

Synergistic Modulation of Composite Donors and π -Spacers in Porphyrin Sensitizers for Enhanced Charge Transfer and Photovoltaic Efficiency: A DFT/TD-DFT Study

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Table S1 Information on the structure, energy levels, and adsorption energy of dye molecules after adsorption onto $(\text{TiO}_2)_{24}$

Dye	Ti–O _a (Å)	Ti–O _b (Å)	HOMO (eV)	LUMO (eV)	E _g (eV)	E _{ads} (eV)
L- $(\text{TiO}_2)_{24}$	2.12	2.17	-5.10	-3.34	1.77	-2.99
T- $(\text{TiO}_2)_{24}$	2.09	2.19	-5.23	-3.52	1.70	-2.72
T-L- $(\text{TiO}_2)_{24}$	2.17	2.09	-5.33	-3.48	1.85	-3.54
TO-L- $(\text{TiO}_2)_{24}$	2.03	2.17	-4.82	-3.35	1.47	-2.45
T-LD- $(\text{TiO}_2)_{24}$	2.11	2.25	-5.14	-3.58	1.56	-2.72

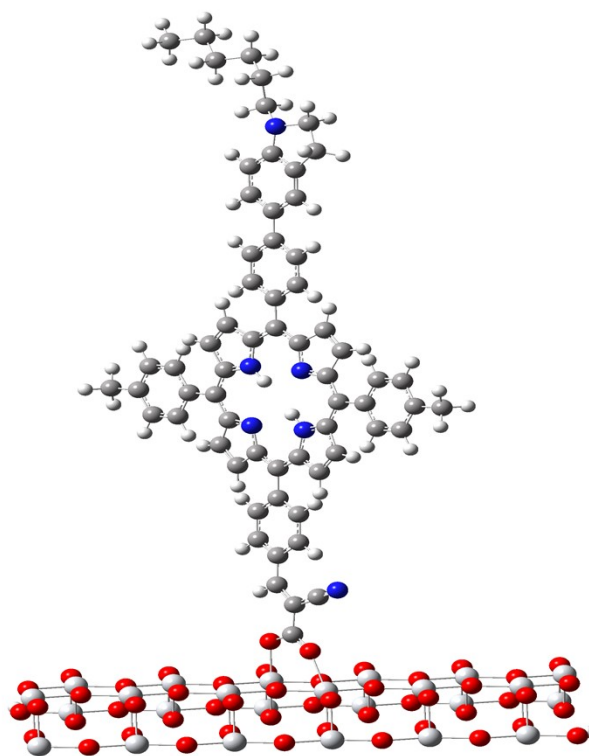


Fig. S1 Dye molecules adsorbed on the $(\text{TiO}_2)_{24}$ cluster model.

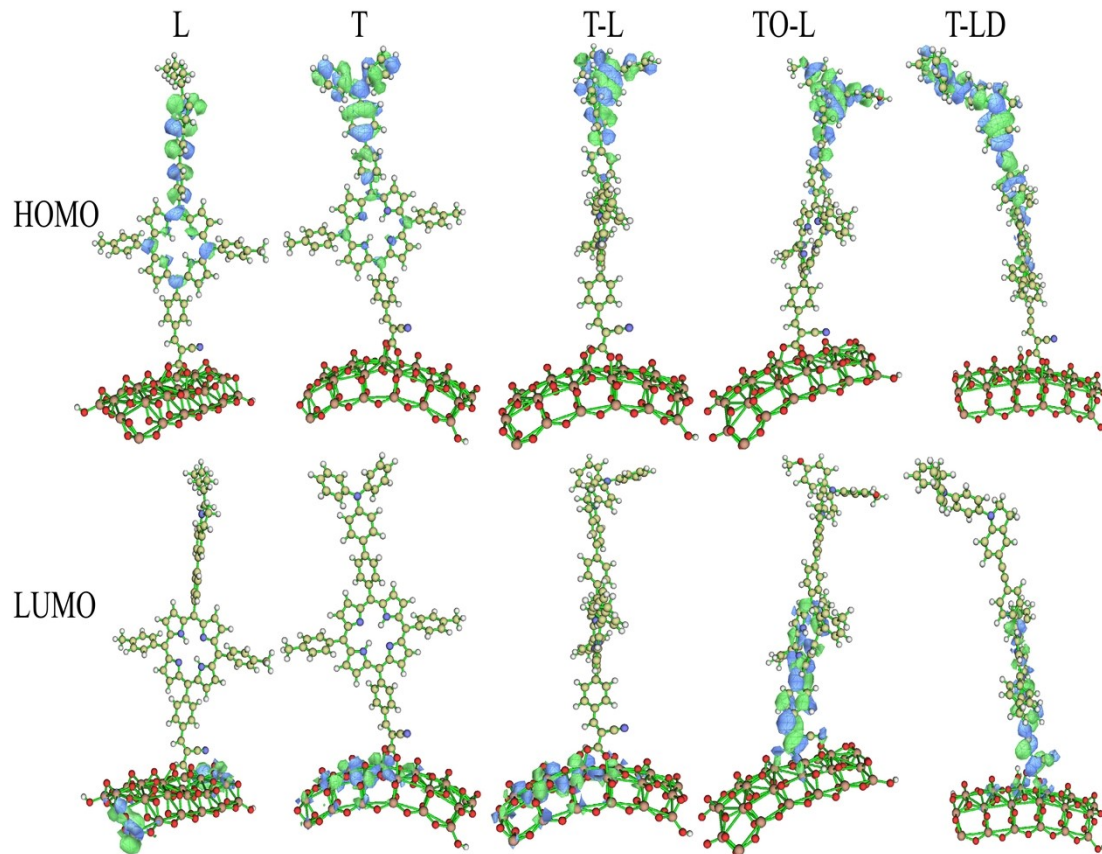


Fig. S2 Molecular orbital distributions of selected dye-(TiO₂)₂₄ complexes.

Table S 2 The conduction-band minimum energy (E_{CBM}), electron-injection distance (r_{in}), electron-recombination distance (r_{re}), injection driving force after conduction-band shift (ΔG^0), electron-injection rate (K_{inj}), injection efficiency (φ_{in}), and charge-collection efficiency (η_{coll}) of the five dye-(TiO₂)₂₄ composite systems.

Dye	E_{CBM} (eV)	r_{in} (Å)	r_{re} (Å)	ΔG^0 (eV)	K_{inj} (s ⁻¹)	φ_{in}	η_{coll}
L-(TiO ₂) ₂₄	-3.74	4.40	28.41	0.86	1.76×10^{14}	0.9994	1
T-(TiO ₂) ₂₄	-3.55	4.37	28.16	0.65	7.60×10^{14}	0.9999	1
T-L-(TiO ₂) ₂₄	-3.53	4.36	34.17	0.63	3.63×10^{14}	0.9997	1
TO-L-(TiO ₂) ₂₄	-3.61	4.20	36.14	0.73	1.25×10^{14}	0.9992	1
T-LD-(TiO ₂) ₂₄	-3.60	4.38	40.30	0.28	1.23×10^{14}	0.9992	1

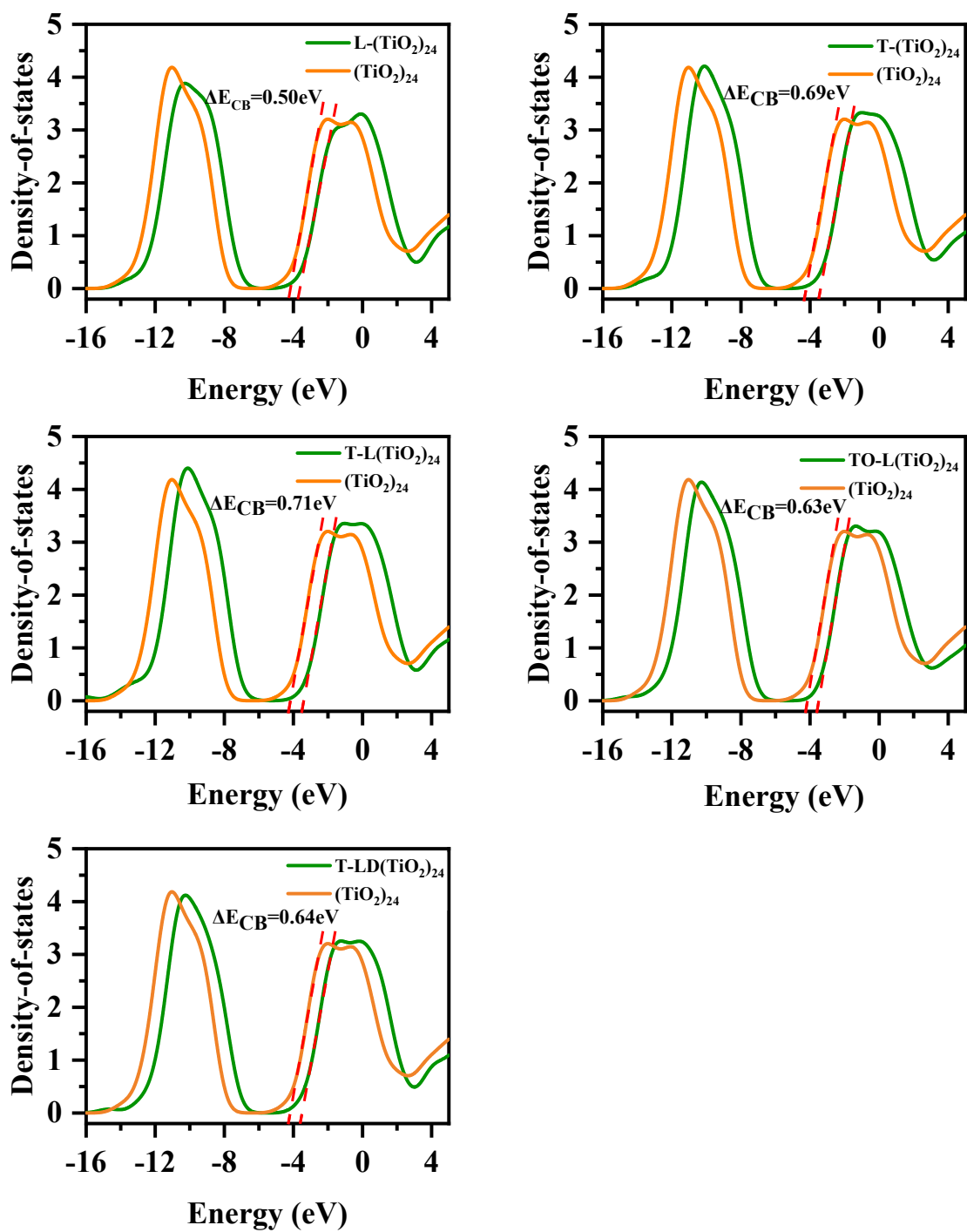


Fig. S3 A schematic illustration of the dye-TiO₂ interaction and the resulting conduction-band minimum shift (ΔE_{CB}) derived from the PDOS analysis.