

Supporting Information for

Acetonitrile solution effect on Ru N749 dye adsorption and excitation at TiO₂ anatase interface

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S1. Assessment of the AN solution state in the present calculation cell

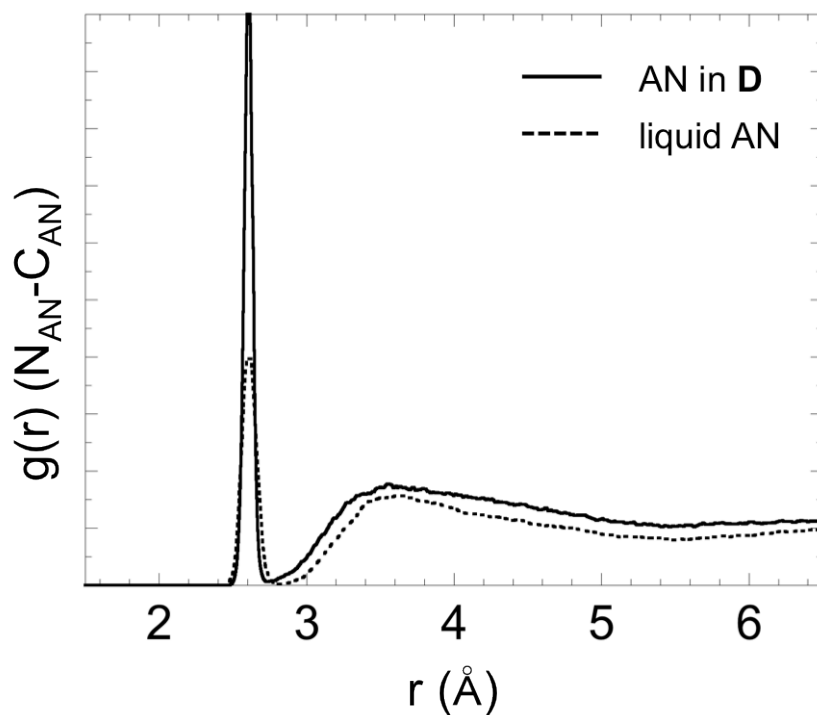


Figure S1. Radial distribution functions from N_{AN} of (N in AN molecule) to C_{AN} (C in AN molecule) of the desorbed (D) state in the present cell (solid line) and the reference cell with liquid AN only (broken line). The peak positions are quite similar, indicating that the AN solution state and the insertion of the counterion, TMA, in the present supercell well reproduce the liquid AN behavior.

S2. Assessment of the adsorption preference depending on the interface slab thickness

Table S2. Duration times of the d2-type and p1-type adsorption states of isonicotinic acid ($C_6H_5NO_2$), a model molecule of the Ru dyes, in the DFT-MD sampling simulations with different thicknesses of the anatase TiO_2 slab. The thicker slab with the 5 layers still indicates the preference of the d2-type state and the coexistence of the p1-type state. Note that the duration times depend on the trajectories, even using the same thickness of the slab. However, the present conclusion still holds.

Trajectory	Duration of the d2-like state (ps)	Duration of the p1-like state (ps)
2-layer slab, trajectory I	4.8	1.9
2-layer slab, trajectory II	3.4	2.9
5-layer slab	1.7	1.1

S3. Detail of the energy sampling data with the error bar

Table S3. The average energies plus constant $\langle E+6183 \rangle$ and the standard deviation σ of the DFT-MD total energy samplings of the adsorption states investigated in this work. Both units are Hartree. In addition to the original sampling for around 4 psec, the additive sampling data for around 1 psec and the total sampling for around 5 psec are also listed. The addition of the sampling does not alter the present conclusion "coexistence of the d2 and p1 states with slightly more preference of the d2". We also found that the standard deviation of the d2 state is usually smaller than the D and p1. This can be attributed to the less structural fluctuation of the d2 state with the two firm anchors. For additional information, we have examined the bidentate bridging mode of the adsorption, labeled as bri, and found that the bri state is less stable than the d2 and p1.

State	Original sampling		Added sampling		Total sampling	
	$\langle E+6183 \rangle$	σ	$\langle E+6183 \rangle$	σ	$\langle E+6183 \rangle$	σ
D	-0.053	0.040	-0.043	0.037	-0.051	0.040
p1	-0.071	0.043	-0.075	0.029	-0.071	0.041
d2	-0.072	0.036	-0.070	0.036	-0.072	0.036
p2	-0.049	0.050	-0.052	0.030		
p1d1	-0.029	0.041	-0.038	0.041		
bri	--	--	-0.035	0.043		

S4. References with the complete author list

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