Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

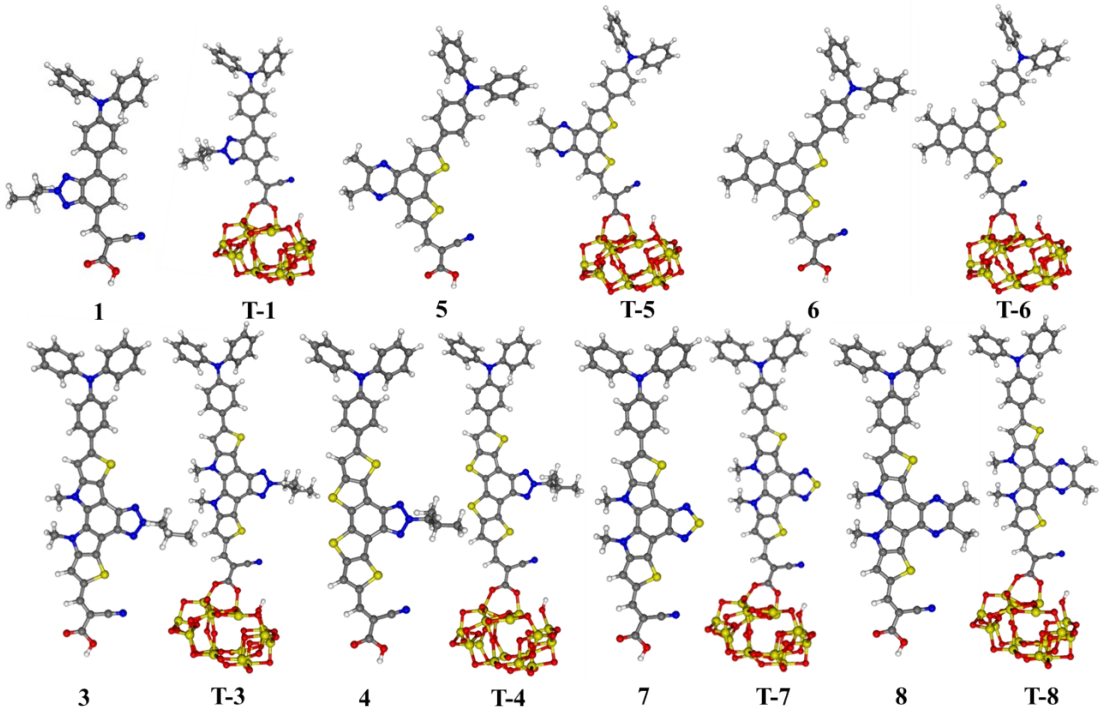
Rigid fused π-spacer in D-π-A type molecule for dye-sensitized solar cell: A computational investigation

Ping Li, Zhixiang Wang, Chongping Song and Houyu Zhang*

State Key Laboratory of Supramolecular Structure and Materials,
Institute of Theoretical Chemistry, Jilin University, Changchun
130012, P. R. China

*E-mail: houyuzhang@jlu.edu.cn

Contents


1 T-1 5 T-5 6 T-6

3 T-3 4 T-4 7 T-7 8 T-8

Fig. S1 Optimized structures of the rest of dyes and their dye-TiO_2 complexes.

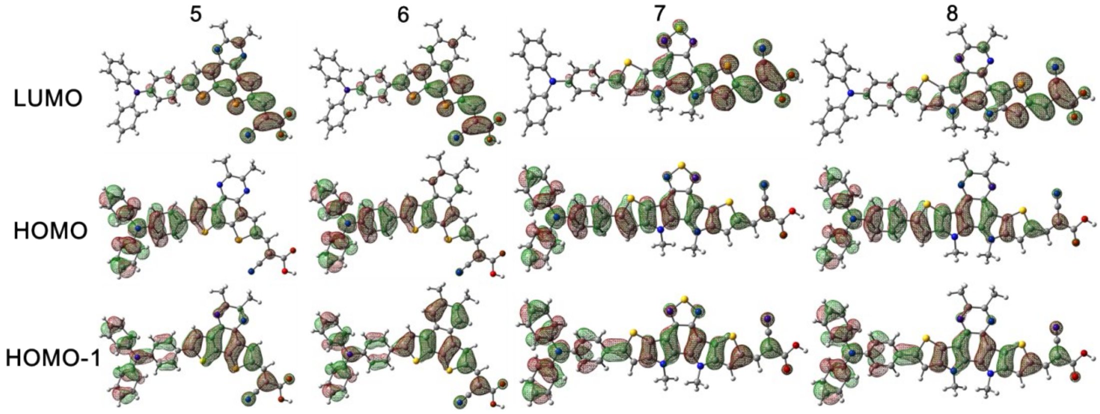


Fig. S2 Spatial distributions of the frontier molecular orbitals for dyes **5-8**.

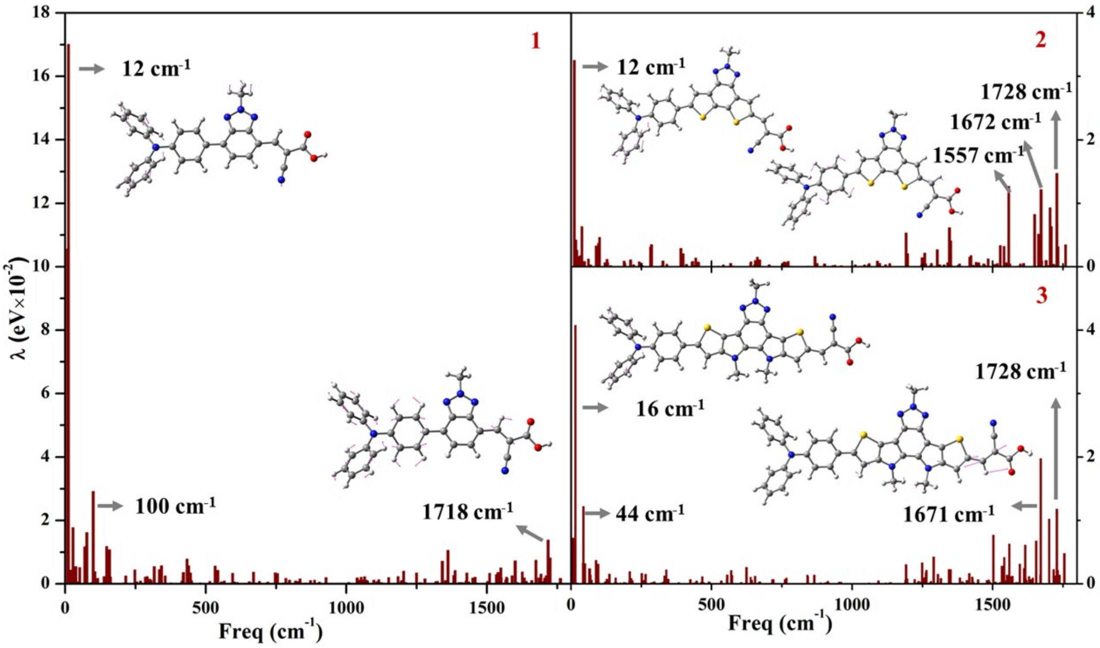


Fig. S3 Contribution of the vibrational modes to the reorganization energy for dyes **1-3**, embeded with the normal modes contribute the most for Λ.

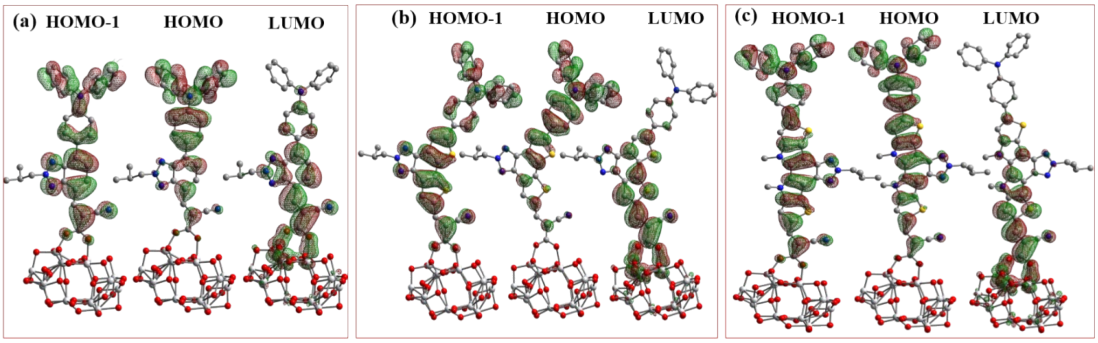


Fig. S4 Frontier molecular orbitals of dye-TiO_2 complexes for **1** (a), **2** (b), and **3** (c) (saturated H atoms are not shown).

The details in calculation of ΔE_{CB}: As indicated in Fig. S5, the comparison of the PDOS of TiO2 in 1-TiO_2 complex and the DOS of pure TiO_2 are made to determine the Δ*ECB*. The linear fittings of DOS profiles at the low energy range for the conduction band are performed. The intercepts of fitted lines with the energy axis are considered as the CB edge, and Δ*ECB* can be approximately evaluated by the difference of intercept at energy axis for two fitted lines.

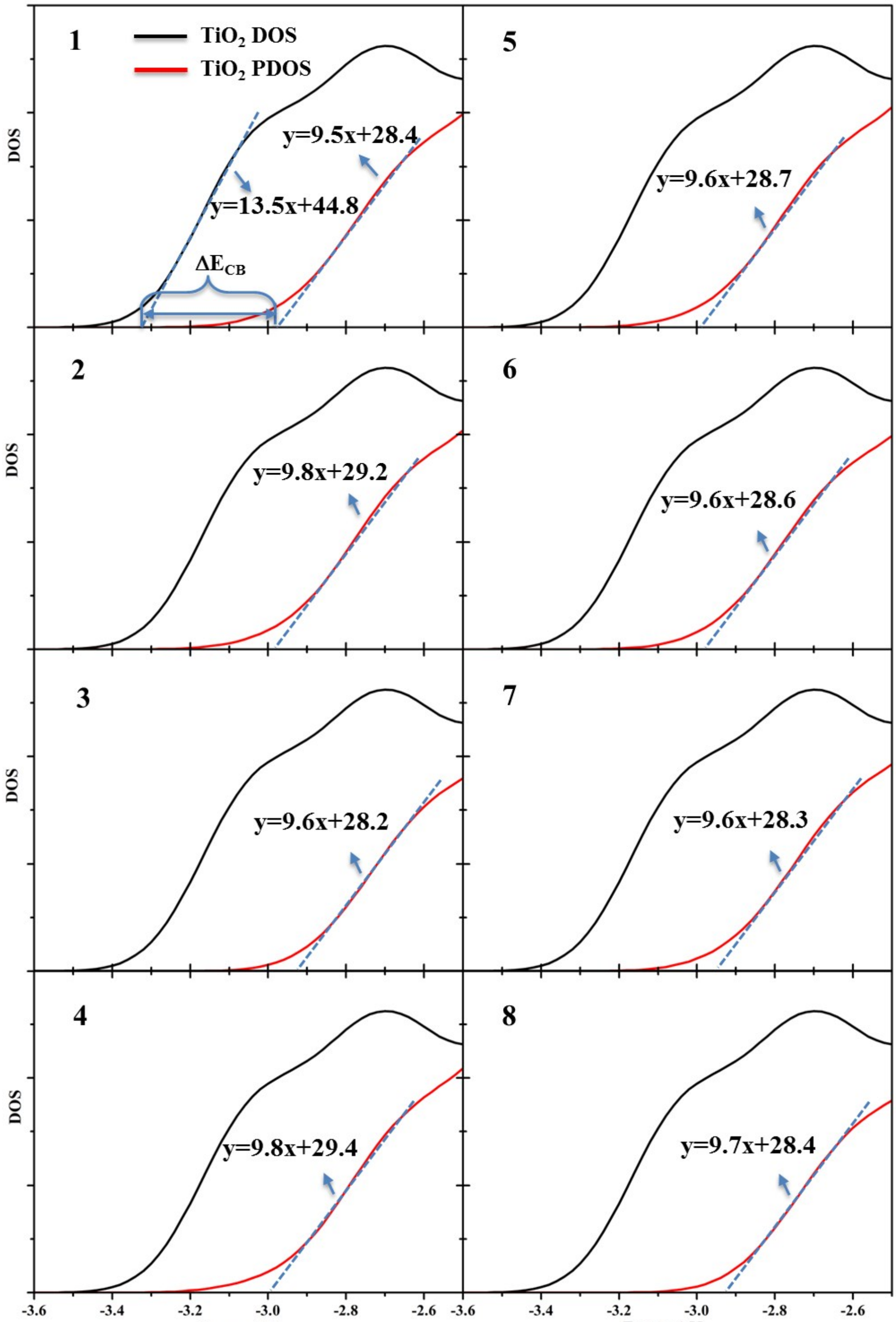


Fig. S5 DOS of TiO_2 and PDOS of TiO_2 in dye-TiO_2 complexes.

Table S1 Calculated HOMO energy levels of dyes **1**, **2**, and **3** in THF with functionals of PBE0, PBE0-1/3, PBE38, and mpw1k, and corresponding experimental values.

	PBE0 (25% HF_{exc})	PBE0-1/3 (33.3% HF_{exc})	PBE38 (37.5% HF_{exc})	MPW1K (42.8% HF_{exc})	Expt.
1	-5.40	-5.70	-5.85	-6.06	-5.80
2	-5.34	-5.63	-5.78	-6.00	-5.76
3	-5.10	-5.38	-5.52	-5.73	-5.48

Table S2 Calculated first singlet excitation energies ($E_{\lambda max}$) and the maximum absorption wavelengths (λ_{max}) of dyes **1**, **2**, and **3** with functionals of PBE0, mpw1k, BHandHLYP, and CAM-B3LYP, and corresponding experimental values. The values denote the percentage of nonlocal Hartree-Fock exchange (HF_{exc}) in parentheses.

		PBE0 (25%)	mpw1k (42.8%)	BHandHLYP (50%)	CAM-B3LYP (19% at SR and 65% at LR)	Expt.
1	$E_{\lambda max}$ /eV	2.25	2.69	2.84	2.85	2.89
	λ_{max}/nm	552	461	437	435	430
2	$E_{\lambda max}$ /eV	2.22	2.68	2.81	2.85	2.86
	λ_{max}/nm	559	462	442	435	434
3	$E_{\lambda max}$ /eV	2.25	2.58	2.65	2.69	2.58
	λ_{max}/nm	552	481	468	461	480

Table S3 Selected bond lengths (Å) and adsorption energies of all investigated dye-TiO_2 complexes.

	Ti-O (H) (Å)	Ti-O (Å)	E_{ads} (kcal mol^{-1})
1	1.95	2.01	-31.64
2	1.95	2.02	-26.09
3	1.95	2.00	-20.78
4	1.95	2.01	-21.58
5	1.95	2.02	-26.88
6	1.95	2.02	-27.12
7	1.95	2.01	-20.60
8	1.95	2.00	-21.51