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Intriguing Photochemistry of the Additives in the Dye-sensitized Solar Cells

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Abstract

Over the years numerous mixes of chemical compounds have been tried in the electrolytes of dye-sensitized solar cells in efforts to improve their efficiency. How these chemicals interact with each other and the photoelectrode has received surprisingly little attention. Here we report results from a systematic study of two I^-/I_3^- electrolytes and their additives using infrared and Raman spectroscopy together with quantum chemical calculations. In the LiI electrolyte competing interactions between lithium cation and the solvent MPN and the additives TBP, NMBI and GuSCN were identified. These interactions could inhibit the interaction of lithium ions with the TiO_2 surface. It was found that under Raman excitation of PMII solution in contact with the photoelectrode, efficient generation of I_3^- takes place. For LiI solution, in addition, a Dye- I_2 complex is formed. The results could be explained

by diffusion limited build-up of I_3^- and depletion of I^- concentrations in the focal area of the excitation beam and by reduction of I_3^- via conduction band electrons of TiO_2 beyond the focal region. To explain the formation of Dye- I_2 complexes in the LiI electrolyte solutions a multi-step regeneration mechanism is proposed. It was found that GuSCN reduces the I_3^- concentration in the electrolyte solutions studied, in the LiI electrolyte in addition it binds to lithium ions and nearly depletes the Dye- I_2 complexes. From infrared spectra, it became clear that preventing water entering the DSCs during the preparation stages in ambient air is a demanding task. The identified interactions paint an intriguing new photochemical landscape of the function of the dye-sensitized solar cells giving guidelines for further development of the devices.

Key words: adsorption, DFT, dye, electrolyte, FTIR, GuSCN, NMBI, photocatalysis, Raman, ruthenium, spectroscopy, TBP, TiO_2 ,

The dye solar cell (DSC) is a potential candidate among third generation solar cells for low-cost photovoltaic applications. Although the high efficiency of 12.3%¹ has been reported, due to the complexity of the system, there is not deep enough understanding of the molecular level interactions of the cell that would give a rationale for improvement of its efficiency and lifetime in a systematic way^{2, 3}. Much of the development work has been done by trial and error: by synthesizing and testing hundreds of dyes and electrolyte mixtures⁴. There have been several degradation issues of DSCs reported in the literature^{5, 6, 7, 8, 9}. Characteristic parameters of the DSCs such as efficiency, open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor, incident light to current conversion efficiency, etc. give the needed information on the performance of the cells. The problem with these standard methods is that they do not give information on ionic and molecular interactions, which lie in the heart of the function of the cell. In order to improve the efficiency, stability and lifetime of DSCs, it is inevitable to understand the mutual interactions of chemical species used in the DSCs.

Molecular modeling is obvious means to gain such information. For realistic quantum chemical simulations, one needs reliable initial boundary conditions and large enough size of the model system. Ab-initio modelling gives useful information on the energetics of the dye TiO_2 interface as well as the interactions between the sensitizer, TiO_2 and the electrolyte constituents^{10, 11, 12, 13, 14}. Yet the outcomes of quantum chemical simulations depend on the method and the relevance of the initial boundary conditions used. A full description of the function of DSCs needs dynamic simulations. Information on the dynamics of redox shuttles and the regeneration mechanisms have been obtained at ab initio molecular dynamics (MD) level of calculation^{15, 16}.

Experimental observations of molecular interactions in the DSCs provide valuable and needed input for modeling. Methods such as infrared and Raman spectroscopies are relatively simple and efficient in unraveling molecular site-selective interactions and hence give hints of which species interact with each other even in a complicated system like the DSC. In most earlier spectroscopic work either attenuated total reflection (ATR) FTIR or Raman spectroscopy has been used to study molecular properties of the DSCs^{7, 8, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32}. Our approach in the present study was to collect both infrared and Raman data in a systematic way for a pool of electrolyte solutions: in solution, in contact with TiO₂ and in contact with sensitized TiO₂.

The photoelectrode of a DSC is made by sensitizing a fired nanoporous anatase TiO₂ thin film. The role of adsorbed water on anatase surfaces and the degree of protonation has been discussed in the literature as it influences dye binding. Both loosely and tightly bound water as well as dissociatively adsorbed water resulting in formation of OH groups on the surface have been reported^{33, 34, 35}. However there is not much information on how much water is present in a DSC when prepared under ambient air. By recording the infrared spectra of I₂ and LiI solutions, 'dry' TiO₂ films and sensitized TiO₂ films immersed in the electrolyte we could get an idea of the amount of water present in the DSCs prepared under ambient air.

Appearances of various redox species in the electrolytes of the DSCs have been studied both experimentally and by quantum chemical methods^{36, 37, 38, 39, 40, 41, 42}. We have used the symmetric I₃⁻ stretching band to monitor conversion of iodide of the electrolyte solution into I₃⁻ on the photoelectrode under Raman illumination and its concentration dependence on electrolyte additives. The addition of GuSCN, in particular, seemed to reduce triiodide

concentrations in the electrolyte solutions.

There are previous spectroscopic and MD simulation reports on iodine binding to thiocyanate ligands of the ruthenium dyes in the DSCs^{16, 18, 43} and in the crystalline state⁴⁴.

We found out that iodine binding in the LiI electrolyte solutions to thiocyanate ligands of the N719, N3, Z907 dyes is dependent on the electrolyte composition and on photoexcitation. No dye-iodine interactions were seen in the PMII electrolyte solutions neither in any of the solutions on contact with the R505 dye that has two cyanide ligands instead of the thiocyanate ligands.

Performances of the DSCs have been found to improve on an addition of chemicals such as 4-tert-Butylpyridine (TBP), 1-methyl-benzimidazole (NMBI) and guanidinium thiocyanate (GuSCN) in the electrolyte solutions^{3, 45}. The addition of 4-tert-butylpyridine (TBP) and 1-methyl-benzimidazole (NMBI) in either I₂/LiI or I₂/PMII electrolyte increases the open circuit voltage and reduces the short circuit current of the DSCs^{2, 46, 47}. It has been suggested that TBP interacts with the TiO₂ surface producing a negative shift of its quasi-Fermi level and reduces recombination of the TiO₂ conduction band electrons with the I₃⁻ ions of the electrolyte⁴⁸. Also interactions between TBP, the sensitizer and TiO₂ have been reported to be the origin of improvement of the open cell voltage^{49, 50}. NMBI has similar effects on the cell performance than TBP but in some cases it works better, and in some cases worse, than TBP. In the present work, we could show that molecular interactions between lithium cation and TBP, as well as NMBI, occur in the LiI electrolyte solutions, which could inhibit the interactions of lithium ions on the photoelectrode and hence improve the performance of the cell.

An addition of GuSCN as the final constituent the LiI and PMII electrolytes has been

shown to increase the short circuit current but also the open circuit voltage of the DSCs^{19, 51, 52}. It has been reported that this additive also increases the stability of the cell⁵³. These improvements have been attributed to adsorption of the compound on TiO₂ to induce a negative shift of the TiO₂ conduction band edge to allow for more efficient electron injection as well as to cover the recombination sites and hence increase electron lifetime⁵¹. In contrast, it has also been stressed that GuSCN does not adsorb on the TiO₂ surface⁵², but rather binds to the dye¹⁹. The major change found on an addition of GuSCN was a decrease of the concentration of photogenerated I₃⁻ in all electrolyte solutions studied. The effect was strongest in the plain solutions and weaker when the solutions were in contact with the photoelectrode. In the LiI electrolyte, in addition, GuSCN seems to bind lithium ions and it nearly depletes the Dye-I₂ complexes from the electrolyte.

Results

Water in the DSCs. Water contamination of the DSCs has been considered to be one of the reasons for the relatively short lifetime of the DSCs⁵. Several of the DSC constituents, such as ruthenium dyes, I₂, LiI, TiO₂ and GuSCN, if exposed to ambient air, rapidly adsorb water. In addition ruthenium dyes and LiI are sensitive to light-induced degradation as mentioned in their material safety data sheets. In the present study OH stretching and bending modes, which are strong infrared absorbers, were used to monitor protonation and water on TiO₂. The spectra were recorded for ‘dry’ TiO₂ films (Figure S1), for the I₂ and LiI solutions in dried 3-methoxypropionitrile (MPN) and for the solutions in contact with TiO₂ (Figure 1) and sensitized TiO₂ films (Figure S2). As a signature of presence of monomeric water in solution the band doublet at 3545 cm⁻¹ and 3629 cm⁻¹ in the infrared spectrum was used. Adsorbed and associated water on ‘dry’ TiO₂ surface a broad red shifted OH stretching band in the frequency region from 2900 cm⁻¹ to 3650 cm⁻¹ was seen in the infrared spectra (Figure S1)²⁸. In the same region the OH groups of the TiO₂ absorb. It has been suggested that the red end of the OH stretching band is due to associated water molecules, while the blue end due to OH stretchings of Ti-OH groups and free OH groups of chemisorbed water on TiO₂^{33, 34, 35}. In the region from 1250 cm⁻¹ to 1750 cm⁻¹ two band groups appeared (Figure S1), one around 1630 cm⁻¹ due to OH bending vibrations of adsorbed and associated water and one around 1380 cm⁻¹ most likely due to CH₃ bending vibrations of the binder residuals of the TiO₂ paste⁵⁴. The spectral fingerprints in both spectral regions, the OH stretching and bending regions, gave direct evidence of water in ‘dry’ nanoporous TiO₂ films. Indeed, nanoporous TiO₂ films are known to adsorb water from the ambient air due to the hydrophilic nature of the TiO₂ surface and the capillary

condensation of water in the smallest nanopores,^{55, 56} even to the extent that they can be used as humidity sensors^{57, 58}. In a DSC, presence of water on TiO₂ surfaces can hinder the excited-state charge transfer which can adversely affect the device performance⁵⁹. To avoid capillary condensation and adsorption of water in the TiO₂ films, it has been recommended that the films are dipped in the dye solutions while they are still warm after the high-temperature annealing step, and dried under dry air or nitrogen^{56,60}. An interesting observation was that the OH bending bands showed significant sample-to-sample variation, although the TiO₂ films were fabricated, handled and measured under practically identical conditions (Figure S1).

Figure 1. FTIR spectra of I₂ and LiI solutions in MPN (red and blue, respectively) and of the same solutions in contact with a TiO₂ film (olive and green, respectively). Dash-dotted line is the reference spectrum of 0.56 mM water solution in deuterated acetonitrile. The bands in the OH bending (δ) and OH stretching (ν) regions are indicative of Ti-OH groups, adsorbed and associated water on TiO₂. The doublet OH stretching peak at 3545 and 3626 cm⁻¹ of water in acetonitrile and in iodine solutions is typical of monomeric water. The

strongly red shifted and broad OH stretching band of the LiI solution from 3600 cm^{-1} to 3200 cm^{-1} is indicative of aggregated water in solution.

Besides adsorbed water contained in TiO_2 , electrolyte additives add to water content in the DSCs. The infrared spectrum of the I_2 solution revealed that water from anhydrous I_2 was dissolved in MPN (Figure 1) giving a spectrum typical of monomeric water, similar to the spectrum of 0.56 mM water in deuterated acetonitrile (Figure 1). Water concentration dissolved from I_2 was estimated to be 0.2 mM , which can be compared to iodine concentration of 50 mM in the solution. Solution of anhydrous LiI in MPN instead showed a very broad and strongly red shifted OH stretching band peaking at about 3450 cm^{-1} and a blue shifted OH bending band at about 1650 cm^{-1} , both typical of associated water in solution (Figure 1). The widths and shifts of the bands reflect complex hydrogen bonding networks of Li^+ and water in MPN.⁶¹ From the spectra of Figure 1 we can estimate that water from I_2 and LiI amounts to 0.5 mM in solutions where both are present. When the solutions were brought in contact with TiO_2 , absorption of the OH groups both in the stretching and the bending regions roughly doubles (Figure 1). We estimate then that the total water content amounts to equivalent of 1 mM in the present preparations. Figure S2 shows that for sensitized films water contamination is similar to that in the plain TiO_2 films. An additional potential water source for the sensitized films comes from the sensitization process itself. We estimate that the water content in the PMII electrolyte is about 70 % from that in the LiI electrolyte.

From the above discussion it is concluded that since titanium lattice atoms, Ti-OH groups and adsorbed water on TiO_2 may serve as binding sites for the dyes, binding in the DSCs

is highly heterogeneous, and may vary from photoelectrode to photoelectrode depending on preparation history of the cell. Presence of water in the DSCs has two side effects, it may hinder electron injection and shorten the lifetime of the cell. Under ambient preparation conditions, according to the present results, avoiding water entering a DSC seems to be a demanding task.

Spectra of individual electrolyte additives. In Figure 2 FTIR spectra of PMII, TBP, NMBI and GuSCN in dry MPN are shown. The strong CN stretching band of the dry solvent, subtracted from all infrared spectra shown, was observed at 2250 cm^{-1} ^{7, 17, 18}.

Figure 2: FTIR spectra of individual electrolyte additives in dry 3-methoxypropionitrile (MPN): PMII (red), TBP (blue), NMBI (olive) and GuSCN (green). Note that the spectrum of the neat solvent has been subtracted from all spectra. Derivative type residue signal at 2050 cm^{-1} is due to varying band shapes of the strong CN stretching bands of the MPN solutions.

PMII, TBP and NMBI in MPN show characteristic and well separated infrared peaks at 1574 cm^{-1} , 1598 cm^{-1} and 1501 cm^{-1} , respectively (Figure 2). Strong characteristic peaks of GuSCN were found at 1667 cm^{-1} and at 2049 cm^{-1} , the former band representing the degenerate NH bending vibration of the Gu^+ cation, while the latter band represents the CN stretching of the SCN^- anion. The infrared peaks of the additives offer a straightforward means for estimation of their concentrations in the DSCs f.e. in aging experiments. The calculated vibrational frequencies with highest infrared intensities in this spectral region were predicted for PMII, TBP and NMBI at 1617 cm^{-1} (aromatic CN stretching), at 1621 cm^{-1} (aromatic CC stretching) and at 1516 cm^{-1} (aromatic CN stretching and CH_3 bending), respectively. The calculated frequency for the degenerate Gu^+ NH_2 bending vibration was 1727 cm^{-1} and the CN stretching frequency of the SCN^- anion 2072 cm^{-1} , in good agreement with the experimentally observed frequencies.

Lithium interactions. Addition of LiI in MPN to make a 0.1 M solution results in emergence of a shoulder at 2277 cm^{-1} ($A = 0.2$) on the blue side of the major CN stretching band of the solvent at 2250 cm^{-1} ($A = 2.4$, Figure 3). The blue shifted band was observed also in other LiI electrolyte solutions devoid of GuSCN in contact with TiO_2 and the sensitized TiO_2 , but not in any of the PMII electrolyte solutions. Hence the peak must be related to lithium cation. Appearance of a similar blue shifted band at 2275 cm^{-1} in the infrared spectrum of LiI in acetonitrile (ACN) has been reported.⁶² DFT calculations and MD simulations have shown that the shift was due to formation of $\text{Li}\dots(\text{ACN})_n^+$ clusters, where the nitrogen atoms of the acetonitriles of the first solvation shell interact with the lithium ion.^{62, 63}

Figure 3: FTIR spectra of 0.05 M iodine (blue), 0.1 M LiI (red), and I_2+LiI (green) solutions in MPN in the CN stretching region. In the insert the solvent spectrum has been subtracted for better visualization of the blue shifted CN stretching band at 2277 cm^{-1} , which is due to the solvent molecules surrounding lithium ions of the solution. Derivative type residue signals in the insert at 2050 cm^{-1} are due to varying band shapes of the CN stretching bands of the MPN solutions.

To explore the interaction between lithium ion and MPN, we performed a DFT calculation and found a stabilization energy of 209 kJmol^{-1} for a $Li\text{-MPN}^+$ complex, where lithium ion binds to the CN group of the solvent (Figure 4a). A blue shifted CN stretching frequency of 2293 cm^{-1} as compared to 2283 cm^{-1} of the ‘free’ MPN was predicted. Hence the blue shifted band at 2277 cm^{-1} (Figure 3) can be safely related to the CN groups of the MPN molecules of the first solvation shell of the lithium ions. We also performed a DFT

calculation on I⁻-MPN interaction, where iodide binds to the methyl group of MPN. A very shallow energy minimum was obtained with the CN stretching frequency red shifted to 2277 cm⁻¹ from 2283 cm⁻¹ of the ‘free’ MPN, in accordance with the results reported for the I⁻-ACN complex,⁶² excluding the possibility of the complex being responsible for the observed blue shift.

Addition of TBP or NMBI to I₂+LiI solution (Figure 4), to the solution in contact with TiO₂ (Figure S3) and to the solution in contact with sensitized TiO₂ (Figures S6 and S7) results in splitting of the characteristic bands of TBP at 1598 cm⁻¹ and of NMBI at 1502 cm⁻¹, with blue shifted shoulders appearing at 1605 cm⁻¹ and at 1513 cm⁻¹, respectively. The splittings were not observed in any spectra of the PMII electrolyte solutions (Figure S3). Then the interaction responsible of the splittings is characteristic of the LiI electrolyte and takes place in the electrolyte and not on the photoelectrode. To explore the origin of the interaction DFT calculations were performed. Stable minimum energy structures and stabilization energies of 245 kJ mol⁻¹ and 356 kJmol⁻¹ were obtained for the Li-TBP⁺ and Li-NMBI⁺ complexes, respectively (Figure 4, b and c). The calculations also predicted the blue shifted frequencies of 1639 cm⁻¹ and 1539 cm⁻¹ of the aromatic CN ring stretching vibrations as compared to the corresponding frequencies of ‘free’ TBP and NMBI vibrations at 1621 cm⁻¹ and at 1516 cm⁻¹, respectively. Since according to DFT results the Li-TBP⁺ and Li-NMBI⁺ complexes have higher stabilization energies than the Li-MPN⁺ complex, it seems likely that in LiI electrolyte solutions with TBP and NMBI added a fraction of lithium ions leave their solvation shells and bind to TBP or NMBI. This interpretation is further supported by the fact that the absorbance of the MPN-Li⁺ CN

stretching band at 2277 cm^{-1} is reduced almost to one-half on addition of TBP or NMBI in I_2+LiI solution (Figure 4).

Figure 4: FTIR spectra of LiI electrolyte solutions showing effects of addition of TBP and NMBI. Colour coding: top image TBP in MPN (red) I_2+LiI (green), $\text{I}_2+\text{LiI}+\text{TBP}$ (blue). Observe the splitting of the aromatic stretching band of TBP at 1598 cm^{-1} and at 1501 cm^{-1} on addition of TBP or NMBI, respectively, followed by concomitant reduction of the intensity of the CN stretching band of the Li-MPN^+ complex at 2277 cm^{-1} . None of the splittings seen in the LiI electrolyte were observable in the PMII electrolyte (Figure S3). On the right minimum energy structures of a) Li-MPN^+ b) Li-TBP^+ and c) Li-NMBI^+

complexes according to DFT calculations are shown. Observe that Li^+ binds to the available lone pair orbitals of the nitrogen atom in all cases. Coloring of the balls, hydrogen (white), carbon (grey), nitrogen (blue), oxygen (red) and lithium ion (violet).

Addition of the fourth component, GuSCN, in the LiI electrolyte is accompanied with an emergence of a clearly resolved shoulder at 2069 cm^{-1} on the blue side of the CN stretching band of the guanidinium SCN^- anion at 2050 cm^{-1} (Figure S3, top images). No such splitting is observed in the PMII electrolyte. Hence the new band must be connected to lithium interaction. We calculated the vibrational CN stretching frequency of the hypothetical LiSCN species assuming it to be responsible of the blue shift. For the minimum energy structure of the complex a blue shift of the CN stretching frequency to 2084 cm^{-1} from non-perturbed SCN^- frequency at 2070 cm^{-1} was predicted (Table 2). In reality Li^+ and SCN^- ions probably form a tightly bound di-ion in solution. The fact that lithium cation binds to TBP, NMBI and SCN^- in the LiI electrolyte means, that the concentration of solvated Li^+ ions of the electrolyte is dramatically reduced, and hence lithium binding to these additives reduce the probability of lithium ions entering the negatively charged TiO_2 in a functioning DSC. This could be an additional reason why these additives often compensate for the effect of Li^+ on the surface charge of TiO_2 , observed as shifting in the conduction band edge potential of TiO_2 vs. the electrolyte ^{64, 65}.

Iodine and iodide interactions. The Raman spectrum of the iodine solution in MPN shows two characteristic peaks, the symmetric stretching band of the triiodide (I_3^-) anion at 113 cm^{-1} (s) and the stretching band of iodine at 168 cm^{-1} (m) (Figure 5, top image). The assignment of the iodine band at 168 cm^{-1} was confirmed by increasing iodine

concentration in solution and observing the concomitant (although not quantitatively proportional) increase of the intensity of the 168 cm^{-1} band in the Raman spectrum (Figure S4). The DFT calculations predicted the Raman active stretching frequencies of I_2 and I_3^- to be 181 cm^{-1} and 144 cm^{-1} , respectively (Table 1). Formation of a charged I_3^- species in a neutral iodine solution requires formation of the counter ion to preserve electroneutrality. A plausible mechanism is self-dissociation of iodine aided by solvent interaction⁶⁶. DFT calculations were performed to test this hypothesis. Stabilization energy of about 270 kJmol^{-1} for the I-MPN^+ complex, where I^+ interacts with the CN group was obtained. For the I-MPN^- complex, where I^- interacts with the CH_3 group, a stabilization energy of 35 kJmol^{-1} was obtained. Hence we suggest that a head on approach of iodine towards the CN group of the solvent is the mechanism to form the charge transfer complex $\text{R-CN-I}^+ - \text{I}^-$, which further splits into R-CN-I^+ and I^- ions in solution. The so formed I^- then moves on to react with molecular iodine to form I_3^- . It is noted that small amounts of I_3^- is formed also in LiI solution but not in the PMII solution.

Addition of LiI or PMII into iodine solution resulted in a dramatic increase of I_3^- concentration in both mixtures and in a total loss of iodine from the solutions (Figure 5 and Figure S5, top). The weak bands in the Raman spectra at 148 cm^{-1} and 226 cm^{-1} are due to asymmetric stretching and the overtone of the symmetric stretching of I_3^- , respectively³⁶. Disappearances of the I_2 bands, and the similar intensities of the I_3^- bands at 113 cm^{-1} , in spite of different iodide concentrations (LiI 0.1M) and (PMII 0.6M), suggest that the initially added iodine has reacted with iodide to form I_3^- and that the excess iodide remains in solution (Figure 5 and Figure S5, top). The result is in full agreement with the known

fact that excess iodide in iodine solution shifts the equilibrium strongly towards I_3^- and negligible amounts of dissolved iodine is left in solution⁶⁷.

Figure 5: Low frequency Raman spectra of the I_2 /LiI electrolyte solutions. The top images show the solution spectra and the bottom images the spectra of the solutions in contact with TiO_2 . Colour coding: iodine solution (red), LiI solution (blue), I_2 +LiI solution (purple), I_2 +LiI+TBP solution (olive), I_2 +LiI+TBP+GuSCN solution (green). Corresponding spectra for the I_2 /PMII electrolyte are shown in Figure S5. The TiO_2 lattice vibration band

at 145 cm^{-1} was used as an internal standard to allow comparison of the intensities of the I_3^- stretching bands at 113 cm^{-1} .

The Raman spectra of LiI and PMII solutions in contact with TiO_2 showed only small traces of I_3^- (Figure 5 and Figure S5, bottom), but to our surprise in I_2+LiI and I_2+PMII solutions the I_3^- concentrations were roughly the same as in the I_2 solution in contact with TiO_2 (Figure 5, and Figure S5, bottom). This means that I_3^- was not generated as efficiently in presence of TiO_2 than in plain I_2+LiI and I_2+PMII solutions. The reason could be recombination of I_3^- ions into I^- ions aided by CB electrons of TiO_2 generated by two photon excitation under intense Raman illumination.

Additions of TBP or NMBI in I_2+LiI and I_2+PMII solutions and the solutions in contact with TiO_2 only slightly reduces the I_3^- concentration but addition of GuSCN results in substantial reduction (Figure 5 and Figure S5). The only spectral change, besides substantial drop of the intensity of the I_3^- band at 113 cm^{-1} , related to GuSCN addition was a small red shift of the NH bending band of the Gu^+ cation to 1660 cm^{-1} (Figure S4) from its solution value of 1667 cm^{-1} (Figure 2) in the infrared spectra. The shift suggests that the Gu^+ cation is involved in the reaction. Tentatively we suggest that guanidinium cations somehow hinder formation of triiodide in the electrolytes without involvement of the dye.

Electrolyte solutions in contact with the photoelectrode: On excitation the electrolyte solutions in contact with the photoelectrode, most of the light is absorbed by the sensitizer, which undergoes a transition from the ground state to the lowest excited electronic states

of the dye. Once excited, the dye undergoes ultrafast electron transfer (injection) to the conduction band (CB) of TiO_2 . The oxidized dye is prone to regeneration via diffusion, which is dependent on the encounters with iodide ions from the electrolyte, and is aided by Coulomb attraction. Under CW illumination a steady state builds up between the electrons injected into the CB of TiO_2 and the electrons lost from TiO_2 in reduction of I_3^- and in recombination with the oxidized dye. Since no external current is taken from the photoelectrode, the situation represents the open-circuit condition of a corresponding illuminated DSC. To learn about photochemistry of the electrolytes, we first discuss the Raman spectra of the LiI and PMII solutions in contact with plain TiO_2 and N719 sensitized TiO_2 (Figure 6).

Figure 6. Low frequency Raman spectra of LiI and PMII solutions in contact with TiO_2 and in contact with N719 sensitized TiO_2 . Notice the bands at 113 cm^{-1} and at 168 cm^{-1} of the LiI solution (in red) are indicative of photoinduced formation of I_2^* and I_3^- on the photoelectrode and the electrolyte solution, respectively. In the PMII solutions, the I_2^* band is missing and the intensity of the 113 cm^{-1} band from the N719 sensitized TiO_2 is about five times as high as the corresponding band of the LiI solution, reflecting the concentration ratio of the two solutions. The anatase lattice vibration band at 145 cm^{-1} was used as an internal intensity standard (scaled to 100).

The Raman spectrum of LiI solution in contact with the photoelectrode (Figure 6, left) shows a strong I_3^- peak at 113 cm^{-1} and a ' I_2 ' peak at 168 cm^{-1} , whereas the spectrum of the solution in contact with plain TiO_2 only a faint feature at 113 cm^{-1} is seen (Figure 6, left). In the corresponding PMII spectra, a very strong I_3^- band at 113 cm^{-1} is seen (Figure 6, right) but the ' I_2 ' peak is missing. The intensity of the 113 cm^{-1} band of the PMII spectrum is about five times as high as that of the LiI spectrum, which matches well the I^- concentration ratio of the two solutions (PMII, 0.6 M and LiI, 0.1 M). It is clear from Figure 6 that photoconversion of iodide ions to triiodide occurs in both solutions extremely efficiently under Raman illumination. Since the only reactant available in the solution to produce I_3^- is the iodide ion, the photoconversion must begin with an encounter of iodide ion and dye cation. Encounters are diffusion controlled and facilitated by Coulomb attraction. The reactions that follow produce I_3^- and store a fair fraction of the photon energy of the excitation light in the chemical bonds of triiodide.

In the confocal Raman experiment, the laser beam in the excitation area has a photon flux corresponding to more than 100 A/cm^2 electron injection rate (10^4 'Suns'). Under a Gaussian laser beam photogeneration of I_3^- in the center of the beam is strongest and a concentration gradient, which drives a steady flux of I_3^- ions towards bulk solution, forms. Triiodide ions have two options to react further away from the high light intensity area, one with CB electrons of TiO_2 and the other with the dye cation. On the other hand, the concentration of the reactant I^- in the center of the laser beam is strongly reduced and diffusion of I^- ions from the bulk solution towards the excitation volume will be initiated.

In equilibrium, the excitation volume becomes practically depleted from I^- , and I_3^- concentration builds up as shown in the Raman spectra of Figure 6. The two electrons created by the total reaction $3I^- \rightarrow I_3^- + 2e$ are conveyed by the dye to the CB of TiO_2 , the two electrons needed for the total reaction $I_3^- + 2e \rightarrow 3I^-$ are provided by the CB of TiO_2 away from the excitation volume. The options for the latter reaction are: 1) reduction of I_3^- directly by the CB electrons from TiO_2 , 2) the reaction of the dye cation and triiodide to form Dye- I_3 complex, that after receiving two electrons from the CB of TiO_2 would then form three iodide ions in solution. For these mechanisms we do not have direct evidence. Proposed diffusion processes are schematically visualized in Figure 7.

Figure 7. Schematic presentation of I^- and I_3^- diffusion processes in LiI and PMII solutions in contact with N719 sensitized TiO_2 under Raman illumination.

The diffusion model explains why the six-fold increase in iodide concentration from 0.1 M in LiI to 0.6 M in PMII solution results in almost equal (five-fold) increase of the intensities of the corresponding 113 cm^{-1} I_3^- Raman bands in the spectra (Figure 6): the rate of dye regeneration, and therefore the build-up of I_3^- concentration within the laser beam, increases proportionally to the bulk concentration of I^- , according to a simple linear diffusion process.

The described processes underline the iodide interactions observable by Raman spectroscopy also in the other solutions in contact with the dyed TiO_2 (Figure 8), which therefore represent the photoelectrochemistry of DSC under high excitation conditions. For example, we note that the dye has no influence on the height of the I_3^- peak in the case of the plain I_2 solutions, but increases only in the presence of I^- (Figure 8 vs. Figure 5, bottom). This further supports the above reasoning that the excess I_3^- is generated specifically via a reaction between the dye cation and I^- , which has been proposed to be the first step of the dye regeneration process in the DSCs^{43, 68}. Further discussion on photogeneration of I_3^- in the Raman excitation volume can be found in Supporting information (Text 1).

Although the detection of photogenerated I_3^- does not alone reveal details about the underlying reaction mechanisms, other features in the Raman and FTIR spectra of the solutions proved to be helpful and will be discussed next.

Figure 8: Low frequency Raman spectra of I^-/I_3^- electrolyte solutions in contact with the N719 sensitized TiO_2 photoelectrode. Colour coding: I_2 solution (red), LiI or PMII solutions (blue), I_2 +LiI or I_2 +PMII solutions (magenta), I_2 +LiI+TBP or I_2 +PMII+TBP solutions (olive), I_2 +LiI+TBP+GuSCN or I_2 +PMII+TBP+GuSCN (green). Solvent was MPN. The anatase lattice vibration band at 145 cm^{-1} was used as an internal intensity standard (scaled to 100).

The infrared spectrum of the iodine solution in contact with the N719 sensitized photoelectrode shows a blue shifted CN stretching band from its solution value of 2106 cm^{-1} to 2130 cm^{-1} (Figure 9, top). Similar blue shifts were observed also for the N3 and Z907 dyes (Figures S6 and S7). To explore the origin of the observed shifts, DFT calculations for the N3 dye and its iodine complexes as representative samples were performed. Stable energy minima were obtained for the N3-I and N3- I_2 complexes, where iodines bind to a thiocyanate ligand of the dye (see Supporting material, Text 2, Figure S8 and Table 3). The complexes have been reported to appear as stable species also in an ab-initio molecular dynamics simulation by Schiffmann et.al.¹⁶ The crystal structure of the N3- I_2 complex has been published and role of iodine interactions in the DSCs discussed.⁴⁴ The present and published results suggest that the blue-shifted CN stretching bands of

N719, N3 and Z907 sensitized photoelectrodes in contact with iodine solution observed in the infrared spectra are due to the ground state Dye-I₂ complexes. When ever iodide was present in the solutions, the I₂-dye complex bands were not seen in the infrared spectra. (Figure 9, top, Figures S6 and S7).

Figure 9: FTIR (top) and Raman (bottom) spectra in the CN stretching region of N719 sensitized photoelectrode in contact with LiI and PMII electrolytes containing the TBP additive. The CN stretching bands of the solvent MPN (2252 cm⁻¹), thiocyanate of the dye (2106 cm⁻¹), thiocyanates of the Dye-I₂ complex (2130 cm⁻¹) as well as the SCN⁻ of GuSCN (2050 cm⁻¹) are shown in the spectra. Colour coding of the solutions : Iodine (red), LiI or PMII (blue), I₂+LiI or I₂+PMII (magenta), I₂+LiI+TBP or I₂+PMII+TBP (olive) and I₂+LiI+TBP+GuSCN or I₂+PMII+TBP+GuSCN (green). Solvent spectrum has been

subtracted from the infrared spectra. The non-resonant CN stretching Raman band of the MPN solvent was used as an internal standard. Corresponding Raman spectra for the NMBI additive are shown in Figure S9.

It was not surprising to see the CN stretching of the excited Dye-I₂ complex at 2131 cm⁻¹ in the Raman spectrum of the iodine solution in contact with the N719 sensitized photoelectrode (Figure 9, bottom). The peak appeared within the experimental error at the same characteristic vibrational frequency as in the ground state FTIR spectrum (Figure 10, top). However, it was surprising to see the shifted Raman band also in LiI, and I₂+LiI solutions as well as in solutions where TBP and NMBI had been added (Figure 10 bottom). Remarkably, the appearance of the 168 cm⁻¹ 'I₂' peak in the low frequency Raman spectra of different samples with LiI present (Figure 8, left), correlates exactly with the appearance of the dye-I₂ complex in the CN stretching region of the same samples (Figure 9, bottom left). This tells us that the 168 cm⁻¹ 'I₂' peak represents the vibration of the dye-bound I₂, since whenever iodide is present in excess in I₂ solution the concentration of free iodine is negligible⁶⁷.

Adding TBP to the I₂+LiI solution in contact with the photoelectrode had practically no effect on the triiodide concentration but it roughly halved the Dye-I₂ concentration (Figure 8, left and Figure 9, bottom, left). Addition of 0.25 M of GuSCN on the other hand, halved the triiodide concentration and nearly depleted the Dye-I₂ complexes (Figure 8, left and Figure 9, bottom, left). In the I₂/PMII electrolyte, addition of GuSCN reduces the triiodide concentration only about 30% (Figure 8, right), much less than what was found in plain solution or in the solution in contact with TiO₂. The reason may be related to the build-up

of the high I_3^- concentration in the excitation volume. The mechanisms of TBP, NMBI and GuSCN inhibition of formation of the Dye- I_2 complex and of reductions of I_3^- concentrations, with different efficiencies remains to be further explored.

An intriguing question is: What is the mechanism for the photoinduced formation of I_3^- in the LiI and PMII solutions in contact with the photoelectrode and what is the mechanism that can also explain formation of the Dye- I_2 intermediate in the LiI electrolyte. A possible reaction scheme that could explain the photoreactions observed in the LiI electrolyte is depicted in the reactions (i-vii) below. At 530 nm Raman excitation, the dye absorbs most of the light and becomes excited (i). Immediately after excitation ultrafast electron injection to the CB of TiO_2 takes place and the dye cation is formed (ii). Next iodide and the dye cation interact (iii), which, due to Coulombic attraction, is more likely to occur, than an encounter between iodide and the neutral excited dye. In this process, an electron is returned to the oxidized dye and the Dye-I complex formed. Characteristic to the steps that follow thereafter, and which lead to the concurrently observed photogeneration of I_3^- and formation of

Figure 10: Comparison of selected infrared and Raman spectra from Figure 9 for I_2 +MPN, LiI+MPN and PMII+MPN solutions in contact with N719 sensitized TiO_2 photoelectrode. The blue shifted CN stretching band at 2130 cm^{-1} of the Dye- I_2 complex is seen in the infrared and Raman spectra. Unexpectedly the Raman spectrum of the LiI solution (blue) also shows the blue shifted band at 2033 cm^{-1} indicative of the formation of the excited N719- I_2 complex without presence of iodine in solution. The PMII solution does not give rise to shifted CN stretching peak neither in the infrared nor in the Raman spectrum. The band at 2277 cm^{-1} in the infrared spectrum of the LiI solution is due to CN stretching of the MPN molecules of the first solvation shell lithium ions in solution (top). Solvent spectrum has been subtracted from all infrared spectra shown. Derivative type residual solvent signal around 2250 cm^{-1} is due to different band shapes of the solution spectra.

the Dye- I_2 intermediate, is that they must take place without free iodine, since there is none available in the LiI solution, or in solutions containing both iodine and iodide. Then under

intense Raman photon flux the Dye-I complex is excited, electron is injected to the CB of TiO₂ and the Dye-I⁺ complex is formed. Iodide encounter with the Dye-I⁺ cation then produces the Dye-I₂ intermediate (iv-vi).

Finally, an encounter of iodide ion and the Dye-I₂ complex completes the cycle and produces I₃⁻ and the dye in the ground state (vii). This reaction scheme could also explain why the Dye-I₂ complex was seen with FTIR in the dark with the plain I₂ solution, but never when I⁻ was available. Further argument in favour of reaction (vii) is that according to our DFT calculations, the N3-I₂ LUMO level is shifted about 0.2 eV towards negative energy from the N3 LUMO level, making electron injection from the complex less efficient than from N3 or N3-I. An alternative mechanism to produce I₃⁻ could be photoexcitation of the Dye-I₂ complex via a third photon, followed by electron injection and an iodide encounter with the Dye-I₂⁺ to produce the Dye-I₃ radical. Yet, one would expect this complex to be quite unstable since the I₃ radical itself is known to be a very weakly bound compound⁶⁸ and hence the complex could be decomposed by CB electrons from TiO₂ to form three iodide ions and the ground state dye. Formation of the Dye-I₂ complex through

the scheme (i-vii) would be favourable when the excitation rate of the dye is high and the I^- concentration is low, which are exactly the special conditions under the intense Raman laser beam for the LiI electrolyte in contact with the photoelectrode. The proposed regeneration mechanism for the high light intensity conditions is worth considering also for the normal operating conditions of the DSCs, where the mechanism could be the same, only the rate of photoconversion much lower.

For the PMII solutions in contact with the photoelectrode we saw efficient photoconversion of iodide to triiodide but no signatures of the Dye- I_2 complex. Neither we saw signs of the iodine complex in the infrared spectra of R505 sensitized photoelectrode in contact with the I_2 solution. The CN stretching band of the R505 dye appeared in the infrared spectra always at 2080 cm^{-1} in the electrolyte solutions studied (Figure S10). The R505 dye has cyanine ligands instead to thiocyanate ligands in the N3, N719 and Z907 dyes. Hence the regeneration mechanism in these cases is most likely different from the scheme (i-vii). One option, already proposed in the literature is a ‘soft’ encounter of the dye cation and iodide anion, where the dye cation is reduced and an iodine atom is formed (viii). Iodine atoms have not been directly identified in the electrolytes but formation of the iodine radical anion as a secondary product has been observed in the transient absorption spectra of $Ru(bpz)_2(deeb)^{2+}$ sensitized photoelectrode in contact with an organic iodide TBAI (tetrabutylammonium iodide) solution^{69, 42}.

To explore the energetics of formation of the iodine radical anion and the possible next regeneration steps to produce triiodide, high level quantum chemical calculations were performed. The reaction between iodine atom and iodide to form iodine radical anion

according to the calculations is thermodynamically favourable (ix). For the next reaction steps there are two options: 1) the iodine radical anion reacts with an iodine atom to form triiodide (x), 2) two iodine radical anions react to form triiodide and iodide ion (xi). From these reactions the latter reaction (xi) is widely considered as a final step of the regeneration reaction in the DSCs^{43, 67}.

We find that the reaction (x) in acetonitrile is much more exogenic than the reaction (xi). In addition the disproportionation reaction of two $\text{I}_2^\bullet$ anions face Coulombic repulsion, making the reaction barrier most likely higher than that of the reaction (x). Which of the two channels is favoured depends on the probabilities of iodine atom – iodine radical anion (x) on one hand and iodine radical anion – iodine radical anion (ix) encounters on the other. Probabilities of these encounters depend on the lifetimes of the two species in the electrolytes, for which we do not have direct evidence. On simple diffusion grounds reaction (x) would be favoured since diffusion constant of iodine atom is most likely larger than that of the iodine radical anion in the electrolyte.

Both proposed reaction schemes (i-vii) or (i-ii and viii) include an encounter with iodide and the dye cation as the first regeneration step. In both cases, either in ‘soft’ iodine encounter with the dye to produce iodine atom or in formation of the Dye-I intermediate, depletion of the dye cation will occur. Indeed disappearance of the dye cation signal in

transient absorption experiments for the N3 and N719 sensitized photoelectrodes in contact with full electrolyte has been seen in the time window from a few ps all the way up to nanoseconds, the kinetics being highly multiexponential⁷⁰. The present spectroscopic results support the interpretation that the few ps component is connected to the encounter of iodide and the dye cation. This time domain has been verified also in a recent MD simulation⁷¹. The transient kinetics at later times up to nanoseconds would then corresponds time evolution of the second phase reactions (iv) – (vii) or (ix) – (xi).

Discussion. The spectroscopic results discussed above underline the complexity of ionic interactions taking place in iodide–triiodide electrolytes used in the DSCs. One of the important observations of the present study was complexity of lithium interactions in the electrolyte solution. In previous studies increase of lithium concentration in the electrolyte has been seen as slight lowering of the V_{OC} , but as improved photocurrent generation in the DSCs. Improved performance has been ascribed to lowering of the conduction band edge of TiO_2 due to lithium adsorption, which improves electron injection efficiency and hence the performance of the cell^{72,73,74}. Here we have shown that lithium plays a much more complicated role. Firstly in pure electrolyte solvent MPN, lithium ions seem to be strongly solvated. The addition of TBP or NMBI in the electrolyte makes a substantial proportion of the ions leave the solvation shell and bind to the nitrogen lone pair electrons of these additives. Finally, addition of GuSCN seems to remove the rest of iodide ions from the solvation shells to form thiocyanine-lithium charge transfer complexes. TBP, NMBI and GuSCN share the common property of binding lithium in the electrolyte thus reducing its mobility and adsorption probability on TiO_2 .

The second important finding was observation of the persistent presence of water in the DSCs prepared under ambient air. At least three sources of water were identified, iodine and LiI and water adsorbed on TiO₂ under ambient air conditions. Also, sensitization of the TiO₂ film is subject to water exposure. For all the prepared photoelectrodes varying amounts of water were observed, equivalent roughly to 1 mM, which can be compared f.e. to iodine concentration of 50 mM of the electrolytes. Water influences the performance of the DSCs in several ways, it is harmful to the dye, it reduces the injection efficiency⁵⁹, it breaks the protective organized solvent layer next to the TiO₂ surfaces⁷⁵ and it may bind to the protonated sites of TiO₂ as well as form aggregates on the TiO₂ surfaces. Since the dye can bind besides to titanium atoms of TiO₂, also to adsorbed water and the OH groups on TiO₂, in a DSC there will always be a distribution of dye binding sites as well as binding energies. This is in line with the multiexponential injection kinetics reported in the literature⁷⁶. The amount of water entering the cell is dependent on its preparation history. Avoiding water contamination during the preparation stages is a prerequisite for improvement of efficiency and the lifetime of the DSCs.

Raman spectroscopic results gave abundant information of the role of iodide photochemistry in the DSCs. Though during Raman illumination the photon flux entering the photoelectrode is about 10000 times higher than that of full Sun, the basic photochemical reactions observed most likely are the same also under low intensity conditions in functioning DSCs. One of the most striking findings of the present work was very efficient conversion of iodide ions into tri-iodide ions in LiI and PMII solutions in contact with the photoelectrode under Raman illumination. Accumulation of triiodide and depletion of iodide in the center region of the excitation beam could be understood via a simple

diffusion model. In these reactions, a part of photon energy is converted into chemical energy of the triiodide bonds.

The final observation was that GuSCN in the electrolyte solutions roughly halves triiodide concentration. The effect is weaker in electrolytes in contact with the photoelectrode, probably due to high I_3^- concentration created under Raman illumination. We did not observe any other spectral changes, that could be related to this phenomenon, except the reductions of the 113 cm^{-1} I_3^- band intensity in the Raman spectra. Tentatively Gu^+ and triiodide could react near TiO_2 surface to form iodide anions. It is known that this additive improves the cell efficiency, the interactions related to improvement still remain unclear with the spectral results of the present work at hand.

Conclusions

We have studied complex photochemistry of the additives in two I/I_3^- electrolytes of dye sensitized solar cells by systematically recording their infrared and Raman spectra in solution, in the solutions in contact with plain and sensitized TiO_2 films. Infrared spectra revealed that the organic DSC additives can be clearly identified in the spectra. It was found out that lithium ions have multiple interactions with the electrolyte constituents, including the solvent MPN and the additives TBP, NMBI and GuSCN. Interactions could inhibit Li^+ ions entering the TiO_2 surfaces of the photoelectrode. Efficient diffusion controlled accumulation of photogenerated I_3^- was observed under intense Raman illumination for LiI and PMII solutions in contact with the photoelectrode. In LiI electrolyte solutions devoid of GuSCN, regeneration at the photoelectrode seems to involve formation of Dye-I and/or Dye- I_2 intermediates. Iodine binding was confirmed to occur via a thiocyanate ligand of

the dye, and was seen in the dark by FTIR only when no I^- was in the solution, whereas under the Raman excitation it occurred in the LiI electrolyte solutions, but not in the PMII electrolyte solutions. For the regeneration reactions in the studied electrolytes two different mechanisms were proposed: 1) a multistep scheme explaining formations of triiodide and the Dye- I_2 intermediate in the LiI electrolyte, 2) a mechanism that involves ‘soft’ encounter of iodide and the dye cation to form the reduced dye and iodine atom, followed by iodine atom reactions to produce triiodide. Besides near depletion of the Dye- I_2 complexes and solvated lithium ions in the LiI electrolyte, GuSCN efficiently reduced concentrations of the photogenerated I_3^- in both electrolytes. Finally, infrared absorbance measurements showed varying presence of water in the prepared cells, which depends on the preparation history of the cells under ambient air. The present study paints an intriguing new photochemical landscape of the fundamental ionic and molecular interactions of the dye-sensitized solar cells using iodide-triiodide electrolytes. Revelation of multiple ionic and molecular interactions in the electrolytes studied give fundamental information for controlling the function of the additives in the DSCs.

Methods

Materials and sample preparation. The dyes N3, N719, Z907, R505 were used as obtained from Solaronix. Electrolyte chemicals used were as follows: iodine (I_2 , Sigma–Aldrich, $\geq 99.8\%$), Lithium iodide (LiI, Aldrich, 99.9%), 1-propyl-3-methylimidazolium iodide (PMII, Solaronix), 4-tert-butylpyridine (TBP, Aldrich, 96%), 1-Methylbenzimidazole (NMBI, Aldrich, 99%), Guanidinium thiocyanate (GuSCN, Sigma, $\geq 99\%$) in 3-methoxypropionitrile (MPN, AlfaAesar, 99%). To avoid water contamination in the samples, the solvent used was distilled at 165 °C over $CaCl_2$ and stored under molecular sieves. Furthermore, the chemicals which were prone to absorb moisture from ambient air (LiI, GuSCN), were dried in an oven. The handling of the chemicals during the sample preparations was done in a manner to avoid unnecessary exposure to the ambient air and samples were stored in a desiccator.

For Raman measurements, the photoelectrodes were prepared on FTO glass (TEC 15) and the cells sealed with a thin microscope cover glass. The TiO_2 (Dyesol paste) films were prepared by screen printing and sintering the at 450°C for 30 minutes. The TiO_2 films were about 12 μm thick. Sintered films were sensitized in 0.32 mM dye solutions of N3, N719, Z907 and R505 dyes in ethanol (99.5 wt.%) or in acetonitrile (99.5 wt.%) over night. The electrodes were sealed with a 25 μm thick Surlyn film spacer (DuPont) and the electrolyte solutions were injected into the cells through holes drilled in the photoelectrode substrates. The holes were then sealed with Surlyn foils and a thin cover glass. For the infrared measurements, TiO_2 films were made by doctor blading on CaF_2 substrates (2 mm thick

and 25 mm in diameter). Films were sintered and sensitized as described above. A 70 μm Teflon spacer separated the photoelectrode from the counter CaF_2 window having two filling holes, which were connected to teflon tubing to allow injection of the electrolyte solutions in the cell without disassembling the cell between the fillings. The windows were pressed against each other in a brass cell mount. All infrared measurements were done in absorbance mode. The signal to noise ratio obtained was about two orders of magnitude

higher as compared to infrared ATR spectra reported for DSCs in the literature. Schematic presentation of infrared and Raman experiments is depicted in Figure 11.

Figure 11. Schematic presentation of the experimental arrangements for FTIR and Raman measurements used in the present study.

In total 16 mixtures of the electrolyte constituents in MPN for both the LiI and the PMII electrolytes were prepared. In total 88 infrared spectra, including measurements for four different sensitizers, and 20 Raman spectra were recorded. The following standard concentrations of the solutions were used throughout the experiments 0.05 mol/L of I₂, 0.1 mol/L of LiI, 0.6 mol/L of PMII, 0.5 mol/L of TBP, 0.5 mol/L of NMBI, and 0.25-0.5

mol/L of GuSCN. These can be compared to the 11.2 mol/L concentration of the pure solvent.

Raman measurements. The Raman spectra of the DSCs were measured using a HORIBA Jobin Yvon LabRam 300 micro-Raman spectrometer providing the 514 nm line from an argon laser for excitation. The power of the argon laser was set to 1.35 mW and a 600 line/mm⁻¹ grating was used in all measurements. The spot size at the sample (diameter) was on average approximately 24 μm leading to an excitation power density of about 3×10^6 W/m². Data acquisition settings were set at an average of 5 cycles of 30 seconds. Excitation power and measurement parameters were kept constant in all measurements in order to maximize comparability of the data. Raman spectra were excited through the counter electrode side of the cell at 180° collection geometry. On 514 nm laser excitation iodine, triiodide and the sensitizers experience resonance Raman effect and give strong signals in the Raman spectra, while the rest of the constituents are transparent to excitation wavelength and experience normal Raman scattering and are overshadowed by the resonance lines (except the CN stretching band of the solvent). A discussion on experimental conditions on the photoelectrode in the focal region of the Raman excitation light is given in Text 3 of Supporting information.

FTIR measurements. A Nicolet Magna-IR 760 spectrometer in the wavenumber range from 1200 cm⁻¹ to 4000 cm⁻¹ was used to record the infrared spectra in absorbance mode. First FTIR spectra of the individual electrolyte constituents and then their binary, ternary

and quaternary mixtures were recorded in solution. Then the spectra of the same solutions in contact with plain TiO₂ and the N3, N719, Z907 and R505 sensitized TiO₂ were recorded.

Computational methods: Standard Gaussian03 package⁷⁷ was used to calculate minimum energy structures and infrared and Raman spectra of the compounds and their complexes. For molecules containing iodine or ruthenium the core potential LANL2DZ was used together with the 6-311 (5d, 7f) basis set for lighter atoms, otherwise the 6-311**G (5d, 7f) basis set was used. Calculations were run on a 64 bit PC using an Intel(R) Core(TM) i5-3470 CPU @ 3.2 GHz and 8 GB installed memory under Windows 7 operating system. For the ruthenium dyes and their iodine complexes, typical CPU times for energy minimization ranged from 40 to 60 hours.

Calculations for regeneration reactions were performed using Restricted Open-Shell Møller–Plesset perturbation theory of the second order and aug-cc-pVDZ basis set using GAMESS(US) program package.⁷⁸ Effective core potentials (ECP) were applied for iodine atoms.⁷⁹ All calculations were carried out using C1 symmetry group. Solvent was modeled with C-PCM method.⁸⁰ Built-in solvent parameters for acetonitrile from GAMESS(US) were used (dielectric constant $\epsilon=35.94$ and solvent radius $R_{\text{solv}}=2.137$). At first, geometries of I₂, I₃⁻, I₂⁻ were optimized in both acetonitrile and vacuum. Then hessian has been calculated at the optimized geometries and Zero-point correction to the energy has been made.

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Tables

Table 1. Calculated vibrational frequencies (cm^{-1}) and infrared and Raman intensities (a.u.) of iodine, iodine radical anion, lithium iodide and tri-iodide anion. See methods for details of the DFT calculations. Greek letters refer to the symmetries of the vibrations in question. Numbering of vibrations of triiodide anion follow Herzberg convention.

I₂			I₂⁻			LiI			I₃⁻ (lin)			
cm^{-1}	IR	Raman	cm^{-1}	IR	Raman	cm^{-1}	IR	Raman	cm^{-1}	IR	Raman	assign
181.4	0	2.5	85.8	0	509	670.7	62	43	95.5	0	42	σ_{g+} , ν_1
									144.2	62	0	σ_{u+} , ν_2
									48.0	0.6	0	π_u , ν_3, ν_4

Table 2. Calculated vibrational frequencies (cm^{-1}) and Infrared and Raman intensities of thiocyanate anion and its iodine and lithium complexes. See methods for details of the DFT calculations. In the assignment columns ν and δ refer to stretching and bending vibrations, respectively. Subscripts i, o, s and as refer to in-plane, out-of-plane, symmetric and anti-symmetric vibrations, respectively. Greek letters refer to the symmetries of the vibrations in question. Numbering of vibrations of thiocyanate anion follow Herzberg convention.

NCS-				NCS_I $_2^-$				LiNCS			
(linear)				(bent)				(linear)			
cm^{-1}	IR	Raman	assign	cm^{-1}	IR	Raman	assign	cm^{-1}	IR	Raman	assign
2071.8	353	174	σ_g, ν_1	2140.7	136	694	$\nu(\text{CN})$	2084.4	1476	102000	$\nu(\text{CN})$
657.9	8.4	6.5	σ_g, ν_2	638.4	0.7	29	$\nu(\text{SC})$	785.7	0.93	7550	$\nu_{\text{as}}(\text{LiNS})$
412.6	1.4	0	$\pi_u, \nu_{3,4}$	425.7	0.4	2.0	$\delta_i(\text{NCS})$	486.1	119	43700	$\nu_s(\text{LiNS})$
				404.3	3.2	2.5	$\delta_o(\text{NCS})$	449.5	1.66	154	$\delta_i(\text{NCS})$
				185.2	74	53	$\nu(\text{S-I})$	373.5	32.6	640	$\delta_i(\text{LiNCS})$
				125.6	23	30	$\nu(\text{I-I})$	116.8	70.2	812	$\delta(\text{LiNC})$

Table 3. Selection of calculated vibrational frequencies (cm^{-1}) and Infrared and Raman intensities of the N3 dye and its iodine complexes. See methods for details of the DFT calculations. In the assignment columns ν and δ refer to stretching and bending vibrations, respectively. Total number of normal modes of the compounds are indicated as 3N-6, where N is the number of atoms. Subscripts s and as refer to symmetric and anti-symmetric vibrations, respectively.

N3 3N-6=171				N3_I 3N-6=174				N3_I2 3N-6=177			
cm^{-1}	IR	Raman	assign	cm^{-1}	IR	Raman	assign	cm^{-1}	IR	Raman	assign
2125.3	1328	418	$\nu_s(\text{CN})$	2138.7	549	7217	$\nu(\text{CN-I})$	2165.7	620	6451	$\nu(\text{CN-I}_2)$
2115.4	1276	80	$\nu_{as}(\text{CN})$	2119.8	1350	350	$\nu(\text{CN})$	2119.5	1354	400	$\nu(\text{CN})$
792.4	26	80	$\nu_{as}(\text{CS})$	749.2	16	59	$\nu(\text{CS-I})$	738.2	29	50	$\nu(\text{CS-I}_2)$
439.1	10.3	22	$\delta_s(\text{NCS})$	437.4	12	13	$\delta(\text{NCS})$	439.1	29	6.2	$\delta(\text{NCS})$
436.8	7.7	6.1	$\delta_{as}(\text{NCS})$	432.9	3.5	12	$\nu(\text{NCS-I})$	432.5	3.6	7.2	$\delta(\text{NCS-I}_2)$
				126.6	1.1	50	$\nu(\text{I-S})$	155.8	52	21	$\nu(\text{S-I})$
								133.6	0.1	43	$\nu(\text{I-I})$