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

Targeted and selective HOMO energy control by fine regulation of molecular planarity and its effect on interfacial charge transfer process in dye-sensitized solar cells

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Table S1 Optical and electrochemical properties of four dyes measured in solvent and on TiO_2.

	λ_{max}[a] / nm	ε_{max}[a] / M^{-1} cm^{-1}	λ_{PL}[a] / nm	$\tau_{solution}$[a] / ns	λ_{max}[b] / nm	Energy loss / eV	H[c] / V *vs* NHE	E_{0-0}[d] / V	L[e] / V *vs* NHE
CS-25	497	13900	588	5.94	483	0.39	0.73	2.00	-1.27
CS-26	483	16400	592	5.51	476	0.47	0.79	2.05	-1.26
CS-27	478	18300	612	5.37	472	0.57	0.80	2.07	-1.27
CS-28	471	16700	614	4.14	468	0.61	0.83	2.09	-1.26

[a] Absorption of the dyes in $CHCl_3$/MeOH (v/v, 1/4). [b] Absorption of the dyes adsorbed on 3 μm TiO_2. [c] HOMO levels of the dyes were extracted from the CVs of the dyes. H = HOMO, L = LUMO. [d] The E_{0-0} values were estimated from the onset wavelength of absorption spectra of dye-loaded TiO_2 films. [e] The LUMO level were calculated by followed equation: LUMO = HOMO - E_{0-0}.

Table S2 Optical and electrochemical properties of **CS-25 - 28** calculated by Gaussian 09 program.

	λ_{max}[a] / nm	PL / nm	Energy loss[b] / eV	H[c] / V *vs* NHE	E_{0-0} / V	L[c] / V *vs* NHE
CS-25	522	669	0.52	0.60	2.12	-1.52
CS-26	499	668	0.63	0.63	2.16	-1.53
CS-27	489	658	0.65	0.68	2.21	-1.53
CS-28	483	650	0.66	0.70	2.23	-1.53

[a] The maximum absorption wavelengths were obtained by TD-DFT calculations (MPWPW91/6-311G (d,p)) at the optimized geometries of ground states, which was simulated at B3LYP/6-311G (d,p) level. H = HOMO, L = LUMO. [b] The energy loss is calculated from the energy difference between absorption peak and photoluminescence peak. [c] The HOMO and LUMO levels were simulated by DFT calculations at B3LYP/6-311G (d,p) level at the optimized geometries of ground states.

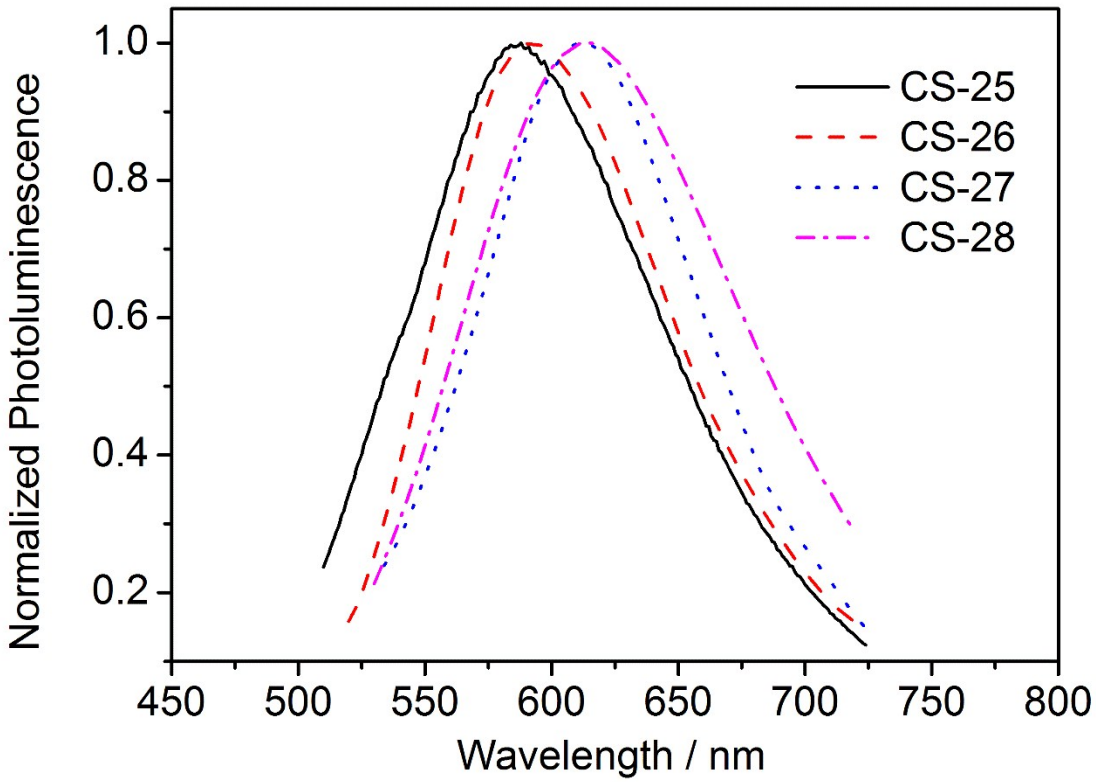

Fig. S1. Normalized photoluminescence spectra of **CS-25 - 28** measured in $CHCl_3$/MeOH (v/v, 1/4).

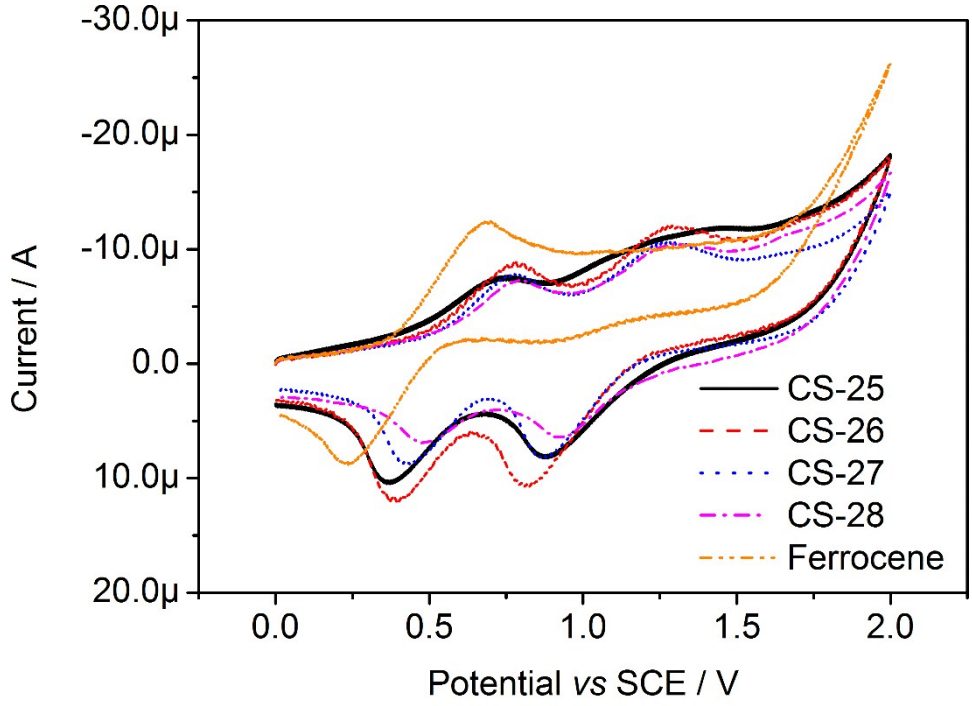

Fig. S2. Cyclic voltammograms of **CS-25 - 28** in CH_3CN. A dye-loaded TiO_2 electrode was used as the working electrode and a Pt wire was used as the counter electrode with a SCE reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphoric was used as the supporting electrolyte. After the measurement, ferrocene was added as the external reference for calibration (0.63 V *vs* NHE).

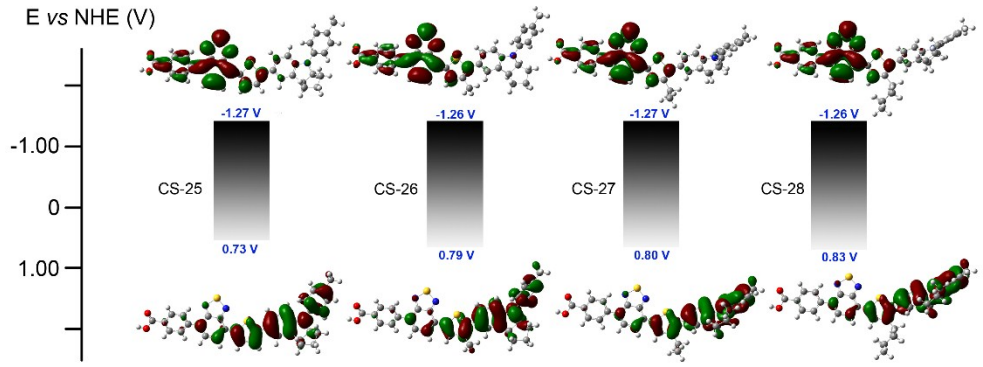

Fig. S3 Optimized geometries of the ground singlet states and first equilibrium excited singlet states of **CS-25 - 28**, as well as their HOMOs and LUMOs with their experimental values.

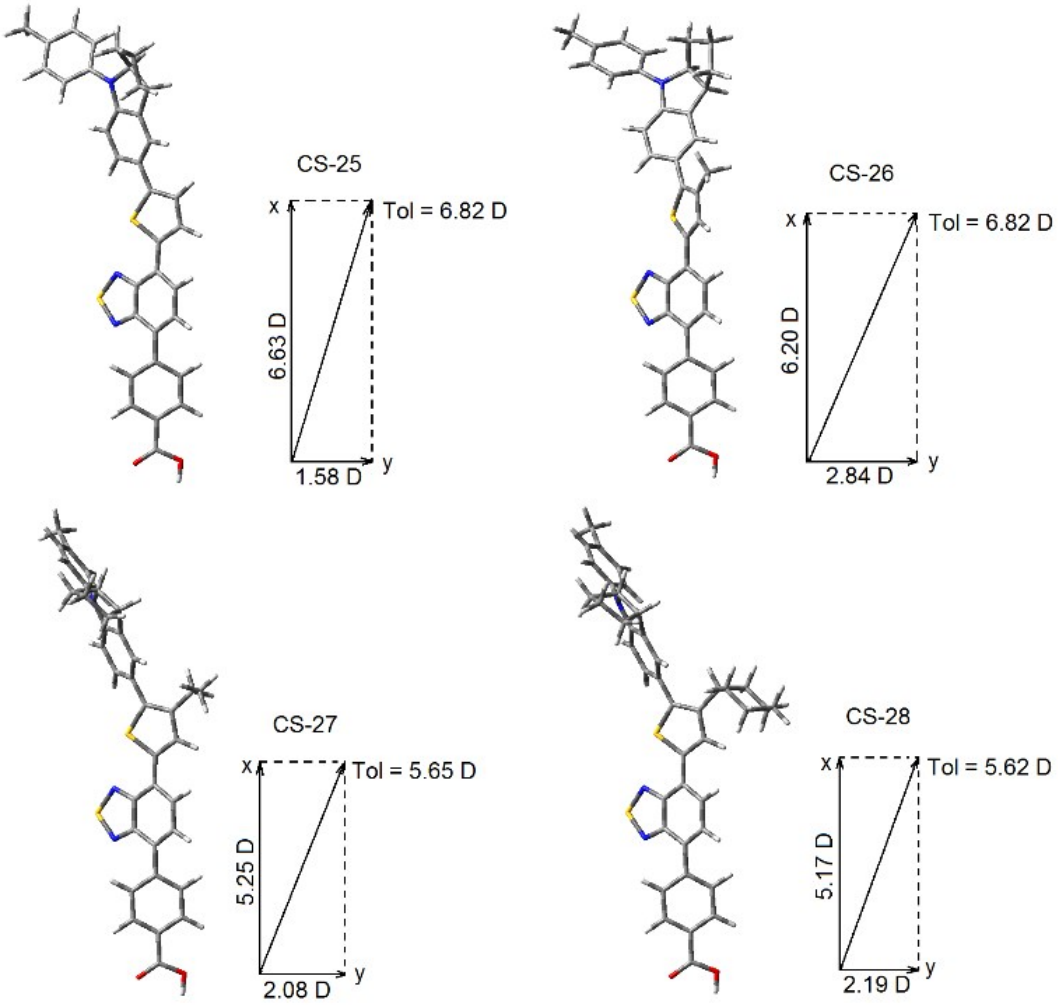

Fig. S4 The vertical dipole moments of **CS-25** - **28** calculated at their optimized geometries of the ground singlet states.