Charge Carrier Dynamics in Novel Solar Materials:

Ultrafast Spectroelectrochemistry

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Ultrafast Spectroelectrochemistry

Alireza Honarfar

DOCTORAL DISSERTATION

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Abstract:

The constant increase in global energy demand makes it inevitable to find clean means of energy production. Among renewable energy sources, the Sun is the most available source which makes it a versatile solution for energy needs. Tremendous efforts are made to invent and develop new materials for light to energy conversion. The main question is how the newly developed materials react to light and what can be done to make them more efficient. Through this dissertation a summary of the results for charge carrier dynamics in novel solar materials is represented. We studied a range of new iron-based molecules which exhibit excited state lifetimes up to ns. They can be used for dye sensitized solar cells (DSSCs) to replace expensive rare elements such as Ruthenium. We studied conjugated polymers that can reach efficiency up to 14% in organic photovoltaics. We also studied how structure and composition modification may lead to better performance for light-harvesting in perovskites. Through our studies we realized that, apart from perfecting solar materials and their performances, there is still a greater need for finding the correct energy level's configuration at interfaces. This can yield better and efficient charge separation and extraction which can directly influence the performance and efficiency of the solar cells. There are various methods for manipulation of energy levels and charge carrier dynamics in materials and interfaces. As an example, by changing their composition or structure. Manipulations of charges at interfaces can also be done on existing materials via external sources for example by application of a bias. It is important if changes are variable, controlled and can be reversible. Therefore, we examined electrochemistry as a versatile method for direct manipulation of charges at the interfaces and in the sample under study. CdSe quantum dots (QDs) sensitized on TiO_2, were chosen as a model system, replicating the photoanode of QDs sensitized solar cells. Specific objective of our studies was to investigate how the photo-physics of the QDs might change under influence of extra charges provided by electrochemistry. We used ultrafast spectroelectrochemistry as the combination of electrochemistry for direct manipulation of charges and ultrafast pump-probe spectroscopy measurements to directly probe the charge carrier's dynamics in QDs. By using this combination, we observed that slight increase in the charges at QDs-TiO_2 interface, significantly affect charge extraction from QDs. If applied bias is sufficient enough, it leads to negative charging of the QDs. Where photo excitation of such negative charged QDs leads to rapid negative trion decay in QDs. We also demonstrated that positive charging of QDs can be achieved by using electrochemistry. Photo excitation of the positively charged QDs also induce rapid positive trion decay. We strived to present the potential of spectroelectrochemistry as a supplement to ultrafast spectroscopy methods. The unique advantage of spectroelectrochemical measurement is that induced changes can be reversed which enable comparison of different configurations with similar experimental conditions. Further studies are needed to develop the required knowledge of the photophysical processes in solar materials to achieve ultimate performance and efficiency for light conversion.

Key words: charge carrier dynamics, quantum dots, solar-cells, trion decay

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Dedicated to those who supported me

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Abstract:

The constant increase in global energy demand makes it inevitable to find clean means of energy production. Among renewable energy sources, the Sun is the most available source which makes it a versatile solution for energy needs. Tremendous efforts are made to invent and develop new materials for light to energy conversion. The main question is how the newly developed materials react to light and what can be done to make them more efficient. Through this dissertation a summary of the results for charge carrier dynamics in novel solar materials is represented. We studied a range of new iron-based molecules which exhibit excited state lifetimes up to ns. They can be used for dye sensitized solar cells (DSSCs) to replace expensive rare elements such as Ruthenium. We studied conjugated polymers that can reach efficiency up to 14% in organic photovoltaics. We also studied how structure and composition modification may lead to better performance for light-harvesting in perovskites. Through our studies we realized that, apart from perfecting solar materials and their performances, there is still a greater need for finding the correct energy level's configuration at interfaces. This can yield better and efficient charge separation and extraction which can directly influence the performance and efficiency of the solar cells. There are various methods for manipulation of energy levels and charge carrier dynamics in materials and interfaces. As an example, by changing their composition or structure. Manipulations of charges at interfaces can also be done on existing materials via external sources for example by application of a bias. It is important if changes are variable, controlled and can be reversible. Therefore, we examined electrochemistry as a versatile method for direct manipulation of charges at the interfaces and in the sample under study. CdSe quantum dots (QDs) sensitized on TiO_2, were chosen as a model system, replicating the photoanode of QDs sensitized solar cells. Specific objective of our studies was to investigate how the photo-physics of the QDs might change under influence of extra charges provided by electrochemistry. We used ultrafast spectroelectrochemistry as the combination of electrochemistry for direct manipulation of charges and ultrafast pump-probe spectroscopy measurements to directly probe the charge carrier's dynamics in QDs. By using this combination, we observed that slight increase in the charges at QDs-TiO_2 interface, significantly affect charge extraction from QDs. If applied bias is sufficient enough, it leads to negative charging of the QDs. Where photo excitation of such negative charged QDs leads to rapid negative trion decay in QDs. We also demonstrated that positive charging of QDs can be achieved by using electrochemistry. Photo excitation of the positively charged QDs also induce rapid positive trion decay. We strived to present the potential of spectroelectrochemistry as a supplement to ultrafast spectroscopy methods. The unique advantage of spectroelectrochemical measurement is that induced changes can be reversed which enable comparison of different configurations with similar experimental conditions. Further studies are needed to develop the required knowledge of the photophysical processes in solar materials to achieve ultimate performance and efficiency for light conversion.

Popular Science Summary

Most of the energy needed for human life is provided by fossil-based fuels, that leaves behind large amounts of carbon dioxide and other products that cause harm to nature. Global warming and climate change are the visible evidence of that harm which everyone can clearly witness. To reduce the damages to nature, it is inevitable to find new means of clean energy production. Since ever, the Sun has provided generous amounts of energy for the planet Earth to thrive. This availability around globe makes it a versatile source for renewable energy production on global scale. Therefore, we need to develop materials and methods that can efficiently convert light to other forms of energy. These materials also need to be produced by the processes that require low cost and cause little damage to nature. Through this thesis we studied a range of new solar materials, which shows promising properties that can be used for efficient light to energy conversion. In the simplest process, when the light strikes a solar material, its energy is being transferred to electrons and holes in the material. To generate electricity, these electrons and holes needs to be separated and extracted from the material. These reactions happen in a very short time and largely depends on the material properties and the extraction process which take place at the interfaces. The holy grail is to find an efficient material which can be used on a large scale to solve global energy needs. There are various solar materials which among them we studied molecules, organic polymers, perovskites, and nano sized semiconductors. Each of these materials are made of elements which some of them contain rare and expensive elements or toxic elements that can cause environmental damage and health risk. Therefore, it is important to find materials that are environmentally friendly, easy to make and cheap so they can be used on global scale. We studied state-of-the-art molecules that are made of iron, which is a cheap abundant element, to replace commonly used rare expensive elements such as Ruthenium (Ru) and Osmium (Os). We also studied organic polymers that can convert light to electricity with conversion efficiency of up to 14%. We also evaluated how replacing Lead (Pb) in perovskites can affect their efficiency in light harvesting and what can be done to make them more efficient. Through our studies we also realized that extraction of charges from solar materials is also affected by configuration of energy levels at interfaces of solar-material and electrodes. Therefore, we studied how changes at interfaces may affect light harvesting and if it can cause major energy loss in solar materials.

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List of Publications

This thesis is based on the following papers, which will be referred to it by their Roman numerals in the text. Papers are reprinted with permission from corresponding journals and enclosed with the same order only to the printed version.

I **A low-spin Fe (iii) complex with 100-ps ligand-to-metal charge transfer photoluminescence**

Pavel Chábera, Yizhu Liu, Om Prakash, Erling Thyrhaug, Amal El Nahhas, Alireza Honarfar, Sofia Essén, Lisa A. Fredin, Tobias C. B. Harlang, Kasper S. Kjær, Karsten Handrup, Fredric Ericson, Hideyuki Tatsuno, Kelsey Morgan, Joachim Schnadt, Lennart Häggström, Tore Ericsson, Adam Sobkowiak, Sven Lidin, Ping Huang, Stenbjörn Styring, Jens Uhlig, Jesper Bendix, Reiner Lomoth, Villy Sundström, Petter Persson & Kenneth Wärnmark,

Nature., **2017**, 543, 7647, p. 695-699

II **FeII Hexa N-Heterocyclic Carbene Complex with a 528 ps Metal-To-Ligand Charge-Transfer Excited-State Lifetime**

Pavel Chábera, Kasper S. Kjaer, Om Prakash, Alireza Honarfar, Yizhu Liu, Lisa A. Fredin, Tobias C.B. Harlang, Sven Lidin, Jens Uhlig, Villy Sundström, Reiner Lomoth, Petter Persson & Kenneth Wärnmark,

Journal of Physical Chemistry Letters., **2018**, 9, 3, p. 459-463 5 p.

III **Luminescence and reactivity of a charge-transfer excited iron complex with nanosecond lifetime**

Kasper Skov Kjær, Nidhi Kaul, Om Prakash, Pavel Chábera, Nils W. Rosemann, Alireza Honarfar, Olga Gordivska, Lisa A. Fredin, Karl-Erik Bergquist, Lennart Häggström, Tore Ericsson, Linnea Lindh, Arkady Yartsev, Stenbjörn Styring, Ping Huang, Jens Uhlig, Jesper Bendix, Daniel Strand, Villy Sundström, Petter Persson, Reiner Lomoth, Kenneth Wärnmark

Science. , 2019, 363, 6424, p. 249-253

IV **Unveiling Excitonic Dynamics in High-Efficiency Nonfullerene Organic Solar cells to Direct Morphological Optimization for Suppressing Charge Recombination**

Xiaoyu Liu, Yajie Yan, Alireza Honarfar, Yao Yao, Kaibo Zheng & Ziqi Liang

Advanced Science. , 2019, 6, 8, 1802103.

V **14.7% Efficiency Organic Photovoltaic Cells Enabled by Active Materials with a Large Electrostatic Potential Difference**

Huifeng Yao, Yong Cui, Deping Qian, Carlito S. Ponseca, Alireza Honarfar, Ye Xu, Jingming Xin, Zhenyu Chen, Ling Hong, Bowei Gao, Runnan Yu, Yunfei Zu, Wei Ma, Pavel Chabera, Tönu Pullerits, Arkady Yartsev, Feng Gao & Jianhui Hou

Journal of the American Chemical Society. , 2019,141, 19, p. 7743-7750

VI **Composition Engineering in Two-Dimensional Pb–Sn-Alloyed Perovskites for Efficient and Stable Solar cells**

Y Chen, Y Sun, J Peng, P Chábera, A Honarfar, K Zheng, Z Liang

ACS applied materials & interfaces , 2018, 10 (25), 21343-21348

VII **Photostability and Photodegradation Processes in Colloidal CsPbI3 Perovskite Quantum Dots**

Rui An, Fengying Zhang, Xianshao Zou, Yingying Tang, Mingli Liang, Ihor Oshchapovskyy, Yuchen Liu, Alireza Honarfar, Yunqian Zhong, Chuanshuai Li, Huifang Geng, Junsheng Chen, Sophie E. Canton, Tonu Pullerits & Kaibo Zheng,

ACS Applied Materials and Interfaces. , 2018,10, 45, p. 39222-39227 6 p.

VIII **Benefiting from Spontaneously Generated 2D/3D Bulk-Heterojunctions in Ruddlesden−Popper Perovskite by Incorporation of S-Bearing Spacer Cation**

Yajie Yan, Shuang Yu, Alireza Honarfar, Tõnu Pullerits, Kaibo Zheng & Ziqi Liang

Advanced Science. , 2019, 6, 14, 1900548.

IX **Photoexcitation Dynamics in Electrochemically Charged CdSe Quantum Dots: From Hot Carrier Cooling to Auger Recombination of Negative Trions**

Alireza Honarfar, Hassan Mourad, Weihua Lin, Alexey Polukeev, Ahibur Rahaman, Mohamed Abdellah, Pavel Chabera, Galina Pankratova, Lo Gorton, Kaibo Zheng, and Tönu Pullerits,

ACS Applied. Energy Materials. 2020,

X Excited State Dynamics in Electrochemically Positively Charged CdSe Nanocrystals

manuscript to be submitted to ACS Nano

My Contribution to the Publications:

Each publication obtained by contribution of all authors whose works and efforts were equally important and appreciated. Nonetheless my contribution defined here is not an indication of being the only one who did the work or being solely responsible for the measurements or the results. Sometimes it is hard to judge individual contributions in a large project when everyone has worked together to reach a common goal.

I I performed electrochemistry and spectroelectrochemistry, took part in transient absorption spectroscopy, and contributed to the writing of the paper.

II I performed spectroelectrochemistry, took part in transient absorption spectroscopy, and contributed to the writing of the paper.

III I performed transient absorption spectroscopy, performed data analysis, and contributed to the writing of the paper.

IV I performed transient absorption spectroscopy, performed data analysis, and contributed to the writing of the paper.

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VIII I performed transient absorption spectroscopy, performed data analysis, and contributed to the writing of the paper.

IX I led the planning of the experiments, performed the experiments, data analysis and wrote main part of the paper.

X I led the planning of the experiments, performed the experiments, data analysis and wrote main part of the manuscript.

Publications Not Included in Thesis

Articles which are not included in this thesis, may not be perceived as less important nor as forgotten, they just simply did not fit to the main goal and subject of this thesis. These are also part of my learning journey through my PhD. They provided me a great resource of learning and practicing research along with others. This is an honor for me to be involved in so much research. They are not only a publication on paper, but also lots of memories of hard work and joy of working together. I 'm glad that my contribution had an impact on these works.

I Beating Darwin-Bragg losses in lab-based ultrafast X-ray experiments

Wilfred K. Fullagar, Jens Uhlig, Ujjwal Mandal, Dharmalingam Kurunthu, A. El Nahhas, Hideyuki Tatsuno, Alireza Honarfar, Fredrik Parnefjord Gustafsson, Villy Sundström, Mikko R J Palosaari, Kimmo M. Kinnunen, Ilari J. Maasilta, Luis Miaja Avila, Galen C. O'Neil, Young Il Joe, Daniel S. Swetz & Joel N. Ullom,

Structural Dynamics., 2017, 4, 4, 044011.

II Electronic structure and excited state properties of iron carbene photosensitizers - A combined X-ray absorption and quantum chemical investigation

Fredric Ericson, Alireza Honarfar, Om Prakash, Hideyuki Tatsuno, Lisa A. Fredin, Karsten Handrup, Pavel Chabera, Olga Gordivska, Kasper S. Kjær, Yizhu Liu, Joachim Schnadt, Kenneth Wärnmark, Villy Sundström, Petter Persson & Jens Uhlig

Chemical Physics Letters. , 2017, 683, p. 559-566

III Inorganic Ions Assisted Anisotropic Growth of CsPbCl3 Nanowires with Surface Passivation Effect

Yingying Tang, Xianyi Cao, Alireza Honarfar, Mohamed Abdellah, Chaoyu Chen, José Avila, Maria-Carmen Asensio, Leif Hammarström, Jacinto Sa, Sophie E. Canton, Kaibo Zheng, Tõnu Pullerits, and Qijin Chi,

ACS Applied Materials and Interfaces. ,2018, 10, 35, p. 29574–29582

IV Ultrafast dynamics in QD based photoelectrochemical cells

Alireza Honarfar, Hassan Mourad, Mohamed Abdellah, Pavel Chabera, Galina Pankratova, Lo Gorton, Kaibo Zheng & Tönu Pullerits,

Physical Chemistry of Semiconductor Materials and Interfaces XVIII. ,2019, SPIE, Vol. 11084. 110840L

V Photodetector Based on Spontaneously Grown Strongly Coupled MAPbBr3/N-rGO Hybrids Showing Enhanced Performance

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ACS Applied Materials and Interfaces., 2020, 12, 1, p. 858-867 10 p.

VI Electron Transfer Mediated by Iron Carbonyl Clusters Enhance Light-Driven Hydrogen Evolution in Water by Quantum Dots

Chuanshuai Li, Ahibur Rahaman, Weihua Lin, Hassan Mourad, Jie Meng, Alireza Honarfar, Mohamed Abdellah, Meiyuan Guo, Michael G. Richmond, Kaibo Zheng & Ebbe Nordlander,

ChemSusChem, 2020, 13, 3252.

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Advanced functional materials, 2020, 30 (31), 2002124

VIII Observing the Structural Evolution in the Photodissociation of Diiodomethane with Femtosecond Solution X-Ray Scattering

Matthijs R Panman, Elisa Biasin, Oskar Berntsson, Markus Hermann, Stephan Niebling, Ashley J Hughes, Joachim Kübel, Kalina Atkovska, Emil Gustavsson, Amke Nimmrich, Asmus O Dohn, Mads Laursen, Diana B Zederkof, Alireza Honarfar, Kensuke Tono, Tetsuo Katayama, Shigeki Owada, Tim B Van Driel, Kasper Kjaer, Martin M Nielsen, Jan Davidsson, Jens Uhlig, Kristoffer Haldrup, Jochen S Hub, Sebastian Westenhoff

Physical Review Letters, 2020, 125 (22), 226001

Abbreviations

QDs	Quantum Dots
SCs	Solar Cells
DSSC	Dye-Sensitized Solar Cells
OPV	Organic Photovoltaics
Ru	Ruthenium
PSCs	Perovskite based Solar Cells
EL	Electrochemistry
CV	Cyclic Voltammetry
WE	Working Electrode
CE	Counter Electrode
TiO_2	Titanium Dioxide
FTO	Florin doped Tin Oxide
Spec-EL	Spectroelectrochemistry
TA	Transient Absorption Spectroscopy
D	Donor
NFA	Non-Fullerene Acceptor
PCE	Power Conversion Efficiency
CT	Charge Transfer

1 Chapter 1:
Introduction and Methods

1.1 **Introduction**

For extraction of energy from renewable sources tremendous efforts have been caried out. Despite all these efforts and achievements there are many obstacles to combat to reach an efficient global solution. Each method has its own advantages and flaws. Among renewable energy sources, the Sun is available all year round throughout the globe. This availability makes it a versatile functional solution for energy needs. To generate energy from the Sun one needs to capture the light, turn it into separated charges and by an efficient method extract them. Therefore, the devices operation and efficiency depend on how materials react with light. These properties of the material can be determined and changed based on the composition of its atoms. For example, energy bands of a single atom shows a set of discrete levels, energies of which are changed by its atomic number. Molecules' energy bands are like superposition of single atoms. In bulk material the energy level differences become very small such that it becomes a continuum and is different for metals and semiconductors. Very interestingly nanoparticles show properties that lay on the cross border between molecules and bulk crystals. The schematic electronic band structure of the atoms, molecules, nanoparticles, and bulk materials are illustrated in figure 1-1.

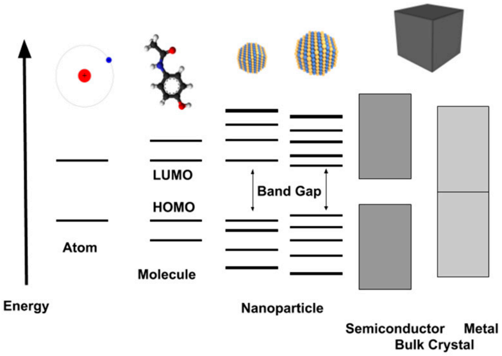


Figure 1-1:simplified band structure for a single atom, a molecule, nanoparticles and bulk materials. Energy level diagram for single atom H, paracetamol molecule, nanoparticles with different sizes and bulk material including semiconductor, insulator and metals. Realistically there are more energy levels even in the simplest atom H.

Among emerging solar cells (SCs), dye-sensitized solar cells (DSSC), organic photovoltaics (OPV) can be seen while they have been developed for decades. The main question is how to develop solar materials and what can be done to make them more efficient. Through this dissertation we report the results of our study of charge carrier dynamics for a range of novel solar materials (molecules, organic conjugated polymers, and perovskites) and how their structure and energy level alignments are affecting their performance for light-harvesting. While a great match between energy levels can be achieved in materials but charges can accumulate at the interfaces due to defects, traps or Schottky barrier formation. Therefore, it is also important to study the effect of these charges at interfaces to be able to make efficient devices. We also propose electrochemistry(EL) as a versatile method for direct manipulation of charges at the interfaces and also in solar materials which can largely affect charge carrier dynamics in devices. The results of our studies can help understanding the existing issues in emerging solar materials.

Fundamentally in SCs, the light will be absorbed by the material. Then for generation of electricity, absorbed light needs to be turned into free charges. These charges must be separated before recombining and by an efficient method being extracted. Therefore, the efficiency of the devices largely depends on the photoinduced charge carrier dynamics[1]. In figure1-2, a simplified schematic of the above-mentioned processes in SCs are illustrated. Apart from perfecting light absorbers, it is also necessary to find the correct energy level configuration for efficient charge separation and extraction which directly influence the performance and efficiency of the device.

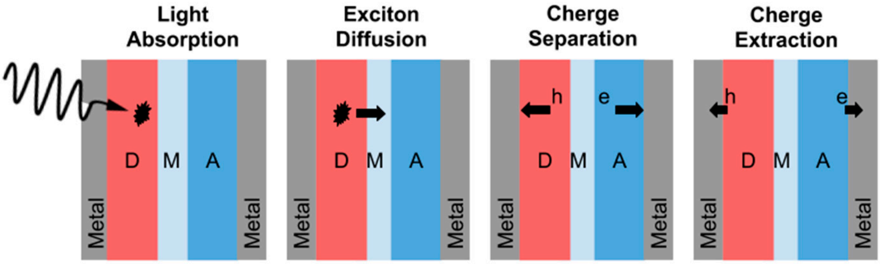


Figure 1-2 : evolution of photoinduced charge carriers in a solar cell
If the photon energy is higher than solar material's energy gap it will be absorbed by Donor (D), generated charges diffuse through medium (M), electrons being transferred to acceptor (A) and eventually separated charges being extracted at the interfaces by the metal contacts

1.1.1 New Iron Age in Solar Cells:

Mostly semiconductor based SCs, initially invented by using semiconductor junctions, where/are the leading of the commercial market. DSSCs, based on photoelectrochemical systems were proposed as one of the promising low-cots, simple to make alternatives[2,3]. In these cells, the light will be absorbed by molecules which usually is made of rear elements such as Ruthenium (Ru). DSSC as a promising light-harvesting method has its own pros but some issues in their construction prevented their large-scale commercialization. As an example, the best performing molecules are made of rare and expensive elements, such as Ru and Os[4]. Tremendous efforts have been made to use abundant elements such as first row transition metals for photophysical and photochemical applications[4,5]. The ubiquity of iron makes it one of the cheapest and most available element as an obvious option to be used on global scale[6]. Usually iron-based complexes suffer from rapid recombination[4,7,8]. This rapid recombination impedes the application of these materials in DSSCs. Developments in chemical synthesis enabled chemists from Lund University to invent a series of iron-based complexes in the effort to overcome the issue of using rare earth elements[7,8]. Laser spectroscopy measurements of the first molecule revealed that it has room temperature photoluminescence and 100 ps charge-transfer excited-state lifetime[9]. It emerged as the first emissive iron-based complex with oxidation state Fe^{3+} (FeIII) which has relatively long excited state lifetime (paper I)[9]. Spectroelectrochemical (Spec-EL) measurements revealed that the Fe^{2+}(FeII) analogue of this complex has interesting absorption features that may lead to better efficiency in light conversion. Initial laser spectroscopy measurements of FeII version revealed exceptionally longer-lived charge-transfer excited-state with lifetime five times longer than its FeIII version. The successful isolation and crystallization of the FeII complex (purer than electrochemically converted), enabled repeating of the measurements that proved similar results as they were previously generated by ultrafast Spec-EL characterization (paper II)[10]. This enabled comparison of the performance of the same iron complex in its different oxidation states. Obtained results provided a piece of knowledge on how-to develop new molecules for better efficiency, that leads to engineering the energy levels of a state-of-the-art complex that shows strong room temperature photoluminescence with a 2-nanosecond lifetime (paper III)[11].

1.1.2 Organic Photovoltaics:

Organic photovoltaics (OPVs) were also demonstrated in a similar period as DSSC, and by the realization of photoinduced electron transfer from a conducting polymer to fullerene acceptor (A), OPVs based on fullerene were extensively investigated[12]. In fullerene based OPVs, a large energy offset is required to compensate the high exciton binding energy (E_B) of donor (D) which is a constrain on the design of the donor polymer and also a mechanism of the energy loss[13]. Obviously, non-fullerene acceptor (NFAs) OPVs have also been developed[12]. In NFA OPVs, both D and NFA, retain molecular structures that allows designing of the optical bandgap and energy levels alignment that can match very well with other organic semiconductors. NFA OPVs with very small energy offset have recently reached efficiency even higher than initially fullerene based[14]. This higher efficiency suggested to be due to better polymer structure, optical absorption and band alignment of the NFAs[12,13,15]. It is also suggested that in NFA OPVs with very small offsets of highest occupied molecular orbital (HOMO) levels, formation of CT state with lower energy loss lead to better efficiencies[14]. In paper IV, we report that in NFA OPVs with very small offsets of both (HOMO) and lowest unoccupied molecular orbital energy levels (LUMO), still efficient electron/hole transfer between donor acceptor can be achieved. Such efficient charge transfer speculated to be the main reason for achieving 10% efficiency (paper IV)[16]. In paper V, we also studied a D-NFA OPV with large LUMO band offset that an efficiency of 14.7% can be achieved in a single-junction OPV[17]. Our measurements suggest that the formation of charge transfer (CT) state with zero energy loss/offset is responsible for efficient charge separation and higher efficiency. The other energy losses mainly influence the open circuit voltage of the OPV (paper V)[17].

1.1.3 Lead Halide Perovskite Based Solar Cells:

Perovskite based solar cells (PSCs) have recently emerged as one of the promising possible solutions in the photovoltaic industry for cheap solution-processable SCs that can be scaled up[18,19]. Over the past few years, a sharp rise in the number of published papers on PSCs indicates the global effort in exploring potentials of these materials for efficient photovoltaic applications. The power conversion efficiency of PSCs has reached more than 25% in a relatively short period of development time. Perovskite has intrinsically large electron mobility, low trap densities and good broadband absorption spectra[20]. When these properties are combined with efficient long-distance charge carrier diffusion, this makes them most suitable material for photovoltaic applications. But since lead halide perovskites usually contain toxic elements, their large-scale application is limited due to potential environmental and health risk. This issue has been a center of many activities in material science to replace the toxic elements completely or partially[21,22]. In our study in paper VI, we observed that partial replacement of Pb with Sn can improve the crystallinity and structure of the absorber film as well as relatively better photo induced charge carrier dynamics[23]. However, the poor reproducibility in device fabrication and instability of these materials is a major challenge to obtain highly efficient large-scale PSC devices. Environmental factors such as humidity and oxygen can be eliminated by encapsulation, but light absorption is necessary for PSC's operation. Long-term photostability is more critical in perovskites nanostructures because their surface to volume ratio is very high. To decipher such degradation, in paper VII we studied the photostability of colloidal $CsPbI_3$ QDs as one of the best performing materials in PSCs[24]. We found that light illumination does induce photodegradation of $CsPbI_3$ QDs. Transient absorption spectroscopy verified that light illumination leads to significant changes in charge carrier dynamics. But interestingly steady state absorption and x-ray characterization showed no differences. SEM images of fresh and degraded samples revealed that possibly detachment of the capping ligand due to light interaction led to the changes in the $CsPbI_3$ QD surface. This cause the transformation of the QDs shape from cubic to spherical while its size is preserved. It is also suggested that aggregation of Pb_0 at the surface, serve as trap states causing PL quenching with a dramatic decrease of PL quantum yield (paper VII)[24]. As mentioned earlier, perovskites are not stable in ambient conditions, especially in presence of oxygen and humidity. Previous studies revealed that one solution for such issues is to incorporate two-dimensional (2D) perovskite phases into conventional 3D perovskite's matrix which led to enhanced long-term stability[25,26]. However, the use of long-organic spacing cations would prevent the charge carrier transport. Therefore, how to arrange the assembly of the 2D:3D hybrid structure to ensure the efficient charge carrier collection, remains to be a challenging task. In paper VIII, we for the first time demonstrated how 2D:3D bulk-heterojunction structures can be simultaneously generated by synthesis at room temperature[27]. In this approach, 3D shapes are epitaxially interconnected with 2D lattices, which ensure the efficient charge carrier transport and hence improve the light to electricity conversion efficiency close to 11.32%. The SCs device based on this structure, without protecting layer show excellent stability and high performance for 270 hours at room temperature in the air with a relatively high humidity[27].

1.1.4 Semiconductor Thin Films and Quantum Dot Sensitized Solar Cells:

Semiconductors and their nanocrystals have been widely investigated and used both as photo absorber and charge carrier transport materials[28,29]. They are also used in fundamental research and in many state-of-the-art interdisciplinary applications[28,29]. QDs are semiconductor nanocrystals with size smaller than exciton Bohr radius (for example for CdSe, exciton Bohr radius is 5.8 nm). Unlike bulk material or molecules, the QD properties can be easily tuned continuously by modifying their size or shape which make them a very attractive material for scientific research and various applications. They have a very large surface to volume ratio which makes them an ideal candidate for photocatalytic reactions. Also, their exceptionally high extinction coefficient is of great advantage for efficient light absorption in SCs with a thin layer. These properties make QDs based SCs a potential strategy that can be easily scaled-up for efficient light-harvesting. By the invention of cheap wet chemistry synthesis of QDs, their application in various fields expanded rapidly. Despite long term development of semiconductor-based devices and all recent advances in QDs applications, QDs based SCs are not commercialized and are only considered as emerging technologies. Recent studies suggest that Auger recombination is responsible for efficiency limit of semiconductor thin films and QDs LEDs[30,31]. Auger recombination in electrically driven applications of QDs (such as LEDs), is due to excess of charge carriers. In SCs this may/can be also a major issue of low performance of devices that incorporate QDs (in general semiconductors)[32,33]. For example, in perovskites it is known that poor film morphology lead to charge accumulation at interfaces that increase charge recombination[23,27]. This charge accumulation at the electrode interface may also eliminates charge extraction from QDs SCs. It may also lead to (positive or negative) charging of the semiconducting material during device operation where photo excitation of such charged semiconductors or QDs leads to rapid Auger recombination[34]. Therefore, we identified a need to scrutiny this issue in SCs and we strived to find a versatile method that can be used for study of these processes in materials with the conditions similar to optoelectronic devices.

1.1.4.1 Why It Is Important to Study the Auger Processes:

The Auger process is exclusively important because it is one of the main energy loss pathways in all photophysical applications of semiconductors. Auger recombination becomes a dominant process in QDs due to confinement effect at nano scales. Interestingly, despite of the Auger process being commonly considered as an energy loss mechanism, a recent study suggests that it can be harnessed for efficient charge extraction[35]. This is of great importance especially in SCs[33]. Despite all efforts and achievements, current studies are limited to availability of experimental results that are mostly done by indirect measurement of Auger processes[30,32–42]. That means, there is a great need for a method which can directly and controllably induce Auger process in matter and has the possibility of tracking the dynamics of charge carriers in matter at shorter time scales. By combining the available knowledge and experience that we gained through our previous studies we realized that this can be achieved by integrating ultrafast laser spectroscopy and EL, known as ultrafast spectroelectrochemistry(ultrafast Spec-EL)[43]. This method can be universally applied to any material (semiconductors, perovskites, ...) with any structure (thin films, nano dot, nanowire). Studying various structures is especially important since recently it has been reported that Auger recombination can be significantly engineered by varying the structure of the QDs in core/shell heterojunctions[38]. In this project our aim is to study charge carrier dynamics in a model system which help to the understanding of the underlying photophysical processes in QDs.

1.1.5 Ultrafast Spectroelectrochemistry

As we realized through our studies, the efficiency of light to electron conversion can be engineered by relative configuration of their energy levels by changing the atomic composition or structure of the complexes via synthesis. While a great match between energy levels can be achieved but charges can accumulate at the interfaces due to defects, traps or Schottky barrier formation. Therefore, it is important to study the effect of these charges at interfaces to be able to make efficient devices. It is appealing if there is a method that can induce such changes in the existing materials that can be controllable and if the induced changes can be reversible. For example, in our previous work with iron complexes we learned that Spec-EL can convert an existing version of a molecule to its different oxidation states and the newly obtained molecule can be studied by both steady state and ultrafast spectroscopy[10]. Therefore, EL can be used easily for direct manipulation of charges in existing materials, that can also be integrated in various in-situ spectroscopy studies. The advantage of the EL method is that it can induce changes in materials independently and the spectroscopy can give information about the performance of the manipulated material (or the full device) under controlled manipulation. This is especially important for studies of semiconductors, since EL can provide controlled variable levels of doping in semiconductors (in contrast to usual doping which is done via permanent inclusion of other materials in their crystal structure)[44]. Such method can be used to study trion decay in QDs too[34,45]. Nonradiative negative or positive trion refers to a three-body interacting system consisting of a combination of an electron-hole pair (e-h) and an additional electron or hole, where the energy of the e-h recombination simultaneously promotes further excitation of the electron or hole respectively (figure 1-3)[34].

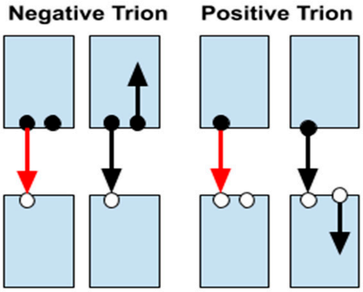


Figure 1-3 : negative and positive trion decay.
Red arrows indicate radiative recombination, black arrows indicate nonradiative recombination.

Since trion is indeed an excited charged QDs, therefore such properties can be manipulated and studied by charging the QDs using EL. In our work (paper IX and X) EL is used as an external source for direct manipulation of the fermi level in the SCs photoanode and ultrafast transient absorption spectroscopy was used for tracking excited state dynamics of the electrons in the QDs and at the interfaces[37]. CdSe QDs is sensitized on the metal oxide layer TiO_2 which replicates SCs photoanodes (on transparent conductive electrodes). Our experimental results revealed that very surprisingly charge accumulation at interfaces, eliminates charge extraction from the QDs. This may provide photophysical ground for upper limit efficiency issues in QDs based SCs. We also anticipated that during device operation if charge accumulation at interfaces lead to charging of the QDs, then photo excitation of such charged QDs certainly induce rapid Auger recombination processes such as trion decay. By using time resolved transient absorption spectroscopy, we observed that in electrochemically charged QDs, excited state rapidly dissociate via non radiative trion decay. Other processes such as polaron formation due to the strong interaction of charges and also electron-electron scattering processes were also observed (paper IX)[37]. The novelty of this method comes to the point where negative and positive charged QDs can be reversibly generated in the same sample having exactly similar working condition. Having obtained that experience, positive charged QDs were successfully generated and by spectroscopic measurements, positive trion dynamics were successfully revealed (paper X). To our knowledge, such experimental results have not been achieved in QDs without shell by direct controlled manipulation of charges and ultrafast measurements. A unique aspect of the proposed method is that it can be universally applied to various materials (molecules, semiconductors, perovskites, ...) with various structures (thin films, nanodot, nanowire) to study their charge carrier dynamics. Therefore, we believe it can be a starting point for further development of the methods and studies of Auger processes in SCs and optoelectronic devices.

1.2 Methods

There are various methods for studies and manipulation of charge carrier dynamics in complexes. Here in this thesis, we used ultrafast laser spectroscopy to study charge carrier dynamics in various novel materials. We also show how EL as a versatile tool can be implemented for studies of charge carrier dynamics in both molecules and semiconductor nanocrystals. We further used the combination of spectroscopy and EL, Spec-EL, for understanding of charge accumulation at interfaces, negative/positive charging of QDs and their underlying photophysical processes in QDs SCs as a step toward their efficient application and development.

1.2.1 Electrochemistry

As it sounds, electrochemistry (EL) is where electricity and chemistry are merged[46,47]. EL is a powerful method that measures the relation between electricity and chemical reactions that involve electron transfer at the interfaces. It is a truly multidisciplinary technique that has existed since the 19th century, implemented in many fields from bio to material science[48–53]. It benefits both laboratory studies and large industrial processes. EL analysis in general can describe the changes in matter (at the atomic scale) by measuring changes in electric charges which can be controlled through an external device. Changes in the matter in response to electrical charge is called reduction /oxidation (Redox in EL language). Typically, in EL the change in the current, i, is measured against changes induced by a voltage stimulus (E) which induce variation in the concentration of chemical reactions (that are coupled with exchanges of electrons between electrodes and sample). One example of electron transfer at the interface is represented in figure 1-4. In this -reaction an

FeIII is adsorbed at the electrode and one electron transfer to this complex, results in a reduction in its oxidation state. So, we can say in EL language that the reaction FeIII + e^-→FeII is a reduction (Red). In general form $Ox+ne^- \rightarrow Red$. Based on similar analogy the reverse reaction FeII - e^-→FeIII is Oxidation (Ox).

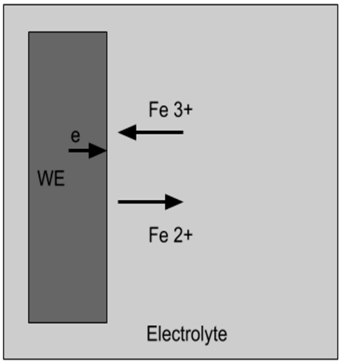


Figure 1-4 : Schematic diagram of an electrochemical reaction at working electrode
FeIII/FeII redox reaction at working electrode (WE). Adapted from [47]

Therefore, if there is a driving force which can introduce charges with sufficient energy to drive a chemical reaction, there will be charges going through interface between electrode and the redox species. The electrode that is driving the reaction, called working electrode (WE). Intuitively due to any of the redox reactions the concentration of reacting materials is changing at the interface. These changes in current and concentration can be explained by the Butler-Volmer equation:

$$i = -nFAk^0\left[{c^0}_{red}\exp\left[\frac{nF(1-\alpha)(E-E^{0'})}{RT}\right] - {c^0}_{ox}\exp\left[\frac{-\alpha nF(E-E^{0'})}{RT}\right]\right] \qquad (1)$$

Which i represent faradaic current, for the changes in the concentration C, of an active material at a plane electrode with area A, n is the number of transferred electrons per mole of electroactive material, k^o as the standard rate constant for the heterogeneous electron transfer at the standard potential (cm/sec); and α is the symmetry factor, a parameter characterizing the symmetry of the energy barrier that has to be surpassed during charge transfer[46,47]. In above Equation E is the applied potential and $E^{o\prime}$ is the standard electrode potential. The difference $E - E^{o\prime}$, called over-voltage, is the amount of the extra energy applied to the electrode beyond the equilibrium potential to drive the reaction at the interface. If there is no current, i=0, for example under equilibrium conditions the Butler-Volmer equation reduces to the Nernst equation[47].

$$E = E^{0'} - \frac{RT}{nF}\ln\frac{[Red]}{[Ox]} \qquad (2)$$

As in EL system electron transfer process between electrode-electrolyte interface is a heterogeneous reaction therefore EL measurement requires the electric contact between different materials that can conduct electricity. Accordingly, in every EL system there must be at least two conductive connections to the electrochemical device(which is called potentiostat). Also, there is ionic conducting material called supporting electrolyte. Usually, the supporting electrolyte is made up of non-electroactive ions and does not contribute to the faradic current (redox reactions) at the interfaces[54]. On the other hand, it does contribute to the current flow in the electrolyte volume and possibly to the capacitive current at the interfaces. A schematic diagram of an EL system is shown in figure 1-5.

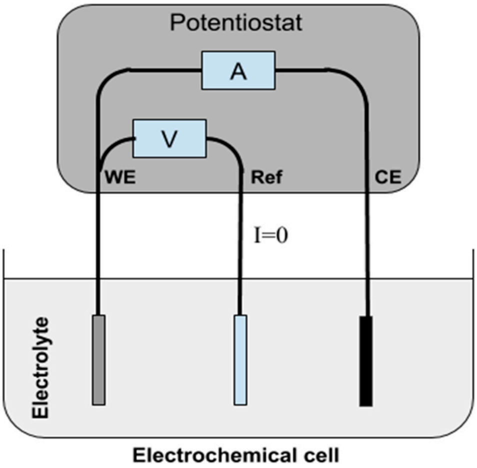


Figure 1-5 : Schematic diagram of an electrochemical system.
The potentiostat is the external device to control or change the voltage or current. Conventional electrochemical measurement consists of three electrodes, working electrode (WE), reference electrode (Ref) and Counter electrode (CE). Adapted from[47]

One should note that an electronic p-n junction cannot be considered as equivalent to an electrochemical cell[47]. The reason is that in contrast to p-n junction, conduction of electricity in EL systems is limited by the conduction of ionic solution via diffusion, migration, and convection of ions. The key difference is that once the maximum conductivity achieved it cannot be further increased (if the solution is not stirred nor disturbed) [47]. The unique aspect of the EL is that the driving force that can drive a reaction can be easily controlled and by measurement of changes in current various parameters can be measured. Therefore, in EL measurement there is always one parameter being controlled, current or voltage, and the other one is being measured. Accordingly, there are various electrochemical measurement techniques. Cyclic voltammetry (CV) is one of the most used techniques to study redox reaction of molecules. In CV, the potential is being controllably changed versus a reference and the current that passes through WE and CE is being measured. As a result, by plotting the voltage and current a cyclic voltammogram (CV) is obtained which typically has a duck shape![54] A CV of FeII[tris(2,2'-bipyridine)] is shown in figure1-6. As the potential is being scanned toward more positive potentials FeII is oxidized to FeIII and concentration of FeII is being depleted near the electrode surface. When the current reaches its maximum, it means that all the FeII near the electrode is converted to FeIII and further conversion is limited by the diffusion of the FeII from the bulk solution. When the scan is reversed, FeIII will be reduced to FeII at the electrode surface until it reaches its original concentration at the beginning of the experiment. The concentration of the FeII and FeIII near the electrode obey the Nernst equation. The potential in the middle of the two peaks corresponds approximately to E^0 which is known for each specific redox couple, for example in this case for FeII / FeIII is known to be 0.77V vs ferrocene[55]. Reference electrode is usually Ag/AgCl electrode that has a stable potential. Sometimes the reference is addressed versus an internal redox couple with a well-known standard potential (E^0), for example Ferrocene is commonly used in all measurements. Reporting potentials versus an internal redox couple has the advantage of being independent of experimental conditions. Since the potential of the reference electrode is different

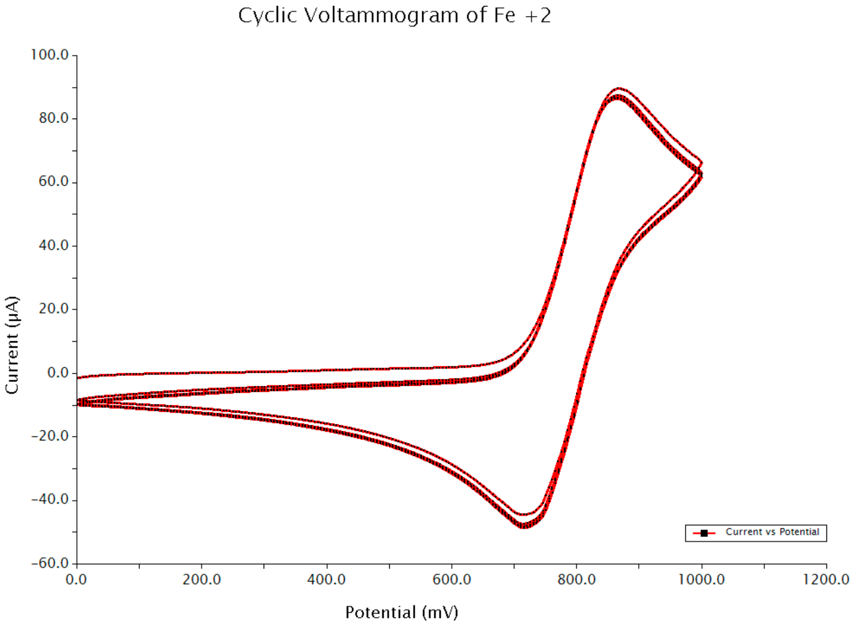


Figure 1-6 : cyclic voltammogram of FeII [tris(2,2'-bipyridine)] complex.
Cyclic voltammogram of FeII [tris(2,2'-bipyridine)] in acetonitrile. Glassy carbon is used as working electrode, Pt as counter electrode, Ag/AgCl as reference. Scan rate 100 mv/s, supporting electrolyte tetrabutylammonium hexafluorophosphate at room temperature.

between experiments due to variations in Ag^+ concentration, electrolyte, or solvent used for non-aqueous measurements[54]. Figure 1-6 is an example of such issue. Usually if the difference between two redox peaks is 57mV the redox reaction is considered reversible. However, reversibility is deduced more thoroughly by measuring the redox peak positions for different scan rates (figure 1-7). When peak positions are plotted versus square root of scan rate, in case of reversibility the plot will be a straight line. Therefore, scan rate plays an important role in CV as well as selection of supporting electrolyte and electrodes[54]. Usually for EL measurements high concentration of supporting electrolyte will be used therefore its purity and solubility is important[54]. Ammonium salts specially NBu_4PF_6 are commonly used supporting electrolytes for EL measurements in organic solvents. For the selection of the electrodes, counter electrode in most of the measurements is Pt mesh or wire with the surface necessarily many times larger than working electrode. Working electrode can be of any material but should be inert (not being oxidized or reduced) within the potential range being used in EL measurement. The potential range for which an electrode can be safely used, is called electrochemical stability window. The range of EL window is not only dependent on the electrode material but also on solvent and supporting electrolyte[56].

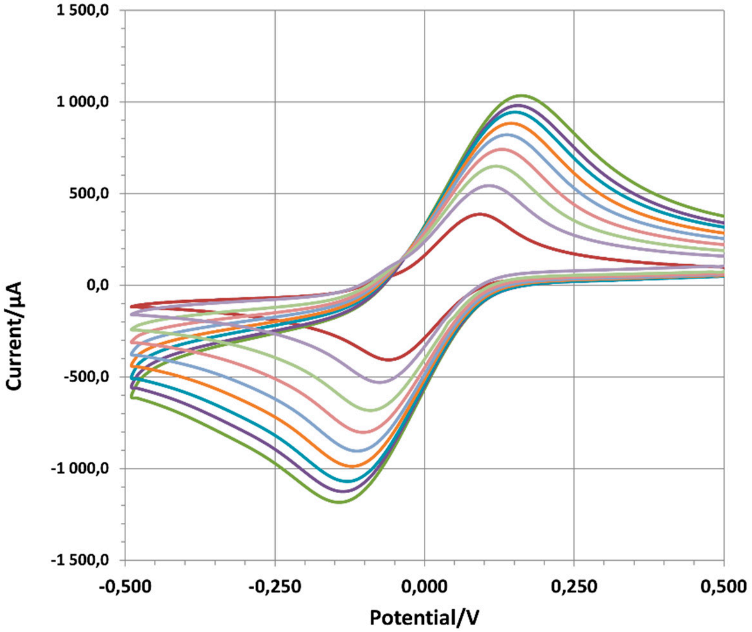


Figure 1-7 : cyclic voltammogram of Ferrocyanide ($K_4Fe(CN)_6$) for different scan rates
Cyclic voltammogram of Ferrocyanide/Ferricyanide couple is measured for different scan rates. Measurements is done in aqueous solution where platinum (Pt) is used as working electrode, Ag/AgCl as reference and Pt as counter electrode. Scan rates are 1000, 800,400,200,100,50,40,20 and,10 mv/s.

EL measurement can also be used to study the band structure of semiconducting materials. For example, CV has been used extensively for evaluating the band gap of QDs[52]. Since in EL measurements, potential is applied versus a reference electrode, therefore negative potentials can be considered as a raise in Fermi level of WE. In contrast, positive potentials correspond to decrease in WE's Fermi level. In semiconductors shift of the Fermi level toward band edge is usually obtained by doping with other elements. Accordingly, in EL measurements as the Fermi level can be shifted controllably, therefore it has similar effect on properties of semiconductor as doping. The advantage of EL for studies of semiconductors is that the induced changes(doping) are variable which enable the study of various configurations of the sample. In figure 1-8, CV measurement of CdSe QDs deposited as thin film on glassy carbon electrode is shown.

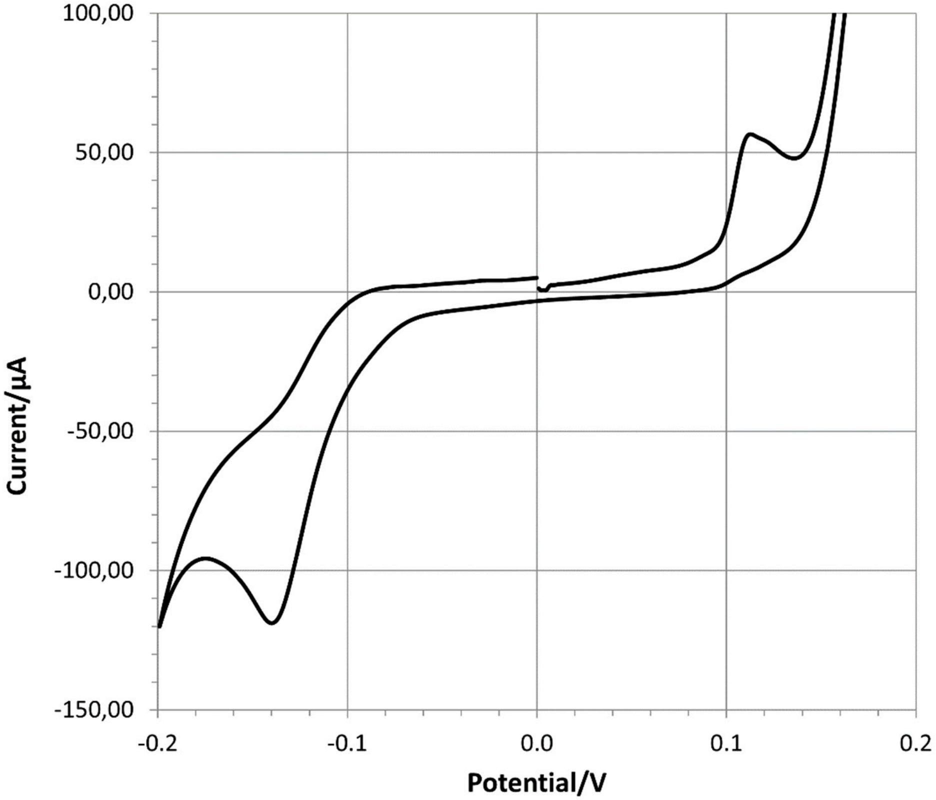


Figure 1-8 : cyclic voltammogram of CdSe QDs on glassy carbon electrode
CdSe QDs are deposited as thin film on glassy carbon electrode. Measurement is done in tetrabutylammonium hexafluorophosphate dissolved in acetonitrile, at room temperature and, scan rate 10mv/s.

1.2.2 UV-VIS Spectroelectrochemistry

Electrochemical techniques by themselves are not suitable for identification of unknown species that can form during redox reactions. Therefore, they are used tremendously in combination with other methods. One of these combinations that covers a very broad range of applications is a combination of EL with spectroscopy (from x-ray to NMR and EPR) which is known as Spec-EL[57]. This method can solve various problems in studies that allows analysis of electron transfer process between electro active complexes and transient redox reactions. In our studies we used steady state absorption spectroscopy in UV-VIS range and EL for identification of redox species. This has been used to identify and confirm the oxidation state of a novel iron complex in the paper I and paper II. It is also a powerful tool to confirm if a complex can be fully converted to redox species. It is very important for spectroscopy measurements because an unknown by-product of EL can interfere with the spectroscopy results and yield completely false information. The CV measurement of FeII [tris(2,2'-bipyridine)] in figure 1-6 can be considered as an example of this. Dissolving FeII [tris(2,2'-bipyridine)] in acetonitrile yield a red solution, while FeIII version of this complexes is blue (if dissolved in dry solvent). Therefore, by measuring the absorption spectra of each of these complexes one can obtain a reference spectrum of their pure form. Then by using EL, conversion of FeII to FeIII and vice versa, can be monitored by measuring the absorption of the sample in EL cell. In figure 1-9, the results of Spec-EL measurement are represented. In this experiment, FeIII is fully converted to FeII by application of negative potential. This reduction is happening very rapidly because the FeIII is an unstable oxidation state of this complex. By application of a positive potential, it

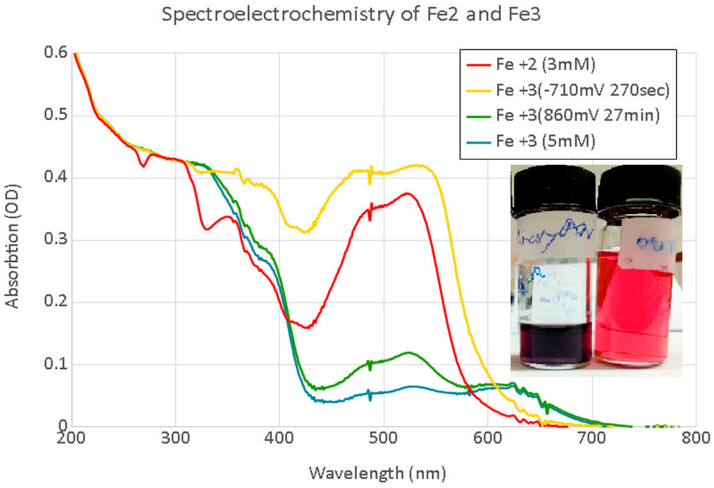


Figure 1-9: Spectroelectrochemical conversion of FeIII [tris(2,2'-bipyridine)].
Pt mesh and wire is used as working and counter electrode, Ag/AgCl as reference electrode. supporting electrolyte tetrabutylammonium hexafluorophosphate in acetonitrile at room temperature.

takes 27 minutes to complete the revers reaction. However, the full reverse reaction is not achieved as can be confirmed from the spectra, therefore there are still some FeII present in the solution. So, despite the reaction seems to be reversible for EL, but it may not be the case for spectroscopy. In semiconductors, the shift of the Fermi level toward band edges can influence the optical properties of the material. This effect has been used for precise identification of conduction band edge in QDs[44]. If the Fermi level is raised or lowered so much that it can reach or goes beyond the band edge, charges can be transferred to the semiconductor. As these extra charges occupy electronic states in the semiconductor, they can induce absorption changes due to state filling effect. This absorption changes can be used to confirm the level of changing in the semiconductor sample under study. A similar approach is used to confirm the presence of negative and positive charges in QDs in paper IX and X respectively.

1.2.2.1 Electrochemical Cell Design:

Combining EL with spectroscopy techniques is an appealing and useful tool. While there are many commercially available EL cells, finding a suitable Spec-EL cell that can accommodate all measurement needs can be an arduous task. The experiments that we have done on nanoparticles were not an exception from this. Normally for optical Spec-EL measurements the cells are constructed in a V-shaped glass cuvette with very thick walls. A commercial Spec-EL cell is shown in figure 1-10.

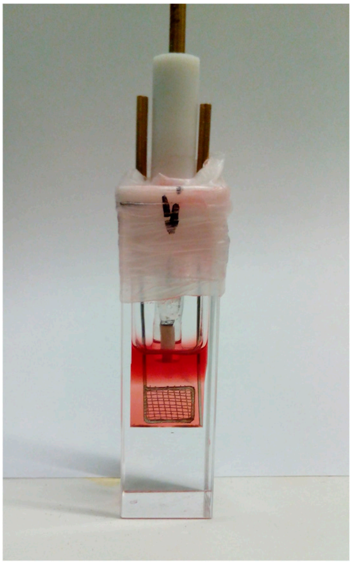


Figure 1-10: conventional commercial spectroelectrochemical cell
Platinum mesh and wire are to be used as working or counter electrode. Ag/AgCl reference electrode is the one in the middle. This Spec-EL cell was used for the measurement of FeIII [tris(2,2'-bipyridine)] that is shown in figure 1-9. Red solution is FeII [tris(2,2'-bipyridine)] in supporting electrolyte tetrabutylammonium hexafluorophosphate in acetonitrile after Spec-EL measurement at room temperature.

To satisfy both requirements of spectroscopy and EL measurements, we took the chance to design and make a series of the Spec-EL cells that can be used for ultrafast laser measurements. The journey went for making cells by drilling and milling the cell body in a piece of glass, illustrated in figure 1-11, and then gluing the electrodes on each side of the cell. This turns out to be a good solution while it was not possible to keep it working for a long time which is needed for all spectroscopic measurements.

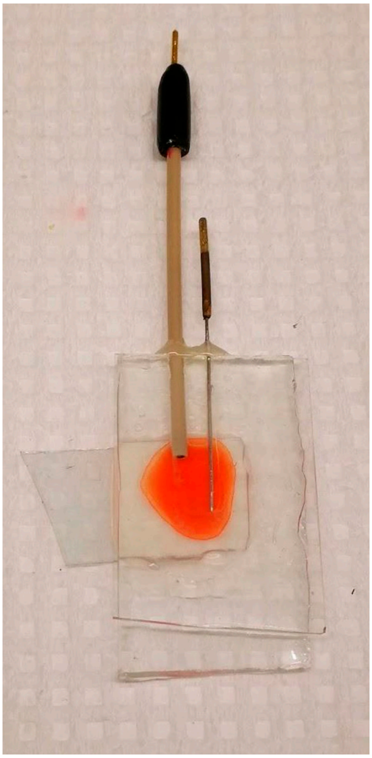


Figure 1-11 : Homemade spectroelectrochemical cell
consisting of FTO as working electrode (CdSe QDs is drop-casted on FTO, orange color), leak less Ag/AgCl reference electrode and a Pt wire as counter electrode.

The other version was built with the idea that the solvent can be degassed, and it can be sealed so it can perform better for EL measurements. But still leaking issues remained a major challenge. A series of glues were tried, including different types of epoxy and hot glue, but all of them were getting loose or leaking after one hour of being in touch with organic solvents such as dichloromethane (DCM).

Figure 1-12 : Homemade spectroelectrochemical cell
TiO_2 coated FTO is used as working electrode, , leak less Ag/AgCl as reference electrode and a Pt plate as counter electrode. High vacuum valve is for degassing of the solvent.

Finally, we realized if the solvent (like DCM) is not hygroscopic the experiments can be done easily in a fresh dry solvent in a normal cell with a normal airtight sealing. For example, the cell which was sealed with Teflon tape could stay functional for few hours which gave the hint of making a much simpler universal cell. Also, by chance we realized that double sided tape provides a lot better sealing than the epoxy glue or hot glue for holding the sample. Double sided tape is cheap, neat and can be easily removed. It enables quick change of the sample. It also resists harsh solvents like DCM for almost a day. In the following you can see the parts and procedure of making an electrochemical cell. In figure 1-15 assembled cell and how it is implemented in spectroscopy experiments is illustrated.

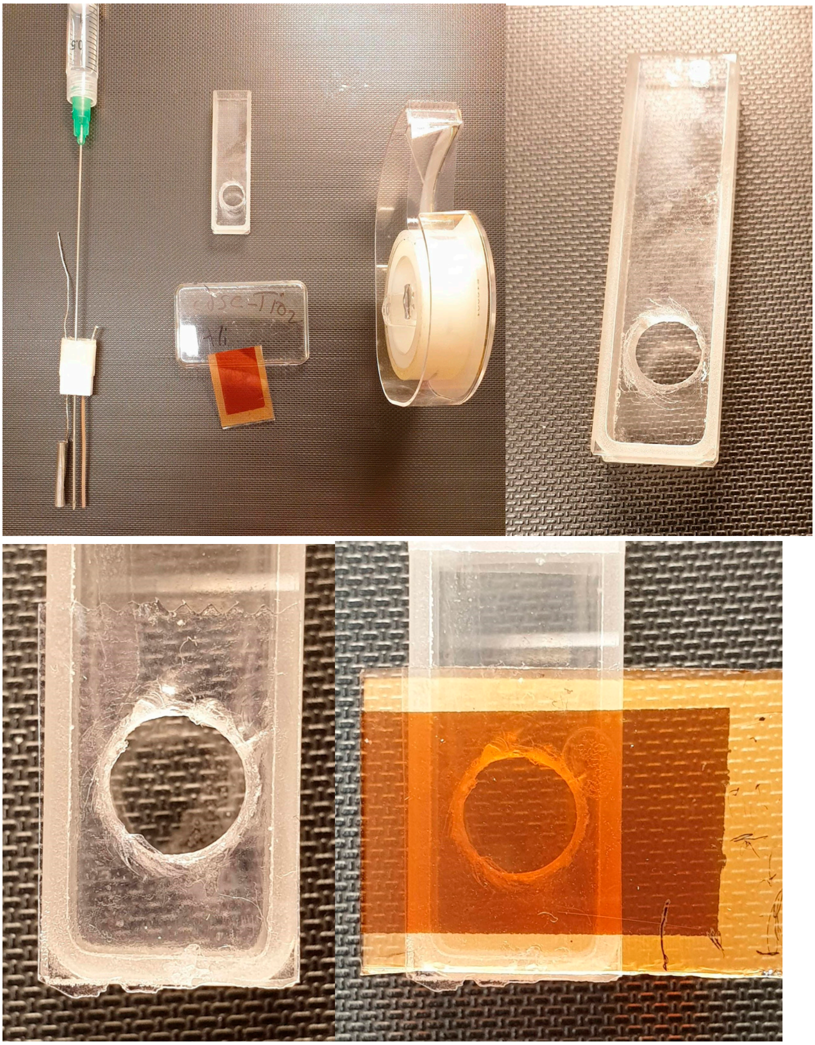


Figure 1-13 : Homemade spectroelectrochemical cell components
The main cell is made of a cuvette with a hole in one side. Sample is made as CdSe QDs sensitized TiO_2 coated FTO. TiO_2-FTO is working electrode, Pt plate as counter electrode and Ag/AgCl wire as pseudo reference. Double sided tape is for fixing the working electrode on the cuvette wall. Teflon cap warped with Teflon tape for sealing.

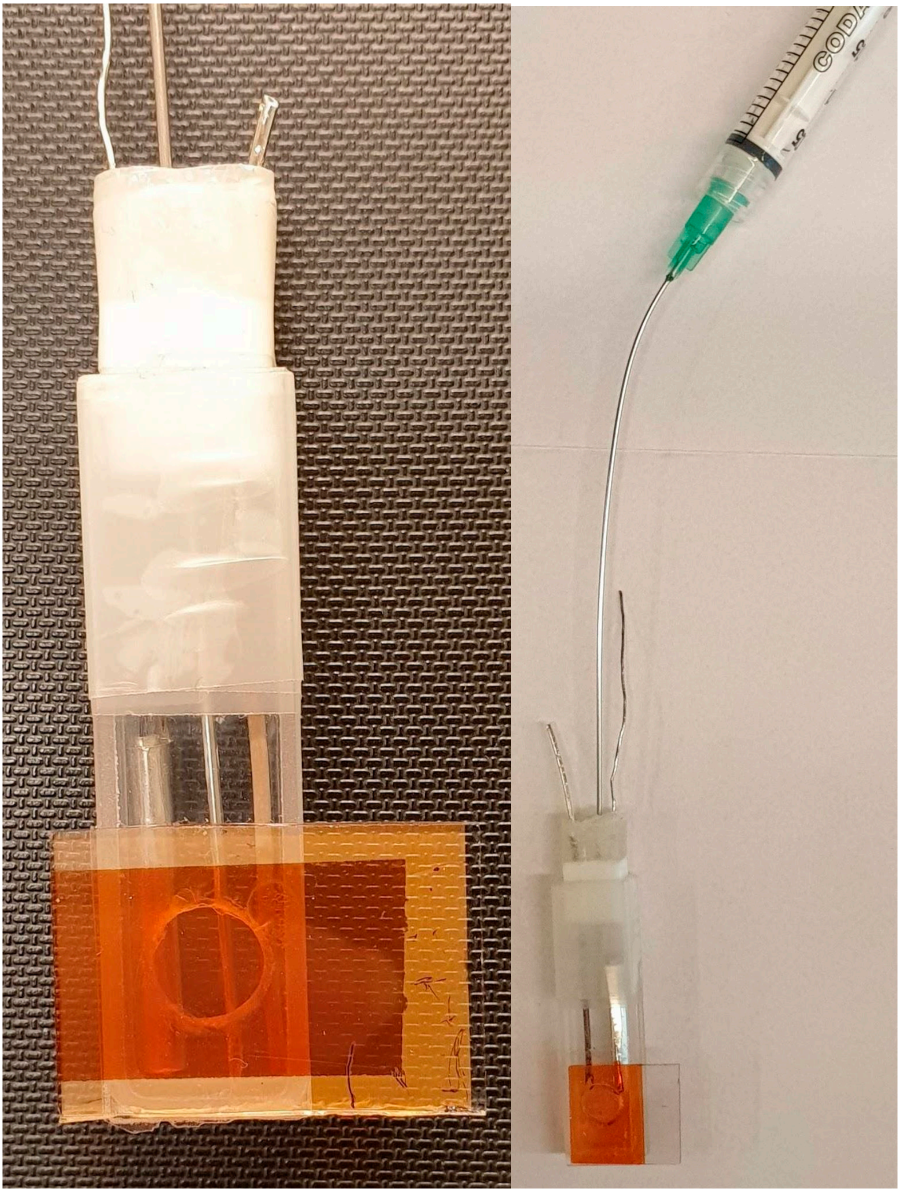


Figure 1-14 : assembled homemade spectroelectrochemical cell

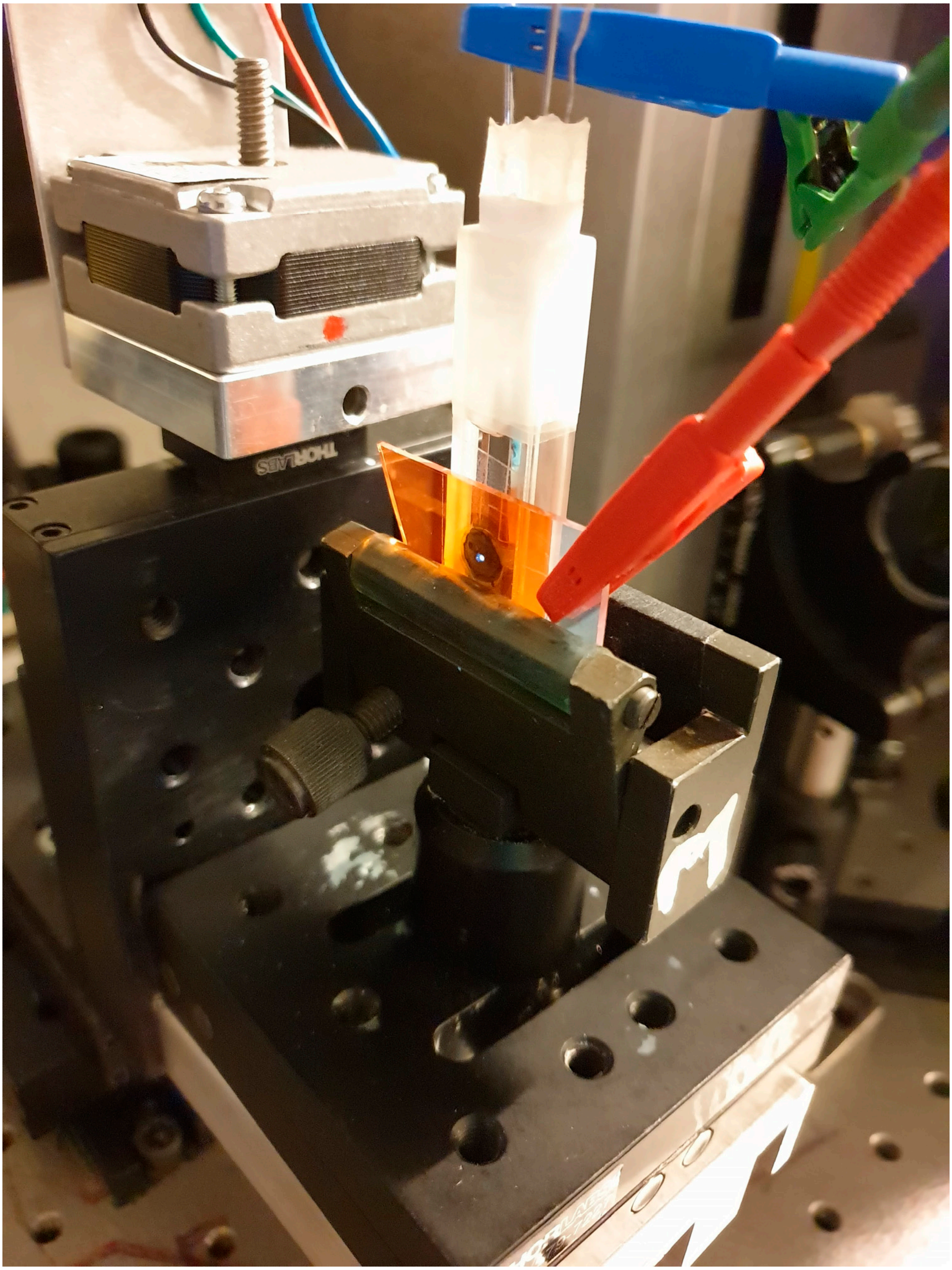


Figure 1-15 : Homemade spectroelectrochemical cell being used for ultrafast laser spectroscopy

One of the main issues of QDs is that during EL measurements it easily gets damaged and will turn into dark/black as you can see in figure 1-16. One reason which is directly related to this situation is the presence of oxygen and water in the solvent or in the QDs film. Therefore, fresh dry solvent, electrolyte and proper drying of the film can affect the experiments.

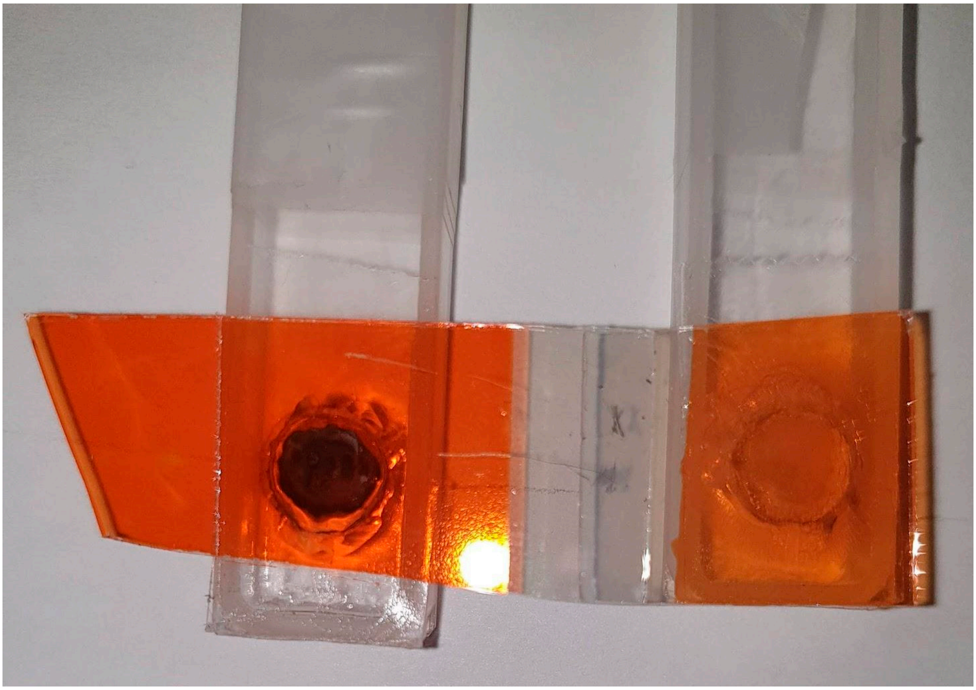


Figure 1-16 : Homemade spectroelectrochemical cell with damaged and undamaged sample

1.2.3 Transient Absorption Spectroscopy

Transient absorption spectroscopy (TA) is the time resolved measurement of the excitation induced absorption changes in matter[20]. In our work the transition to the excited state is induced by ultrafast laser pulses (pump). The absorption changes in time were measured by broad white-light supercontinuum (probe). In the simplest case the absorption changes are an ensemble of ground state bleach, excited state absorption and stimulated emission. For each system it is important to identify these spectral features to be able to interpret data and address different charge carrier mechanisms. In our measurements, the negative signal is ground state bleach, which is depletion of the electrons from the ground state due to excitation by pump pulse. For TA experiments output pulses of SpitfireXP at 796 nm 6mJ 100fs 1KHz were used to generate both pump and probe light. The output of nonlinear optical parametric amplifiers (NOPA) was used as pump and probe. For the generation of broadband white light (350 nm to 1200 nm) as the probe, CaF_2 crystal is used. The data was collected as average of laser pulsed at each delay points as a 2D map, consisting of the evolution of the absorption-spectra-differences in time due to excitation by the pump pulse. Global fitting was used as the main model to fit the experimental data with a multiple number of single exponential decays by using Glotaran software.

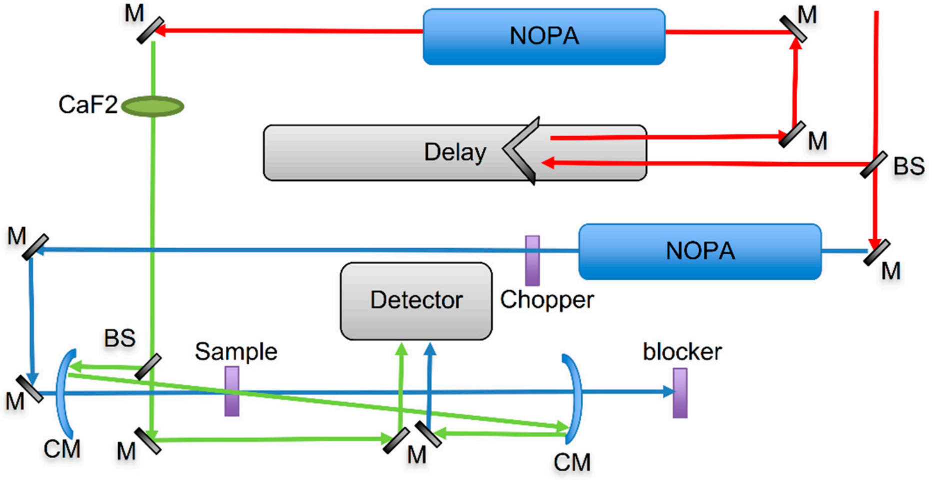


Figure 1-17 : schematic diagram of the transient absorption spectroscopy set up
Incoming laser light split into two beams by a beam splitter (BS), each beam is guided by mirrors (M) to nonlinear optical parametric amplifiers (NOPA), output of one NOPA is used for pump and the other one for generation of white light in a nonlinear optical crystal (CaF_2), white light beam is split into reference and probe which is collected by concave mirrors (CM).

2 Chapter 2: Charge Carrier Dynamics in Novel Solar Materials

For decades, efforts were made to make SCs efficient, cost effective and environmentally friendly. Development of new types of solar energy conversion is accelerated by global demand for energy and public awareness of having clean means of producing energy. The common goal of all scientific light-harvesting activities is to capture solar energy and convert it efficiently to the form of energy that can be used in different ways (electricity or chemical energy). The evolution of photovoltaic SCs can be categorized into four generations:

> 1st. Crystalline silicon based SCs. As initially commercially developed photovoltaic cells, they possessed a large part of the market. But usually, their high production cost and the environmental effect of their fabrication process makes them less favorable for solving the global climate-change issues. Despite all issues, they are largely used since cheaper alternatives are not available yet[58].
>
> 2nd. Inorganic thin-film SCs. Which have great potential for the utility-scale power generation. Since the deposition of thin-film usually requires small amount of materials, cheaper substrates can be used, therefore the energy and consequently the cost for large-scale production are low. But they have less efficiency and suffer photodegradation, so their large-scale commercialization is not achieved yet[58].
>
> 3rd. Solution processable thin film SCs such as dye-sensitized SCs (DSSCs)), organic photovoltaic(OPV), QDs-sensitized SCs (QDSSCs)[59]. This generation is currently under extensive research and development, as emerging alternatives to previous ones to provide higher efficiency at a lower cost because they can be made by solution processable methods[59].
>
> 4th. Known as hybrid SCs such as organic-inorganic SCs and organometal halide perovskite SCs[58].

In this part of the thesis, we study some state-of-the-art materials as promising candidates for SCs applications.

2.1 Dye-Sensitized Solar Cells

Correspond to paper I, II and III

The dye-sensitized solar cells (DSSCs) are considered, as low cost and easy to produce, alternative to the crystalline p-n junction SCs[2,3]. DSSC is actually a photoelectrochemical cell with a working electrode, electrolyte, and counter electrode (platinum is commonly used). Working electrode, consist of a thin mesoporous optically transparent film of a wide band gap n-type semiconductor (typically TiO_2) which is coated with a photo-active complex (known as dye). Since the wide bandgap semiconductor can only absorb a small fraction of solar energy (in the UV region), mainly the dye is responsible for the efficient light absorption and charge injection to TiO_2. Among inorganic and organic dyes, metal complexes containing rare elements such as ruthenium (Ru), Osmium (Os), and Iridium (Ir) have been mainly used in DSSCs[2,3]. Among these complexes, Ru polypyridyl complexes shows broad absorption spectra and long excited state lifetime and also the best efficiency, therefor they have been largely used in DSSCc fabrication. Despite DSSCs were invented as a cost-effective alternative to crystalline SCs but using expensive rare elements such as ruthenium (in dye), platinum (as counter electrode and catalyst) and making conductive glass or plastic (as back contact) remains a major drawback and a challenge for their commercialization. One approach to make DSSCs cost-effective is to develop dyes from inexpensive earth-abundant elements[5,7,8]. Iron as one of the most abundant elements on Earth is one of the promising candidates but simply replacing iron in the trivial existing Ru's molecular structures does not lead to similar functionality. One of the issues in iron-based complexes is that their excited state lifetime is very short (sub picosecond). In the figure 2-1, the difference between excited state energy levels and lifetimes of a typical polypyridyl iron and Ru complex are illustrated.

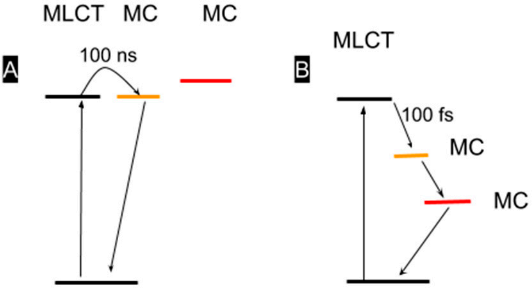


Figure 2-1: Schematic energy levels of a typical Ru- and Fe-polypyridyl complex
Excited state transitions in a typical Ru- (A) and Fe-polypyridyl complex (B) from the MLCT states to MC states usually take place in few hundred nanoseconds while this time scales for iron-based complexes is of the order of 100fs. Adapted from[20]

Therefore, low-lying metal-centered (MC) states are the main reason for short-lived excited-state of these complexes. It is also shown that despite the efficient electron transfer to TiO_2 (with 92% yield), a large amount of energy is lost due to mismatch between energy levels[60]. Among all efforts for making alternative complexes, Wärnmark and his team by using a new ligand design strategy managed to push the energy level of the metal-centered (MC) states higher up. As the consequence, excited state lifetime of the charge transfer state is extended further to 100 ps (paper I)[9]. Electrochemical measurement shows a reversible redox that corresponds to the FeIII/FeII redox couple. Steady state absorption spectra of this iron complex as FeIII and its reduced version (obtained by UV–VIS Spec-EL) as FeII, shows interesting features as represented in figure 2-2. In the UV region, both complexes show similar spectral feature that is related to ligand absorption which is not sensitive to metal oxidation state. In the visible region FeII version shows broad absorption spectra which is an indication of a typical MLCT (/LMCT) states in metal-centered complexes. Interestingly photoexcitation of FeIII led to detectable photoluminescence (PL) at room temperature and PL-excitation spectrum resembles the absorption spectrum of FeIII which provides a proof for its emission. As there were no known emissive iron complexes before, this new iron complex is marked as the first emissive iron complex which in connection with its 100ps lifetime opens up hopes for further development of such complexes for potential photo-active applications[7]. TA measurements also provided valuable information about the transitions of the excited state.

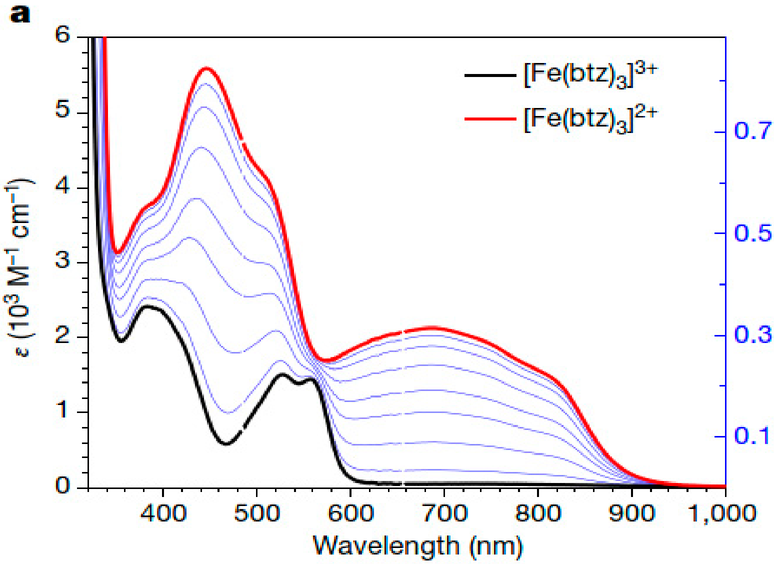


Figure 2-2 : UV-VIS spectroelectrochemical measurements of $[Fe(btz)_3](PF6)_3$ [9]

The TA spectrum consisting of ground-state bleach similar to the absorption spectrum of FeII which further proved that in the excited state charges are being transferred between the ligand and metal. As both excited state and ground-state bleach decay with similar lifetime, it can be interpreted that there are no other transitions involved. Therefore, excited charges remain in the excited state for 100ps. In contrast to FeIII, the FeII version does not efficiently emit photons which indicates that possibly the transition from MLCT state is a forbidden transition. Initially, TA measurement of in-situ generated FeII by Spec-EL, figure 2-3, revealed exceptionally long excited-state lifetime of 528 ps. Successful synthesis, isolation, and crystallization of the FeII complex by chemists, enabled further comparison of this iron complex in its different oxidation states. The 528ps was the longest excited state lifetime reported for any iron-based metal centered complexes at that time (paper II)[10].

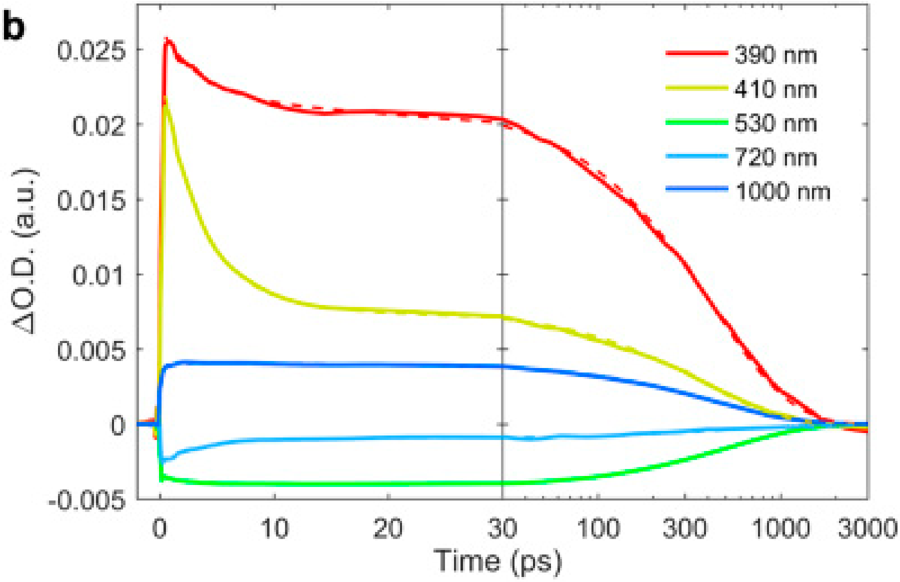


Figure 2-3 : transient absorption decay of [Fe(btz)$_3$](PF6)$_2$ [10]

This result yielded valuable knowledge about how ligand structure can increase the energy of MC states, which enabled further developments of new iron-based complexes by Wärnmark and co-workers. As the result of such developments, a state-of-the-art complex as [FeIII $(phtmeimb)_2]^+$ (phtmeimb = (phenyl[tris (3-methylimidazol-2-ylidene)]borate$)^-$) was synthesized. Interestingly this complex shows two reversible electrochemical redox potentials (paper III)[11]. Which by the help of Spec-EL were attributed to FeIII/FeII and FeIV/FeIII redox reactions. Photo excitation of this complex resulted in very surprising PL with a lifetime of 2 ns. TA of this complex also shows a single exponential decay with nearly 2ns lifetime. Discovery of such iron complexes with nanosecond excited-state lifetime, which is relatively comparable to commonly used dyes in DSSCs, opened up the hope for the potential of iron complexes to replace the rare elements. Application of such complexes may lead to a new era in DSSCs which will be a big step towards the development of environmentally friendly SCs for a better society and a brighter future for humans.

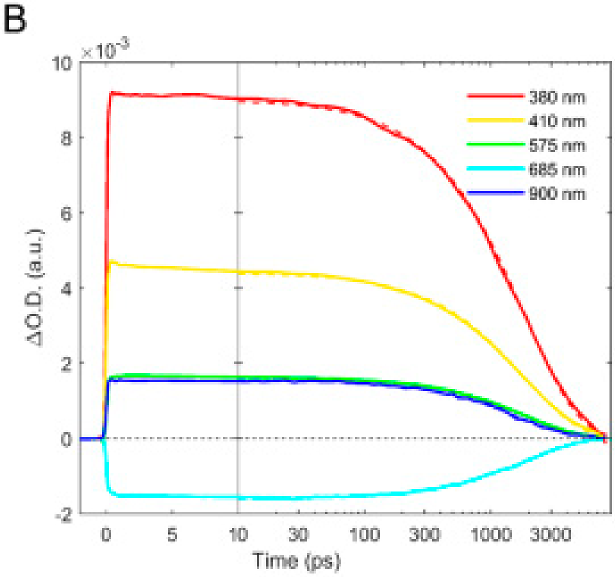


Figure 2-4 : transient absorption decay of [FeIII $(phtmeimb)_2]^+$ [11]

2.2 Organic Photovoltaics

Corresponds to paper IV and V

Organic photovoltaic (OPVs) also have many interesting features such as low cost and flexibility. They can be made by roll-to-roll solution processing on plastic sheets which is a key factor for large-scale cost-effective commercialization. They were first demonstrated by using a single junction copper phthalocyanine and a perylene tetracarboxylic derivative with the power conversion efficiency (PCE) of about 1%[61]. By demonstration of rapid photo induced electron transfer to fullerene (C60), extensive research was done on the fullerene-based devices[13,15]. Despite the good performance of fullerene in bulk heterojunction SCs, it does not absorb visible parts of the spectrum and its electronic structure cannot be tuned. Also, there are restrictions on how a donor polymer could be designed because a large energy offset is required between donor and fullerene acceptor to generate free charges[16,17]. This energy offset is a source of energy loss and also a major limitation for the development of fullerene-based devices[16,17]. Therefore, researchers also explored other possibilities such as non-fullerene acceptor (NFA) based devices[12–15]. The basic advantage of NFA devices is that their electronic structure (for light absorption, energy level alignment and morphology) can be vastly adjusted by designing their molecular structure[12–15]. Accordingly, in contrast to fullerene based OPVs, large energy offset is not necessary in NFA systems. In paper IV, we report the results of our study for a newly developed polymer donor (D) named as PBBF11 (PBBF) and ITIC as NFA[16]. Optical absorption of PBBF and ITIC complement each other, figure 2-5, covering the most range of the visible region. Similar to molecules, energy levels of polymers can be determined by CV. The band alignment of the polymers are also shown in figure 2-5. As it can be seen, very little energy offset exists between D and NFA.

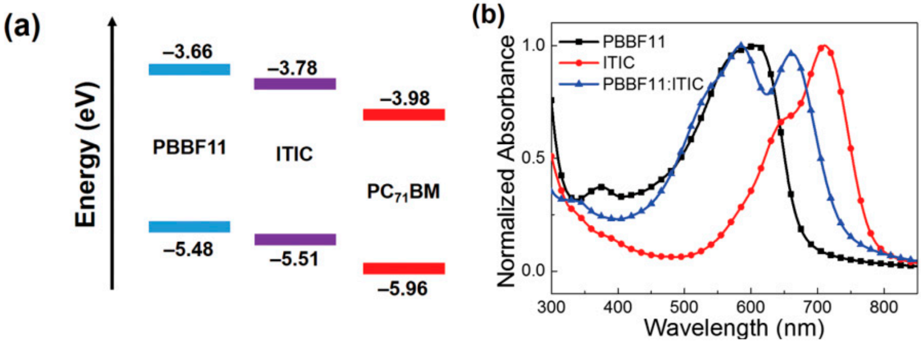


Figure 2-5 : band alignment and steady state absorption spectra of PBBF11, ITIC and PC$_{71}$BM [16]

NFA OPVs with very small energy offset between HOMO levels have recently reached efficiency even higher than initially fullerene based[14]. This higher efficiency suggested to be due to formation of CT state with lower energy loss and better charge carrier dynamic properties[14]. The main question is that if electrons and holes can be transferred between PBBF-ITIC with such very low energy offset of both HOMO and LUMO. Therefore, TA measurement is used to study charge carrier dynamics in the polymer blend. Photoexcitation of only ITIC in the PBBF:ITIC blend led to rapid bleach of the PBBF which is the indication of hole transfer from NFA to D. Further analyses of the kinetics show that hole is transferred within 1ps (figure 2-6). This rapid hole transfer between this D-NFA with very low band offset was expected considering that ITIC has relatively good charge carrier characteristics compared to other NFA materials. In contrast photo excitation of both D-NFA can yields information about both hole and electron transfer to ITIC. Therefore, electron transfer dynamics can be extracted by subtraction of this dynamics from ones obtained from excitation of ITIC only. Electron transfer dynamics in figure 2-6, shows a rapid raise and a slower component. The fast process, 0.2ps, can be the electron transfer by an efficient charge transfer (CT) state and slower one corresponds to the diffusion of electrons away from the interface which is happening within 11ps. It is known that in organic semiconductors, large exciton binding energy led to the formation and dissociation of the CT state[62]. Eventually photo generated charges recombine withing 3ns lifetime which is long enough for efficient charge extraction. Comparing the TA dynamics of each polymer with their blend, figure 2-6, shows that charges are recombining relatively faster, this is believed to be due to the structure of the polymers in the blend. From the x-ray and TEM studies, it is known that the PBBF and ITIC in the blend mix very well together and AFM also revealed homogeneous film morphology caused by this good miscibility. This was suspected to be the cause of faster charge recombination at interfaces. Therefore, $PC_{71}BM$ (PCBM) as additional electron acceptor was added into the PBBF:ITIC system as the third component to modulate film structure and also to improve charge transport.

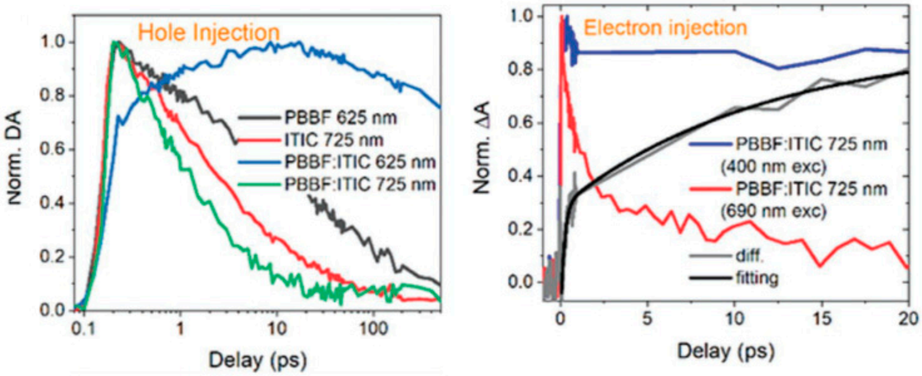


Figure 2-6 : transient absorption decay of PBBF:ITIC [16]

TA results for the various concentrations of PCBM, reflects the possible optimal concentration of PCBM as the one with longer lifetime. Excess of PCBM seems to facilitate charge recombination. From photovoltaic performances the PBBF:ITIC:PCBM (1:1:0.3, wt%) device also delivered higher PCE of 11.4% while for the binary blend it accounts only up to 9.9%. Considering the results of TEM and AFM for the ternary blend it is eventually suggested that PCBM, at its optimal concentration, disperse at the interfaces of PBBF and ITIC which enhance the electron transfer and reduce the recombination at interfaces (paper IV).

As we saw in paper IV, in NFA-based OPVs, rapid electron and hole transfer is feasible despite having very low energy offset between both HOMO and LUMO energy levels. In contrast in paper V, we report the results of our study for a donor polymer, PTO2, and a NFA called IT-4F, with very large band offset which shows PCE of 14.6%[17]. The band alignment of these polymers are shown in figure 2-7 A. In NFA OPVs with low band offset, it is reported that the energy level of the CT state is close or identical to their first excited state which results in efficient charge transfer and lower voltage loss in such systems[63]. Measurements for the energy level of CT state in PTO2:IT-4F interestingly revealed no offset between their excited state and CT, figure 2-7 B. This indicates lower energy losses for PTO2:IT-4F blend compared to PTO2:PCBM (paper V).

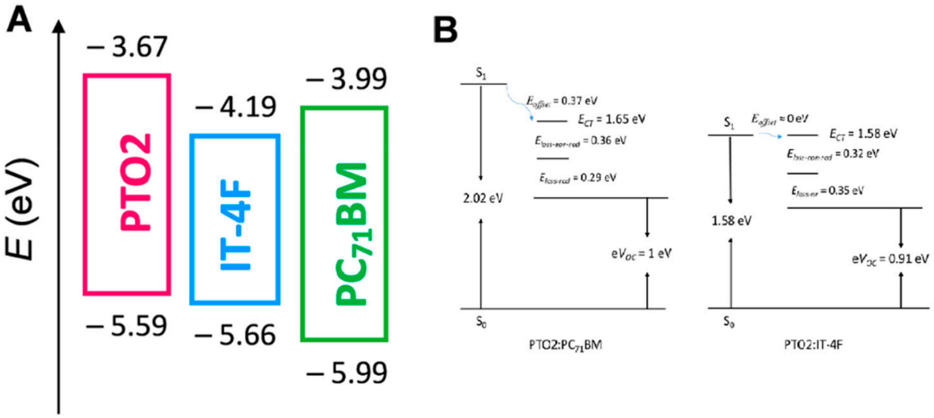


Figure 2-7 : band alignment of PTO2, IT-4F and $PC_{71}BM$ with the energy level diagram for PTO2:$PC_{71}BM$ blend compared to PTO2:IT-4F [17]

TA measurement of each polymer and their blends, as PTO2:IT-4F and PTO2:PCBM, is used to draw conclusions about charge carrier dynamics. For better comparison TA kinetics are shown in figure 2-8. Photoexcitation of only PTO2 and IT-4F shows relatively short-lived excited state in the range of 350 and 70 ps respectively. In contrast their blend shows completely different dynamics. At early times, there is a very fast decay for both blends. This fast decay can be expected since electrons in the excited donor should efficiently transfer to CT state due to it relatively zero band offset. On longer times, there is a significant difference between the kinetics of PTO2:IT-4F and PTO2:PCBM. The PTO2:IT-4F shows longer lifetime and interestingly a raise which appears from 10ps. This raise has been reported in earlier works where it is interpreted as a separation of electron-hole pairs[64,65]. Therefore more charges in PTO2:IT-4F can be harvested compared to PTO2:PCBM. The photovoltaic performance of PTO2:IT-4F and PTO2:PCBM also reflect similar trend. The best performance is obtained for PTO2:IT-4F devices with a PCE of 14.7% and V_{OC} of 0.91 V while PTO2:PCBM device yield PCE up to 5.0% with a V_{OC} of 1.0 V (paper V). As we can see the measured V_{OC} is equal to what was estimated from CT state energy level and other energy losses(paper V). Therefore, CT state and its energy offset in OPVs is a major factor which have direct influence on the efficiency and performance of devices.

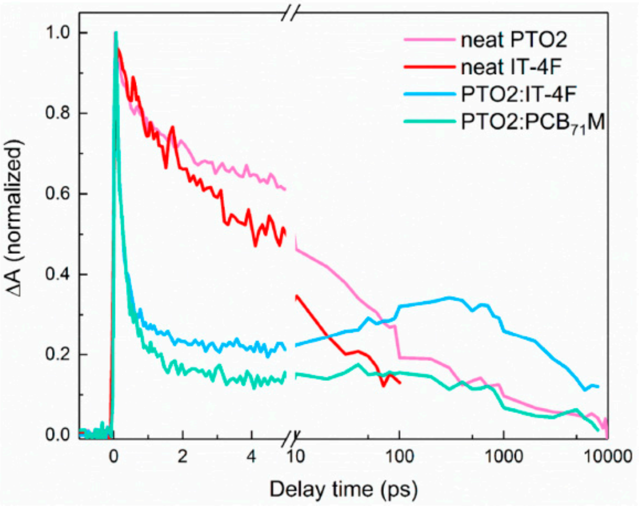


Figure 2-8 : transient absorption decay of PTO2:PC$_{71}$BM blend and PTO2:IT-4F, compared to neat PTO2 and neat IT-4F [17]

2.3 Lead Halide Perovskites

Corresponds to paper VI, VII and VIII

The other competitor of the cheap and easy to make SCs are perovskites. These materials are a very promising for solution-processable thin-film light-harvesting applications. The most important properties of these materials are the low exciton binding energy, long charge diffusion length and high carrier mobilities as high as 25 cm^2/ (V s) which is three orders of magnitude larger than the mobilities in OPVs[66]. These properties are ideal for photo-induced charges to efficiently reach the electrode interfaces with minimal loss. Since the initially developed SCs based on lead halide perovskites contained toxic elements such as lead (Pb), their commercialization was inhibited due to environmental and health risk of such materials. Significant research effort is devoted to developing environmentally friendly alternatives by totally or partially replacing Pb[18,21]. So far, simply replacing Pb with other elements has not been successful. For example, despite the complete replacement of Pb can be achieved by Sn, but oxidization of Sn largely affects the stability and performance of the devices[67,68]. In paper VI, we show the results of our studies for development of a two-dimensional (2D) Ruddlesden−Popper perovskite, where Pb is partially replaced by Sn as $(BA)_2(MA)_3Pb_{4-x}Sn_xI_{13}$ [23]. These 2D perovskites are known for their good stability, where the organic spacing cations can prevent material degradation by water and oxygen[69,70]. We engineered the Pb:Sn ratio X (4:0, 3:1, 2:2, 1:3, 0:4) to find the best device performance. Absorption spectra of these samples in figure 2-9, shows spectral shift to lower energies with the increase in Sn ratio. The optical bandgap for these samples is estimated as 2.09, 2.01, 1.79, 1.77, and 1.67 eV respectively (for X=4:0, 3:1, 2:2, 1:3, 0:4).

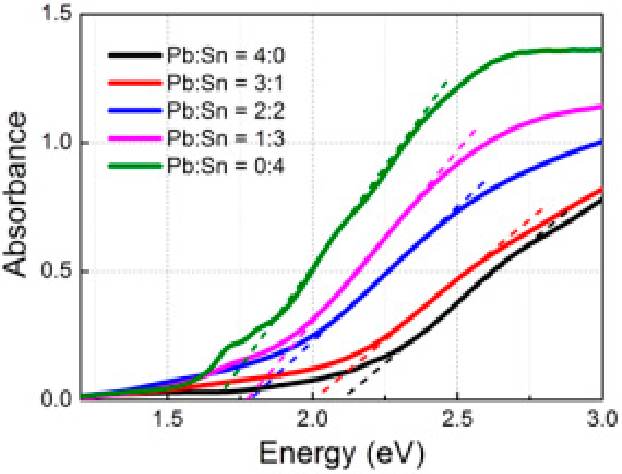


Figure 2-9 : steady state absorption spectra of $(BA)_2(MA)_3Pb_{4-x}Sn_xI_{13}$ for Pb to Sn ratio X (4:0, 3:1, 2:2, 1:3, 0:4)[23]

It is known that addition of Sn increases the ratio of crystal formation between Sn-I_2 and Sn-MA[71,72]. SEM images of these samples confirm the formation of pinholes in the films as the ratio of the Sn increase. Similarly, photovoltaic characterization demonstrates the optimal Pb:Sn ratio to be 3:1. We performed the charge carrier dynamics study by TA measurement to understand the underlying mechanism. TA measurement results are shown in figure 2-10. The TA spectra consist of ground-state bleach which its position is changing by Sn ration similar to the steady-state absorption. But the spectra of GSB is broader when the Sn ration is smaller. It is known that the 2D perovskite films, consist of a mixture of multiple perovskite phases, with n =1, 2, 3, 4 and ≈ ∞, that naturally align in the order of n along the direction perpendicular to the substrate[73]. The number n corresponds to the formation of quantum wells with different thicknesses of the inorganic layer. Analysis of the TA data shows that by increasing of Sn ratio, the charge carrier lifetime is significantly shortened, while there exists an exception for Pb:Sn ratio 3:1. In this case, the longest charge carrier lifetime of 12 ns is obtained. From PL measurements it can also be seen that the sample with Pb:Sn ratio of 3:1, has longest lifetime of 12 ns. These results indicate suppressed charge carrier trapping or recombination in this sample (Pb:Sn ratio of 3:1).

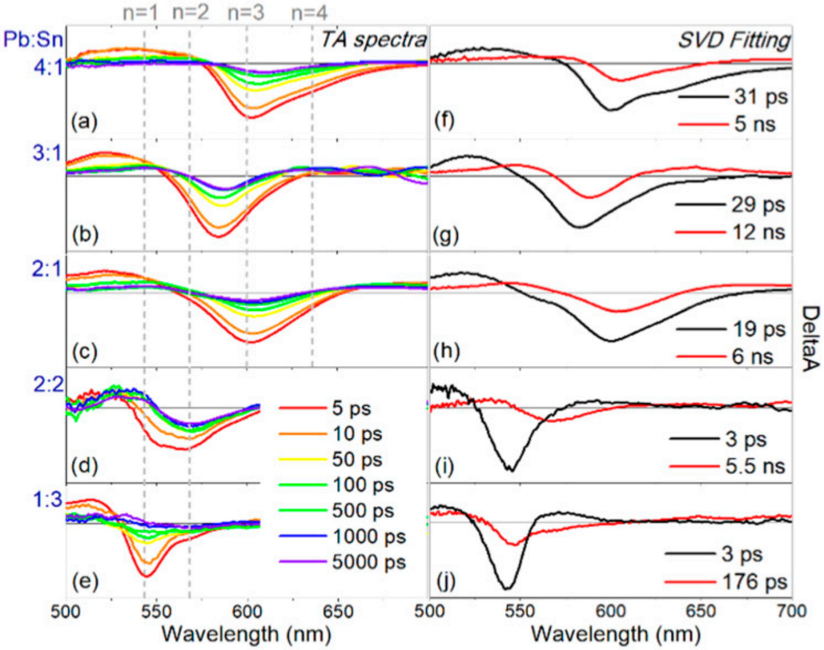


Figure 2-10 : transient absorption spectra evolution for different delay times (left) and SVD fitting (right) of $(BA)_2(MA)_3Pb_{4-x}Sn_xI_{13}$ for Pb to Sn ratio X (4:0, 3:1, 2:2, 1:3, 0:4)[23]

This behavior can be related to the improved structure of the film which can be seen from SEM characterization, where smooth thin films with high surface coverage is formed for Pb/Sn ratio of 3:1. This can be related to the self-assembly characteristic of hybrid 2D perovskites during the crystallization[73]. We also performed the stability test of the devices in nitrogen atmosphere, under constant illumination. The results also revealed the best stability for the sample with Pb:Sn ratio of 3:1, which shows only 10% degradation on its PCE after 400 hours (paper VI).

It is worth mentioning that the stability of perovskite-based solar-cells has significantly improved compared to early demonstrations, which were only able to work up to a few minutes. A large number of efforts are devoted to increasing the stability of perovskite materials for optoelectronic applications. However, in general lead halide perovskites usually suffer from poor stability. This is in particular vital when perovskites are formed in nanostructures. Because with higher surface their reactivity and degradation are accelerated. In paper VII, we studied the photostability of $CsPbI_3$ QDs[24]. Cesium lead halide perovskites, CsPbX3, (X = I, Br, Cl) have shown the highest PCE up to 13% among all QDs SCs[74]. However, cubic phase of the $CsPbI_3$, which shows the best-performing solar-cells, is not stable at room temperature[75,76]. Making $CsPbI_3$ into QD passivated with a surface ligand may effectively prevent its phase transition but previous studies found that light illumination is responsible for such degradation in $CsPbBr_3$ QDs[77]. In our studies for $CsPbI_3$ QDs, interestingly optical absorption and x-ray characterization does not show any noticeable changes[24]. In contrast, PL spectra and its lifetime is changed significantly. TA measurements also yield similar results as PL. TA measurements for fresh and degraded samples, shown in figure 2-12. From TA spectral analysis, GSB can be seen for both samples, while the photoinduced charge carrier's lifetime is significantly different for each sample. The faster decay component with a lifetime of a few 100ps indicates biexciton recombination and hot electron relaxation. The longer-lived transitions can be assigned to trap states and recombination of free charges.

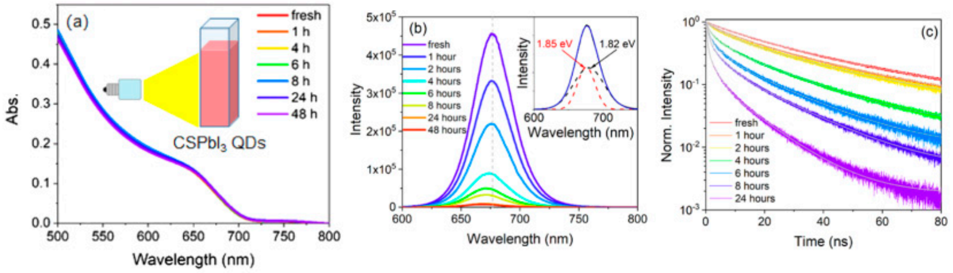


Figure 2-11 : Steady state absorption, photoluminescent intensity and lifetime for $CsPbI_3$ QDs under illumination for 1, 4, 6, 8, 24, 48 hours [24]

In order to understand what is happening during sample degradation, TEM characterization is performed. Surprisingly TEM images revealed gradual conformal changes of QD shape while their average size is preserved (paper VII)[24]. As it can be seen immediately from TEM images, as a result of degradation the shape of the QDs change from cubic to spherical. Analysis of the TEM images shows that the spacing between crystal planes remains intact which explains why XRD results look similar for all samples. This further indicates the light-induced removal of the surface passivating ligand which has been already observed[77].

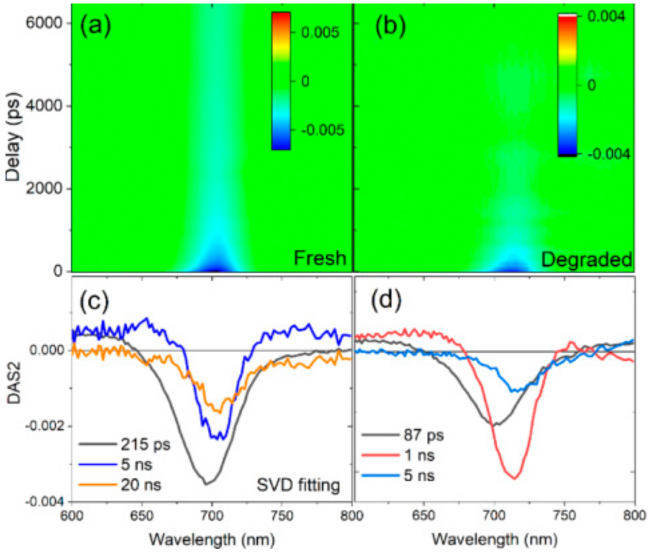


Figure 2-12 : transient absorption measurement for $CsPbI_3$ QDs fresh and after 48 hours light illumination [24]

As we observed lead halide perovskites in general have issues for long-term chemical instability in ambient conditions in the presence of air, humidity, and specifically under light illumination. It has been shown that two dimensional (2D) Ruddlesden–Popper (RP) perovskites have interestingly long-term stability[78,79]. But their power conversion efficiency is limited by the structure of the perovskite film[80]. As we also presented in our studies in Paper VI, 2D RP perovskites form different phases parallel to the surface of the substrate[23,73]. Such hybrid structures are not favorable for efficient charge extraction since the photo-generated charges cannot travel across the long spacing cations and to be collected by the electrodes[79]. One possible solution is to introduce 3D structure into the 2D inorganic lattices to efficiently collect the photo-generated charges[78]. This has been proven to be an effective approach in enhancing the performance of the devices[25]. In paper VIII, we report the results of our study for a novel approach where 2D:3D bulk-heterojunction structures are spontaneously generated by synthesis at room temperature[27]. In this new method we observed that 3D phases are inherently interconnected with 2D lattices by an organic spacer. This method can suppress the issues which have been observed with similar approaches[25,81,82]. Two different organic spacers were sued, named as TEA and as PEA for preparing two different samples as $(TEA)_2MA_3Pb_4I_{13}$ and $(PEA)_2MA_3Pb_4I_{13}$ respectively. The crystal structure and formation of different phases in each sample studied by XRD. Optical absorption of the samples in figure 2-13 B, shows that samples contain a mixture of 2D phases ($n \leq 4$), quasi-2D phases ($n = 5-20$), and 3D phases ($n > 20$). PL emission and XPS further confirm homogeneous phase distribution in TEA sample while in PEA sample only pure 2D or quasi 2D phases are present. We also observed in our previous work (paper VI) that in TA spectra, different phases give different spectral features which can further indicates the difference between phase composition of PEA and TEA samples[23]. TA results are illustrated in figure 2-14. Following the laser excitation, GSB of different phases can be clearly observed in TA spectra which for TEA sample corresponds to several 2D phases with n=2 (at 560 nm), 3 (610 nm), 4 (640 nm), and 3D (750 nm). On the contrary there exist only a 2D phase and quasi-2D (650−700 nm) in the TA spectra of PEA sample. To identify the charge carrier dynamics in TEA sample and how charges being transferred from 2D phases to 3D phase, singular value decomposition (SVD) of the TA measurements were used.

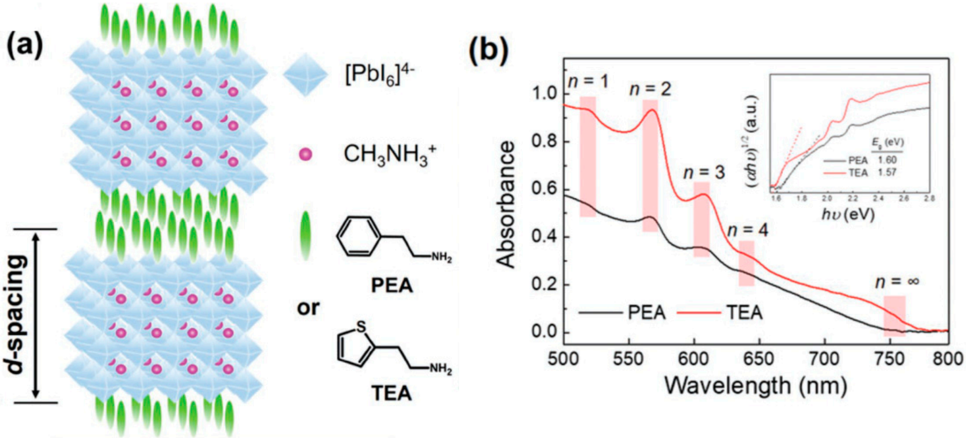


Figure 2-13 : Schematic structure of $(TEA)_2MA_3Pb_4I_{13}$ and $(PEA)_2MA_3Pb_4I_{13}$ and their absorption spectra [23]

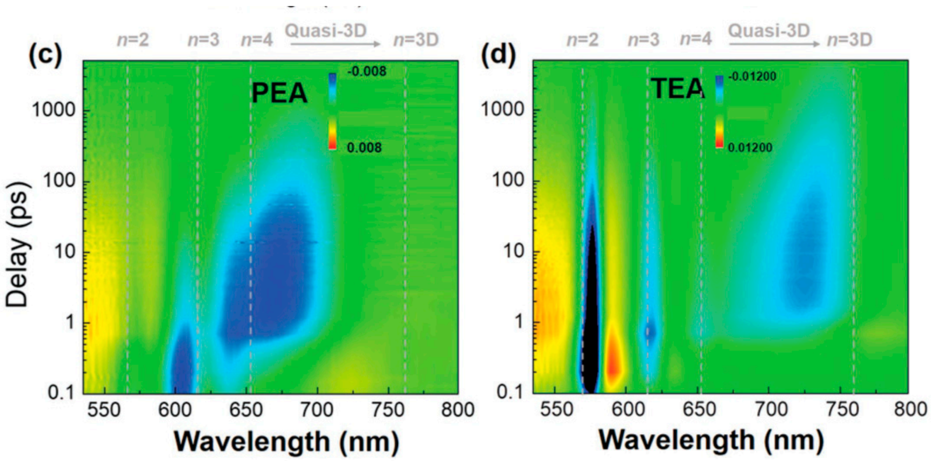


Figure 2-14 : transient absorption measurements for PEA and TEA samples [23]

The results of TA measurements for TEA are illustrated in figure 2-15. TA kinetics for TEA samples can be fitted with two exponential components. The faster decay lifetime corresponds to the relaxation of photo-induced hot carriers and their transfer to the 3D phase. This is followed by a long-lived transition, which is in good agreement with the results of PL decay lifetime. In SVD of TEA sample as indicated earlier, GSB of different phases with n=2,3 and 4 is clearly visible. In the SVD of the fast component for TEA sample, there is a pronounced band from 650 to 750nm. This can be the indication of exciton dissociation at the boundary of the 2D phases or a CT state that contributes to electron transfer at the interfaces. For the long-lived component in the ns range for all samples, a distinct peak observed at 750nm which is very well in agreement with the time-resolved PL lifetimes. According to previous studies of PEA, this is due to the fast nonradiative recombination which is induced by defects or impurities or interphase charge transfer[83]. However, the overall conclusion is that the charge carrier lifetime is significantly improved by the incorporation of 3D phases in TEA sample. Photovoltaic characterization of the TEA PSC shows up to 7.2% PCE which is remarkably high efficiency among other counterparts[69,84]. Previous studies on PEA suggested that crystallinity and crystal orientation in room-temperature fabricated 2D RP perovskites can be further enhanced if they are treated by NH_4Cl and DMSO[83,85].Very importantly NH_4Cl is known to reduce trap/defect states. Similarly, TA studies of NH_4Cl treated TEA (TEA-N in figure 2-15) shows exceptionally long-lived charge recombination which is a clear indication of reduced trap states. While the faster component has increased three times, from 71ps in neat TEA to 250ps in TEA-N. This is in agreement with reported results for NH_4Cl treated samples[83,85]. In contrast DMSO is known to improve the orientation of perovskites and optimize the interfaces. Therefore, DMSO is believed to enhance the inter-phase charge transfer from 2D phase to 3D phase[83,85]. From TA data we can see that DMSO treated TEA (TEA-D figure 2-15), has similar fast component of 70ps as neat film, but the free charge recombination is enhanced compared to neat TEA. The co-treated samples (TEA-D-N in figure 2-15) in TA measurement show a combination of both properties, reduced trap densities and long-lived free charge carriers, with the lifetimes which is interestingly an average of both TEA-N and TEA-D. Therefore, we can interpret that in the co-treated sample, these two competitive processes are in balance. Photovoltaic characterization also proves this concept as the co-treated device result in the best device performance with the PEC of 11.2%. The stability test of the PSCs shows exceptional long stability in ambient conditions.

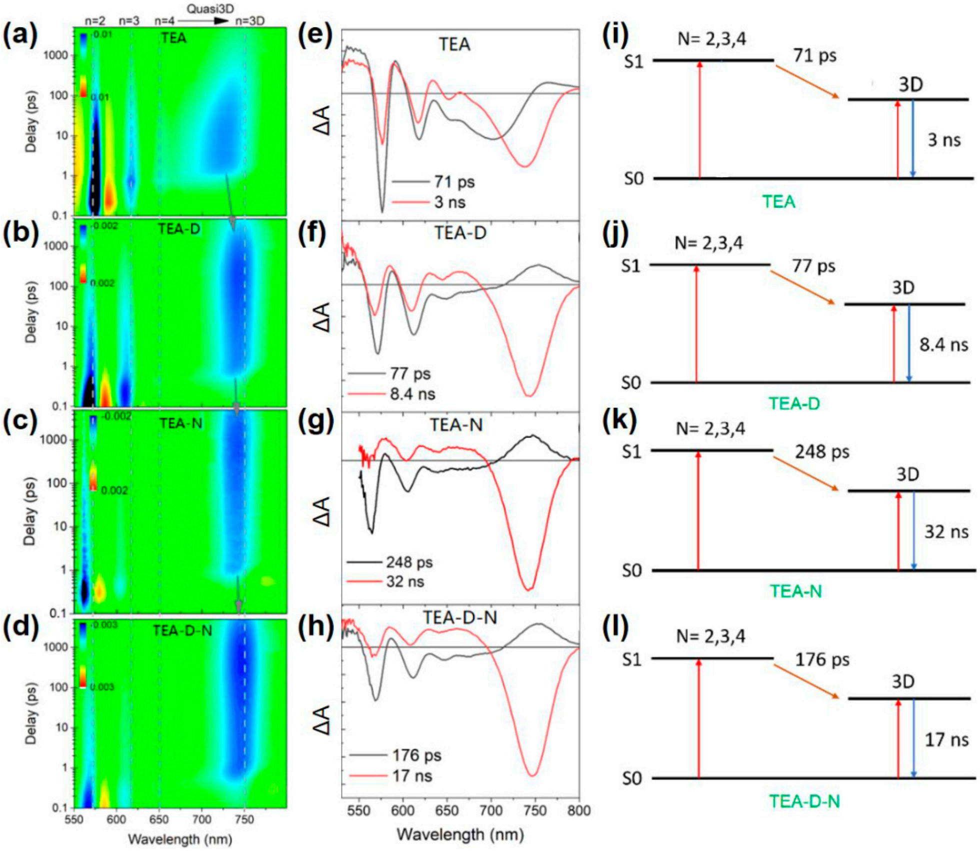


Figure 2-15 : transient absorption measurements for TEA and TEA samples treated with NH_4Cl (TEA-N), treated by DMSO (TEA-D), and treated by both NH_4Cl and DMSO (TEA-D-N) [23]

3 Chapter 3: Ultrafast Spectroelectrochemistry

Corresponds to paper IX and X

As addressed in introduction, semiconductors and their nano structures have been widely investigated and used both as model systems for fundamental research and for many state-of-the-art multidisciplinary applications. They are also the building blocks of almost all types of light-harvesting devices[28,29,58,59]. Therefore, it is important to understand and decipher their underlying photophysical properties. In our earlier studies we observed that in SCs, energy levels and band alignment play an important role for efficient light-harvesting. In DSSCs we observed that manipulation of oxidation-state of iron complexes caused a completely different charge carrier dynamics[9,10]. In OPVs formation of CT state and in perovskites charge accumulation due to imperfect boundaries affect the performance of the devices[17,27,63,80]. But among many non-answered questions, one is how charge accumulation at interfaces may affect the performance of the devices. Our aim is to very specifically investigate how the photo-physics of QDs, as promising emerging photosensitizer, can change under influence of charge accumulation at interfaces. The charges can accumulate at the interfaces due to defects, traps or Schottky barrier formation. This charge accumulation itself is believed to be a source of energy loss in QD-LEDs[30,31]. As explained in introduction, application of EL bias can resemble charge accumulation at interfaces and at higher potentials (energies) it can also led to negative or positive charging of QDs. By using controlled changes of charges at interfaces (provided by EL), we want to know if such charge accumulation at interfaces can affect charge extraction from QDs in QDSSC's photoanodes. Also, in special cases, if the bias can lead to negative or positive charging of QDs (which may occur during device operation), and how photo excitation of such charged QDs affect charge extraction. To achieve this, we used the combination of Spec-EL for direct-controlled manipulation of charges at interfaces (in QDs too) and ultrafast pump-probe spectroscopy measurements to directly probe the charge carrier's dynamics with fs time resolutions. This combination, as ultrafast Spec-EL can enable study of samples (in this case QDs) with working conditions similar to real optoelectronic applications. The results can be used to find if such manipulation can affect charge recombination or extraction and if trion decay in QDs can induce major differences.

We strive very specifically to study positive trion decay. The unique advantage of Spec-EL measurement is that charging of QDs between positive and negative can be reversibly achieved in the same sample and accordingly positive and negative trion dynamics can be measured with exact experimental conditions. This method as a universal tool can also be implemented for studies of the semiconductors, as well as quantum confined systems like atomically thin materials and nanostructures.

Similar to definition of exciton as photo-generated electron-hole (e-h) pair, biexciton refers to two excitons. Nonradiative negative (positive) trion refers to a three-body interacting system consisting of a combination of an e-h pair and an electron (hole), where energy of the e-h recombination simultaneously promotes further excitation of the other electron (hole), illustrated in figure 3-1. Trion is exclusively important because in general it is one of the main energy loss pathways in electro-optical applications of semiconductors. Trion decay as a special type of Auger recombination is a dominant energy loss in charged QDs. Trion decay leads to very fast depopulation of the excited states, undermining the efficiency of the devices. Trion was hypothesized in 1958 and later was experimentally observed in semiconductor quantum wells[86,87]. In 1996 trion decay was also observed in QDs which was explained as photo-induced Auger process[88,89]. Since then, trion decay and Auger process has been observed in various structures and devices.

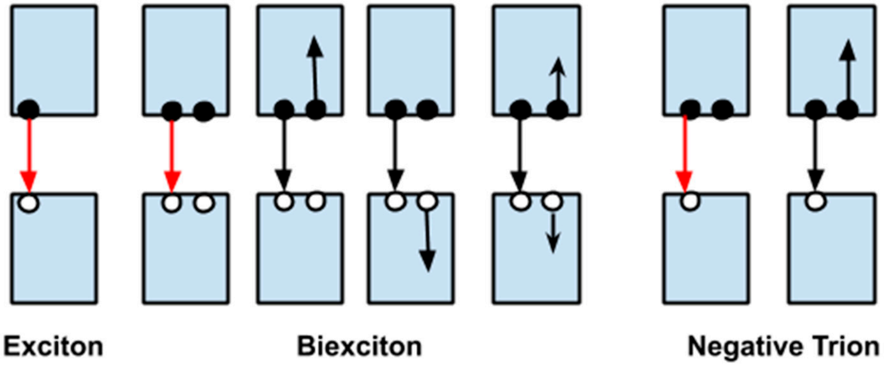


Figure 3-1 : schematic illustration of exciton, biexciton and negative trion decay
Red arrows indicate radiative recombination, black arrows indicate nonradiative recombination.

Despite of recent achievements, measurement of trion decay in QDs with controlled charging (i.e., direct controlled manipulation of charges in QDs as we propose in this thesis) is still not achieved[34,36,38,40,90]. In all recent studies time-resolved photoluminescence spectroscopy (PL) is mainly used which can only measure radiative recombination with ps time resolution, therefore nonradiative processes that usually occur in ultrafast time scales were not studied. In addition, the employed photo/chemical doping(or charging) methods[91], provides only indirect charging, which has various issues since it is not reversible[90]. It is not also reliably controllable[90]. While Auger recombination is commonly considered as an energy loss mechanism, a recent study suggests that it can be harnessed for efficient charge extraction[35]. This is very important for especially SCs and catalysis, but suggested modification method by doping QDs with donor/acceptor elements, is a fundamental material science challenge and have unexpected effects too which are not really understood yet[92]. More importantly the trion is solely studied in core/shell heterojunction structures with a very thick shell to avoid degradation of the QDs. Using core-shell structure do not lead to correct information about electron dynamics in the core material, since core and shell are actively interacting, and part of the charges will be lost by emission from the shell. Certainly, core-shell structure leads to enhancement of stability and performance of the core QDs, it also eliminates surface trap states[93]. But a recent study shows that shell thickness and its structure have a direct effect on the Auger recombination such that it can be inhibited or promoted[38]. Therefore, without knowing exactly how the core behaves, adding a shell can make experimental results twofold blind. In some studies, trion formation is achieved by intense laser excitation which also makes it difficult to quantify the actual charged state of the QDs[94]. As such, more studies are required. For our studies 3nm CdSe QDs are used as photosensitizer. CdSe were chosen as model system since their charge carrier dynamics are well studied and well known.

3.1 Synthesis and Sample Preparation

For many researchers QDs synthesis and sample preparation sound very trivial and may not be very important. However, for successful studies this is the foundation and of great importance to reach the desired results. Preparing high quality sample and finding a reliable preparation method is the art of material science and chemistry. Evaluating the synthesis-repeatability for high-quality QDs is a must for a successful measurement. The field of QDs synthesis is already well established and there exist a huge variety of synthesis approaches to make QDs[28]. But importantly one should look into having good control of the synthesis reaction and its reproducibility. Most aqueous based synthesis methods can be done at room-temperature but requires more work-out and good control over pH. In contrast, hot injection as a simple method is a versatile route to make various QDs. This method itself has a wide variety of routines too. Among hot injection methods finding a very good method can be also very hard since each method has its pros and cons. But in general, one has to find it by trial and error. Through our experience we found two methods the most reliable and reproducible. One of the methods efficiently yield certain size with narrower size distribution (used in our publications)[37]. The other method is very reliable and has extreme control over the synthesis and QDs size[95].

Figure 3-2 : CdSe QDs samples prepared with different sizes

Purification of the sample is also important since presence of impurities can adversely affect the EL and spectroscopy results. For confirming the purification process ^{1}H NMR can be used to confirm the presence of excess ligand or other organic impurities[96]. The synthesized CdSe QDs should also be characterized to ensure the quality, size distribution and shape of the nanoparticles. The absorption and emission spectrum are a god immediate check to be done. A very distinctive exciton peak is a good sign, and the width of the photoluminescence can indicate the size distribution. Usually, electron microscopy is the best to confirm the nanocrystals shape and the size distribution. The size distribution of the QDs has a significant effect on both EL and charge carrier dynamics[52]. To mimic the photo-anode of the QDSSCs, TiO_2 coated FTO-glass is used as working electrode. The FTO slides were coated with TiO_2 paste by using doctor blade and annealing. One should consider that annealing of the TiO_2 can have significant effect on electrode properties too. CdSe QDs are sensitized on TiO_2 by soaking TiO_2 coated FTO slides in a MPA capped QD's solution with basic pH (>10), then washed with distilled water and heated to 100°C under low air pressure to enforce water extraction. QDs films, which together with TiO_2-FTO, replicates the QDSSC's photoanode illustrated in figure 3-3. QDs films were stored in a desiccator over drying agents to make sure it will be dry by the time of the experiments. The volume of the desiccator was be filled with Ar to reduce presence of oxygen. Films were kept in the dark, since photo degradation may degrade samples[97].

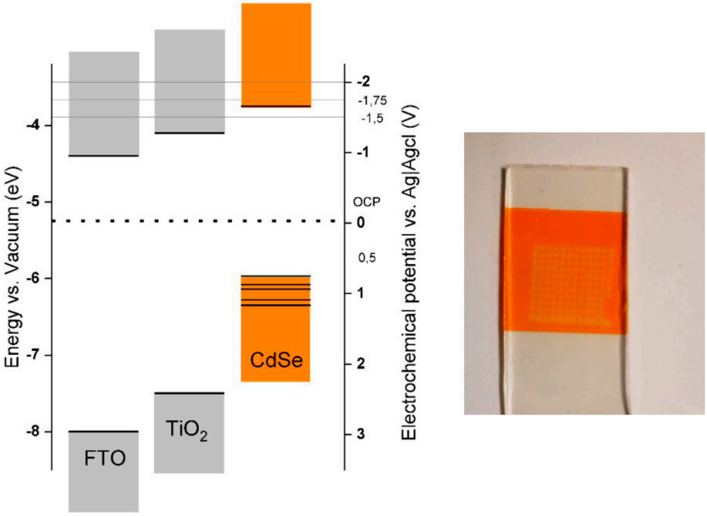


Figure 3-3: schematic illustration of energy levels alignment for FTO, TiO$_2$ [37] and CdSe QDs and photograph of a CdSe sensitized TiO$_2$ coated FTO

3.2 Electrochemical Measurement

Cyclic voltammetry (CV) is a versatile technique that provides information about energies of the redox reactions in molecules. In case of semiconducting materials, CV experiments can give information on the relative energies of the valence and conduction bands of semiconductors[52]. In general, samples for EL measurements can be used as dissolved in solution or deposited as thin film on the electrode surface. The main drawback of experiments in solutions is that usually the signal is too low specially for QDs due to low solubility in polar solvents. The sensitivity issue may overcome by using differential pulse voltammetry, which suppresses the background signal and enhances the sensitivity. But diffusion and migration of QDs away from the electrode surface also makes it impractical to be successfully integrated with spectroscopy measurements. Deposition of the QDs on the electrode surface has the advantage of providing larger electrochemical signal and also facilitating integration with spectroscopy measurements. Therefore, it is not surprising that a large fraction of the studies dealing with the electrochemical properties of QDs have been carried out on films. Thin films are probably very useful approach for studies of solar materials too. In the context of QD characterization, a unique feature of electrochemical methods is that it mainly interact with the surface of the material, therefore in studies it can provide information about surface defects[98–100]. Spectroscopic measurements can be independently integrated with EL to probe the processes that take place between energy levels of the QDs. The electrochemical band gap (ΔE_{el}) is the difference in energy between the first reduction and first oxidation of the QDs. ΔE_{el} can be determined from voltametric experiments while the optical band gap (ΔE_{op}) can be measured from spectroscopic data. Electrochemical measurements can thus be related to spectroscopic observations by the relation,

$$\Delta E_{op} = \Delta E_{el} - \Delta J_{e\text{-}h} \qquad (3).$$

$\Delta J_{e\text{-}h}$ is the exciton binding energy which is the energy that is required to split an exciton into fee charges. Therefore, electrochemical energy gap is expected to be slightly larger than the optical energy gap.

In our studies a conventional three electrode system was used. TiO_2-coated-FTO glass served as working electrode, Pt wire as counter electrode and leak less Ag/AgCl electrode as pseudo reference electrode. The electrochemical cell was our homemade cell as represented in chapter1. In figure 3-4, CV of CdSe QDs on glassy carbon electrode is shown. Since the applied potential is measured against the reference electrode and Ag/AgCl electrode potential is less sensitive to applied bias therefore it is considered to be a fixed potential. Accordingly, in electrochemical measurements application of negative bias corresponds to increase in the Fermi level of the working electrode. In contrast, the positive potential is expected to decrease the Fermi level. If the Fermi level is shifted such that electrons in the electrode has enough energy to be transferred to an electro-active species, a current change can be detected. In measurement of the QDs, as we are dealing with semiconducting materials, the energy levels correspond to those in the conduction (CB) and valence bands (VB). Thus, if the Fermi level of the working electrode is raised so high that it reaches an available energy level in CB or VB, electrons can be injected into that QD's energy level, this also induce a current change in the EL measurement. Therefore, in the CV of the QDs, one can identify the position of the CB and VB in the negative and positive region, respectively. While EL of QDs is an already established and frequently used method still sometimes it is very difficult to identify the reactions and produced species as the result of the EL measurements. Therefore, EL measurements are usually combined with other techniques to better identify the reactions. In our studies we are interested to see if the injected electrons by EL can be verified and how they influence the QDs optical properties. Therefore, while EL is providing controlled charging of the QDs, optical spectroscopy, as independent tool, can simultaneously monitor/confirm induced changes in the QDs.

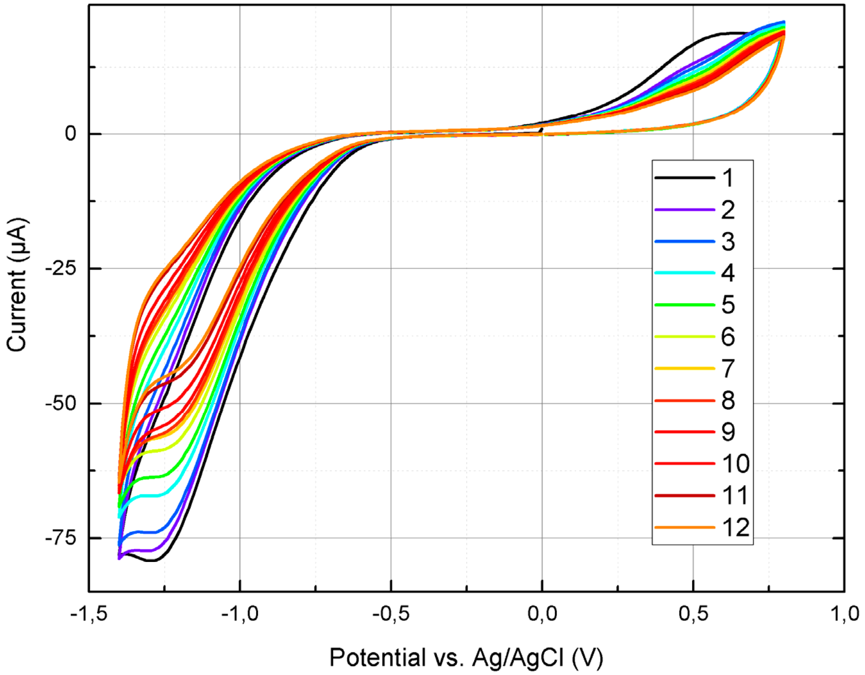


Figure 3-4: CV of CdSe QDs on glassy carbon electrode for multiple scans
CdSe Qds deposited as a thin film on glassy carbon working electrode, Pt wire is used as counter electrode. Measurements are done with tetrabutylammonium hexafluorophosphate in acetonitrile as supporting electrolyte. Measurement is performed for multiple times with scan rate 10mV/s

3.3 Spectroelectrochemistry

Merging EL techniques with spectroscopic methods is known as Spec-EL. In our studies to confirm the electron transfer to the QDs and how its optical property will be changed, steady-state absorption spectroscopy was performed in real time simultaneously during EL measurements. Fundamentally there is a difference between the electron created by light and the electrochemically injected electron. But in both cases the presence of charges in the QDs will induce state filling effect, which influence the absorption of the QDs[44]. Therefore, from spectroscopy point of view, photo-generated charges act the same way as the electrochemically injected charges. By evaluation of the induced changes in the absorption of QDs we can confirm whether the electrochemical electron in/e -jection is actually achieved or not. Therefor correlating the energy levels of the QDs to the electrochemical potential will help understanding of the possible absorption changes. In figure 3-5, CV of 3nm CdSe QDs in relation to its band structure is illustrated. In steady state measurement, presence of an electron in CB, causes absorption changes and new absorption bands to higher energy levels might become visible. The effect is similar to the GSB and excited state absorption (ESA) in TA measurements. As explained earlier, in electrochemical measurements application of negative bias corresponds to increase in the Fermi level of the working electrode. If the Fermi level is shifted so high that electrons in the electrode have the energy equal or higher than QD's first excited state ($1S_e$), the electrons can be transferred from working electrode to

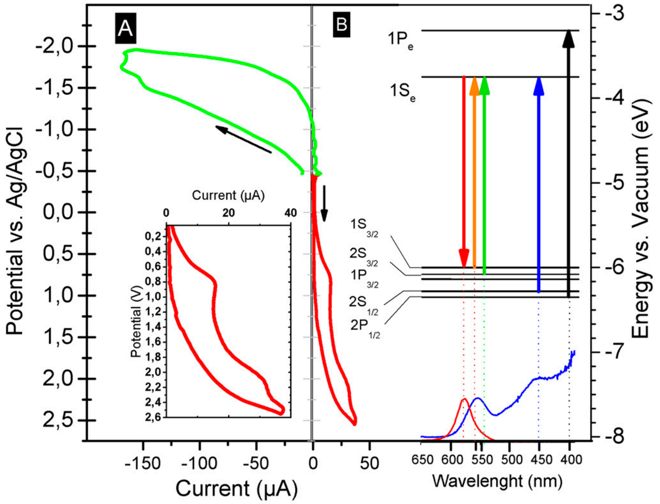


Figure 3-5 : CV measurement of CdSe QDs and it band structure with optical transitions[37]

the QDs. As the result of electron flow, a current change can be detected in CV and also it is expected that absorption transitions to the$1S_e$ state become bleached. The results of Spec-EL for CdSe QDs are presented in figure 3-6. By increase of the negative potential, a constant background is increasing in the absorption spectrum (indicated by a straight dotted line in figure 3-6). This broad absorption spectrum is known to be due to state filling of the TiO_2 [101]. The sigmoidal shape at lower potentials centered at 550nm is the result of the Stark effect due to the presence of an electric field across the QDs film[102]. As a rough estimate, if the QDs layer has a thickness of 1µm and the applied gradient across the film is 10 mV, the resulted electric field is of the order of 10 kV/m. This electric field is enough to induce Stark shift in the absorption spectra of QDs film[102]. By increasing the applied potential to more negative, when it reaches the energy levels higher than QDs, electron can be transferred to QDs. Therefore, a GSB, similar to excited QDs, can be observed. So, we suggest that the electrons that are injected electrochemically to the QDs are present in CB of the QDs[37]. By evaluating the relative amplitude of the induced bleach, electrochemical potential for single (-1.6V vs Ag/AgCl) and double charging (-1.8V vs Ag/AgCl) can be estimated[37]. The double charging is judged base on the fact that at -1.8V absorption spectra two times stronger bleached compared to -1.6V. This is due to the nature of the $1S_e$ (first excited state) of the QDs which has the possibility of accommodating only two electrons.

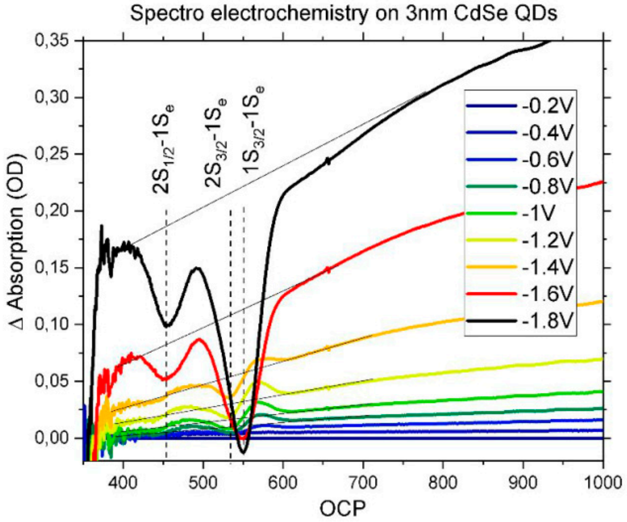


Figure 3-6 : Change in steady state absorption of QDs under application of negative bias where TiO_2 absorption is fitted by a straight line as a constant background.[37]

For the purpose of positive trion studies, we also explored the influence of the positive bias on QDs steady state absorption. Results are represented in figure 3-7. We observed that positive bias also leads to absorption changes as applying sufficient positive potential can led to depopulation of the QD's valence band. Therefore, the optical properties of QDs may also change due to positive charging. The induced changes are weaker than those induced by electron injection to CB, which is in agreement with the recent reported results[103,104]. It may also be possible to use this absorption change for quantification of the positive charges. However, effect of hole is not very well explored in optical absorption of the QDs therefore we leave this as an open question for future works. In general, we observe that Spec-EL method is a versatile tool for direct controlled manipulation of charges in QDs which can be further integrated with ultrafast spectroscopy to study charge carrier dynamic processes in QDs. It can be also used for the systematic study of both positive and negative trion decay in materials.

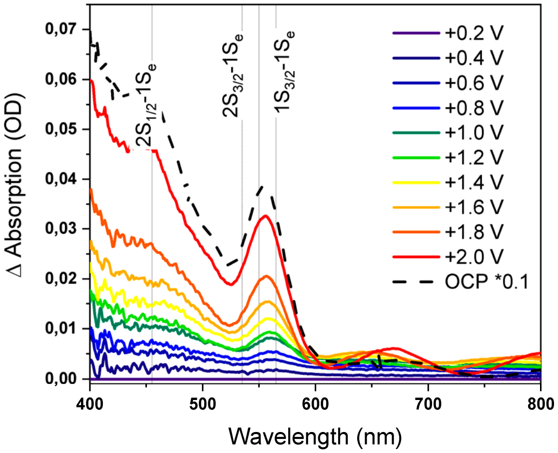


Figure 3-7 : Change in steady state absorption of QDs under application of positive bias

3.4 Transient Absorption Spectroscopy

Integration of Spec-EL into TA measurement allows direct probing of the photo-generated charge carrier dynamics in the QDs under controlled bias. For TA measurements, we used bulk electrolysis or chronoamperometric method. In this method a fixed potential is set for each TA measurement. For the better comparison, TA measurement at OCP is used as our reference. OCP corresponds to open circuit potential as the conditions where no EL bias is applied. Laser pulses with central wavelength 400 nm are used to populate higher-energy levels ($2P_{1/2}-1P_e$ transition). In OCP, following the photo excitation by laser pulse, hot electrons rapidly relax to the QD's CB minimum which induce state filling of $1S_{3/2}-1S_e$ and $2S_{3/2}-1S_e$ transitions (GSB). Then it is followed by electron injection to TiO_2 which is happening relatively fast in few ps. While the electron transport to the bulk of the TiO_2 is a relatively slower process of the order of few hundred ps[105]. Eventually photo-generated charges are recombining on the ns time scale. By increasing the electrochemical negative bias, charge injection and transfer to TiO_2 gradually diminishes. This is an interesting result, which can reflect that in QDs SCs, slight charge accumulation at interfaces can considerably disturb charge extraction from QDs. This may also explain the relatively low efficiency of QD SCs.

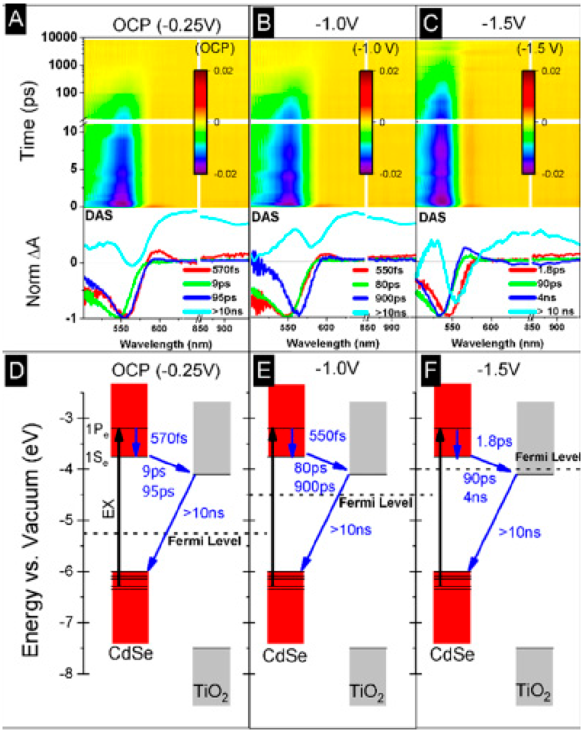


Figure 3-8: transient absorption measurement of CdSe QDs under application of no bias (OCP), -1.0 and -1.5V.[37]

Further increase of the negative bias, led to increase of the Fermi level of the working electrode so high that electrons can be transferred to $1S_e$ state of QDs. This introduces significant changes in TA kinetics. As a result, charge transfer to TiO_2 is completely terminated. Accordingly, the photo generated charges and EL injected electrons are confined in the QDs. This is one of the reasons that TiO_2 has been used in our studies. Because firstly, it can provide information about both electron transfer and also intrinsically act as hole blocker. Second, as the result of EL bias, at high negative potentials, TiO_2 will also act as a barrier for photo generated charges, so charges will be confined in QDs. In contrast to charge injection to TiO_2, relaxation of hot electrons become faster due to electron−electron scattering effect[106]. This is expected due to the fact that at -1.75V an additional electron (by EL) is already present in QDs. The other interesting feature which is observed in TA measurements is formation of polaron due to Coulombic repulsion between these electrons[107,108]. As in QDs, charges are confined in a small region, Coulombic interaction is larger and have a long-distance effect leading to the preferable localization of the additional charges at the surface[109]. These dynamics are followed by a relatively fast Auger recombination which is due to negative trion decay. Similarly at -2V, for the double charged QDs, relaxation of hot electrons and polaron followed by Auger recombination due to negative tetron decay[110]. After negative trion decay, QDs is expected to be in its ground state while our TA results

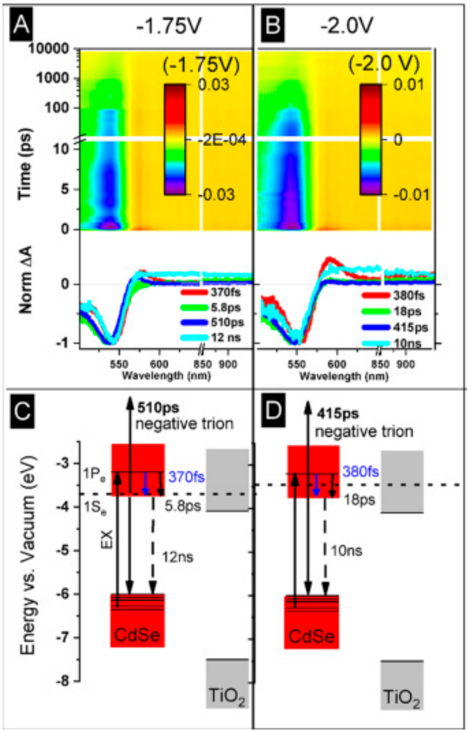


Figure 3-9 : transient absorption measurement of CdSe QDs under application of -1.75 and -2.0V.[37]

still show longer lived decay which corresponds to those QDs which lost their charges and do not contribute to the negative trion decay. This loss of charges can be due to polaron formation which can push electrons to the surface of the QDs. Also a recent study shows that charging of the QDs may lead to changes in the QD's surface and formation of trap states, which may not be visible in absorption[100].

As already discussed, positive bias decreases the Fermi level in FTO- TiO_2. If the Fermi level reaches the energy levels lower than QD's VB, holes can be injected to the VB. The results of TA measurements under applied positive bias are summarized in figure 3-10. At OCP, typical hot electron relaxation (with lifetime 400-500 fs) and both electron transfer and injection to TiO_2 can be clearly observed. Upon application of slight positive bias, faster electron injection and faster recombination is observed. This faster recombination is attributed to depletion of trap states and possibly increased Coulomb interaction. Further increase of the positive bias, lead to significant changes in TA kinetics such that the new kinetics can be fitted with only three components. As it is visible from the SVD analysis of the TA data, charge injection to TiO_2 is again terminated. This is indeed interesting result, which may provide further insight for the development of QDs devices. However, within our experimental uncertainties, hot electron relaxation and the charge trapping remains relatively unchanged. These relaxations are followed by a fast decay of the range of 200 to 300 ps, due to positive trion decay. Surprisingly, application of higher positive potentials does not induce significant changes in the lifetime of the positive trion decay. This may be the result of the large density of states in the VB and also insensitivity of the TA measurements to hole dynamics.

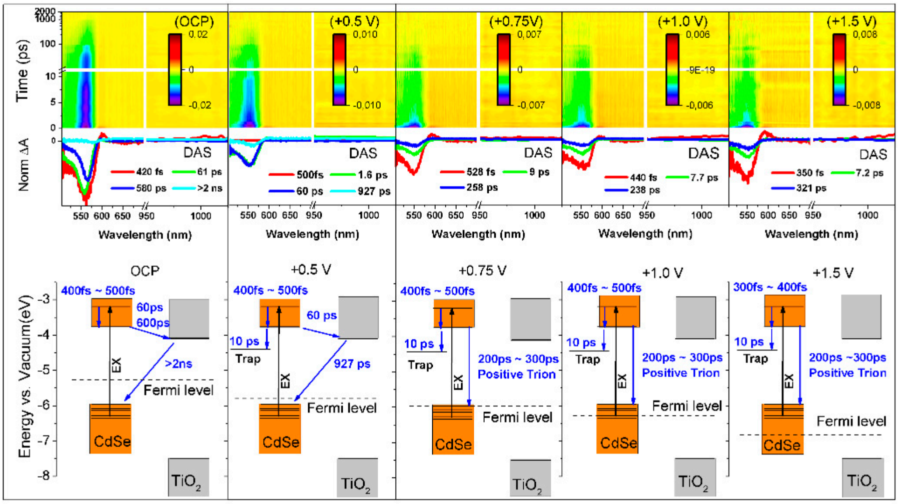


Figure 3-10 : transient absorption measurement of CdSe QDs under application of no bias (OCP), +0.5, +0.75, +1.0 and +1.5V

4 Conclusion

Through the journey of this PhD, we explored various materials and their charge carrier dynamics as well as their performance as promising light harvesting materials.

*- Advancement in the field of ligand synthesis provided the necessary tool for engineering of the band alignments of iron complexes. This led to the advent and development of new iron complexes. A set of methods were used to study these materials. Spectroelectrochemical measurements provided extra aid for identification and evaluation of different versions of existing complexes. Our studies showed that iron complexes can also reach ns long lifetime as a result of increasing in the energy of metal cantered states. They can also have photoemission at room temperature. These developments opened up a new path for possible replacement of rare expensive elements with earth abundant ones, especially iron as cheap and environmentally friendly alternative. Hopefully in the near future, further development of such complexes can yield the performance of the usually used dyes (or even better). These promising achievements can introduce a step change in the development of the solar-cells which the Author believe it can be a new iron age in human history.

*-We also studied organic conjugated polymers for photovoltaic applications. Our results for two different types of donor polymers, with different band energy offsets, reflects that regardless of band offset between donor and acceptor, the band offset for the charge transfer state is a major factor for efficient charge separation and higher efficiency in OPVs.

*-Perovskites as new promising solar materials have many useful properties. But they suffer from degradation. Replacement of Pb with other elements such as Sn can largely increase the stability and light harvesting performance. We also realized that light can also induce changes on the surface and structure of the perovskites, therefore their charge carrier performance is significantly degraded. As an alternative, one can achieve the combination of replacing elements and incorporation of better surface passivating layers in perovskites by using 2D/3D hybrid structures. We demonstrated that such structure could reach high power conversion efficiency compared to only 2D or 3D perovskites. We also observed that such 2D/3D structure can reach good working stability.

As we realized through our studies, band alignment and energy levels at interfaces can largely affect charge carrier dynamics and the performance of the SC devices. Therefore, we further studied how charge carrier performance may be affected due to changes of charges at interfaces. We used electrochemistry as a versatile tool to provide controlled energy level manipulation which can resemble charge accumulation at QDs-TiO_2 interfaces. This is to resemble the possible variations of charge accumulation that can occur at interfaces in solar cells due to defects and trap states as well as Schottky barrier formation between semiconductors and metals. For our studies we selected CdSe QDs as a model system and we surprisingly observed that:

*- Application of slight negative bias diminish charge extraction from the QDs.

*- Further increase in negative bias, led to negative charging of the QDs.

*- The number of charges can be estimated by using spectroelectrochemical measurements.

*- Charge extraction is completely terminated if QDs is negatively charged

*- Photo excitation of negatively charged QDs led to rapid Auger decay of negative trion.

*- For the positive charged QDs, steady-state absorption changes can also be detected.

*- Surprisingly, positive bias also led to termination of the charge extraction from QDs too.

*- Photo excitation of positively charged QDs also led to fast Auger decay of positive trion.

Future works

In the continuation of the works that were done through this thesis, following works can be beneficial for further understanding of the underlying photophysical processes in solar materials.

*- Using spectroelectrochemical measurements as a versatile method for identification and evaluation of different versions of newly developed complexes.

*- Similar spectroelectrochemical measurements can be implemented for studies of the polymers and perovskites.

*- Recent studies shows that QDs can be stably charged and remain charged for very long times by freezing the electrolyte. Similar results can be achieved by using ionic liquids or solid-state electrolytes.

*- Quantitative evaluation of positive charging of QDs.

*- Using experimental studies that can directly measure electrons/holes dynamics at sub-femtosecond times (ideally attosecond) for studies of positive trion and evaluation of contribution of hole dynamics in QDs.

*- Trion decay can be utilized for optical gain and realization of QDs lasing.

References

(1) Ponseca, C. S.; Chábera, P.; Uhlig, J.; Persson, P.; Sundström, V. Ultrafast Electron Dynamics in Solar Energy Conversion. *Chem. Rev.* **2017**, *117* (16), 10940–11024. https://doi.org/10.1021/acs.chemrev.6b00807.

(2) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110* (11), 6595–6663. https://doi.org/10.1021/cr900356p.

(3) Grätzel, M. Dye-Sensitized Solar Cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2003**, *4* (2), 145–153. https://doi.org/10.1016/S1389-5567(03)00026-1.

(4) Chábera, P.; Lindh, L.; Rosemann, N. W.; Prakash, O.; Uhlig, J.; Yartsev, A.; Wärnmark, K.; Sundström, V.; Persson, P. Photofunctionality of Iron(III) N-Heterocyclic Carbenes and Related D5 Transition Metal Complexes. *Coordination Chemistry Reviews* **2021**, *426*, 213517. https://doi.org/10.1016/j.ccr.2020.213517.

(5) Wenger, O. S. Photoactive Complexes with Earth-Abundant Metals. *J. Am. Chem. Soc.* **2018**, *140* (42), 13522–13533. https://doi.org/10.1021/jacs.8b08822.

(6) Frey, P. A.; Reed, G. H. The Ubiquity of Iron. *ACS Chem. Biol.* **2012**, *7* (9), 1477–1481. https://doi.org/10.1021/cb300323q.

(7) Wenger, O. S. Is Iron the New Ruthenium? *Chemistry – A European Journal* **2019**, *25* (24), 6043–6052. https://doi.org/10.1002/chem.201806148.

(8) Wenger, O. S. A Bright Future for Photosensitizers. *Nature Chemistry* **2020**, *12* (4), 323–324. https://doi.org/10.1038/s41557-020-0448-x.

(9) Chábera, P.; Liu, Y.; Prakash, O.; Thyrhaug, E.; Nahhas, A. E.; Honarfar, A.; Essén, S.; Fredin, L. A.; Harlang, T. C. B.; Kjær, K. S.; Handrup, K.; Ericson, F.; Tatsuno, H.; Morgan, K.; Schnadt, J.; Häggström, L.; Ericsson, T.; Sobkowiak, A.; Lidin, S.; Huang, P.; Styring, S.; Uhlig, J.; Bendix, J.; Lomoth, R.; Sundström, V.; Persson, P.; Wärnmark, K. A Low-Spin Fe(III) Complex with 100-Ps Ligand-to-Metal Charge Transfer Photoluminescence. *Nature* **2017**, *543* (7647), 695–699. https://doi.org/10.1038/nature21430.

(10) Chábera, P.; Kjaer, K. S.; Prakash, O.; Honarfar, A.; Liu, Y.; Fredin, L. A.; Harlang, T. C. B.; Lidin, S.; Uhlig, J.; Sundström, V.; Lomoth, R.; Persson, P.; Wärnmark, K. FeII Hexa N-Heterocyclic Carbene Complex with a 528 Ps Metal-to-Ligand Charge-Transfer Excited-State Lifetime. *J. Phys. Chem. Lett.* **2018**, *9* (3), 459–463. https://doi.org/10.1021/acs.jpclett.7b02962.

(11) Kjær, K. S.; Kaul, N.; Prakash, O.; Chábera, P.; Rosemann, N. W.; Honarfar, A.; Gordivska, O.; Fredin, L. A.; Bergquist, K.-E.; Häggström, L.; Ericsson, T.; Lindh, L.; Yartsev, A.; Styring, S.; Huang, P.; Uhlig, J.; Bendix, J.; Strand, D.; Sundström, V.; Persson, P.; Lomoth, R.; Wärnmark, K. Luminescence and Reactivity of a Charge-Transfer Excited Iron Complex with Nanosecond Lifetime. *Science* **2019**, *363* (6424), 249–253. https://doi.org/10.1126/science.aau7160.

(12) Cheng, P.; Li, G.; Zhan, X.; Yang, Y. Next-Generation Organic Photovoltaics Based on Non-Fullerene Acceptors. *Nature Photonics* **2018**, *12* (3), 131–142. https://doi.org/10.1038/s41566-018-0104-9.

(13) Menke, S. M.; Ran, N. A.; Bazan, G. C.; Friend, R. H. Understanding Energy Loss in Organic Solar Cells: Toward a New Efficiency Regime. *Joule* **2018**, *2* (1), 25–35. https://doi.org/10.1016/j.joule.2017.09.020.

(14) Zheng, Z.; Awartani, O. M.; Gautam, B.; Liu, D.; Qin, Y.; Li, W.; Bataller, A.; Gundogdu, K.; Ade, H.; Hou, J. Efficient Charge Transfer and Fine-Tuned Energy Level Alignment in a THF-Processed Fullerene-Free Organic Solar Cell with 11.3% Efficiency. *Advanced Materials* **2017**, *29* (5), 1604241. https://doi.org/10.1002/adma.201604241.

(15) Lu, L.; Kelly, M. A.; You, W.; Yu, L. Status and Prospects for Ternary Organic Photovoltaics. *Nature Photonics* **2015**, *9* (8), 491–500. https://doi.org/10.1038/nphoton.2015.128.

(16) Liu, X.; Yan, Y.; Honarfar, A.; Yao, Y.; Zheng, K.; Liang, Z. Unveiling Excitonic Dynamics in High-Efficiency Nonfullerene Organic Solar Cells to Direct Morphological Optimization for Suppressing Charge Recombination. *Advanced Science* **2019**, *6* (8), 1802103. https://doi.org/10.1002/advs.201802103.

(17) Yao, H.; Cui, Y.; Qian, D.; Ponseca, C. S.; Honarfar, A.; Xu, Y.; Xin, J.; Chen, Z.; Hong, L.; Gao, B.; Yu, R.; Zu, Y.; Ma, W.; Chabera, P.; Pullerits, T.; Yartsev, A.; Gao, F.; Hou, J. 14.7% Efficiency Organic Photovoltaic Cells Enabled by Active Materials with a Large Electrostatic Potential Difference. *J. Am. Chem. Soc.* **2019**, *141* (19), 7743–7750. https://doi.org/10.1021/jacs.8b12937.

(18) Grätzel, M. The Light and Shade of Perovskite Solar Cells. *Nature Materials* **2014**, *13* (9), 838–842. https://doi.org/10.1038/nmat4065.

(19) Chen, Y.; He, M.; Peng, J.; Sun, Y.; Liang, Z. Structure and Growth Control of Organic–Inorganic Halide Perovskites for Optoelectronics: From Polycrystalline Films to Single Crystals. *Advanced Science* **2016**, *3* (4), 1500392. https://doi.org/10.1002/advs.201500392.

(20) Ponseca, C. S.; Chábera, P.; Uhlig, J.; Persson, P.; Sundström, V. Ultrafast Electron Dynamics in Solar Energy Conversion. *Chem. Rev.* **2017**, *117* (16), 10940–11024. https://doi.org/10.1021/acs.chemrev.6b00807.

(21) Giustino, F.; Snaith, H. J. Toward Lead-Free Perovskite Solar Cells. *ACS Energy Lett.* **2016**, *1* (6), 1233–1240. https://doi.org/10.1021/acsenergylett.6b00499.

(22) Fu, H. Review of Lead-Free Halide Perovskites as Light-Absorbers for Photovoltaic Applications: From Materials to Solar Cells. *Solar Energy Materials and Solar Cells* **2019**, *193*, 107–132. https://doi.org/10.1016/j.solmat.2018.12.038.

(23) Chen, Y.; Sun, Y.; Peng, J.; Chábera, P.; Honarfar, A.; Zheng, K.; Liang, Z. Composition Engineering in Two-Dimensional Pb–Sn-Alloyed Perovskites for Efficient and Stable Solar Cells. *ACS Appl. Mater. Interfaces* **2018**, *10* (25), 21343–21348. https://doi.org/10.1021/acsami.8b06256.

(24) An, R.; Zhang, F.; Zou, X.; Tang, Y.; Liang, M.; Oshchapovskyy, I.; Liu, Y.; Honarfar, A.; Zhong, Y.; Li, C.; Geng, H.; Chen, J.; Canton, S. E.; Pullerits, T.; Zheng, K. Photostability and Photodegradation Processes in Colloidal CsPbI3 Perovskite Quantum Dots. *ACS Appl. Mater. Interfaces* **2018**, *10* (45), 39222–39227. https://doi.org/10.1021/acsami.8b14480.

(25) Grancini, G.; Roldán-Carmona, C.; Zimmermann, I.; Mosconi, E.; Lee, X.; Martineau, D.; Narbey, S.; Oswald, F.; De Angelis, F.; Graetzel, M.; Nazeeruddin, M. K. One-Year Stable Perovskite Solar Cells by 2D/3D Interface Engineering. *Nature Communications* **2017**, *8* (1), 15684. https://doi.org/10.1038/ncomms15684.

(26) Bai, Y.; Xiao, S.; Hu, C.; Zhang, T.; Meng, X.; Lin, H.; Yang, Y.; Yang, S. Dimensional Engineering of a Graded 3D–2D Halide Perovskite Interface Enables Ultrahigh Voc Enhanced Stability in the p-i-n Photovoltaics. *Advanced Energy Materials* **2017**, *7* (20), 1701038. https://doi.org/10.1002/aenm.201701038.

(27) Yan, Y.; Yu, S.; Honarfar, A.; Pullerits, T.; Zheng, K.; Liang, Z. Benefiting from Spontaneously Generated 2D/3D Bulk-Heterojunctions in Ruddlesden−Popper Perovskite by Incorporation of S-Bearing Spacer Cation. *Advanced Science* **2019**, *6* (14), 1900548. https://doi.org/10.1002/advs.201900548.

(28) *Colloidal Quantum Dot Optoelectronics and Photovoltaics*; Konstantatos, G., Sargent, E. H., Eds.; Cambridge University Press: Cambridge, 2013. https://doi.org/10.1017/CBO9781139022750.

(29) Brennan, K. F. *The Physics of Semiconductors: With Applications to Optoelectronic Devices*; Cambridge University Press: Cambridge, 1999. https://doi.org/10.1017/CBO9781139164214.

(30) Bae, W. K.; Park, Y.-S.; Lim, J.; Lee, D.; Padilha, L. A.; McDaniel, H.; Robel, I.; Lee, C.; Pietryga, J. M.; Klimov, V. I. Controlling the Influence of Auger Recombination on the Performance of Quantum-Dot Light-Emitting Diodes. *Nature Communications* **2013**, *4* (1), 2661. https://doi.org/10.1038/ncomms3661.

(31) Anikeeva, P. O.; Madigan, C. F.; Halpert, J. E.; Bawendi, M. G.; Bulović, V. Electronic and Excitonic Processes in Light-Emitting Devices Based on Organic Materials and Colloidal Quantum Dots. *Phys. Rev. B* **2008**, *78* (8), 085434. https://doi.org/10.1103/PhysRevB.78.085434.

(32) Vossier, A.; Hirsch, B.; Gordon, J. M. Is Auger Recombination the Ultimate Performance Limiter in Concentrator Solar Cells? *Appl. Phys. Lett.* **2010**, *97* (19), 193509. https://doi.org/10.1063/1.3510474.

(33) Makarov, N. S.; McDaniel, H.; Fuke, N.; Robel, I.; Klimov, V. I. Photocharging Artifacts in Measurements of Electron Transfer in Quantum-Dot-Sensitized Mesoporous Titania Films. *J. Phys. Chem. Lett.* **2014**, *5* (1), 111–118. https://doi.org/10.1021/jz402338b.

(34) Jha, P. P.; Guyot-Sionnest, P. Trion Decay in Colloidal Quantum Dots. *ACS Nano* **2009**, *3* (4), 1011–1015. https://doi.org/10.1021/nn9001177.

(35) Singh, R.; Liu, W.; Lim, J.; Robel, I.; Klimov, V. I. Hot-Electron Dynamics in Quantum Dots Manipulated by Spin-Exchange Auger Interactions. *Nature Nanotechnology* **2019**, *14* (11), 1035–1041. https://doi.org/10.1038/s41565-019-0548-1.

(36) Cohn, A. W.; Rinehart, J. D.; Schimpf, A. M.; Weaver, A. L.; Gamelin, D. R. Size Dependence of Negative Trion Auger Recombination in Photodoped CdSe Nanocrystals. *Nano Lett.* **2014**, *14* (1), 353–358. https://doi.org/10.1021/nl4041675.

(37) Honarfar, A.; Mourad, H.; Lin, W.; Polukeev, A.; Rahaman, A.; Abdellah, M.; Chábera, P.; Pankratova, G.; Gorton, L.; Zheng, K.; Pullerits, T. Photoexcitation Dynamics in Electrochemically Charged CdSe Quantum Dots: From Hot Carrier Cooling to Auger Recombination of Negative Trions. *ACS Appl. Energy Mater.* **2020**. https://doi.org/10.1021/acsaem.0c02478.

(38) Hou, X.; Kang, J.; Qin, H.; Chen, X.; Ma, J.; Zhou, J.; Chen, L.; Wang, L.; Wang, L.-W.; Peng, X. Engineering Auger Recombination in Colloidal Quantum Dots via Dielectric Screening. *Nature Communications* **2019**, *10* (1), 1750. https://doi.org/10.1038/s41467-019-09737-2.

(39) Žídek, K.; Zheng, K.; Abdellah, M.; Lenngren, N.; Chábera, P.; Pullerits, T. Ultrafast Dynamics of Multiple Exciton Harvesting in the CdSe–ZnO System: Electron Injection versus Auger Recombination. *Nano Lett.* **2012**, *12* (12), 6393–6399. https://doi.org/10.1021/nl303746d.

(40) Park, Y.-S.; Bae, W. K.; Pietryga, J. M.; Klimov, V. I. Auger Recombination of Biexcitons and Negative and Positive Trions in Individual Quantum Dots. *ACS Nano* **2014**, *8* (7), 7288–7296. https://doi.org/10.1021/nn5023473.

(41) Makarov, N. S.; Guo, S.; Isaienko, O.; Liu, W.; Robel, I.; Klimov, V. I. Spectral and Dynamical Properties of Single Excitons, Biexcitons, and Trions in Cesium–Lead-Halide Perovskite Quantum Dots. *Nano Lett.* **2016**, *16* (4), 2349–2362. https://doi.org/10.1021/acs.nanolett.5b05077.

(42) Zídek, K.; Zheng, K.; Abdellah, M.; Lenngren, N.; Chábera, P.; Pullerits, T. Ultrafast Dynamics of Multiple Exciton Harvesting in the CdSe-ZnO System: Electron Injection versus Auger Recombination. *Nano Lett.* **2012**, *12* (12), 6393–6399.

(43) Knowles, K. E.; Koch, M. D.; Shelton, J. L. Three Applications of Ultrafast Transient Absorption Spectroscopy of Semiconductor Thin Films: Spectroelectrochemistry, Microscopy, and Identification of Thermal Contributions. *J. Mater. Chem. C* **2018**, *6* (44), 11853–11867. https://doi.org/10.1039/C8TC02977F.

(44) Spittel, D.; Poppe, J.; Meerbach, C.; Ziegler, C.; Hickey, S. G.; Eychmüller, A. Absolute Energy Level Positions in CdSe Nanostructures from Potential-Modulated Absorption Spectroscopy (EMAS). *ACS Nano* **2017**, *11* (12), 12174–12184. https://doi.org/10.1021/acsnano.7b05300.

(45) Honarfar, A.; Mourad, H.; Abdellah, M.; Chabera, P.; Pankratova, G.; Gorton, L.; Zheng, K.; Pullerits, T. Ultrafast Dynamics in QD Based Photoelectrochemical Cells. In *Physical Chemistry of Semiconductor Materials and Interfaces XVIII*; International Society for Optics and Photonics, 2019; Vol. 11084, p 110840L. https://doi.org/10.1117/12.2529771.

(46) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*, second Edition.; JOHN WILEY, 2008.

(47) Lefrou, C.; Fabry, P.; Poignet, J.-C. *Electrochemistry: The Basics, With Examples*; Springer-Verlag: Berlin Heidelberg, 2012. https://doi.org/10.1007/978-3-642-30250-3.

(48) Hederstedt, L.; Gorton, L.; Pankratova, G. Two Routes for Extracellular Electron Transfer in Enterococcus Faecalis. *Journal of Bacteriology* **2020**, *202* (7). https://doi.org/10.1128/JB.00725-19.

(49) Pankratova, G.; Hederstedt, L.; Gorton, L. Extracellular Electron Transfer Features of Gram-Positive Bacteria. *Analytica Chimica Acta* **2019**, *1076*, 32–47. https://doi.org/10.1016/j.aca.2019.05.007.

(50) Gorton, L. Chemically Modified Electrodes for the Electrocatalytic Oxidation of Nicotinamide Coenzymes. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases* **1986**, *82* (4), 1245–1258. https://doi.org/10.1039/F19868201245.

(51) Wang, C.; Shim, M.; Guyot-Sionnest, P. Electrochromic Nanocrystal Quantum Dots. *Science* **2001**, *291* (5512), 2390–2392. https://doi.org/10.1126/science.291.5512.2390.

(52) Ingole, P. P. A Consolidated Account of Electrochemical Determination of Band Structure Parameters in II–VI Semiconductor Quantum Dots: A Tutorial Review. *Phys. Chem. Chem. Phys.* **2019**, *21* (9), 4695–4716. https://doi.org/10.1039/C8CP06847J.

(53) Boehme, S. C.; Walvis, T. A.; Infante, I.; Grozema, F. C.; Vanmaekelbergh, D.; Siebbeles, L. D. A.; Houtepen, A. J. Electrochemical Control over Photoinduced Electron Transfer and Trapping in CdSe-CdTe Quantum-Dot Solids. *ACS Nano* **2014**, *8* (7), 7067–7077. https://doi.org/10.1021/nn501985e.

(54) Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner’s Guide to Cyclic Voltammetry. *J. Chem. Educ.* **2018**, *95* (2), 197–206. https://doi.org/10.1021/acs.jchemed.7b00361.

(55) Conradie, J.; von Eschwege, K. G. Cyclic Voltammograms and Electrochemical Data of FeII Polypyridine Complexes. *Data in Brief* **2020**, *31*, 105754. https://doi.org/10.1016/j.dib.2020.105754.

(56) Benck, J. D.; Pinaud, B. A.; Gorlin, Y.; Jaramillo, T. F. Substrate Selection for Fundamental Studies of Electrocatalysts and Photoelectrodes: Inert Potential Windows in Acidic, Neutral, and Basic Electrolyte. *PLOS ONE* **2014**, *9* (10), e107942. https://doi.org/10.1371/journal.pone.0107942.

(57) Kaim, W.; Klein, A. *Spectroelectrochemistry*; RSC Publishing, 2008. https://doi.org/10.1039/9781847558404.

(58) Kumar, P. *Organic Solar Cells: Device Physics, Processing, Degradation, and Prevention*; CRC Press, Taylor et Francis Group: Boca Raton, FL, 2017.

(59) Ananthakumar, S.; Kumar, J. R.; Babu, S. M. Third-Generation Solar Cells: Concept, Materials and Performance - An Overview. In *Emerging Nanostructured Materials for Energy and Environmental Science*; Rajendran, S., Naushad, Mu., Raju, K., Boukherroub, R., Eds.; Environmental Chemistry for a Sustainable World; Springer International Publishing: Cham, 2019; pp 305–339. https://doi.org/10.1007/978-3-030-04474-9_7.

(60) Harlang, T. C. B.; Liu, Y.; Gordivska, O.; Fredin, L. A.; Ponseca, C. S.; Huang, P.; Chábera, P.; Kjaer, K. S.; Mateos, H.; Uhlig, J.; Lomoth, R.; Wallenberg, R.; Styring, S.; Persson, P.; Sundström, V.; Wärnmark, K. Iron Sensitizer Converts Light to Electrons with 92% Yield. *Nature Chemistry* **2015**, *7* (11), 883–889. https://doi.org/10.1038/nchem.2365.

(61) Tang, C. W. Two-layer Organic Photovoltaic Cell. *Appl. Phys. Lett.* **1986**, *48* (2), 183–185. https://doi.org/10.1063/1.96937.

(62) Vandewal, K.; Albrecht, S.; Hoke, E. T.; Graham, K. R.; Widmer, J.; Douglas, J. D.; Schubert, M.; Mateker, W. R.; Bloking, J. T.; Burkhard, G. F.; Sellinger, A.; Fréchet, J. M. J.; Amassian, A.; Riede, M. K.; McGehee, M. D.; Neher, D.; Salleo, A. Efficient Charge Generation by Relaxed Charge-Transfer States at Organic Interfaces. *Nature Materials* **2014**, *13* (1), 63–68. https://doi.org/10.1038/nmat3807.

(63) Liu, J.; Chen, S.; Qian, D.; Gautam, B.; Yang, G.; Zhao, J.; Bergqvist, J.; Zhang, F.; Ma, W.; Ade, H.; Inganäs, O.; Gundogdu, K.; Gao, F.; Yan, H. Fast Charge Separation in a Non-Fullerene Organic Solar Cell with a Small Driving Force. *Nature Energy* **2016**, *1* (7), 1–7. https://doi.org/10.1038/nenergy.2016.89.

(64) Pal, S. K.; Kesti, T.; Maiti, M.; Zhang, F.; Inganäs, O.; Hellström, S.; Andersson, M. R.; Oswald, F.; Langa, F.; Österman, T.; Pascher, T.; Yartsev, A.; Sundström, V. Geminate Charge Recombination in Polymer/Fullerene Bulk Heterojunction Films and Implications for Solar Cell Function. *J. Am. Chem. Soc.* **2010**, *132* (35), 12440–12451. https://doi.org/10.1021/ja104786x.

(65) De, S.; Pascher, T.; Maiti, M.; Jespersen, K. G.; Kesti, T.; Zhang, F.; Inganäs, O.; Yartsev, A.; Sundström, V. Geminate Charge Recombination in Alternating Polyfluorene Copolymer/Fullerene Blends. *J. Am. Chem. Soc.* **2007**, *129* (27), 8466–8472. https://doi.org/10.1021/ja068909q.

(66) Ponseca, C. S.; Savenije, T. J.; Abdellah, M.; Zheng, K.; Yartsev, A.; Pascher, T.; Harlang, T.; Chabera, P.; Pullerits, T.; Stepanov, A.; Wolf, J.-P.; Sundström, V. Organometal Halide Perovskite Solar Cell Materials Rationalized: Ultrafast Charge Generation, High and Microsecond-Long Balanced Mobilities, and Slow Recombination. *J. Am. Chem. Soc.* **2014**, *136* (14), 5189–5192. https://doi.org/10.1021/ja412583t.

(67) Hao, F.; Stoumpos, C. C.; Cao, D. H.; Chang, R. P. H.; Kanatzidis, M. G. Lead-Free Solid-State Organic–Inorganic Halide Perovskite Solar Cells. *Nature Photonics* **2014**, *8* (6), 489–494. https://doi.org/10.1038/nphoton.2014.82.

(68) K. Noel, N.; D. Stranks, S.; Abate, A.; Wehrenfennig, C.; Guarnera, S.; Haghighirad, A.-A.; Sadhanala, A.; E. Eperon, G.; K. Pathak, S.; B. Johnston, M.; Petrozza, A.; M. Herz, L.; J. Snaith, H. Lead-Free Organic–Inorganic Tin Halide Perovskites for Photovoltaic Applications. *Energy & Environmental Science* **2014**, *7* (9), 3061–3068. https://doi.org/10.1039/C4EE01076K.

(69) Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I. A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability. *Angewandte Chemie International Edition* **2014**, *53* (42), 11232–11235. https://doi.org/10.1002/anie.201406466.

(70) Chen, Y.; Sun, Y.; Peng, J.; Tang, J.; Zheng, K.; Liang, Z. 2D Ruddlesden–Popper Perovskites for Optoelectronics. *Advanced Materials* **2018**, *30* (2), 1703487. https://doi.org/10.1002/adma.201703487.

(71) Hao, F.; Stoumpos, C. C.; Guo, P.; Zhou, N.; Marks, T. J.; Chang, R. P. H.; Kanatzidis, M. G. Solvent-Mediated Crystallization of CH3NH3SnI3 Films for Heterojunction Depleted Perovskite Solar Cells. *J. Am. Chem. Soc.* **2015**, *137* (35), 11445–11452. https://doi.org/10.1021/jacs.5b06658.

(72) Anaya, M.; P. Correa-Baena, J.; Lozano, G.; Saliba, M.; Anguita, P.; Roose, B.; Abate, A.; Steiner, U.; Grätzel, M.; E. Calvo, M.; Hagfeldt, A.; Míguez, H. Optical Analysis of CH 3 NH 3 Sn x Pb 1−x I 3 Absorbers: A Roadmap for Perovskite-on-Perovskite Tandem Solar Cells. *Journal of Materials Chemistry A* **2016**, *4* (29), 11214–11221. https://doi.org/10.1039/C6TA04840D.

(73) Liu, J.; Leng, J.; Wu, K.; Zhang, J.; Jin, S. Observation of Internal Photoinduced Electron and Hole Separation in Hybrid Two-Dimentional Perovskite Films. *J. Am. Chem. Soc.* **2017**, *139* (4), 1432–1435. https://doi.org/10.1021/jacs.6b12581.

(74) Sanehira, E. M.; Marshall, A. R.; Christians, J. A.; Harvey, S. P.; Ciesielski, P. N.; Wheeler, L. M.; Schulz, P.; Lin, L. Y.; Beard, M. C.; Luther, J. M. Enhanced Mobility CsPbI3 Quantum Dot Arrays for Record-Efficiency, High-Voltage Photovoltaic Cells. *Science Advances* **2017**, *3* (10), eaao4204. https://doi.org/10.1126/sciadv.aao4204.

(75) Beal, R. E.; Slotcavage, D. J.; Leijtens, T.; Bowring, A. R.; Belisle, R. A.; Nguyen, W. H.; Burkhard, G. F.; Hoke, E. T.; McGehee, M. D. Cesium Lead Halide Perovskites with Improved Stability for Tandem Solar Cells. *J. Phys. Chem. Lett.* **2016**, *7* (5), 746–751. https://doi.org/10.1021/acs.jpclett.6b00002.

(76) Swarnkar, A.; Marshall, A. R.; Sanehira, E. M.; Chernomordik, B. D.; Moore, D. T.; Christians, J. A.; Chakrabarti, T.; Luther, J. M. Quantum Dot–Induced Phase Stabilization of α-CsPbI3 Perovskite for High-Efficiency Photovoltaics. *Science* **2016**, *354* (6308), 92–95. https://doi.org/10.1126/science.aag2700.

(77) Chen, J.; Liu, D.; Al-Marri, M. J.; Nuuttila, L.; Lehtivuori, H.; Zheng, K. Photo-Stability of CsPbBr3 Perovskite Quantum Dots for Optoelectronic Application. *Sci. China Mater.* **2016**, *59* (9), 719–727. https://doi.org/10.1007/s40843-016-5123-1.

(78) Grancini, G.; Nazeeruddin, M. K. Dimensional Tailoring of Hybrid Perovskites for Photovoltaics. *Nature Reviews Materials* **2019**, *4* (1), 4–22. https://doi.org/10.1038/s41578-018-0065-0.

(79) Tsai, H.; Nie, W.; Blancon, J.-C.; Stoumpos, C. C.; Asadpour, R.; Harutyunyan, B.; Neukirch, A. J.; Verduzco, R.; Crochet, J. J.; Tretiak, S.; Pedesseau, L.; Even, J.; Alam, M. A.; Gupta, G.; Lou, J.; Ajayan, P. M.; Bedzyk, M. J.; Kanatzidis, M. G.; Mohite, A. D. High-Efficiency Two-Dimensional Ruddlesden–Popper Perovskite Solar Cells. *Nature* **2016**, *536* (7616), 312–316. https://doi.org/10.1038/nature18306.

(80) Snaith, H. J.; Abate, A.; Ball, J. M.; Eperon, G. E.; Leijtens, T.; Noel, N. K.; Stranks, S. D.; Wang, J. T.-W.; Wojciechowski, K.; Zhang, W. Anomalous Hysteresis in Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2014**, *5* (9), 1511–1515. https://doi.org/10.1021/jz500113x.

(81) Cohen, B.-E.; Wierzbowska, M.; Etgar, L. High Efficiency and High Open Circuit Voltage in Quasi 2D Perovskite Based Solar Cells. *Advanced Functional Materials* **2017**, *27* (5), 1604733. https://doi.org/10.1002/adfm.201604733.

(82) Bai, Y.; Xiao, S.; Hu, C.; Zhang, T.; Meng, X.; Lin, H.; Yang, Y.; Yang, S. Dimensional Engineering of a Graded 3D–2D Halide Perovskite Interface Enables Ultrahigh Voc Enhanced Stability in the p-i-n Photovoltaics. *Advanced Energy Materials* **2017**, *7* (20), 1701038. https://doi.org/10.1002/aenm.201701038.

(83) Yu, S.; Yan, Y.; Chen, Y.; Chábera, P.; Zheng, K.; Liang, Z. Enabling Room-Temperature Processed Highly Efficient and Stable 2D Ruddlesden–Popper Perovskite Solar Cells with Eliminated Hysteresis by Synergistic Exploitation of Additives and Solvents. *J. Mater. Chem. A* **2019**, *7* (5), 2015–2021. https://doi.org/10.1039/C8TA09146C.

(84) Cao, D. H.; Stoumpos, C. C.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G. 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications. *J. Am. Chem. Soc.* **2015**, *137* (24), 7843–7850. https://doi.org/10.1021/jacs.5b03796.

(85) Yan, Y.; Wu, Q.; Zhao, Y.; Chen, S.; Hu, S.; Zhu, J.; Huang, J.; Liang, Z. Air-Stable and Self-Driven Perovskite Photodiodes with High On/Off Ratio and Swift Photoresponse. *Small* **2018**, *14* (41), 1802764. https://doi.org/10.1002/smll.201802764.

(86) Kheng, K.; Cox, R. T.; d' Aubigné, M. Y.; Bassani, F.; Saminadayar, K.; Tatarenko, S. Observation of Negatively Charged Excitons X^- in Semiconductor Quantum Wells. *Phys. Rev. Lett.* **1993**, *71* (11), 1752–1755. https://doi.org/10.1103/PhysRevLett.71.1752.

(87) Lampert, M. A. Mobile and Immobile Effective-Mass-Particle Complexes in Nonmetallic Solids. *Phys. Rev. Lett.* **1958**, *1* (12), 450–453. https://doi.org/10.1103/PhysRevLett.1.450.

(88) Efros, Al. L.; Rosen, M. Random Telegraph Signal in the Photoluminescence Intensity of a Single Quantum Dot. *Phys. Rev. Lett.* **1997**, *78* (6), 1110–1113. https://doi.org/10.1103/PhysRevLett.78.1110.

(89) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. Fluorescence Intermittency in Single Cadmium Selenide Nanocrystals. *Nature* **1996**, *383* (6603), 802–804. https://doi.org/10.1038/383802a0.

(90) Wu, K.; Lim, J.; Klimov, V. I. Superposition Principle in Auger Recombination of Charged and Neutral Multicarrier States in Semiconductor Quantum Dots. *ACS Nano* **2017**, *11* (8), 8437–8447. https://doi.org/10.1021/acsnano.7b04079.

(91) Rinehart, J. D.; Schimpf, A. M.; Weaver, A. L.; Cohn, A. W.; Gamelin, D. R. Photochemical Electronic Doping of Colloidal CdSe Nanocrystals. *J. Am. Chem. Soc.* **2013**, *135* (50), 18782–18785. https://doi.org/10.1021/ja410825c.

(92) Sahu, A.; Kang, M. S.; Kompch, A.; Notthoff, C.; Wills, A. W.; Deng, D.; Winterer, M.; Frisbie, C. D.; Norris, D. J. Electronic Impurity Doping in CdSe Nanocrystals. *Nano Lett.* **2012**, *12* (5), 2587–2594. https://doi.org/10.1021/nl300880g.

(93) van der Stam, W.; Grimaldi, G.; Geuchies, J. J.; Gudjonsdottir, S.; van Uffelen, P. T.; van Overeem, M.; Brynjarsson, B.; Kirkwood, N.; Houtepen, A. J. Electrochemical Modulation of the Photophysics of Surface-Localized Trap States in Core/Shell/(Shell) Quantum Dot Films. *Chem. Mater.* **2019**, *31* (20), 8484–8493. https://doi.org/10.1021/acs.chemmater.9b02908.

(94) Park, Y.-S.; Bae, W. K.; Pietryga, J. M.; Klimov, V. I. Auger Recombination of Biexcitons and Negative and Positive Trions in Individual Quantum Dots. *ACS Nano* **2014**, *8* (7), 7288–7296. https://doi.org/10.1021/nn5023473.

(95) Zlateva, G.; Zhelev, Z.; Bakalova, R.; Kanno, I. Precise Size Control and Synchronized Synthesis of Six Colors of CdSe Quantum Dots in a Slow-Increasing Temperature Gradient. *Inorg. Chem.* **2007**, *46* (16), 6212–6214. https://doi.org/10.1021/ic062045s.

(96) Knauf, R. R.; Lennox, J. C.; Dempsey, J. L. Quantifying Ligand Exchange Reactions at CdSe Nanocrystal Surfaces. *Chem. Mater.* **2016**, *28* (13), 4762–4770. https://doi.org/10.1021/acs.chemmater.6b01827.

(97) Žídek, K.; Zheng, K.; Chábera, P.; Abdellah, M.; Pullerits, T. Quantum Dot Photodegradation Due to CdSe-ZnO Charge Transfer: Transient Absorption Study. *Appl. Phys. Lett.* **2012**, *100* (24), 243111. https://doi.org/10.1063/1.4729382.

(98) Houtepen, A. J.; Hens, Z.; Owen, J. S.; Infante, I. On the Origin of Surface Traps in Colloidal II–VI Semiconductor Nanocrystals. *Chem. Mater.* **2017**, *29* (2), 752–761. https://doi.org/10.1021/acs.chemmater.6b04648.

(99) van der Stam, W.; Grimaldi, G.; Geuchies, J. J.; Gudjonsdottir, S.; van Uffelen, P. T.; van Overeem, M.; Brynjarsson, B.; Kirkwood, N.; Houtepen, A. J. Electrochemical Modulation of the Photophysics of Surface-Localized Trap States in Core/Shell/(Shell) Quantum Dot Films. *Chem. Mater.* **2019**, *31* (20), 8484–8493. https://doi.org/10.1021/acs.chemmater.9b02908.

(100) du Fossé, I.; ten Brinck, S.; Infante, I.; Houtepen, A. J. Role of Surface Reduction in the Formation of Traps in N-Doped II–VI Semiconductor Nanocrystals: How to Charge without Reducing the Surface. *Chem. Mater.* **2019**, *31* (12), 4575–4583. https://doi.org/10.1021/acs.chemmater.9b01395.

(101) Maity, P.; Mohammed, O. F.; Katsiev, K.; Idriss, H. Study of the Bulk Charge Carrier Dynamics in Anatase and Rutile TiO2 Single Crystals by Femtosecond Time-Resolved Spectroscopy. *J. Phys. Chem. C* **2018**, *122* (16), 8925–8932. https://doi.org/10.1021/acs.jpcc.8b00256.

(102) Colvin, V. L.; Cunningham, K. L.; Alivisatos, A. P. Electric Field Modulation Studies of Optical Absorption in CdSe Nanocrystals: Dipolar Character of the Excited State. *J. Chem. Phys.* **1994**, *101* (8), 7122–7138. https://doi.org/10.1063/1.468338.

(103) Zheng, K.; Žídek, K.; Abdellah, M.; Zhang, W.; Chábera, P.; Lenngren, N.; Yartsev, A.; Pullerits, T. Ultrafast Charge Transfer from CdSe Quantum Dots to P-Type NiO: Hole Injection vs Hole Trapping. *J. Phys. Chem. C* **2014**, *118* (32), 18462–18471. https://doi.org/10.1021/jp506963q.

(104) Grimaldi, G.; Geuchies, J. J.; van der Stam, W.; du Fossé, I.; Brynjarsson, B.; Kirkwood, N.; Kinge, S.; Siebbeles, L. D. A.; Houtepen, A. J. Spectroscopic Evidence for the Contribution of Holes to the Bleach of Cd-Chalcogenide Quantum Dots. *Nano Lett.* **2019**, *19* (5), 3002–3010. https://doi.org/10.1021/acs.nanolett.9b00164.

(105) Žídek, K.; Zheng, K.; Ponseca, C. S.; Messing, M. E.; Wallenberg, L. R.; Chábera, P.; Abdellah, M.; Sundström, V.; Pullerits, T. Electron Transfer in Quantum-Dot-Sensitized ZnO Nanowires: Ultrafast Time-Resolved Absorption and Terahertz Study. *J. Am. Chem. Soc.* **2012**, *134* (29), 12110–12117. https://doi.org/10.1021/ja3029679.

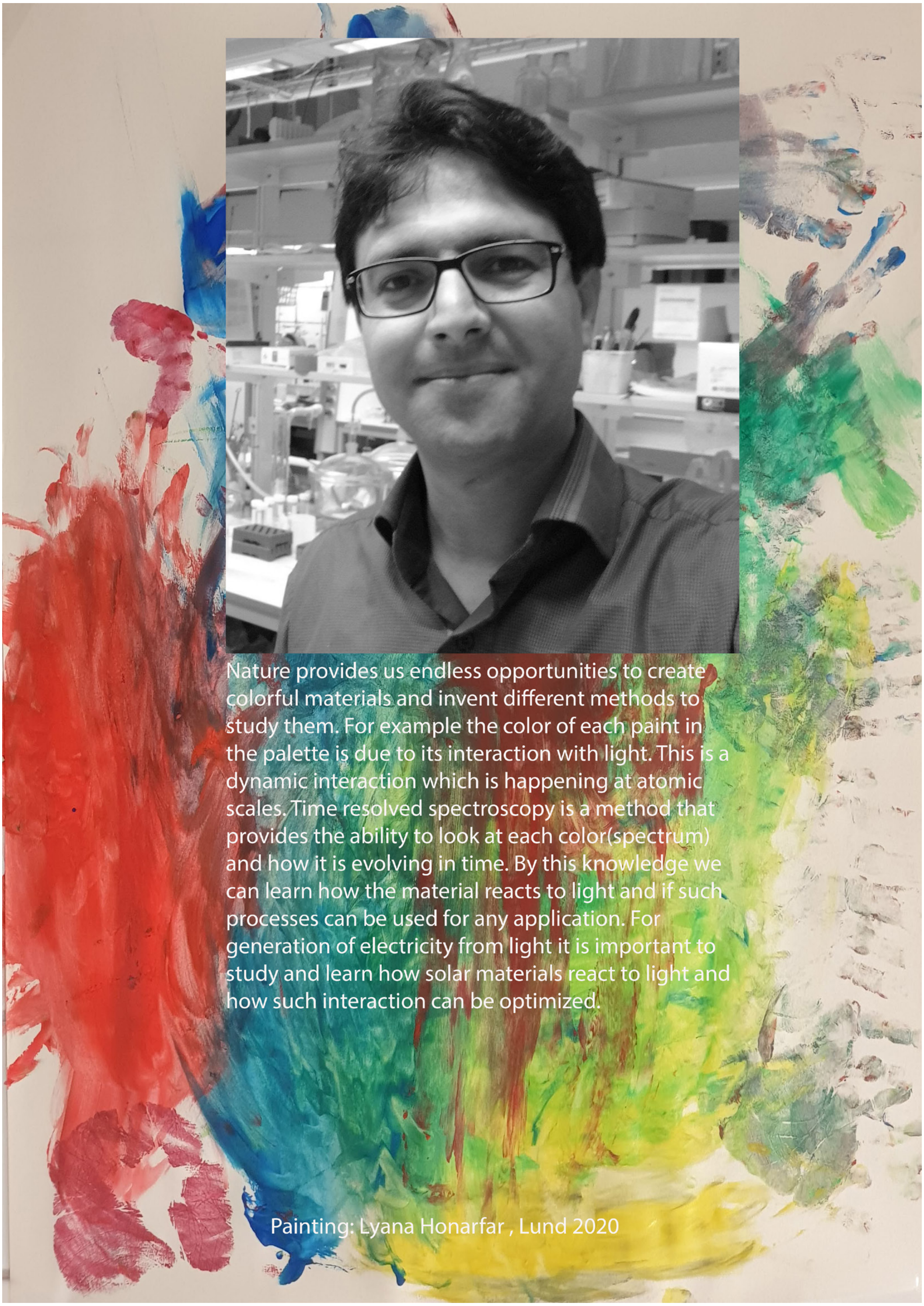
(106) Chen, J.; Messing, M. E.; Zheng, K.; Pullerits, T. Cation-Dependent Hot Carrier Cooling in Halide Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2019**, *141* (8), 3532–3540. https://doi.org/10.1021/jacs.8b11867.

(107) Zheng, K.; Abdellah, M.; Zhu, Q.; Kong, Q.; Jennings, G.; Kurtz, C. A.; Messing, M. E.; Niu, Y.; Gosztola, D. J.; Al-Marri, M. J.; Zhang, X.; Pullerits, T.; Canton, S. E. Direct Experimental Evidence for Photoinduced Strong-Coupling Polarons in Organolead Halide Perovskite Nanoparticles. *J. Phys. Chem. Lett.* **2016**, *7* (22), 4535–4539. https://doi.org/10.1021/acs.jpclett.6b02046.

(108) Karki, K. J.; Widom, J. R.; Seibt, J.; Moody, I.; Lonergan, M. C.; Pullerits, T.; Marcus, A. H. Coherent Two-Dimensional Photocurrent Spectroscopy in a PbS Quantum Dot Photocell. *Nature Communications* **2014**, *5* (1), 5869. https://doi.org/10.1038/ncomms6869.

(109) Leatherdale, C. A.; Kagan, C. R.; Morgan, N. Y.; Empedocles, S. A.; Kastner, M. A.; Bawendi, M. G. Photoconductivity in CdSe Quantum Dot Solids. *Phys. Rev. B* **2000**, *62* (4), 2669–2680. https://doi.org/10.1103/PhysRevB.62.2669.

(110) Hartstein, K. H.; Erickson, C. S.; Tsui, E. Y.; Marchioro, A.; Gamelin, D. R. Electron Stability and Negative-Tetron Luminescence in Free-Standing Colloidal n-Type CdSe/CdS Quantum Dots. *ACS Nano* **2017**, *11* (10), 10430–10438. https://doi.org/10.1021/acsnano.7b05551.



Nature provides us endless opportunities to create colorful materials and invent different methods to study them. For example the color of each paint in the palette is due to its interaction with light. This is a dynamic interaction which is happening at atomic scales. Time resolved spectroscopy is a method that provides the ability to look at each color(spectrum) and how it is evolving in time. By this knowledge we can learn how the material reacts to light and if such processes can be used for any application. For generation of electricity from light it is important to study and learn how solar materials react to light and how such interaction can be optimized.

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