Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

The Dynamics of Light-Induced Interfacial Charge Transfer of Different Dyes in Dye-Sensitized Solar Cells Studied by Ab Initio Molecular Dynamics

Lanlan He‡[a], Yu Guo‡[a] and Lars Kloo*[a]

Department of Chemistry, Applied Physical Chemistry, KTH Royal Institute of Technology,
Stockholm SE-10044, Sweden.

*Corresponding author:

Email address: larsa@kth.se

The re-organization energy (optimized method)

Table S1. The reorganization energy of protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 obtained from ADF and Gaussian 16

Table S2. The re-organization energies of the protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems as well as the deprotonated L1-TiO_2 system with acetonitrile effect (the latter in the column of deprotonated L1-TiO_2) as obtained from the statistical optimization method

Table S3. The average of electronic coupling for protonated and deprotonated L1-TiO2, D35-TiO2 and LEG4-TiO2.

Fig. S1(a-f) The electronic coupling of electron transfer, hole transfer and charge recombination for the deprotonated Li1-L1-TiO_2 and Li2-L1-TiO_2 systems

Implicit solvent effect on the interfacial geometry of the L1+TiO_2 model.

Fig. S2 The molecular structure of the deprotonated L1-TiO_2 model system

Fig. S3(a-d) The distances of Ti-O1, O1-O, C-O1 and C-O2 in the 30~45 ps aiMD simulation time range with (red) and without (black) solvent effects

Fig. S4 Angle O-Ti-O distribution of solvent and non-solvent systems for aiMD snapshots

Fig. S5(a-b) The dihedral angle of O-Ti-O-C and Ti-O-C-C with and without solvent effect.

Structural analysis for aiMD with 1.0 fs time step size

Fig. S6(a-i) The hydrogen bonding information of protonated systems. The bond length O-H of cyanoacrylic acid of the dye, the distance of O…H, O comes from TiO_2 and H comes from the dye, and hydrogen bonding angle O-H…O.

Fig. S7(a-c). The distance between the Ti atom of TiO_2 and the O atom of carboxylic acid. The black lines represent protonated systems; the red lines represent deprotonated systems

Fig. S8(a-b). The distance between the O atom of TiO_2 and the O atom of cyanoacrylic acid of the protonated and deprotonated dye. The black, red and blue lines stand for L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems, respectively

Fig. S9(a-c) Angle O-Ti-O distributions. Black and red lines represent the protonated and deprotonated systems

Fig. S10(a-f) Torsion Φ and Ψ distributions. Black and red lines represent the protonated and deprotonated systems

The analysis of structural properties and electronic coupling and rate of electron transfer for aiMS with 0.5 fs time step size

Fig. S11(a-c). The electronic coupling of electron transfer, hole transfer and charge recombination for protonated L1-TiO_2 system.

Fig. S12(a-g). The structural date of protonated L1TiO2 system. Ti-O bond, hydrogen bond (HB) distance H…O, O-Ti-O angle, hydrogen bonding angle H…O-H, torsion C-O-Ti-O, torsion Φ and torsion Ψ.

Table S4. The date of electron coupling of charge transfer (electron transfer, hole transfer and charge recombination) and the corresponding structural data bond Ti-O, hydrogen bonding length H…O, angle O-Ti-O, hydrogen bonding angle O…H-O, torsion C-O-Ti-O, Φ and Ψ for 20 continuous snapshots.

The relations between scanning of Ti-O(dye) distance and charge-transfer rates

Figure S13(a-f). The relations of distance Ti-O and electronic coupling/rate of charge transfer.

Input file for electronic coupling calculation

The re-organization energy calculated by optimization method. The formulas of optimization method[27] for re-organization energies calculation are shown in equation S1.

$$\lambda_e = (E_0^- - E_-) + (E_-^0 - E_0)$$

$$\lambda_h = (E_0^+ - E_+) + (E_+^0 - E_0) \qquad \text{(S1)}$$

where λ_e and λ_h represent the re-organization energies of electron and hole hopping, respectively. The energy E_0 stands for the energy of the neutral dye molecule which has been fully optimized geometry. E_0^- and E_0^+ are the energies of the anion and cation in the optimized ground-state geometry of the neutral dye molecule, respectively. E_- and E_+ refer to the energies of the relaxed geometries of the anionic and cationic states of the respective dye molecule. E_-^0 and E_+^0 are the energies of the neutral molecule calculated using the optimized geometries of the anionic and cationic states, respectively.

Table S1. The reorganization energy of protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 obtained from ADF and Gaussian 16

		Protonated systems			**Deprotonated systems**		
		L1-TiO_2	D35-TiO_2	LEG4-TiO_2	L1-TiO_2	D35-TiO_2	LEG4-TiO_2
ADF	λ_e（eV）	0.30	0.28	0.21	0.30	0.27	0.27
	λ_h（eV）	0.45	0.33	0.24	0.21	0.71	0.23
G16	λ_e（eV）	0.62	1.49	0.46	1.03	1.00	0.48
	λ_h（eV）	0.28	0.43	0.29	0.78	1.10	0.83

Table S1 gives the re-organization energy of electron and hole hopping of deprotonated and protonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 obtained from ADF software and Gaussian 16. For the protonated systems, the re-organization energies of electron hopping obtained from ADF are 0.30, 0.28 and 0.21 eV for L1-TiO_2, D35-TiO_2 and LEG4-TiO_2, respectively, and yielded by Gaussian 16 are 0.62, 1.49 and 0.46 eV, respectively. The re-organization energy of electron hopping of protonated D35TiO_2 system obtained from Gaussian 16 is 1.21 eV too much larger than that obtained from ADF. The re-organization energies of hole hopping obtained from ADF are 0.45, 0.33 and 0.24 eV for L1-TiO_2, D35-TiO_2 and LEG4-TiO_2, respectively, and yielded by Gaussian 16 are 0.51, 0.43 and 0.29 eV, respectively, which are in a reasonable range. For the deprotonated systems, the re-organization energies of electron hopping obtained from ADF are 0.30, 0.27 and 0.27 eV for L1-TiO_2, D35-TiO_2 and LEG4-TiO_2, respectively, and yielded by Gaussian 16 are 1.03, 1.34 and 1.35 eV, respectively. The re-organization energy of electron hopping of deprotonated systems obtained from Gaussian 16 are 0.73, 1.07 and 1.08 eV larger than those obtained from ADF, respectively. The re-organization energies of hole hopping obtained from ADF are 0.21, 0.71 and 0.23 eV for L1-TiO_2, D35-TiO_2 and LEG4-TiO_2, respectively, and yielded by Gaussian 16 are 0.78, 0.18 and 0.15 eV, respectively. The above values show the difference from ADF and Gaussian 16. Moreover, the re-organization energy obtained from Marcus-Hush method cannot reflect the changing of re-organization energy produced by different configurations. Therefore, to find out a statistical method to calculate re-organization energy is essential.

Table S2. The re-organization energies of the protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems as well as the deprotonated L1-TiO_2 system with acetonitrile effect (the latter in the column of deprotonated L1-TiO_2) as obtained from the statistical optimization method

	L1-TiO_2		**D35-TiO_2**		**LEG4-TiO_2**	
unit(eV)	[d]p	[e]dep	[d]p	[e]dep	[d]p	[e]dep
λ_e	0.81	0.76/0.75	0.76	0.74	0.81	0.82
λ_h	0.99	1.71/1.00	1.05	1.19	1.01	1.13

λ_{rec}	1.14	1.02/1.11	1.13	0.86	1.10	0.86

[d and e] represent the protonated and deprotonated systems, respectively.

Table S3 lists the average of electronic coupling when considering 95%, 5% and 100% of the data, respectively. The corresponding average of electronic coupling are listed below. Most of the data show that only 5% data are also not too sensitive to influence the average value of the total electronic coupling. These suggest that the data of electronic coupling are in the steady state.

Table S3. The average of electronic coupling for protonated and deprotonated L1-TiO2, D35-TiO2 and LEG4-TiO2.

		L1-TiO_2		**D35-TiO_2**		**LEG4-TiO_2**	
Average	[d]EC(eV)	protonated	deprotonated	protonated	deprotonated	protonated	deprotonated
[a]et	95%	0.0575	0.2515	0.1778	0.1341	0.0633	0.1498
	5%	0.0436	0.2921	0.1907	0.1158	0.0791	0.1078
	100%	0.0566	0.2555	0.1791	0.1314	0.0686	0.1455
[b]ht	95%	0.0020	0.0108	0.0014	0.0067	0.0016	0.0080
	5%	0.0016	0.0125	0.0010	0.0049	0.0019	0.0074
	100%	0.0019	0.0109	0.0013	0.0065	0.0017	0.0079
[c]Cr	95%	0.0463	1.1520	0.0944	1.1437	0.0367	1.1448
	5%	0.0371	0.9777	0.1008	0.6487	0.0619	1.2330
	100%	0.0454	1.1350	0.0950	1.0952	0.0400	1.1538

[a,b and c] represent the electron transfer, hole transfer and charge recombination, respectively. d represent the corresponding electronic coupling.

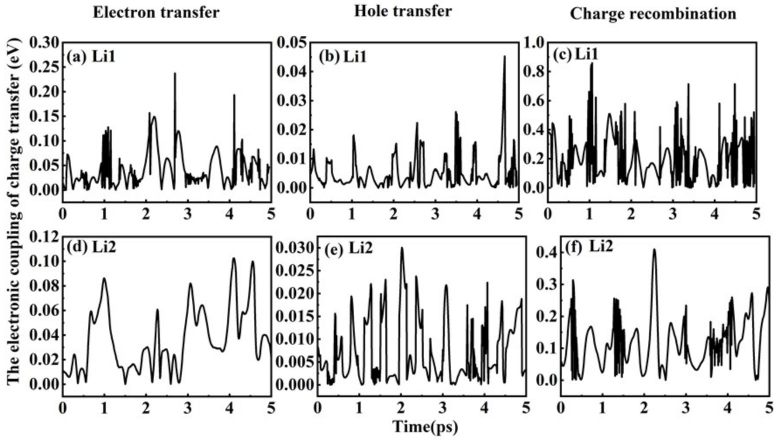


Fig. S1(a-f) The electronic coupling of electron transfer, hole transfer and charge recombination for the deprotonated Li1-L1-TiO_2 and Li2-L1-TiO_2 systems.

Implicit solvent effect on the interfacial geometry of the L1+TiO_2 model.

In order to study the solvent effects on interfacial geometry of the dye and TiO_2, the bond length, bond angle and dihedral angles of the deprotonated L1-TiO_2 interface model (see Figure S2) have been analyzed. The aiMD snapshots were selected from 30~45 ps in the simulations in acetonitrile solvent (PCM) and gas phase. The bond length of Ti-O1, O1-O, C-O1 and C-O2 of the deprotonated L1-TiO_2 system (for definitions, see Figure 1) with and without considering solvent effects are depicted in Fig. S3(a-d), which are represented by red and black curves, respectively. The Ti-O1 distances including solvent effects are 1.81~1.90 Å; shorter than the 1.80-1.97 Å obtained in the gas phase, as shown in Fig. S3(a). This indicates that the interaction between the dye O1 and the Ti atoms gets stronger when considering solvent effects, which indicates a stronger adsorption of deprotonated L1 on the TiO_2 surface. This is consistent with the results of Fang et al.[41] Fig. S3(b) shows that the O1-O distance ranges from 3.39 ~ 3.73 Å in acetonitrile, longer than those in gas phase, 3.25~3.63 Å, which may be coupled to the polarity of acetonitrile (as modelled by PCM). Fig. S3(c) and Fig. S3(d) show the fluctuation of the dye bond length C-O1 and C-O2 when including solvent effects and not. The reason for the lengths of the distances C-O1 and C-O2 when including the effects of acetonitrile showing damped fluctuations may also be attributed to the polarity of acetonitrile. The difference between the bond lengths of C-O1 in acetonitrile and those in gas phase are quite small, ranging from 1.30~1.39 Å and 1.21~1.41 Å, respectively. However, the bond lengths of C-O2 in acetonitrile (1.17~1.26 Å) are more obviously fluctuating less than those in gas phase (1.12~1.34 Å).

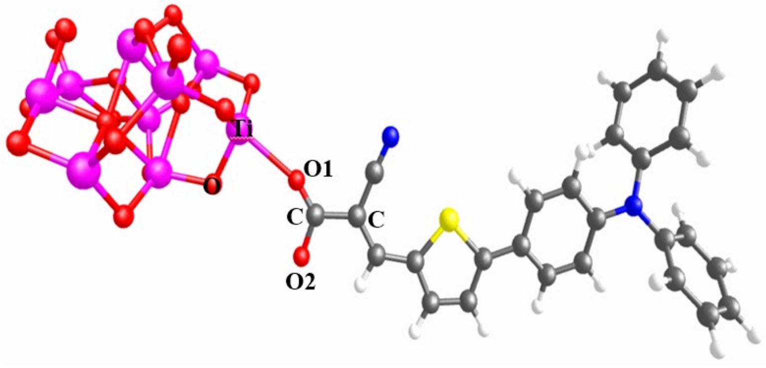


Fig. S2 The molecular structure of the deprotonated L1-TiO_2 model system used in this study

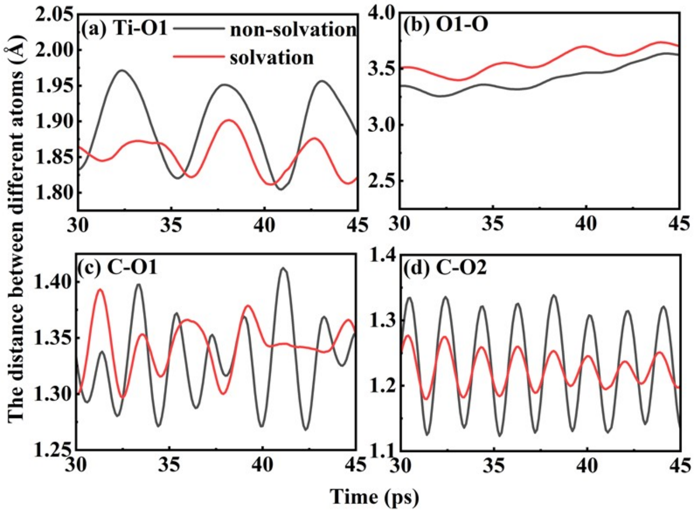


Fig. S3(a-d). The distances of Ti-O1, O1-O, C-O1 and C-O2 in the 30~45 ps aiMD simulation time range with (red) and without (black) solvent effects

To compare the geometrical difference with and without solvent effect, two trajectories for aiMD simulations are performed with and without considering implicit acetonitrile as solvent effect. The angle distribution of O-Ti-O and dihedral angle distribution of O-Ti-O-C and Ti-O-C-C from 30-45 ps ab initio molecular dynamicare depicted in Fig. S4 and S5(a-b). The angle O-Ti-O and dihedral angle O-Ti-O-C of deprotonated L1-TiO2 system in gas phase and in implicit acetonitrile are very similar. The absolute value of dihedral angle Ti-O-C-C in gas phase and implicit acetonitrile are close to 180°. In conclusion, the implicit acetonitrile doesn't influence the geometrical properties of angle O-Ti-O and dihedral angle O-Ti-O-C/Ti-O-C-C a lot.

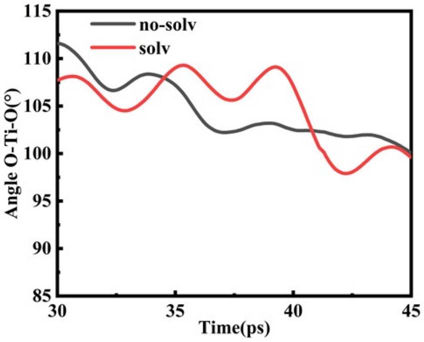


Fig. S4 Angle O-Ti-O distribution of solvent and non-solvent systems for aiMD snapshots.

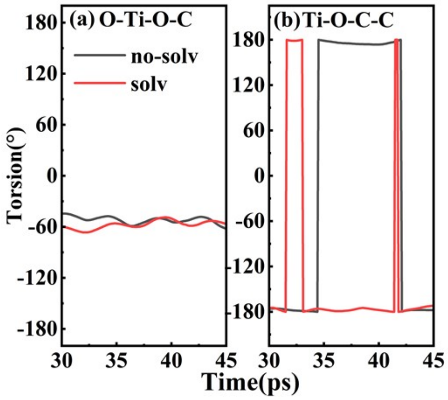


Fig. S5(a-b) The dihedral angle of O-Ti-O-C and Ti-O-C-C with and without solvent effect.

Structural analysis for aiMD with 1.0 fs time step size

Hydrogen bonding analysis. During the aiMD simulations, all protonated and deprotonated dye stay vertically above the TiO_2 cluster surface. As a consequence of the interaction between TiO_2 and the dye, hydrogen bonding O-H…O forms for all the protonated systems, which is from one oxygen atom of TiO_2 and the O-H of cyanoacrylic acid of the dye. The hydrogen bonding information including hydrogen bond length and hydrogen bond angle is outlined in Fig. S6(a-f), which consists of the hydrogen bonding length O…H and angle O-H…O. Fig. S6(a-b), S6(c-d) and S6(e-f) present the hydrogen bonding length of O…H and angle O-H…O for protonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems, respectively. The hydrogen bonding length O…H change from 1.40~1.80, 1.40~1.90 and 1.49~1.90 Å for the systems of L1-TiO_2, D35-TiO_2 and LEG4-TiO_2, respectively, which demonstrates the strong hydrogen bonding interaction. For the first 35 ps, the fluctuating range of O…H distance of D35-TiO_2 is from 1.40~.90 Å which is bigger than those of L1-TiO_2 and LEG4-TiO_2 systems. However, for the 35-50 ps, the fluctuating range of O…H distance of D35-TiO_2 gets smaller from 1.50~1.70 Å, which suggests the growing strength of hydrogen bonding. For L1-TiO_2 and LEG4-TiO_2 systems, the fluctuating range of O…H distance are mainly from 1.55~1.70 Å and 1.50~1.65 Å, which demonstrates the stable of hydrogen bonding. The range of hydrogen bonding angle O-H…O of L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems change from 147~176, 143~169 and 146~169°, respectively, which show a large fluctuating range. For L1-TiO_2 system, the fluctuating center of the hydrogen bonding angle is 160 and the main fluctuating is 5 up and down the center value. For D35-TiO_2 system, the fluctuating center of the hydrogen bonding angle is 155 and the main fluctuating is 5 up and down the center value, which are smaller than those of L1-TiO_2 systems. For LEG4-TiO_2 system, most hydrogen bonding angle range from 157~165°, which are the biggest hydrogen bonding angle among the three systems. The hydrogen bonding length and angle analysis suggest that the hydrogen bonding strength of the LEG4-TiO_2 system is slightly stronger than L1-TiO_2 and the hydrogen bonding strength of the

D35-TiO_2 system is slight weaker than other two systems. We cannot find that there is any relation between the hydrogen bonding information and the rate or electronic coupling of protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2.

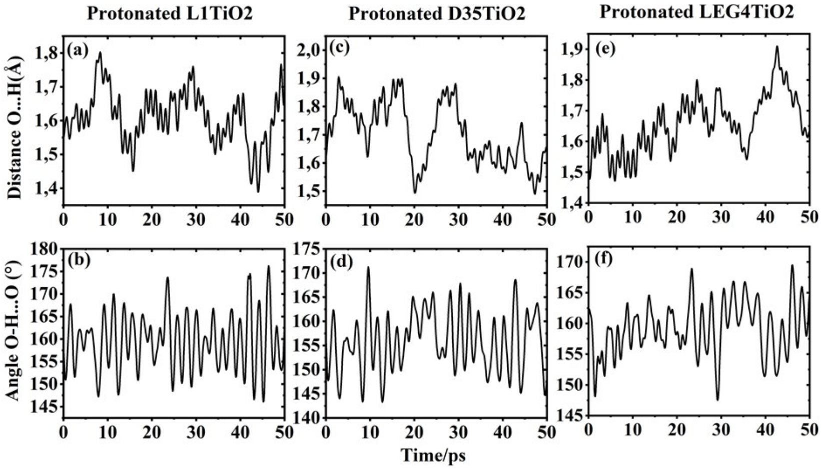


Fig. S6(a-i) The hydrogen bonding information of protonated systems. The bond length O-H of cyanoacrylic acid of the dye, the distance of O…H, O comes from TiO_2 and H comes from the dye, and hydrogen bonding angle O-H…O.

Ti-O bond length analysis.

After optimization, one oxygen atom of cyanoacrylic acid of the dye (protonated-L1, deprotonated-L1, protonated-D35, deprotonated-D35, protonated-LEG4 and deprotonated-LEG4) connects to one Ti atom of TiO_2 with a bonding distance. During the process of aiMD simulation, the distances of Ti-O of all the six systems are fluctuating. In order to compare the distance of Ti-O of protonated systems and deprotonated systems directly, we outlined the corresponding protonated dye-TiO_2 and deprotonated dye-TiO_2 in Fig. 7(a-c). Fig. 7(a), S7(b) and S7(c) show the distance Ti-O of L1-TiO_2, D35-TiO_2 and LEG4-TiO_2, respectively, with the black lines representing protonated systems and the red lines representing deprotonated systems. According to Fig. S8(a-c), the Ti-O distances of protonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems range from 1.90~2.11, 1.90~2.05 and 1.89~2.05 Å, which are longer than those of deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems ranging from 1.80~2.01, 1.81~1.98 and 1.81~1.96 Å. Most Ti-O distance for deprotonated are smaller than the normal Ti-O bond length (~2.0 Å).[27] This is due to the lack of the proton of the cyanoacrylic acid acts as an anchoring role to form hydrogen bonding with TiO_2 to restrict the oxygen atom of cyanoacrylic acid of the protonated dye to further approach to the Ti atom, which has been verified in hydrogen bonding analysis. It indicates that the interaction of Ti-O for deprotonated systems is stronger than those of protonated systems, which leads to the stronger electronic coupling of charge transfer of deprotonated systems. The Ti-O distance don't have any relation with the rate or electronic coupling of charge transfer for protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2.

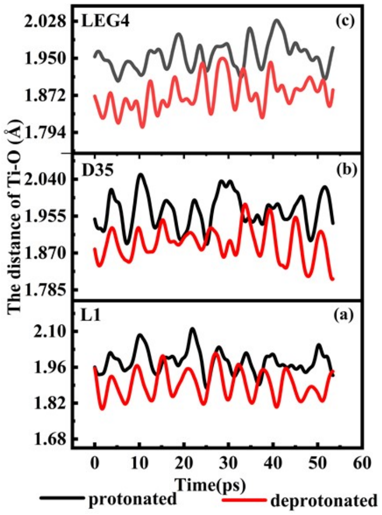


Fig. S7(a-c). The distance between the Ti atom of TiO_2 and the O atom of carboxylic acid. The black lines represent protonated systems; the red lines represent deprotonated systems.

O-O distance analysis. In order to further investigate the geometrical properties of the protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems, the distance between the oxygen atom of cyanoacrylic acid O-H of protonated dye as well as the oxygen atom of cyanoacrylic acid of deprotonated dye, which is not connecting to the Ti atom, and the oxygen atom of the semiconductor TiO_2 are exhibited in Fig. S8(a-b). Fig. S8(a) and S8(b) show the O-O distance of protonated and deprotonated systems, respectively, with the black, red and blue lines representing L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems, respectively. The distances between the O atoms of TiO_2 and the oxygen atoms of O-H group of cyanoacrylic acids of the protonated-L1TiO_2, D35TiO_2 and LEG4TiO_2 systems range from 2.52-2.82 Å, which are apparently smaller than those of deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems. The O-O distance of deprotonated L1-TiO_2 system is initially close to that of the protonated systems. However, with the aiMD proceeding, the O-O distance gradually gets away from each other on account of the electrostatic repulsion. Ultimately, the O-O distance of deprotonated L1TiO_2 system approach those of deprotonated D35-TiO_2 and LEG4-TiO_2 systems, which range from 3.3-3.6 Å. The O-O distance analysis of protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems also verifies the hydrogen atom of cyanoacrylic acid of the protonated dye acting as an anchor during the configuration changing of protonated systems. We have never found any relationship between the O-O distance changing and the rate or electronic coupling of charge transfer for protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2.

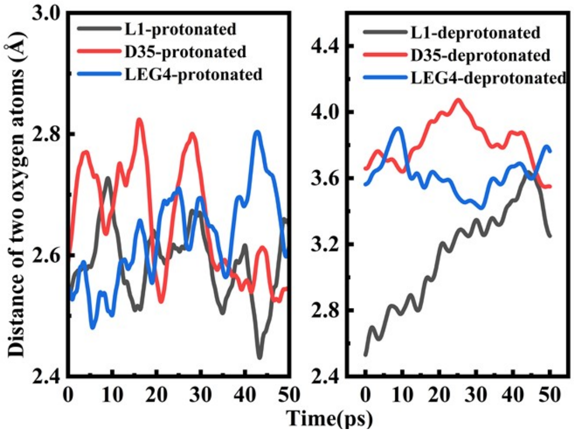


Fig. S8(a-b). The distance between the O atom of TiO_2 and the O atom of cyanoacrylic acid of the protonated and deprotonated dye. The black, red and blue lines stand for L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems, respectively.

Angle distribution analysis. The O-Ti-O angle distributions for L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems are depicted in Fig. S9(a-c) with the black and rad curves representing the O-Ti-O distributions of protonated and deprotonated systems, respectively. The angle O-Ti-O distributions of protonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems range from 83.0~93.6, 88.3~101.1 and 81.4~97.9°, respectively, which correlates well with the results (84~96°) of the first principle.[27] For deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems, angle O-Ti-O distributions range from 88.9~111.6, 99.3~118.4 and 91.9~115.4°, respectively. The most striking feature of Figure 11 is that the angle O-Ti-O of deprotonated systems is bigger than those of protonated systems, which is on account of lack of the proton. It is in agreement with the analysis of hydrogen bonding, Ti-O and O-O distance. However, the angle O-Ti-O analysis don't show any relationship with the rate or electronic coupling of charge transfer for protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems.

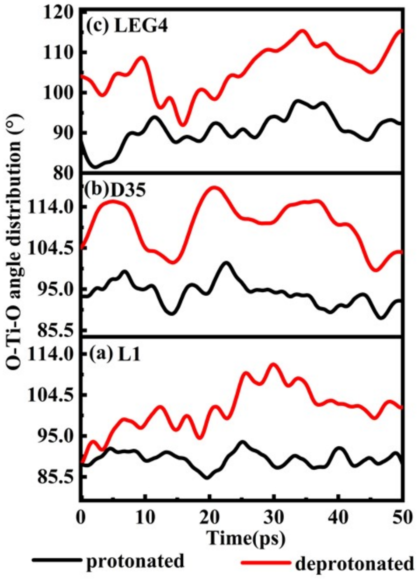


Fig. S9(a-c) Angle O-Ti-O distributions. Black and red lines represent the protonated and deprotonated systems

Torsion Φ and Ψ analysis. To unravel whether there exists any linear relation between torsion Φ/Ψ and the rate of electron transfer, the torsions Ψ and Φ derived from the first 50ps aiMD simulation have been outlined in figure S10(a-f). The torsions Φ and Ψ are stated in Figure 11, which are the torsion S-C-C-C between cyanoacrylic acid and thiophene and torsion C-C-C-C between thiophene and triphenylamine group. Fig. S10(d-f) show that the torsion Φ of protonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 varies from 168.1~180.0, 168.6~180.0 and 164.7~179.9°, respectively, which are approach to those of deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 systems 159.7~180.0, 159.6~180.0 and 164.3~180.0°, respectively. The torsion Ψ of protonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 varies from 154.9~179.9, 158.3~180.0 and 151.2~172.0°, respectively, which are approach to those of deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2 142.6~175.0, 140.7~166.5 and 138.8~170.8°, respectively. The Φ differences between protonated systems and deprotonated systems are slightly small than those of Ψ, which elucidates the hindered function of the interface interaction between dyes and TiO_2. But, the relation between torsions Φ/Ψ and the rate or electronic coupling of charge transfer of protonated and deprotonated L1-TiO_2, D35-TiO_2 and LEG4-TiO_2.

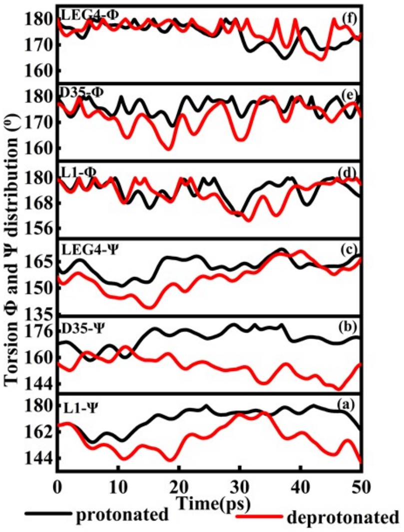


Fig. S10(a-f) Torsion Φ and Ψ distributions. Black and red lines represent the protonated and deprotonated systems

The analysis of structural properties and electronic coupling and rate of electron transfer for aiMS with 0.5 fs time step size.

Figure S11(a-c) and S12 (a-g) depict the electronic coupling of electron transfer, hole transfer and charge recombination and the structural properties Ti-O bond length, hydrogen bonding length H…O, angle O-Ti-O, hydrogen bonding angle O…H-O, torsion C-O-Ti-O, Φ and Ψ. Comparing Fig. S12(a-c) and Fig. S13(a-g), we cannot find any relationship between electronic coupling of charge transfer and the structural properties.

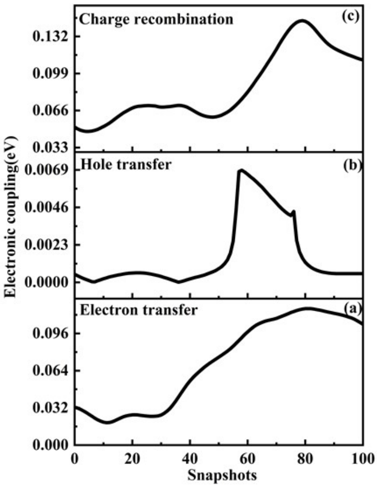


Fig. S11(a-c). The electronic coupling of electron transfer, hole transfer and charge recombination for protonated L1-TiO_2 system.

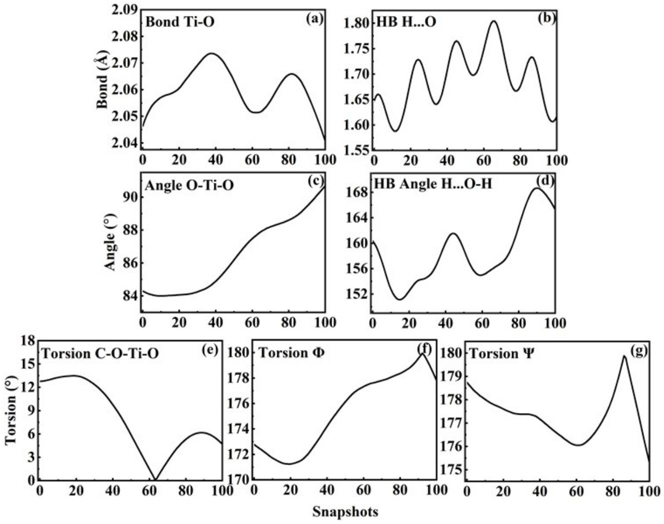


Fig. S12(a-g). The structural date of protonated L1TiO2 system. Ti-O bond, hydrogen bond (HB) distance H…O, O-Ti-O angle, hydrogen bonding angle H…O-H, torsion C-O-Ti-O, torsion Φ and torsion Ψ.

Table S4. The date of electron coupling of charge transfer (electron transfer, hole transfer and charge recombination) and the corresponding structural data bond Ti-O, hydrogen bonding length H…O, angle O-Ti-O, hydrogen bonding angle O…H-O, torsion C-O-Ti-O, Φ and Ψ for 20 continuous snapshots.

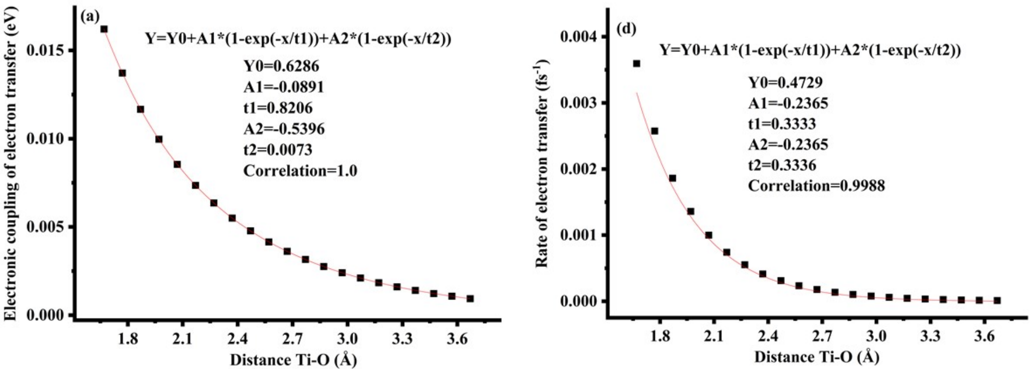
snapshots	^{a}et (eV)	^{b}ht (eV)	^{c}cr (eV)	Ti-O (Å)	H…O (Å)	O-Ti-O (°)	O…H-O (°)	C-O-Ti-O (°)	Φ (°)	Ψ (°)
1	0.0326	0.0005	0.0513	2.0463	1.6480	84.2979	160.3355	12.7606	172.7756	178.7419
2	0.0318	**0.0041**	0.0497	2.0483	1.6571	84.2372	159.9350	12.7909	172.6646	178.6485
3	0.0308	0.0032	0.0485	2.0501	**1.6605**	84.1847	159.4037	12.8193	172.5660	178.5564
4	0.0295	0.0024	0.0478	2.0516	1.6585	84.1367	158.7283	12.8620	172.4606	178.4671
5	0.0280	0.0017	**0.04739**	2.0528	1.6515	84.0995	157.9599	12.9136	172.3638	178.3858
6	0.0264	0.0011	0.0474	2.0540	1.6415	84.0707	157.1264	12.9650	172.2579	178.3147
7	0.0248	0.0005	0.0477	2.0548	1.6298	84.0455	156.2189	13.0306	172.1484	178.2469
8	0.0232	0.00001	0.0483	2.0555	1.6175	84.0249	155.2557	13.1010	172.0357	178.1788
9	0.0217	**0.0001**	0.0492	2.0561	1.6062	84.0095	154.3166	13.1629	171.9200	178.1268
10	0.0206	0.0016	0.0504	2.0567	1.5975	84.0014	153.4306	13.2192	171.8123	178.0676
11	0.0197	0.0022	0.0517	2.0572	1.5912	**84.0001**	152.7208	13.2706	171.7201	178.0125
12	**0.0193**	0.0027	0.0532	2.0575	1.5877	84.0027	152.1325	13.3167	171.6312	177.9568
13	0.0194	0.0033	0.0548	2.0578	1.5880	84.0093	151.6768	13.3534	171.5569	177.9060
14	0.0200	0.0037	0.0565	2.0580	1.5918	84.0121	151.3554	13.3880	171.4830	177.8630
15	0.0210	0.0041	0.0585	2.0582	1.5989	84.0223	151.1673	13.4226	171.4146	177.8211
16	0.0222	0.0045	0.0604	2.0584	1.6087	84.0267	151.1180	13.4448	171.3523	177.7812
17	0.0234	0.0048	0.0623	2.0587	1.6213	84.0303	151.2131	13.4615	171.3004	177.7479

18	0.0244	0.0051	0.0641	2.0591	1.6363	84.0357	151.4315	13.4770	171.2697	177.7135
19	0.0251	0.0054	0.0655	2.0594	1.6533	84.0457	151.7462	13.4921	171.2510	177.6803
20	0.0257	0.0056	0.0669	2.0600	1.6713	84.0539	152.1206	13.4935	171.2387	177.6423

^{a} represents electronic coupling of electron transfer, ^{b} represents electronic coupling of hole transfer, ^{c} represents electronic coupling of charge recombination

In 20 snapshots, there is only one break point for electronic coupling of electron transfer. The electronic couplings of electron transfer decrease from snapshot 1 to snapshot 12, which are 0.0326, 0.0318, 0.0308, 0.0295, 0.0280, 0.0264, 0.0248, 0.0232, 0.0217, 0.0206, 0.0197 and 0.0193 eV, respectively. While the electronic couplings of electron transfer increase from snapshot 13, which are 0.1940, 0.0200, 0.0210, 0.0222, 0.0234, 0.0244, 0.0251 and 0.0257 eV, respectively. The electronic couplings of hole transfer are 0.0005, 0.0041, 0.0032, 0.0024, 0.0017, 0.0011, 0.0005, 0.00001, 0.0001, 0.0016, 0.0022, 0.0027, 0.0033, 0.0037, 0.0041, 0.0045, 0.0048, 0.0051, 0.0054 and 0.0056 eV, respectively for 20 continuous snapshots, which suggests two break points for electronic coupling of hole transfer at snapshots 2 and 9. While the electronic couplings of charge recombination decrease from snapshot 1 to snapshot 5, which are 0.0513, 0.0497, 0.0485, 0.0478 and 0.04739 eV, respectively, and increase from snapshot 6. The data of Ti-O bond length, hydrogen bonding length H…O, hydrogen bonding angle H…O-H and torsion Φ do not have any break point for the 20 continuous snapshots. The bond length of Ti-O is ascending from 2.0463 to 2.0600 Å for the 20 continuous snapshots. The hydrogen bond length H…O increases from snapshot 1 (1.648 Å) to snapshot 3 (1.6605 Å) and decreases from snapshot 3 (1.6605 Å) to snapshot 20 1.6713 Å, which states a break point snapshot 3. The angle O-Ti-O decreases from snapshot 1 (84.2979°) to snapshot 11 (84.0001°), while increases from snapshot 11 (84.0001°) to snapshot 20 (84.0539°). However, for hydrogen bond angle O…H-O, torsion C-O-Ti-O, Φ and Ψ, never one break point appears from the 20 continuous snapshots. The hydrogen bond angle O…H-O is descending from snapshot 1 (160.3355°) to snapshot 20 (152.1206°). Torsion C-O-Ti-O is ascending from snapshot 1 (12.7606°) to snapshot 20 (13.4939°). Torsion Φ and Ψ are descending from snapshots 1 (172.7756) and (178.7419°) to snapshots 20 (171.2387) and (177.6423).

The relations between scanning of Ti-O(dye) distance and charge-transfer rates



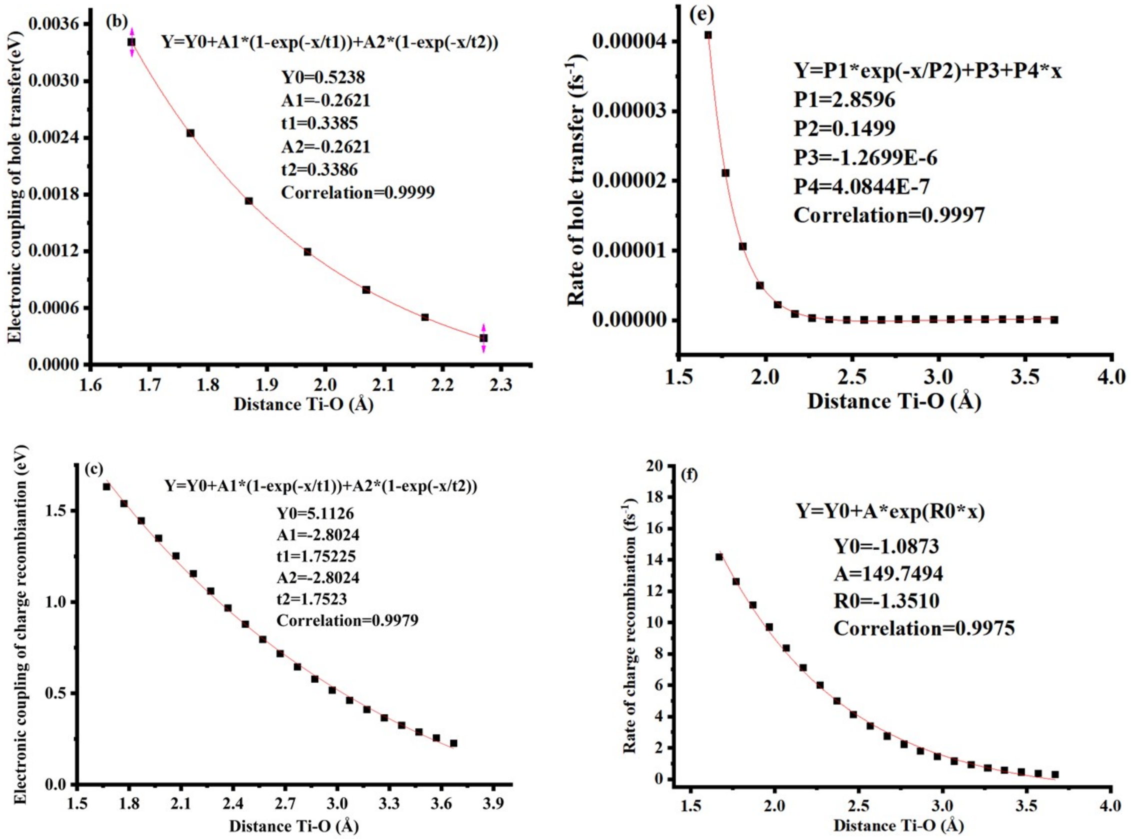


Figure S13(a-f). The relations of distance Ti-O and electronic coupling/rate of charge transfer.

Input file for electronic coupling calculation

File 1

ATOMS

1	C	16.3302314657	1.7872762139	-3.7018509564
2	C	15.1516263429	2.4631288445	-3.4125253411
3	C	14.0915280055	1.8057398672	-2.7278226717
4	C	14.2683023845	0.4577922356	-2.3569687481
5	C	15.3751356215	-0.2473340850	-2.8004775541
6	C	16.4196467611	0.4215056770	-3.4172107385
7	H	17.0807456609	2.3067093371	-4.3638288237
8	H	15.0049893404	3.4430293646	-3.8390272213
9	H	13.4715208991	0.0432261941	-1.7687046120
10	H	15.3072818462	-1.3171853421	-2.8279796352
11	N	12.9419080927	2.5567981383	-2.2822812143
12	C	13.2003293559	3.8100817403	-1.6642938323
13	C	12.6191449267	5.0041092632	-2.0857256819
14	C	14.0190511873	3.8106360279	-0.4878254936
15	C	12.8560637446	6.1136437039	-1.4264746931
16	H	12.0336535036	5.0108647733	-2.9852676687

```
 17    C     14.2473531184    4.9131151539    0.2831845412
 18    H     14.3423229691    2.8652637972   -0.1292543714
 19    C     13.6041139105    6.1329217600   -0.2256643341
 20    H     12.5656286910    7.0070773466   -1.9029806772
 21    H     14.8845124946    4.9908500570    1.1413531206
 22    C     11.6351543245    2.1341168631   -2.5106264032
 23    C     10.5112183564    2.6423274545   -1.8360648406
 24    C     11.3417878298    1.1079201308   -3.4514113331
 25    C      9.2510651946    2.4046315044   -2.2521849992
 26    H     10.7463517843    3.4988733385   -1.2130702155
 27    C     10.0498463038    0.7853883572   -3.8046188476
 28    H     12.2017497873    0.6280187018   -3.9353070988
 29    C      8.9518348605    1.5014976592   -3.3113308285
 30    H      8.3748263910    2.8955412378   -1.7566628726
 31    H      9.9982497213   -0.1207793950   -4.3634265411
 32    C      7.6034362439    1.2249147513   -3.7043329629
 33    C      7.1829505432    0.2218198777   -4.5358427314
 34    S      6.1689249938    2.1136199675   -2.9731661859
 35    C      5.8032135076   -0.0316085594   -4.4446466253
 36    H      7.8135798767   -0.3518486672   -5.1752013321
 37    C      5.1343209322    0.9062074243   -3.5990774873
 38    H      5.3503757080   -0.8628463691   -4.9675535882
 39    C      3.7223838608    0.8324079727   -3.3086322469
 40    H      3.3098034469   -0.1794763746   -3.4809839693
 41    C      2.9705361670    1.6959213423   -2.5833453649
 42    C      3.4626956297    2.9685521935   -2.1560706201
 43    N      3.9806592533    3.9930631575   -1.8731133609
 44    C      1.6042701799    1.3796687906   -2.1529423186
 45    O      0.9190942028    2.0000426280   -1.3004385461
 46    O      1.1352922747    0.3479770539   -2.8278192325
 47    H      0.1554998238    0.2331206924   -2.5264320299
 48    H     17.2627590633   -0.1397518637   -3.9038974808
 49    H     13.4993691412    7.0055024471    0.4103531965
END

CHARGE 0.0 0.0
BASIS
type TZ2P
core None
createoutput None
END
NUMERICALQUALITY GOOD
RELATIVISTIC SCALAR ZORA MAPA
XC
GGA PW91
DISPERSION GRIMME4 s6=1.0 s8=0.7728 a1=0.3958 a2=4.9341
END
```

File 2

```
ATOMS
  1   Ti    -0.9827897798    1.9307593980   -0.5073315145
  2    O    -3.0537724498    2.1665031148   -0.8761333498
  3    O    -1.3269176706    0.6132069963   -1.7548143608
  4    O    -1.0223636892    1.1489507692    1.0423834941
  5   Ti    -2.3903701714    0.4100043896    2.1937600227
  6    O    -1.7126819309    0.0555054423    3.5972202804
  7    O    -3.2873733077   -1.1310651272    1.4286254619
  8    O    -3.7955055816    1.6250057559    1.9556172781
```

```
  9    Ti     -4.7801013827    2.1449338596    0.6329145191
 10     O      -3.7162551824    4.4865047668   -2.3521169252
 11    Ti      -2.9991813199    4.0828027185   -0.7716808457
 12     O      -1.2323145086    3.7914365296   -0.4724516582
 13     O      -4.2853759772    3.9533782357    0.5418211671
 14     O      -5.7060730104    2.7030920330   -1.3407994576
 15    Ti     -3.1420574288    0.4280152027   -1.8995666556
 16     O      -3.9338724031    1.2701048409   -3.2078791999
 17     O      -4.6954821358    0.3820738918   -0.4602909168
 18     O      -3.4174989678   -1.3514646041   -1.5303670418
 19    Ti     -4.3075386779   -1.4348395854    0.0384795999
 20     O      -6.5104272439    1.4636304254    1.0329139758
 21     O      -6.1255633900   -1.6052818267    0.1065069418
 22    Ti     -6.6258660320    0.1633769528   -0.2009442083
 23    Ti     -4.7967952910    2.9528576180   -2.8368939978
 24     O      -8.7398106468    3.4035393661   -1.8366138962
 25    Ti     -7.4383857116    2.5258929247   -2.1601991885
 26     O      -6.3906070298    3.0499708931   -3.6473121927
 27     O      -7.5277355585    0.6092599535   -1.6533080651
END

BASIS
type TZ2P
core None
createoutput None
END
NUMERICALQUALITY GOOD
RELATIVISTIC SCALAR ZORA MAPA
XC
GGA PW91
DISPERSION GRIMME4 s6=1.0 s8=0.7728 a1=0.3958 a2=4.9341
END
```

File 3

```
ATOMS
  1   C   16.3302314657 1.7872762139 -3.7018509564    f=Region_1 b=Region_1
  2   C   15.1516263429 2.4631288445 -3.4125253411    f=Region_1 b=Region_1
  3   C   14.0915280055 1.8057398672 -2.7278226717    f=Region_1 b=Region_1
  4   C   14.2683023845 0.4577922356 -2.3569687481    f=Region_1 b=Region_1
  5   C   15.3751356215 -0.2473340850 -2.8004775541   f=Region_1 b=Region_1
  6   C   16.4196467611 0.4215056770 -3.4172107385    f=Region_1 b=Region_1
  7   H   17.0807456609 2.3067093371 -4.3638288237    f=Region_1 b=Region_1
  8   H   15.0049893404 3.4430293646 -3.8390272213    f=Region_1 b=Region_1
  9   H   13.4715208991 0.0432261941 -1.7687046120    f=Region_1 b=Region_1
 10   H   15.3072818462 -1.3171853421 -2.8279796352   f=Region_1 b=Region_1
 11   N   12.9419080927 2.5567981383 -2.2822812143    f=Region_1 b=Region_1
 12   C   13.2003293559 3.8100817403 -1.6642938323    f=Region_1 b=Region_1
 13   C   12.6191449267 5.0041092632 -2.0857256819    f=Region_1 b=Region_1
 14   C   14.0190511873 3.8106360279 -0.4878254936    f=Region_1 b=Region_1
 15   C   12.8560637446 6.1136437039 -1.4264746931    f=Region_1 b=Region_1
 16   H   12.0336535036 5.0108647733 -2.9852676687    f=Region_1 b=Region_1
 17   C   14.2473531184 4.9131151539 0.2831845412     f=Region_1 b=Region_1
 18   H   14.3423229691 2.8652637972 -0.1292543714    f=Region_1 b=Region_1
 19   C   13.6041139105 6.1329217600 -0.2256643341    f=Region_1 b=Region_1
 20   H   12.5656286910 7.0070773466 -1.9029806772    f=Region_1 b=Region_1
 21   H   14.8845124946 4.9908500570  1.1413531206    f=Region_1 b=Region_1
 22   C   11.6351543245 2.1341168631 -2.5106264032    f=Region_1 b=Region_1
 23   C   10.5112183564 2.6423274545 -1.8360648406    f=Region_1 b=Region_1
```

```
 24   C   11.3417878298 1.1079201308 -3.4514113331    f=Region_1 b=Region_1
 25   C    9.2510651946 2.4046315044 -2.2521849992    f=Region_1 b=Region_1
 26   H   10.7463517843 3.4988733385 -1.2130702155    f=Region_1 b=Region_1
 27   C   10.0498463038 0.7853883572 -3.8046188476    f=Region_1 b=Region_1
 28   H   12.2017497873 0.6280187018 -3.9353070988    f=Region_1 b=Region_1
 29   C    8.9518348605 1.5014976592 -3.3113308285    f=Region_1 b=Region_1
 30   H    8.3748263910 2.8955412378 -1.7566628726    f=Region_1 b=Region_1
 31   H    9.9982497213 -0.1207793950 -4.3634265411   f=Region_1 b=Region_1
 32   C    7.6034362439 1.2249147513 -3.7043329629    f=Region_1 b=Region_1
 33   C    7.1829505432 0.2218198777 -4.5358427314    f=Region_1 b=Region_1
 34   S    6.1689249938 2.1136199675 -2.9731661859    f=Region_1 b=Region_1
 35   C    5.8032135076 -0.0316085594 -4.4446466253   f=Region_1 b=Region_1
 36   H    7.8135798767 -0.3518486672 -5.1752013321   f=Region_1 b=Region_1
 37   C    5.1343209322 0.9062074243 -3.5990774873    f=Region_1 b=Region_1
 38   H    5.3503757080 -0.8628463691 -4.9675535882   f=Region_1 b=Region_1
 39   C    3.7223838608 0.8324079727 -3.3086322469    f=Region_1 b=Region_1
 40   H    3.3098034469 -0.1794763746 -3.4809839693   f=Region_1 b=Region_1
 41   C    2.9705361670  1.6959213423 -2.5833453649   f=Region_1 b=Region_1
 42   C    3.4626956297  2.9685521935 -2.1560706201   f=Region_1 b=Region_1
 43   N    3.9806592533  3.9930631575 -1.8731133609   f=Region_1 b=Region_1
 44   C    1.6042701799  1.3796687906 -2.1529423186   f=Region_1 b=Region_1
 45   O    0.9190942028  2.0000426280 -1.3004385461   f=Region_1 b=Region_1
 46   O    1.1352922747  0.3479770539 -2.8278192325   f=Region_1 b=Region_1
 47   H    0.1554998238  0.2331206924 -2.5264320299   f=Region_1 b=Region_1
 48   H   17.2627590633 -0.1397518637 -3.9038974808  f=Region_1 b=Region_1
 49   H   13.4993691412  7.0055024471 0.4103531965   f=Region_1 b=Region_1
 50  Ti  -0.9827897798  1.9307593980  -0.5073315145  f=Region_2 b=Region_2
 51   O   -3.0537724498  2.1665031148 -0.8761333498   f=Region_2 b=Region_2
 52   O   -1.3269176706  0.6132069963 -1.7548143608   f=Region_2 b=Region_2
 53   O   -1.0223636892  1.1489507692  1.0423834941   f=Region_2 b=Region_2
 54  Ti  -2.3903701714  0.4100043896  2.1937600227   f=Region_2 b=Region_2
 55   O   -1.7126819309  0.0555054423  3.5972202804   f=Region_2 b=Region_2
 56   O   -3.2873733077 -1.1310651272  1.4286254619   f=Region_2 b=Region_2
 57   O   -3.7955055816  1.6250057559  1.9556172781   f=Region_2 b=Region_2
 58  Ti  -4.7801013827  2.1449338596  0.6329145191   f=Region_2 b=Region_2
 59   O   -3.7162551824  4.4865047668 -2.3521169252   f=Region_2 b=Region_2
 60  Ti  -2.9991813199  4.0828027185 -0.7716808457   f=Region_2 b=Region_2
 61   O   -1.2323145086  3.7914365296 -0.4724516582   f=Region_2 b=Region_2
 62   O   -4.2853759772  3.9533782357  0.5418211671    f=Region_2 b=Region_2
 63   O   -5.7060730104  2.7030920330  1.3407994576    f=Region_2 b=Region_2
 64  Ti  -3.1420574288  0.4280152027 -1.8995666556    f=Region_2 b=Region_2
 65   O   -3.9338724031  1.2701048409 -3.2078791999    f=Region_2 b=Region_2
 66   O   -4.6954821358  0.3820738918 -0.4602909168    f=Region_2 b=Region_2
 67   O   -3.4174989678 -1.3514646041 -1.5303670418    f=Region_2 b=Region_2
 68  Ti  -4.3075386779 -1.4348395854  0.0384795999    f=Region_2 b=Region_2
 69   O   -6.5104272439  1.4636304254  1.0329139758    f=Region_2 b=Region_2
 70   O   -6.1255633900 -1.6052818267  0.1065069418    f=Region_2 b=Region_2
 71  Ti  -6.6258660320  0.1633769528 -0.2009442083    f=Region_2 b=Region_2
 72  Ti  -4.7967952910  2.9528576180 -2.8368939978    f=Region_2 b=Region_2
 73   O   -8.7398106468 3.4035393661 -1.8366138962     f=Region_2 b=Region_2
 74  Ti  -7.4383857116  2.5258929247 -2.1601991885    f=Region_2 b=Region_2
 75   O   -6.3906070298  3.0499708931 -3.6473121927    f=Region_2 b=Region_2
 76   O   -7.5277355585  0.6092599535 -1.6533080651    f=Region_2 b=Region_2
END

CHARGE 0.0 0.0
BASIS
type TZ2P
```

```
core None
createoutput None
END
XC
GGA PW91
END
NUMERICALQUALITY GOOD
RELATIVISTIC SCALAR ZORA MAPA
SYMMETRY NOSYM
TRANSFERINTEGRALS
Fragments
Region_1 T1.T21
Region_2 T2.T21
DISPERSION GRIMME4 s6=1.0 s8=0.7728 a1=0.3958 a2=4.9341
END
```