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A Systematic Study via Ab-initio MD of the effect solvation by Room Temperature Ionic Liquid has on the structure of a Chromophore Titania Interface

Aaron Byrne[†] and Niall J. English[*,‡]

[†]*Department of Chemical and Bioprocess Engineering / Complex Adaptive Systems Laboratory / School of Physics, University College Dublin, Belfield, Dublin 4, Ireland*

[‡]*Department of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland*

E-mail: niall.english@ucd.ie

Abstract

Ab-initio, density functional theory (DFT)-based molecular dynamics (MD) has been carried out to investigate the effect with which the choice of functional has on the structural properties of a $[\mathrm{bmim}]^+[\mathrm{NTf2}]^-$ room-temperature ionic liquid (RTIL), solvating a N719 sensitising dye adsorbed onto an anatase-titania (101) surface. A systematic, fully crossed study has been carried out, comparing the BLYP and PBE functionals, both unsolvated and solvated by the RTIL as well as with and without Grimme D3 dispersion corrections.

Introduction

In dye-sensitised solar cells (DSCs), the semiconductors optical band gap is bridged by a light-absorbing, or sensitising, dye. DSCs needs to have charge replenished continuously: thus, it is necessary to have some form of redox electrolyte (usually I-/I3- in an organic solvent) as the third primary component. This allows dye-to-electrolyte hole transfer, whilst electrons injected into the semiconductor move through it into the external circuit, recombining at the cathode. A key reason underlying DSCs buoyant prospects lies in their facile manufacture, not requiring high-purity materials, unlike silicon-based photovoltaic technology. Extending DSC lifetimes substantially through replacing a volatile electrolyte with low-volatility room-temperature ionic liquids (RTILs) has great potential. RTILs liquid-like electrical properties and solid-like physical ones (e.g., low flammability, volatility and toxicity),[1] serves to render these as excellent candidates for DSCs.

In previous work,[2] though Density Functional Theory (DFT)-based molecular dynamics (MD), we determined that dispersion and solvation effects can have a dramatic affect on the structure and adsorption modes of the DSC interface, applied to a prototypical and well-studied N719 dye. In essence, explicit dispersion interactions in the solvated system led to the average separation between the cations and anions decreasing by 0.6 , the mean distance between the cations and the surface decreasing by about 0.5 and significant altering of the RTILs layering in the first layer surrounding the dye, with the cation being on average 1.5 further from the centre of the dye. Inclusion of explicit dispersion effects in vacuo resulted in unphysical kinking of the adsorbed N719 dyes configuration. The compelling, and unaddressed, question remains however, whether these effects are confounded by the choice of functional. This present study sets out to explore whether choice of functional is important to future work involving MD for these type of large, challenging ab-initio simulation systems.

Although, PBE and B3LYP are two of the most widely used DFT functionals available, the decision was made to rule B3LYP out as a suitable candidate due to the work by Izgorodina et al.,[3] which showed that the B3LYP functional suffered from systematic errors in

calculating the properties of ionic liquids. Hence, in the present work, we make a comparison for the N719-on-titania system (with and without RTIL) between the two GGA functionals PBE (Perdew-Burke-Ernzerhof) and BLYP
(Becke-Lee-Yang-Parr).

Here, the structural properties of this interface were studied in depth for the various systems simulated, through the use of pair distribution functions (PDFs). Mosconi et al[4] demonstrated that the solvent played an important role in determining the stability of the dye on the anatase which is vital to any design of DSC. Indeed, this motivates us in the present study to carry out a systematic, fully-crossed comparison BLYP and PBE functionals for both RTIL-solvated and in vacuo systems, with and without Grimme D3 dispersion corrections, to assess the structural properties of these complex systems.

Methodology

The computational model is the same as that employed in previous work[2] and summarised below.

The sensitizing dye used in our simulations was N719:
cis-di(thiocyanato)-bis(2,2'-bipyridl-4-carboxylate-4'-carboxylic acid)
-ruthenium(II), with no counterions and two surface bound protons, necessary for charge neutrality. Previous work by DeAngelis et al[5] has shown this to be a realistic representation of N719.

In our initial configuration the dye was chemically adsorbed to the TiO_2 surface through two carboxylate groups, one of which was bidentate bridging and the other monodentate. This starting adsorbed configuration of the dye is similar to the configuration labelled as I_1 in the study by Schiffmann et al.,[6] in which they found it to be the most stable when surface protons were taken into account.

The RTIL used in these simulations was 12 cation-anion pairs of 1-butyl

-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][NTf$_2$], consisting of 480 atoms in total. The starting configuration for the liquid was one that had been relaxed via classical MD.

The semiconductor substrate consisted of an anatase titania surface $(TiO_2)_{96}$ (288 atoms), periodic in x and y and exposing two parallel (101) surfaces perpendicular to the z-axis, of $2.3 \times 2.1\,\mathrm{nm}^2$ surface area.

The DSC model with explicit solvent used in this study is composed of 827 atoms and has 4300 valence electrons. In the in vacuo case, there were 347 atoms and 2530 valence electrons.

The solar cells were simulated using ab-initio MD for 8.5 ps with a 1 fs time-step at 300 K in an NVT ensemble, using BOMD as implemented in CP2K,[7–13] using a 400 Ry cut-off, triple zeta basis sets and the BLYP, BLYP-D, PBE and PBE-D functionals, where the additional dispersion is accounted for by means of the Grimme D3 semi-empirical corrections.

To enable accurate comparisons and study how the inclusion of dispersion and/or solvation effects influences the structure and dynamics of this interface, eight ab-initio simulations were run using the conditions described below. For the simulations of systems including explicit dispersion effects, the Grimme D3 dispersion corrections[14,15] were added to the functional. The temperature was fixed by coupling the systems to a Nose-Hoover[16] thermostat with a time period of 0.15 ps, and the virial-estimated,[17] pressure was found to average to 1 atm.

The eight ab-initio simulations carried out, allow for a fully crossed experimental design between;

- BLYP system I; no dispersion corrections, no solvation.
- PBE system I; no dispersion corrections, no solvation.
- BLYP system II; with dispersion corrections, no solvation.
- PBE system II; with dispersion corrections, no solvation.

- BLYP system III; no dispersion corrections, with [bmim][NTf_2] solvation.
- PBE system III; no dispersion corrections, with [bmim][NTf_2] solvation.
- BLYP system IV; with dispersion corrections, with [bmim][NTf_2] solvation.
- PBE system IV; with dispersion corrections, with [bmim][NTf_2] solvation.

Different pair distribution functions,[17] $g_{ij}(r)$, averaged over an interval of 1000 time steps were also calculated for each system, at the outset, between 1 and 2 ps and then later between 7.5 and 8.5 ps, enabling us to explore changes to the structure of the interface for each system as a function of relaxation time.

Results and Discussion

Relaxed Geometries

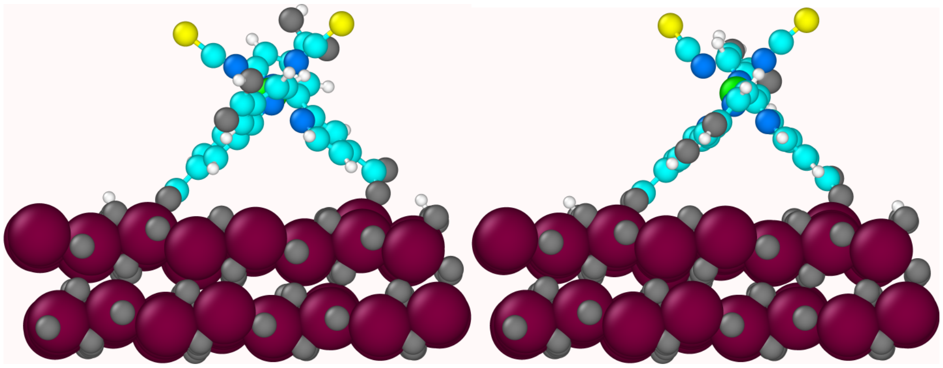
Representative configurations of the structure of the dye at the end of the eight systems simulations can be seen from a front and side perspective in Figures 1, 2, respectively. PBE system I and PBE system II both show explicit hydrogen bonding to the surface, with PBE system II undergoing the greatest changes to the dyes initial binding modes.

None of the systems simulated with BLYP bend towards the surface to the same degree as that seen in the unsolvated PBE cases, although there is some evidence of BLYP system II beginning this process (see Figure S28b). Also, the only simulation to exhibit a proton transfer event from the surface to the dye was PBE system II which was simulated using PBE-D in the absence of ionic liquid. Evidence suggests that this setup then has the longest range interactions of the systems studied.

All four of the systems solvated by [bmim][NTf_2] remain stable throughout their trajectories, largely helped by the solvation effects of the surrounding ionic liquid. Additionally, a visual inspection of the trajectories of the solvated systems shows no discernible difference between those simulated with the different functionals.

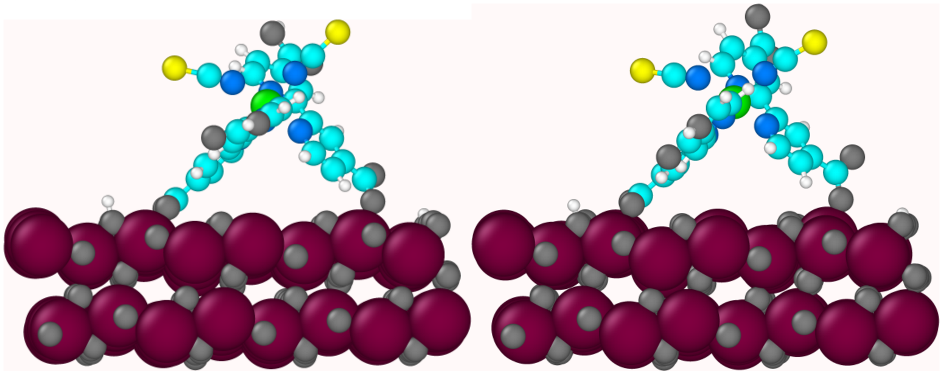
(a) BLYP System Type I

(b) BLYP System Type II



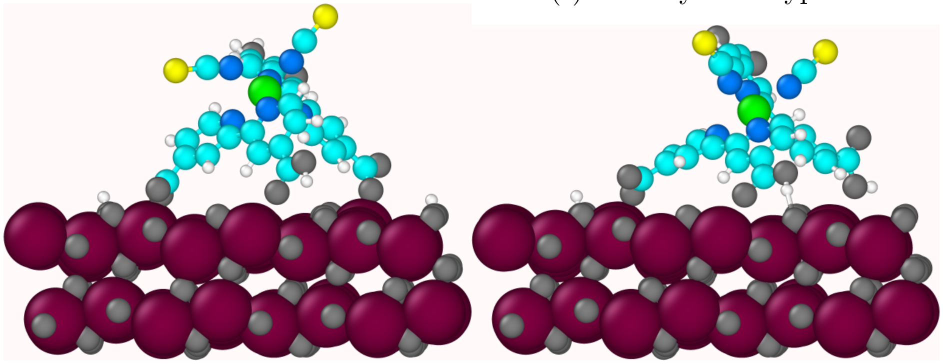
(c) BLYP System Type III

(d) BLYP System Type IV



(e) PBE System Type I

(f) PBE System Type II



(g) PBE System Type III

(h) PBE System Type IV

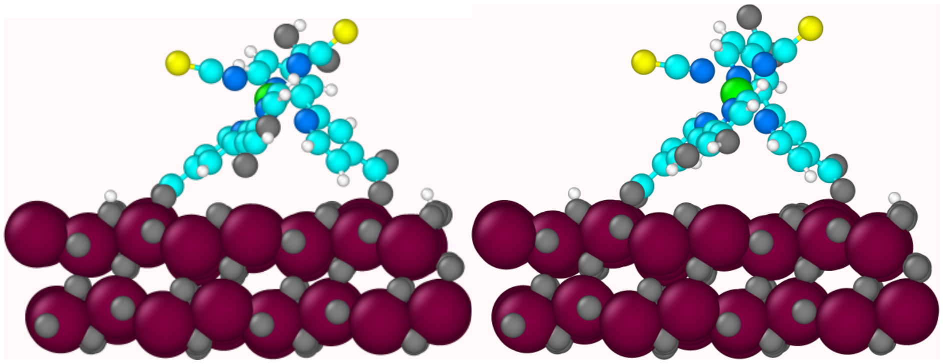
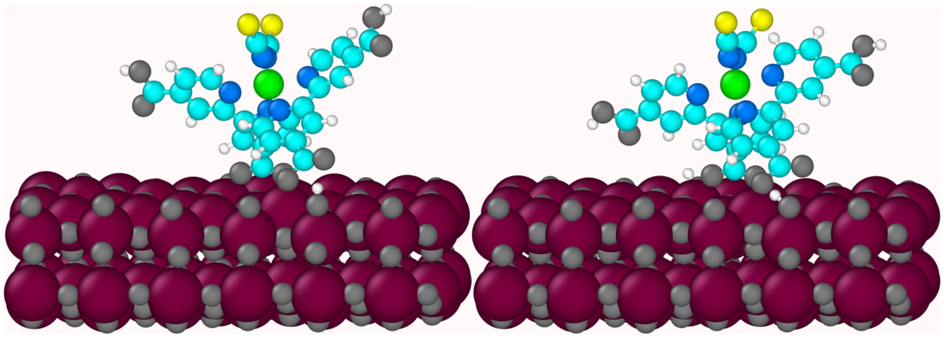


Figure 1: Frontal view showing the relaxed geometries of the eight systems under consideration. Carbon shown in light blue, nitrogen in dark blue, oxygen in grey, hydrogen in white, titanium in purple, sulphur in yellow and ruthenium in green. System types; I: unsolvated, II: unsolvated with dispersion corrections, III: solvated , IV: solvated with dispersion corrections. Solvated systems are shown without solvent for ease of viewing.

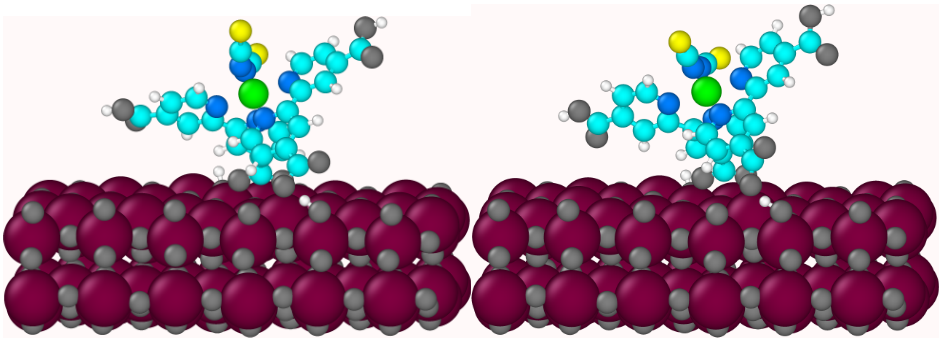
(a) BLYP System Type I

(b) BLYP System Type II



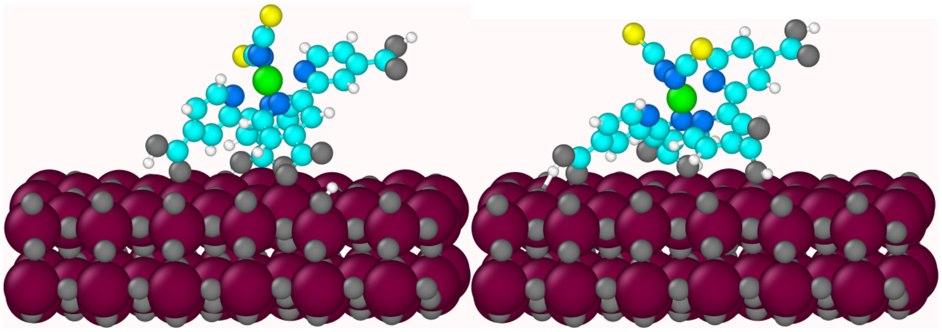
(c) BLYP System Type III

(d) BLYP System Type IV



(e) PBE System Type I

(f) PBE System Type II



(g) PBE System Type III

(h) PBE System Type IV

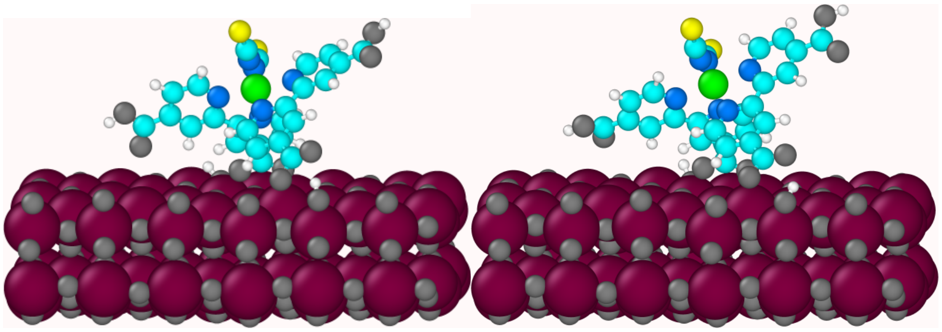


Figure 2: Side view showing the relaxed geometries of the eight systems under consideration. Refer to the caption of Figure 1 for atom and system descriptions.

Structural Distribution

The effect of functional choice, solvation and/or the addition of empirical D3 dispersion corrections on the structure of the interface can be determined from the PDFs shown in the following figures. The top left panels, labelled ‘a’, display the results of a simulation of type I, an unsolvated DFT simulation of the interface using the BLYP functional. Moving horizontally, the top right panels, labelled ‘b’, correspond to simulations of type II and were performed using BLYP-D3. The effect with which the addition of dispersion has on the unsolvated surface can be ascertained by comparing the plots in the ‘a’ and ‘b’ of these figures.

The ‘c’ panels contain the PDFs belonging to a simulation of type III, similar to system I but now solvated by the RTIL [bmim][NTf_2]. To the right of this, the ‘d’ panels contain the results from a BLYP simulation of type IV, where the surface is both solvated by the RTIL and dispersion corrections have also been added to the functional. The bottom four panels ‘e - h’ correspond to the same simulation type as ‘a - d’ but with the PBE functional used instead of BLYP. Each plot contains structural information averaged over both an early stage of the simulation and a latter stage to see what, if any, structural re-organisation takes place during the course of the simulations.

Carbon Backbone

In the PDF for the carbon atoms in the dye with the other carbon atoms in the dye, (see Figure S4), we note that again the choice of functional has minimal effect on the structure towards which the dye relaxes. The 1.5 Å dominant peak comes from the carbons in the pyridine rings and is identical in all eight plots, likewise the other near-structure (< 5 Å), displays almost identical locations of peaks. In some of the plots involving solvation and dispersion effects there is a slight longer-range alteration to the structure which could be due to the planes of the rings having a smaller angle between them, this is particularly visible at 5.2 Å in Figure S4d.

If instead this effect was due to some alteration of the carbons in the binding carboxyl groups then we would expect to see something similar occurring in the PDF for the carbon atoms in the dye with the nitrogen atoms of the dye, Figure S5, and we do not. There is also very little difference in the arrangement of the carbons around the ruthenium atom at the center of the dye, (see Figure S7).

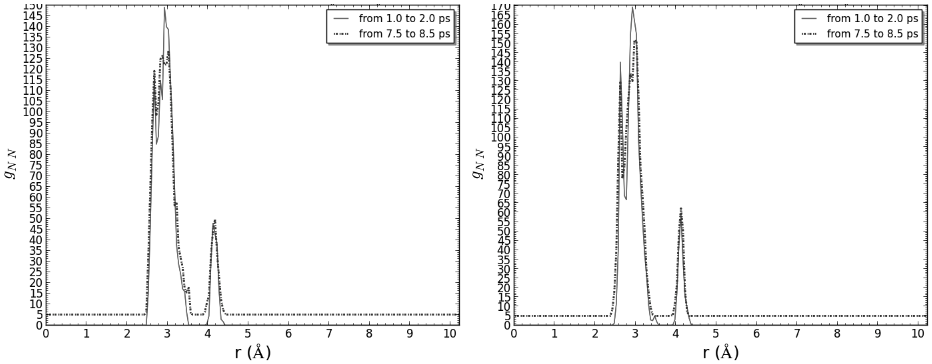
Figure S6 shows the PDF for the carbon and sulphur atoms of the dye. The peak at 1.8 Å is due to the carbon-sulphur proximity in the thiocyano N−C−S groups. The lack of a sharp structure further out indicates the mobility of the two thiocyano arms. When dispersion is added to the BLYP functional we see the nearest approach of the sulphur atoms with the carbon backbone decreasing over the course of the unsolvated simulation to 3.1 Å, (see Figure S6b), where as it stays at around 4 Å for the other systems studied.

Metal Complex

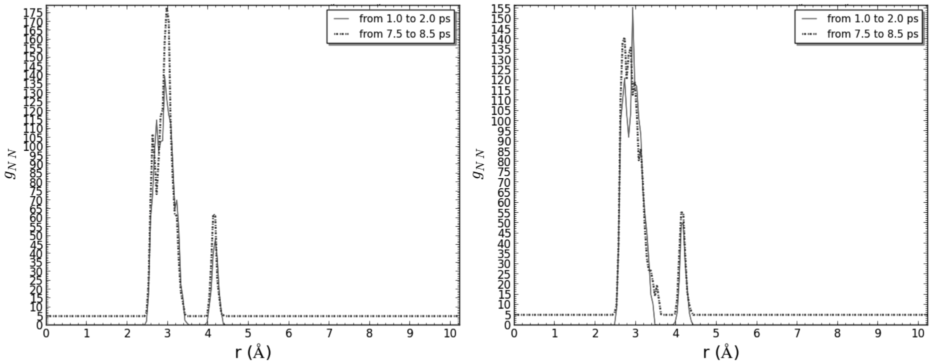
The metal complex structure at the centre of the dye is largely unaffected by the inclusion of the ionic liquid. Likewise dispersion corrections and choice of functional have no noticeable effect, (see Figure 3 and Figure S8). Perhaps surprising about this structure is that the N-N interatomic distance surrounding the Ru atom is not uniformly distributed and a splitting of the main peak is visible in its PDF for all systems to some extent, (see for instance Figure 3h).

Anatase Surface

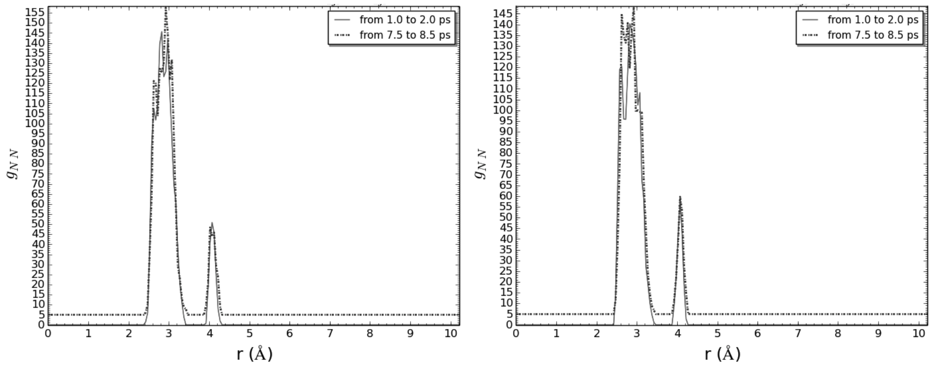
In regards to the structure of the titania surface, neither the addition of dispersion corrections nor the strongly ionic solvent have any noticeable effect. This can be seen from Figures S1-S3. The surface changes little over the duration of the simulation and can be considered quite stable, as expected of anatase (101).[18] The choice of GGA functional on the structure of the surface also has limited effect with crystallographic peaks occurring in almost identical positions.



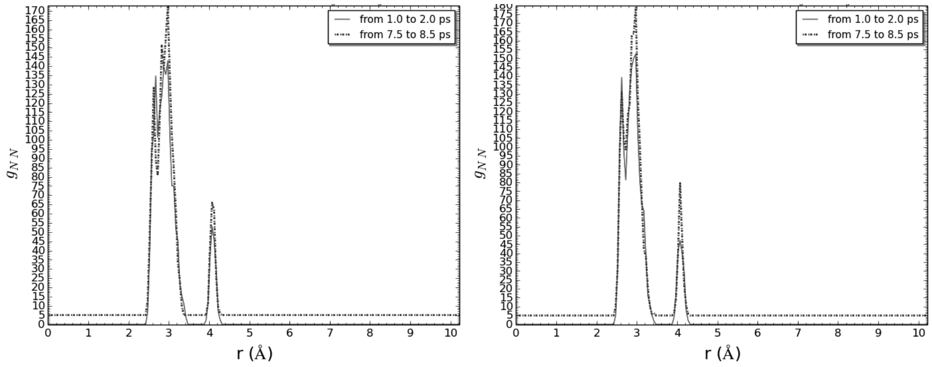
(a) BLYP System Type I (b) BLYP System Type II



(c) BLYP System Type III (d) BLYP System Type IV



(e) PBE System Type I (f) PBE System Type II



(g) PBE System Type III (h) PBE System Type IV

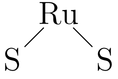
Figure 3: Pair distribution functions for N - N in the N719 dye. Early structure shown with a continuous line, later structure with a dashed line and shifted upwards.

Hydrogens of the Dye

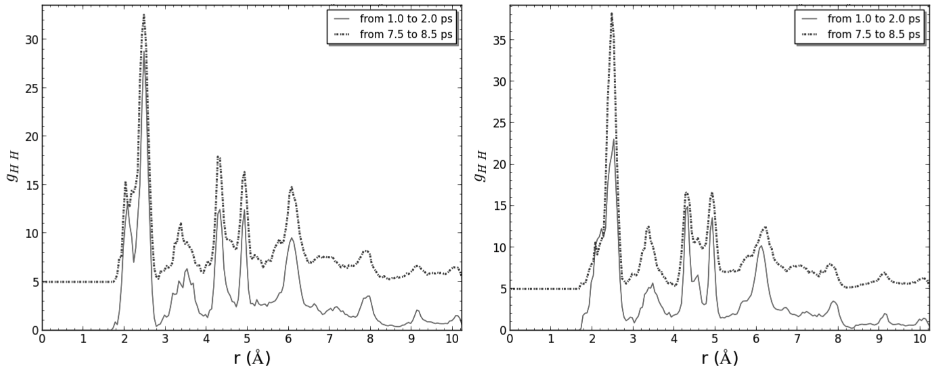
We see in Figure 4 that the locations of the H-H peaks are largely unaffected across the different simulations. This would imply that there is little ‘twisting’ distortion in the ring geometry of the dye molecule which direct visualisation confirms (see Figure 2). The system II simulations (unsolvated with dispersion), for BLYP (Figure 4b) and PBE (Figure 4f) show the nearest peak at 2 Å being decreased/increased respectively. The remaining internal structure of the dye undergoes little alteration across all eight of the simulations, as indicated by the PDFs of Figures S9-S12.

Thiocyano Moieties

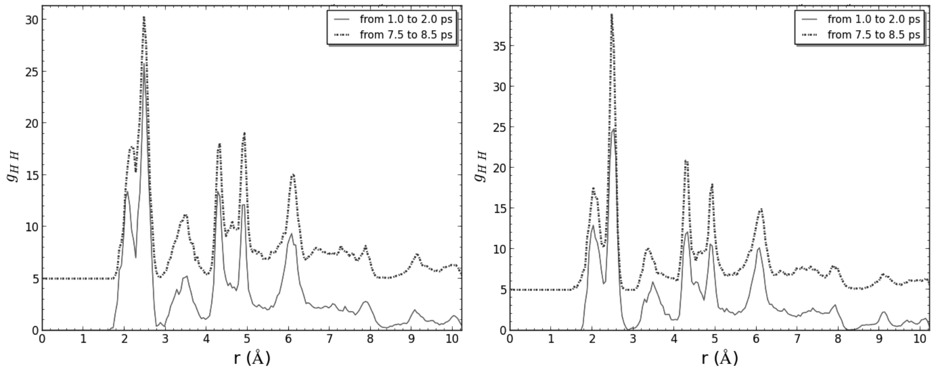
The PDFs for atomic combinations which involve the thiocyano arms of the N719 dye molecule are visible in Figures S13 - S16. What is instantly clear is that there is a lot more variation to the structure displayed by this chemical group than by the other more rigid parts of the N719 dye. These two arms are largely free to move about during the course of the simulation and each of the eight different simulations exhibit significantly altered structural profiles which can largely be attributed to random motion.

The motion of the sulphurs at the end of the thiocyano arms is not radial in nature. This can be inferred from the largely static locations of peaks in Figures S13 and S15. The large differences in structure displayed is then because of the bending mode between the  angle, rather than the S—Ru stretch mode, where the ruthenium atom acts as the centre of the dye.

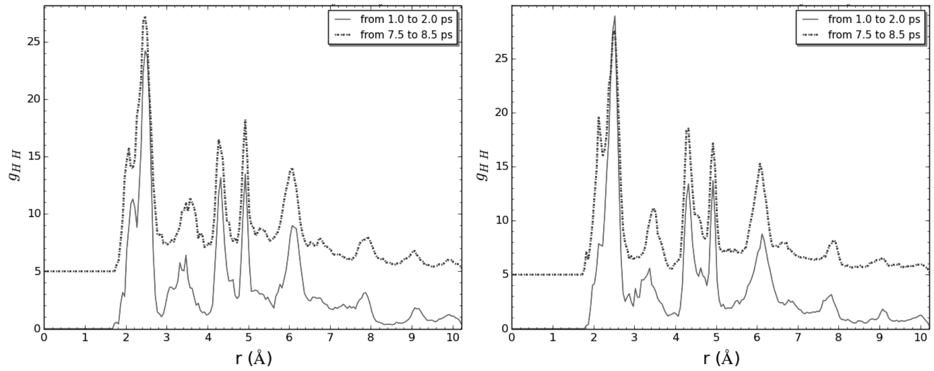
Examining the closest approach distance of the two sulphur atoms averaged over a picosecond at the end of the simulation, (see Figure S16), distances of [5.5, 7 , 7.1 , 7.8 , 5 , 6.4 , 7.8, 7.1] Å would be observed for plots labelled ‘a - h’ respectively. This suggests that in the solvated simulations, labelled by ‘c,d,g,h’ the sulphurs are further apart on average than in the unsolvated simulations, forced further away by the presence of the solvent molecules.


(a) BLYP System Type I

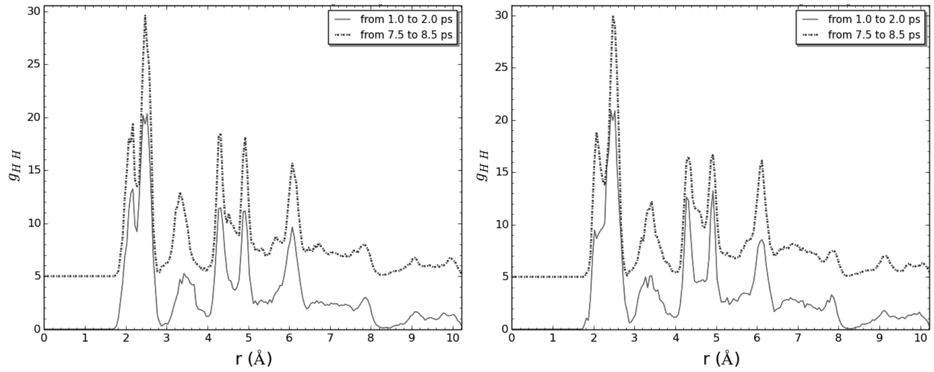
(b) BLYP System Type II


(c) BLYP System Type III

(d) BLYP System Type IV


(e) PBE System Type I

(f) PBE System Type II


(g) PBE System Type III

(h) PBE System Type IV

Figure 4: Pair distribution functions for H - H in the N719 dye. Early structure shown with a continuous line, later structure with a dashed line and shifted upwards.

Carboxyl Oxygens

The oxygen atoms of the dye belong to one of the four carboxyl group located at the extremities of the N719 dye. There is no noticeable difference in structure for the PDFs of these oxygens with either the carbon backbone of the dye or with themselves (see Figures S17 and S20). This is particularly interesting in the case of the unsolvated PBE-D simulation, Figure S20f, as it shows then that the rotation of the carboxylate oxygen atom about the bonded carbon atom discussed in previous work[2] didn't alter the distance with the oxygen atom on the other side of the bond. Although the absence of the solvent makes this result questionable it could be a demonstration of the proposed mechanism by Schiffman et al.[6] for the translation of the dye along the anatase surface.

The second layer of the distribution for the oxygen and nitrogen atoms in the dye, located 6Å away (see Figure S18), undergoes a slight alteration of at most 0.1 Å for the four unsolvated systems, with the solvated systems being unaffected.

Over the course of the simulation the suplhur atoms have the most mobility of any of the dyes chemical groups and Figure 5 again shows this, in a similar way to that discussed above. The unsolvated systems simulated using BLYP and BLYP-D exhibit the most structural change in this regard within a simulation, although the two are of opposite direction (see Figure 5a, 5b).

Using the ruthenium atom as an approximation to the centre of the of dye and looking at the PDF of it with the carboxyl oxygens at the extremities, (see Figure S19), the only system which shows any deviation is the unsolvated PBE one, as can be seen by the alteration to the single peak in Figure S19e. Both the unsolvated PBE and unsolvated PBE-D simulations bend towards the surface but the simulation with dispersion makes contact further along the titania surface than the system without dispersion. Bearing this in mind and using these Ru-O PDFs, we can infer that the bending towards the surface for the unsolvated PBE system has resulted in a distance contraction of 0.5 Å between the carboxylic acid group which does the bending and the dyes centre. That is to say that rather than the PBE-D system II simulation's distance between these atoms being elongated, it is actually the PBE system I dye which is contracted.

There is a slight, 0.1 Å , shift 'closer' in the location of the sole structural peak in Figure S19 when the functional is changed from BLYP to PBE. This effect is also visible upon closer inspection of many of the other peaks presented in the supplementary information, but are not as clearly distinguishable.

Surface-Dye

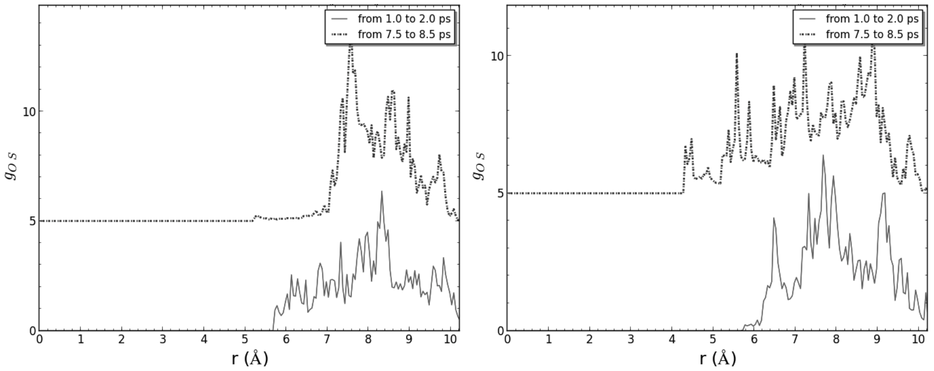
Overall there seems to be limited effect due to the alteration of DFT functional on the dye-titania interface. Taking Figure S25 as an example, we see that the nearest carbon atoms to the surface are distributed about 3 Å away from it. Dispersionless PBE simulations, plots labelled 'e' and 'g', result in the nearest distance being shortened by 0.05 Å ,compared with the respective BLYP simulations, namely plots 'a' and 'c'. Upon solvation however, this effect isn't observed.

Across all possible pairs, there is one system which is consistently different from the other seven, the unsolvated PBE-D, system II simulation. In Figure S26f we see that the location of the first layer is at least 0.4 Å closer than in any of the other PDFs and the reason as to why this system exhibits such different behaviour has been discussed previously.

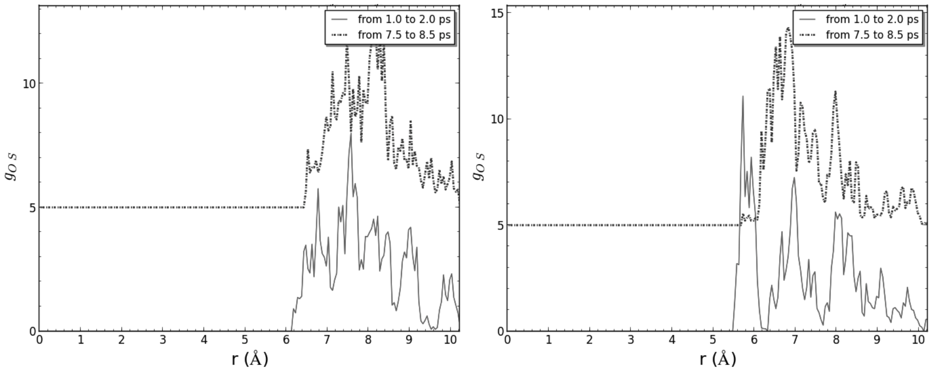
While not as extreme, in some cases the unsolvated BLYP-D, system II simulation mimics some of the behaviour of its PBE counterpart. For instance, Figure S27 shows the two system II simulations to have evolved towards an average titania sulphur separation of less than 7 Å while the other systems all exhibit separations of around 8 Å.

Studying the PDFs for the oxygen atoms in the surface with the hydrogen atoms of the dye allow us to determine whether the dye changes its orientation relative to the surface. These PDFs are shown in Figure S28. If the location of the first peak is 2 Å or above then the system hasn't bent towards the surface where as if the first peak is 1.5 Å then hydrogen bonding between the carboxylic acid and the surface has occurred altering the binding mode

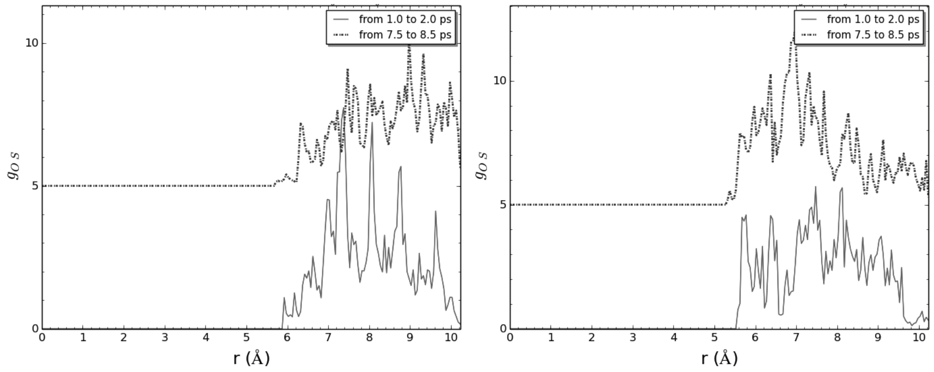
(a) BLYP System Type I (b) BLYP System Type II



(c) BLYP System Type III (d) BLYP System Type IV



(e) PBE System Type I (f) PBE System Type II



(g) PBE System Type III (h) PBE System Type IV

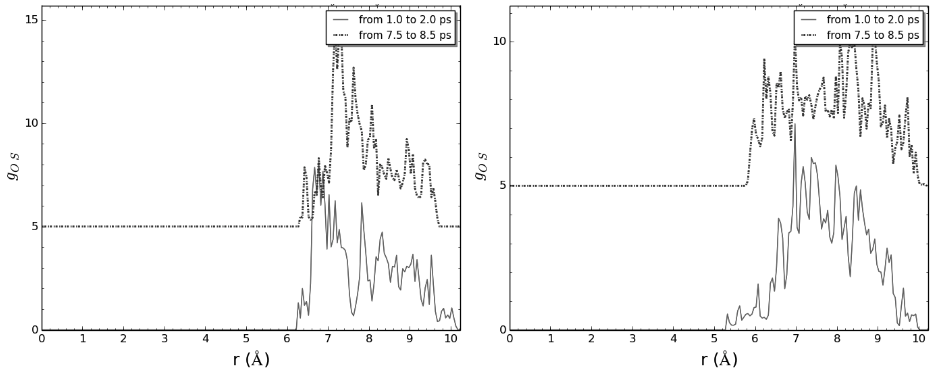


Figure 5: Pair distribution functions for O - S in the N719 dye. Early structure shown with a continuous line, later structure with a dashed line and shifted upwards.

of the dye. The exact binding mode on the surface is still debated,[5],[19] with it being likely that multiple modes are present in an experimental sample and that modes can fluctuate.

The unsolvated PBE simulations, Figures S28e and S28f, demonstrate this changing of their binding modes, while the BLYP simulations or any of the solvated simulations do not. While not visible from solely inspecting the final configuration of BLYP-D system II (see Figure 2b), this system appears to spend some of its trajectory with its carboxylic acid hydrogen atom quite close to the surface, (see the peak at 1.9 Å in Figure S28b), and a physisorption H-bonding might develop if that simulation were extended for a long enough time.

Surface-RTIL

RTILs have notoriously long relaxation times on the order of microseconds so determining their relaxed-state properties is not possible with ab-initio methods. However, certain properties of the liquids interactions can still be inferred from the simulations carried out in this work. Figure S33 shows the PDFs for the centre of mass (COM) of either the cations or anions with the Ti atoms in the titania surface. In the simulations without dispersion corrections, the cation-Ti mean separation is the same for BLYP and PBE functionals, Figures S33a and S33e , however, when dispersion is included, the mean separation for PBE-D is 0.7 Å further apart than that of BLYP-D. There is less of a significant effect for the anions.

Addition of dispersion corrections to solvated systems affects the cation more than the anion and the BLYP simulations more than those of PBE. The change in nearest approach mean separations with addition of dispersion for the BLYP functional is 1.2 Å for the cations and 0.2 Å for the anions, while for PBE the change is only 0.5 Å for the cations and non-existent for the anions.

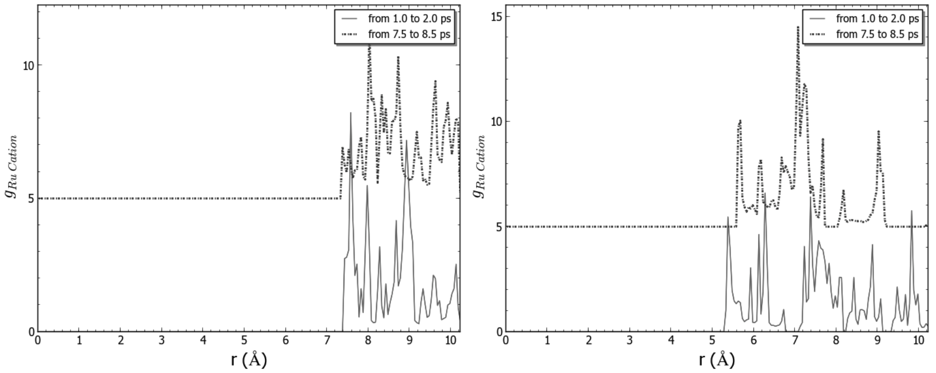
Dye-RTIL

The distribution of the cations and anions centres of mass around the carbon skeleton of the dye is shown in Figure S37, note the clearly visible layering of the ionic liquid. In the BLYP-D simulations, the cations relax towards a configuration whereby they are closer than the anions to the carbons in the dye by 1 Å. Conversely in the PBE-D simulations, the anions are closer to the carbon skeleton by about the same amount. The addition of dispersion to the BLYP functional pulls the first layer of the cations (anions) closer by 0.8 (0.4) Å, while in the PBE simulations dispersion has the effect of the nearest layer of the liquid being pushed away from the carbon atoms (see for instance Figures S37g and S37h).

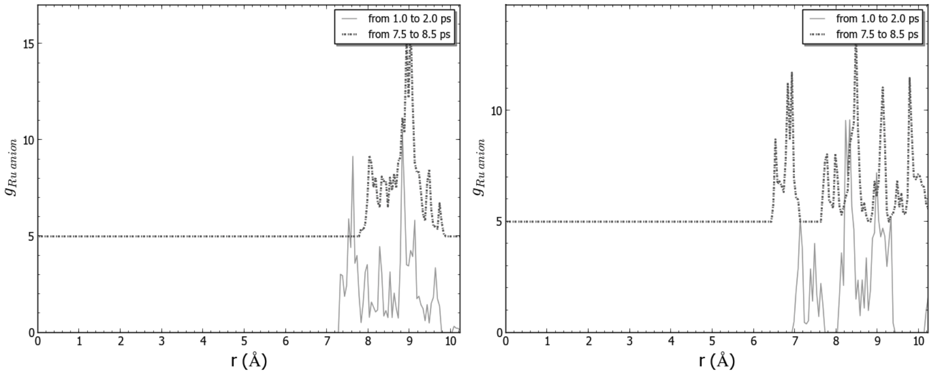
This change in the layering of the ionic liquid which surrounds the dye can be best investigated by studying Figure 6 as the ruthenium atom acts as one central point and the PDF is then akin to a radial distribution function. Over the life of the simulations we see the liquids alter their configurations relative to the dye. The first layer of the anions COM is 7.1 Å away from the Ru atom early on when simulated with BLYP-D, and the other simulations carried out with BLYP, PBE and PBE-D all largely agree with this. As the liquid rearranges itself this first layer moves to an average separation of 8 Å for BLYP, 6.4 Å for BLYP-D, 7.6 Å for PBE and 7.6 Å for PBE-D. For the cations, BLYP-D results in the liquid being 1.5 Å closer to the dye than with just BLYP alone, where as PBE-D results in the first layering being pushed further away by 1.4 Å compared with PBE.

The addition of dispersion corrections to the PBE functional for solvated systems actually results in forcing the cation to an outer layer, as mentioned in previous work. This is quite different than for the BLYP functional where longer-range interactions tend to pull the liquid closer to the dye for both the cations and anions but predominantly for the cation. Figures S38b and S39b also demonstrate this effect.

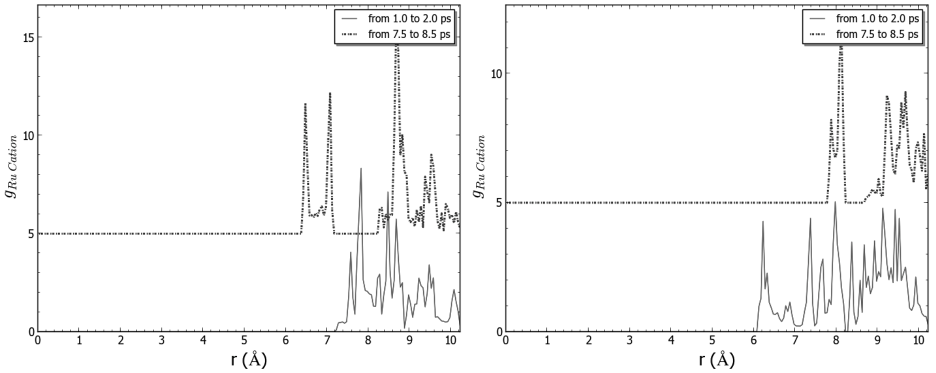
(a) BLYP Type III Cation COM (b) BLYP Type IV Cation COM



(c) BLYP Type III Anion COM (d) BLYP Type IV Anion COM



(e) PBE Type III Cation COM (f) PBE Type IV Cation COM



(g) PBE Type III Anion COM (h) PBE Type IV Anion COM

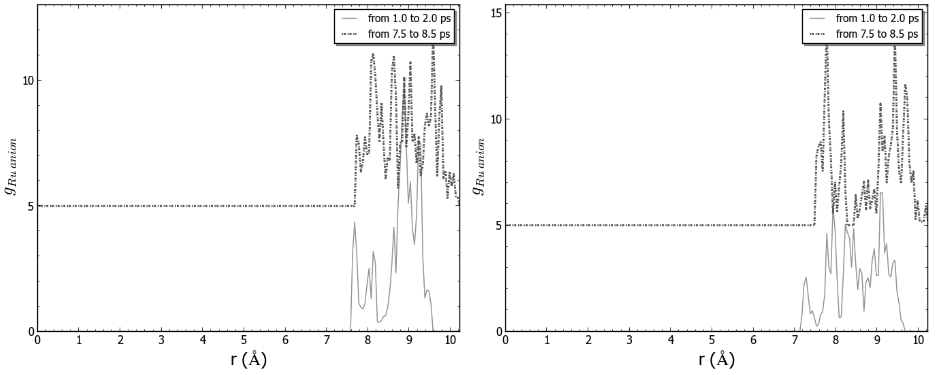


Figure 6: Pair distribution functions for the Ru atom in the dye and the ionic centers of mass in the liquid. Early structure shown with a continuous line, later structure with a dashed line and shifted upwards.

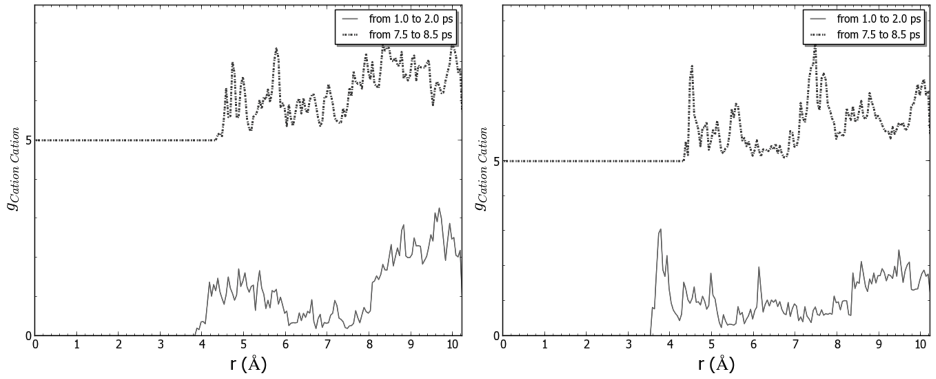
RTIL Internal Structure

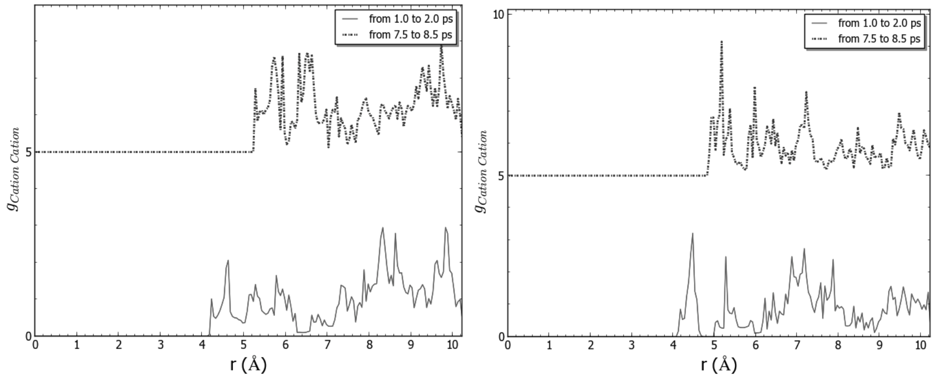
This section looks at the arrangement of the liquid ions amongst themselves, it does so by studying three PDF figures, 7 - 9, which show the distributions of the COM of the anions and cations as well those for the head atoms of the molecules. The head atom for NTf_2 is the sole nitrogen atom at the vertex while for bmim it is the nitrogen ring atom furthest from the tail. The figures show PDFs between the cation-cation, anion-anion and cation-anion arrangements respectively.

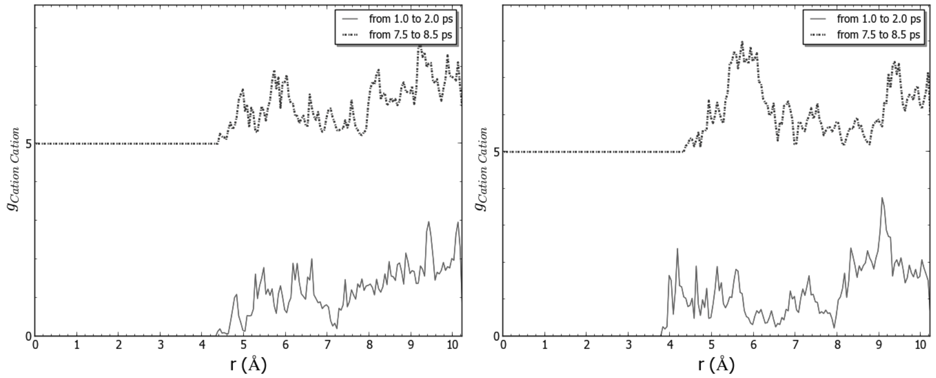
We can see from Figure 7, that the distributions for BLYP and PBE, system III, of the head atoms of the cation largely agree with one another, while the COM distribution for BLYP is more 'front-loaded' than the COM for PBE. The situation changes slightly, when dispersion effects are included, BLYP-D has a nearer peak for its head distribution than its COM one, indicating that some partial alignment of the cations takes place in a head-to-head fashion. PBE-D shows less alignment, with the distributions for the head atom and COM being quite similar in the first layer, which would result from a random orientation of the cations.

As we wish to simulate room temperature ionic liquids, we know that dispersion corrections are a necessity in order to capture the longer range behaviour these liquids exhibit and thus the plots of system IV, namely 'b','d','f' and 'h' are most important to this discussion. The first peak in the COM distribution for BLYP-D is about an Angstrom closer than that of PBE-D indicating that in the BLYP-D simulations the cations are on average closer together than in the PBE-D simulated system.

Looking then to the anions by examining Figure 8, we see that all eight plots have their closest anion-anion distance in the 6.1 - 6.4 Å range. The COMs of the anions are slightly closer for both BLYP and BLYP-D than for PBE or PBE-D. The PDFs for the PBE-D simulation of system IV, plots 'f' and 'h' show that the COM has more dominant early peaks than those belonging to the head atoms distribution, indicating that there is an alignment present in the liquid whereby the anions do not face each other head-on.


(a) BLYP Type III Cation Head
(b) BLYP Type IV Cation Head


(c) BLYP Type III Cation COM
(d) BLYP Type IV Cation COM


(e) PBE Type III Cation Head
(f) PBE Type IV Cation Head

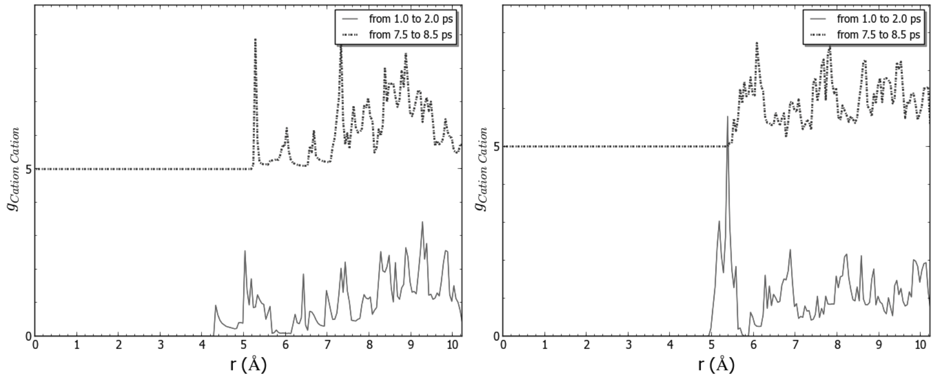
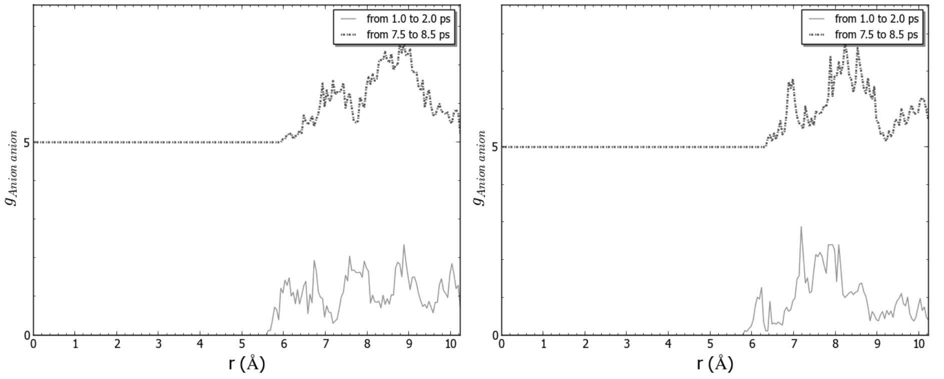
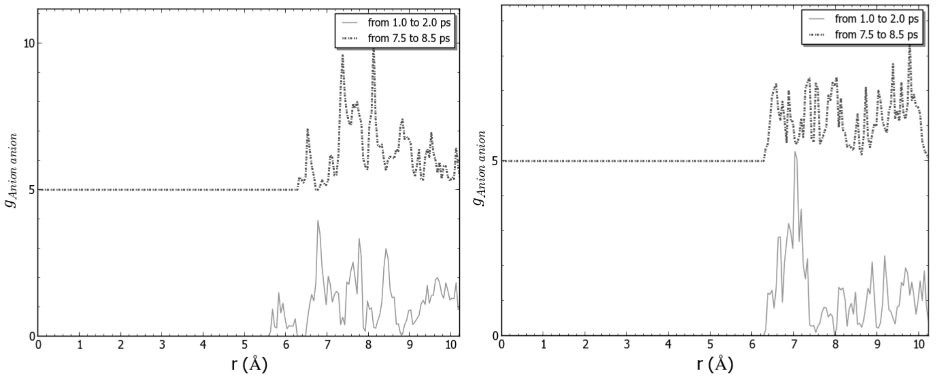
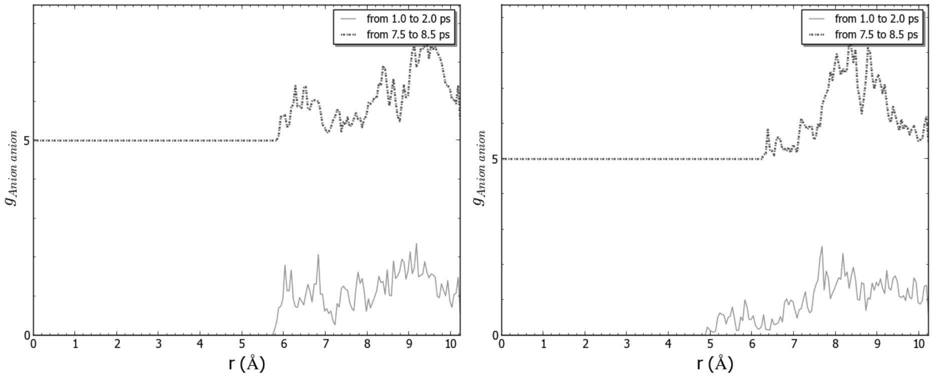

(g) PBE Type III Cation COM
(h) PBE Type IV Cation COM

Figure 7: Pair distribution functions for the (head-nitrogen atom)/(COM) of the cations in the RTIL with the (head-nitrogen atom)/(COM) of the other cations. Early structure shown with a continuous line, later structure with a dashed line and shifted upwards.


(a) BLYP Type III Anion Head (b) BLYP Type IV Anion Head


(c) BLYP Type III Anion COM (d) BLYP Type IV Anion COM


(e) PBE Type III Anion Head (f) PBE Type IV Anion Head

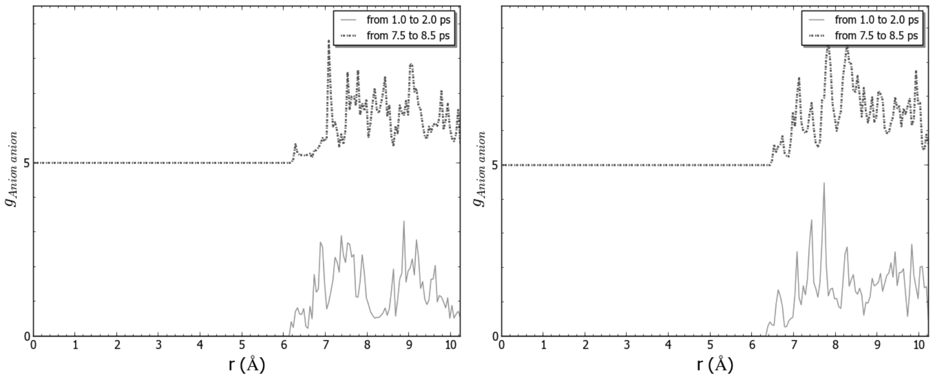
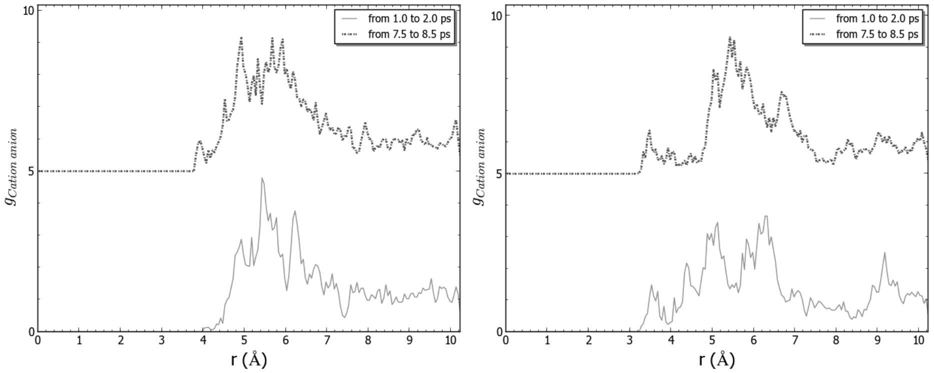
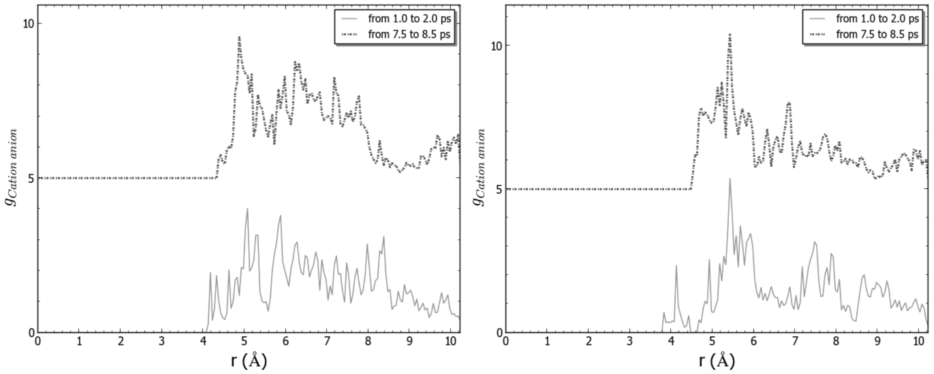
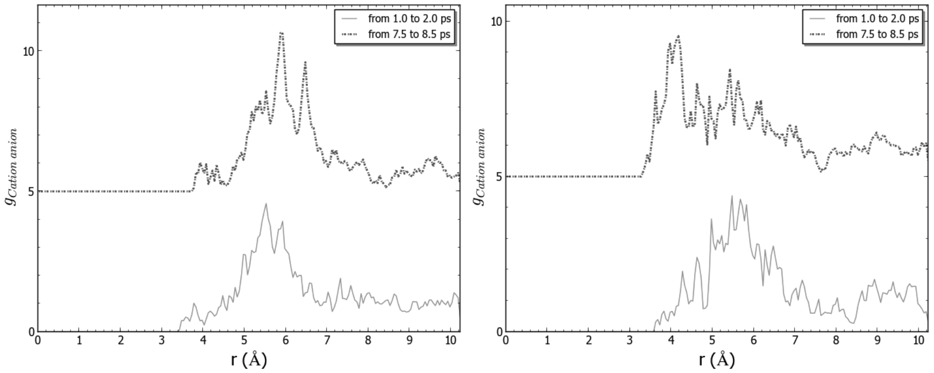

(g) PBE Type III Anion COM (h) PBE Type IV Anion COM

Figure 8: Pair distribution functions for the (head-nitrogen atom)/(COM) of the anions in the RTIL with the (head-nitrogen atom)/(COM) of the other anions. Early structure shown with a continuous line, later structure shown with a dashed line and shifted upwards.


(a) BLYP Type III Ion Head (b) BLYP Type IV Ion Head


(c) BLYP Type III Ion COM (d) BLYP Type IV Ion COM


(e) PBE Type III Ion Head (f) PBE Type IV Ion Head

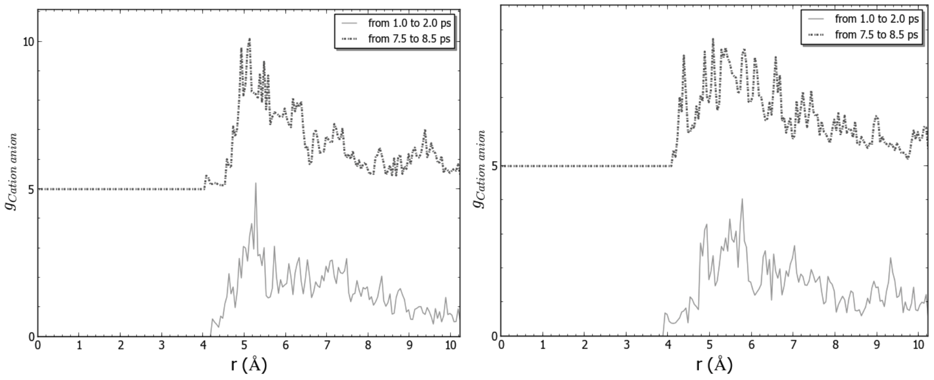

(g) PBE Type III Ion COM (h) PBE Type IV Ion COM

Figure 9: Pair distribution functions for the (head-nitrogen atom)/(COM) of the anions in the RTIL with the (head-nitrogen atom)/(COM) of the cations. Early structure shown with a continuous line, later structure shown with a dashed line and shifted upwards.

Comparing Figure 9a with Figure 9b we see that the anions and cations point more towards each other when dispersion corrections are included in the BLYP functional. The COM of the two systems with and without dispersion corrections are quite similar but the distribution of their head atoms are 0.6 Å closer in the BLYP-D case. This indicates that the dispersion corrections have an orientational effect, not changing the distance of the layers between the ions but their alignments with respect to each other. We would expect the head atoms to have some alignment due to this being close to where the charge imbalance on the molecules reside.

In the case of the PBE functional, we see that there is an orientational and translational effect. The orientational effect from dispersion corrections can be inferred from the larger peak at 3.6 Å in Figure 9f when compared with the same location in the adjacent plot, (Figure 9f). Similarly the translational effect can be seen from inspecting Figure 9g and Figure 9h which shows the COM of the cations and anions to be on average 0.6 Å closer together when dispersion corrections are added to the PBE functional.

A comparison of the PDFs from the BLYP and PBE functionals show the structure of the anions and cations to be quite similar, where as we find some deviation in comparing BLYP-D with PBE-D. The PDFs for the head atoms from the simulations with dispersion corrections included (Figures 9b, 9f) show that the PBE-D functional has a stronger orientational alignment of the cations and anions than does the BLYP-D functional. Additionally the COM plots reveal that the cations and anions are slightly closer together in the case of PBE-D by about 0.2 Å.

Conclusions

Two of the most commonly used functionals are PBE and B3LYP, however work by Izgorodina et al.[3] showed that B3LYP suffered from systematic errors in calculating the properties of ionic liquids and hence to look at whether the choice of functional had a strong influence on the results we compared PBE against another GGA functional namely BLYP.

In regards to the structure of the titania surface itself, neither the addition of dispersion corrections nor solvation by the strongly ionic solvent has any noticeable effect. This surface is stable throughout the simulations as is the carbon backbone of the N719 dye with neither group showing any real differences in their structure upon change of functional. The PDFs for some of the carboxylate oxygens do show however that the PBE functional results in some structural peaks being shifted by 0.1 Å closer than for the BLYP functional. The metal complex at the centre of the dye is also largely unaffected by changes to the dispersion treatment, functional or presence of solvent.

The structure of the dye is largely unaffected by solvation with the bipyridine rings and anchoring groups retaining their geometry. The exception to this is the thiocyano moieties which are more free to move about during the simulations. The radial distribution of the thiocyano arms is unchanged, but their angular distribution is altered by the presence of the solvent, being further apart from one another in the solvated simulations.

In the simulations involving the RTIL and without dispersion corrections, the cation-Ti mean separation is the same for the BLYP and PBE functionals, however, when dispersion is included, the mean separation for PBE-D is 0.7 Å further apart than that of BLYP-D. There is less of a significant effect for the anions. Hence while the choice of functional has a limited effect on the structures of the surface and the adsorbed dye, it can result in a considerably different layering of the ionic liquid.

Addition of dispersion corrections to solvated systems affects the cation more than the anion and the BLYP simulations more than those of PBE. The change in nearest approach mean separations between the RTIL and titania surface upon addition of dispersion for the BLYP functional is 1.2 Å for the cations and 0.2 Å for the anions, while for the PBE functional, the change is only 0.5 Å for the cations and non-existent for the anions. In the BLYP-D simulations, the cations relax towards a configuration whereby they are closer than the anions to the carbons in the dye by 1 Å. Conversely in the PBE-D simulations, the anions are closer to the carbon skeleton by about the same amount. The addition of dispersion to the BLYP functional pulls the first layer of the cations (anions) closer by 0.8 (0.4) Å, while in the PBE simulations dispersion has the effect of the nearest layer of the liquid being pushed away from the carbon atoms.

A comparison of the PDFs from the BLYP and PBE functionals show the structure of the anions and cations to be quite similar, where as we find some deviation in comparing BLYP-D with PBE-D with the cations and anions being slightly closer together in the case of PBE-D by about 0.2 Å. Dispersion corrections also have the effect of introducing more of an orientational alignment within the liquid, something which would be expected of a real liquid.

In a choice between which of the functionals studied here would be of use for future work, we would recommend the use of PBE-D as the empirical dispersion corrections are necessary for the realistic modelling of the RTIL, yet alter the underlying functional less than in the case of BLYP. Future work will delve deeper into this comparison by analysing properties other than structure.

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- Additional Structural Properties: Remaining pair distribution functions generated from ab-initio MD for all pairwise atom type combinations of the DSC.

References

1. Ohno, H. *Electrochemical aspects of ionic liquids*; John Wiley & Sons, 2011.

2. Byrne, A.; English, N. J.; Schwingenschlogl, U.; Coker, D. F. Dispersion and solvation effects on the structure and dynamics of N719 adsorbed to anatase titania (101) surfaces in room-temperature ionic liquids: An ab initio molecular simulation study. *J. Phys. Chem. C* **2015**,

3. Izgorodina, E. I.; Bernard, U. L.; MacFarlane, D. R. Ion-pair binding energies of ionic liquids: can DFT compete with ab initio-based methods? *J. Phys. Chem. A* **2009**, *113*, 7064–7072.

4. Mosconi, E.; Selloni, A.; De Angelis, F. Solvent effects on the adsorption geometry and electronic structure of dye-sensitized TiO_2: a first-principles investigation. *J. Phys. Chem. C* **2012**, *116*, 5932–5940.

5. De Angelis, F.; Fantacci, S.; Selloni, A.; Nazeeruddin, M. K.; GräTzel, M. First-principles modeling of the adsorption geometry and electronic structure of Ru (II) dyes on extended TiO_2 substrates for dye-sensitized solar cell applications. *J. Phys. Chem. C* **2010**, *114*, 6054–6061.

6. Schiffmann, F.; VandeVondele, J.; Hutter, J.; Wirz, R.; Urakawa, A.; Baiker, A. Protonation-dependent binding of ruthenium bipyridyl complexes to the anatase (101) surface. *J. Phys. Chem. C* **2010**, *114*, 8398–8404.

7. Lippert, G.; Hutter, J.; Parrinello, M. A hybrid Gaussian and plane wave density functional scheme. *Mol. Phys.* **1997**, *92*, 477–488.

8. VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **2005**, *167*, 103–128.

9. VandeVondele, J.; Hutter, J. An efficient orbital transformation method for electronic structure calculations. *J Chem Phys* **2003**, *118*, 4365–4369.

10. Lippert, G.; Hutter, J.; Parrinello, M. The gaussian and augmented-plane-wave density functional method for ab initio molecular dynamics simulations. *Theor. Chem. Acc.* **1999**, *103*, 124–140.

11. Krack, M.; Parrinello, M. All-electron ab-initio molecular dynamics. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2105–2112.

12. Grotendorst, J. *High performance computing in chemistry*; John von Neumann Institute for Computing, 2004.

13. Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. CP2K: atomistic simulations of condensed matter systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, *4*, 15–25.

14. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys* **2010**, *132*, 154104.

15. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J Comput Chem* **2006**, *27*, 1787–1799.

16. Hoover, W. G. Canonical dynamics: equilibrium phase-space distributions. *Phys. Rev. A* **1985**, *31*, 1695.

17. Allen, M. P.; Tildesley, D. J. *Computer simulation of liquids*; Oxford university press, 1989.

18. Hengerer, R.; Bolliger, B.; Erbudak, M.; Grätzel, M. Structure and stability of the anatase TiO_2 (101) and (001) surfaces. *Surf. Sci.* **2000**, *460*, 162–169.

19. Pastore, M.; De Angelis, F. Computational modelling of TiO2 surfaces sensitized by organic dyes with different anchoring groups: adsorption modes, electronic structure

and implication for electron injection/recombination. *Phys. Chem. Chem. Phys.* **2012**, *14*, 920–928.