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

Supporting information

Insight into the Effects of Modifying π-bridges on the Performance of Dye-sensitized Solar Cells Containing Triphenylamine Dyes

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General information

All solvents and reagents were purchased from commercial suppliers and used as received unless otherwise specified. *N*, *N*-Dimethylformamide were dried and distilled from CaH_2, toluene and tetrahydrofuran were dried and distilled from Na.

The ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker DRX (300 MHz) NMR spectrometer. The mass spectra were measured in ESI Mass Spectrometer (LCQ Fleet).

Experimental

Fabrication of DSSCs

We cleaned the FTO glass plates (15 Ω per square) with detergent solution in ultrasonic bath for 0.5h two times before preparing the TiO_2 film by screen printing and then washed by water and ethanol. The FTO glass plates were then treated with 40 mM $TiCl_4$ (aqueous) at 70°C for 30 min and washed with water and ethanol. The TiO_2 films were prepared by sintered gradually up to 500°C and kept at this temperature before cooling. The TiO_2 films were immersed in 40mM $TiCl_4$ at 70°C for 30 min again and washed with water and ethanol. Finally the films were sintered at 500°C for 30min. After cooling to 25°C, the films were immersed into 0.3 mM ZHG dyes solution in THF/ethanol (1:1) for 18 h at room temperature to complete the loading of sensitizers. The photoanodes were sealed with platinum counter electrodes by a hot-melt film (25-μm-thick Surlyn, Dupont). The electrolytes were introduced to the cells via one predrilled hole back in the counter electrodes and thin glass covers by heating with electric soldering iron. The I^-/I_3^- electrolyte consisted of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 30 mM I_2, 50 mM LiI, 0.5 M tert-butylpyridine and 0.1 M guanidiniumthiocyanate (GuNCS) in a mixed acetonitrile and valeronitrile (85:15, V/V) solvent.

Device characterization

The photocurrent–voltage (J–V) curves of the devices were measured on a Keithley 2400 source meter under an irradiance of 100 mW cm^{-2} at the surface of a testing cell by a xenon light source (Oriel). The incident photo-to-electron conversion efficiency (IPCE) spectra of the devices were measured using a DC method. The light source was a 300 W xenon lamp (Oriel 6258) coupled with a flux controller to improve the stability of the irradiance. The single wavelength was selected by a monochromator (Cornerstone 260 Oriel74125). Light intensity was measured by a NREL traceable Si detector (Oriel 71030NS), and the short-circuit currents of the devices were measured by an optical power meter (Oriel 70310).

Theoretical calculations

Density function theory (DFT) calculations were performed at the **DFT-B3LYP/6-31G(d,p)** level with the Gaussian 09 suite of programs.

UV-Vis absorption spectra and electrochemical properties

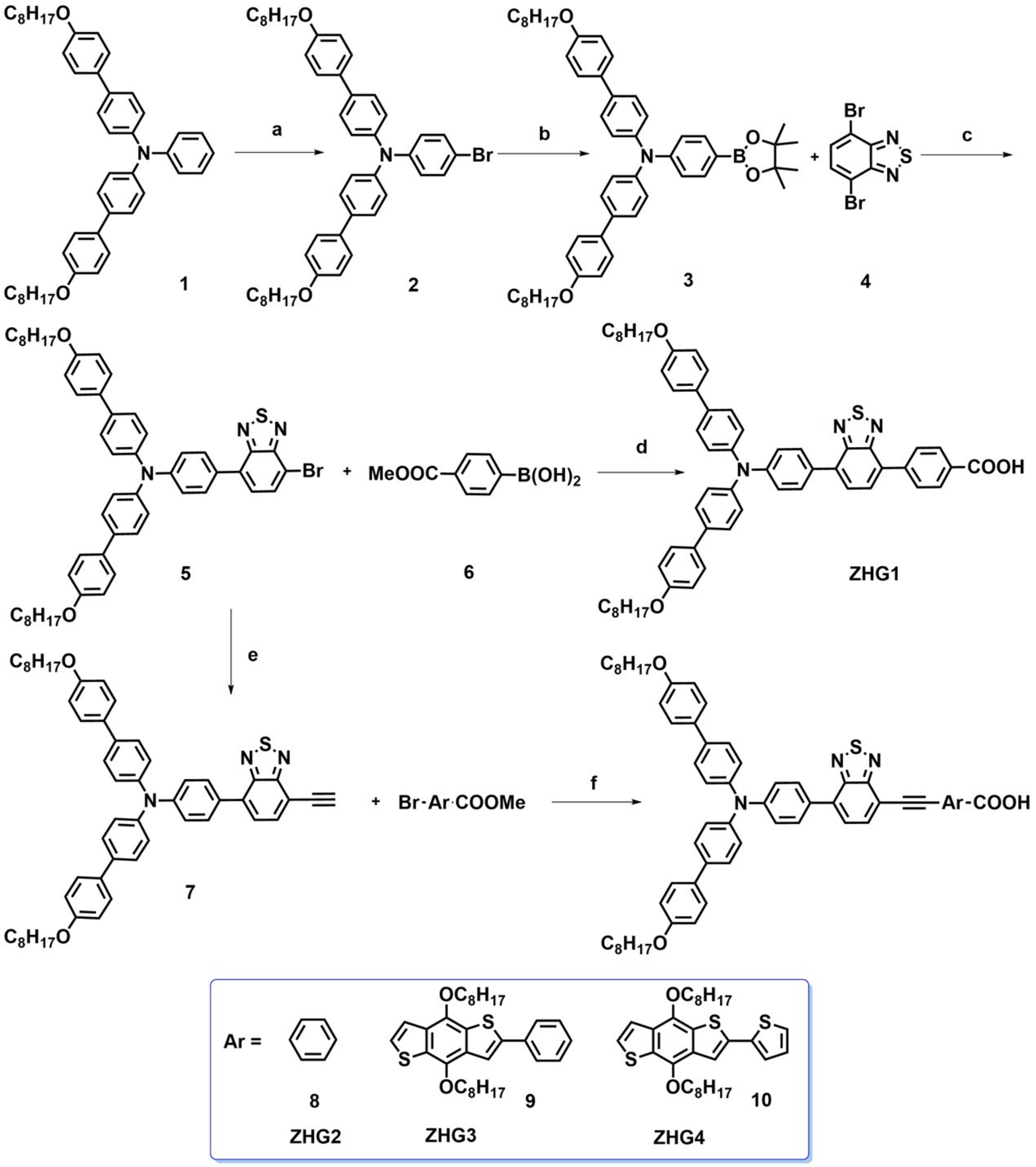
UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. For the absorption spectra of the dyes on TiO_2, a blank TiO_2 film was used for baseline correction before testing. Quasi-reversible oxidation and reduction waves were recorded on a Chenhua CHI660D model Electrochemical Workstation (Shanghai). Electrochemical Impedance Spectroscopy was studied using a Chenhua CHI660I model Electrochemical Workstation (Shanghai).

X-ray photoelectron spectroscopy measurements

The X-ray photoelectron spectra were measured with an PHI 5000 Versa Probe equipped with a hemispherical electron energy analyzer using the Al Kα radiation (hv =1486.6 eV) and an energy step of 0.1 eV. The electron take-off angle was 45°. Photoelectron spectra were recorded in constant analyzer energy mode. The spectra are energy calibrated by setting the Ti2$p_{3/2}$ substrate signal to 457.3 eV. Charging and radiation effects during the measurements were monitored and were found negligible for all spectra in these investigations.

Experimental section:

Synthesis of the dye ZHG dyes



Scheme S1 Reagents and conditions: (a) NBS, THF, rt; (b) $Pd(PPh_3)_4$, Bis(pinacolato)diboron, KOAc, 1,4-Dioxane, 100°C; (c) $Pd(PPh_3)_4$, K_2CO_3, 1,4-Dioxane/H_2O, 100 °C; (d) i: $Pd(PPh_3)_4$, K_2CO_3, 1,4-Dioxane/H_2O, 100 °C; ii: NaOH, MeOH/THF/H_2O; (e) i: $Pd(PPh_3)Cl_2$, Et_3N, CuI, Trimethylsilylacetylene, 90°C; ii: K_2CO_3, MeOH/THF; (f) i: $Pd_2(dba)_3$, $AsPh_3$, THF/Et_3N; ii: NaOH, MeOH/THF/H_2O.

Synthesis of compound 2

A mixture of compound 2 (2.92 g, 4.472 mmol) was dissolved in 30 ml DMF in 0°C. NBS (0.955g, 5.366mmol) was dissolved in 20ml DMF and was added to the DMF solution of compound 2 slowly. After the addition the reaction was returned to room temperature and stirred at the same time for 4 hours. Then the reaction was quenched by 300ml water and appeared light yellow solid. After filtration, 2.7g target product was obtained and the yield was 82%. ^{1}HNMR ($CDCl_3$, 300Hz) δ_H 7.49 (m, 8H), 7.37 (d, *J* = 8.67, 2H) 7.16 (d, *J* = 7.53, 4H) 7.04 (d, *J* = 8.40, 2H) 6.97 (d, *J* = 8.47, 4H) 4.00 (m, 4H) 1.82 (m, 4H) 1.49 (m, 4H) 1.32 (m, 16H) 0.92 (m, 6H)

Synthesis of compound 3

A mixture of compound 2 (6.3 g, 8.61 mmol), bis(pinacolato)diboron (2.6 g, 10.33 mmol), $Pd(dppf)Cl_2$ (0.314 g, 0.43 mmol) and AcOK (1.01g, 10.33 mmol) in 100 ml 1,4-dioxane was heated at 100°C overnight under N_2. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (3/1) gives out 3.5g target compound. The yield is 52%. ^{1}HNMR ($CDCl_3$, 300Hz) δ_H 7.72 (d, *J* = 8.43 Hz, 2H) 7.52 (d, *J* = 8.70 Hz, 4H) 7.47 (d, *J* = 8.58 Hz, 4H) 7.19 (d, *J* = 8.52 Hz, 4H) 7.13 (d, *J* = 8.43 Hz, 2H) 6.97 (d, *J* = 8.73 Hz, 4H) 4.00 (m, 4H) 1.82 (m, 4H) 1.49 (m, 4H) 1.32 (m, 28H) 0.91 (m, 6H)

Synthesis of compound 5

A mixture of compound 3 (1.8 g, 2.31 mmol), 4 (1.02 g, 3.47 mmol), $Pd(PPh_3)_4$ (0.133 g, 0.12mmol) and K_2CO_3 (0.963g, 6.93 mmol) in 100 ml 1,4-dioxane/H_2O was heated at 100°C overnight under N_2. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (5/1) gives out 0.92 g target compound. The yield is 46%. ^{1}HNMR ($CDCl_3$, 300Hz) δ_H 7.91 (d, *J* = 7.65 Hz, 1H) 7.85 (d, *J* = 8.58 Hz, 2H) 7.54 (m, 9H) 7.27 (m, 6H) 6.97 (d, *J* = 8.76 Hz, 4H) 4.00 (m, 4H) 1.82 (m, 4H) 1.49

(m, 4H) 1.32 (m, 16H) 0.91 (m, 6H)

Synthesis of compound 7

A mixture of compound 5 (2.6 g, 2.31 mmol), Trimethylsilylacetylene (1.5 g, 15 mmol), $Pd(PPh_3)_2Cl_2$ (0.132 g, 0.3mmol), PPh_3 (0.157 g, 0.6 mmol) and CuI (0.114g, 0.6 mmol) in 50 ml Et_3N was heated at 90°C overnight under N_2. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (2/1) gives out 2.60 g red solid. The yield is 98%. ^{1}HNMR ($CDCl_3$, 300Hz) δ_H 7.91 (d, *J* = 8.64 Hz, 2H) 7.85 (d, *J* = 7.44 Hz, 1H) 7.65 (d, *J* = 7.41 Hz, 1H) 7.52 (m, 8H) 6.97 (d, *J* = 8.76 Hz, 4H) 4.00 (m, 4H) 1.82 (m, 4H) 1.49 (m, 4H) 1.32 (m, 16H) 0.91 (m, 6H) 0.36 (s, 9H). Then the solid was dissolved in mixed solution of MeOH/THF, 10g K_2CO_3 was added into the solution and stirred at room temperature overnight. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (2/1) gives out 1.81 g target compound. The yield is 96%. The compound 7 was used in the next step without further purification.

Synthesis of the dye ZHG1

A mixture of compound 5 (0.48 g, 0.554 mmol), compound 6 (0.15 g, 0.830 mmol), $Pd(PPh_3)_4$ (0.064 g, 0.0554 mmol) and K_2CO_3 (0.23g, 1.662 mmol) in 35 ml mixed solution of 1,4-dioxane/H_2O (6/1, V/V) was heated at 100°C overnight under N_2. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (2/1) gave corresponding ester and then was dissolved in MeOH/THF/H_2O (1/1/1) mixed solution, NaOH (1 g, 250 mmol) was added and stirred overnight at room temperature. The solution pH was neutralized to 3 with 1M HCl and the precipitation was filtered to give the **ZHG1** dye (0.32 g, 0.35 mmol, 63%) as light red solid. ^{1}HNMR ($CDCl_3$, 300Hz) δ_H 8.27 (d, J = 8.0 Hz, 2H), 8.08 (d, J = 8.0 Hz, 2H) 7.90 (d, J = 8.2 Hz, 2H) 7.79 (d, J = 7.4 Hz, 1H) 7.74 (d, J = 7.3 Hz, 1H) 7.53-7.48 (m, 8H) 7.30-7.24 (m, 6H) 6.99-6.95 (m, 4H) 4.01-3.98 (m, 4H) 1.84-1.79 (m, 4H) 1.34-1.31 (m, 20H) 0.91-0.89 (m, 6H) ^{13}CNMR (75 MHz, $CDCl_3$) δ 171.25, 158.47, 153.97, 148.09, 145.82, 142.64, 135.85, 133.78, 132.78, 131.01, 130.40, 130.01, 129.14, 128.82, 128.61, 127.62, 127.43, 126.96, 126.54, 125.43, 125.08, 123.98, 122.72, 115.74, 114.72, 113.69, 68.02, 31.74, 30.22, 29.23, 27.58, 25.99, 22.58, 14.03. MS (ESI): Calcd. for $C_{59}H_{61}N_3O_4S$, 908.21; found, 907.00.

Synthesis of the dye ZHG2

A mixture of compound 7 (0.24 g, 0.295 mmol), compound 8 (0.15 g, 0.590 mmol), $Pd_2(dba)_3$ (0.054g, 0.059mmol) and $AsPh_3$ (0.18g, 0.59 mmol) in 52 ml mixed solution of THF/Et_3N (25/1, V/V) was heated at 70°C overnight under N_2. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (1/1) gave corresponding ester and then was dissolved in MeOH/THF/H_2O (1/1/1) mixed solution, NaOH (1 g, 250 mmol) was added and stirred overnight at room temperature. The solution pH was neutralized to 3 with 1M HCl and the precipitation was filtered to give the **ZHG2** dye (0.12 g, 0.13mmol, 54%) as red solid. ^{1}HNMR (THF-*d8*, 300Hz) δ_H 8.00 (d, J = 6.3 Hz, 1H), 7.97-7.94 (m, 4H) 7.84 (d, J = 5.6 Hz, 1H) 7.79 (d, J = 5.6 Hz, 1H) 7.75 (d, J = 7.3 Hz, 1H) 7.69 (d, J = 6.1 Hz 1H) 7.62 (d, J = 6.1 Hz 2H) 7.46-7.43 (m, 7H) 7.14-7.12 (m, 5H) 6.85 (d, J = 6.5 Hz 4H) 3.91-3.87 (m, 4H) 1.70-1.67 (m, 4H) 1.40-1.38 (m, 4H) 1.26-1.22(m, 16H) 0.80-0.78 (m, 6H) ^{13}CNMR (75 MHz, THF-*d8*) δ 164.07, 156.79, 153.52, 151.12, 146.39, 143.96, 134.14, 132.39, 131.27, 130.61, 129.43, 128.90, 128.80, 128.33, 128.17, 127.66, 126.41, 126.32, 125.32, 125.23, 124.33, 124.23, 123.08, 122.07, 120.39, 113.61, 112.53, 111.50, 92.47, 86.23, 65.61, 29.89, 27.45, 27.38, 27.35, 24.13, 20.63, 11.52. MS (ESI): Calcd. for $C_{61}H_{61}N_3O_4S$, 932.24; found 931.25.

Synthesis of the dye ZHG3

A mixture of compound 7 (0.23 g, 0.283 mmol), compound 9 (0.281 g, 0.42 mmol), $Pd_2(dba)_3$ (0.053 g, 0.057 mmol) and $AsPh_3$ (0.173 g, 0.57 mmol) in 52 ml mixed solution of THF/Et_3N (25/1, V/V) was heated at 70°C overnight under N_2. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (1/1) gave corresponding ester and then was dissolved in MeOH/THF/H_2O (1/1/1) mixed solution, NaOH (1 g, 250 mmol) was added and stirred overnight at room temperature. The solution pH was neutralized to 3 with 1M HCl and the precipitation was filtered to give the **ZHG3** dye (0.13 g, 0.09 mmol, 32%) as rufous solid. ^{1}HNMR (THF-*d8*, 300Hz) δ_H 8.00-7.74 (m, 10H), 7.44-7.43 (m, 8H) 7.13 (d, *J* = 5.5 Hz, 6H) 6.85 (d, *J* = 6.27 Hz, 4H) 4.27-4.25 (m, 4H) 3.90-3.87 (m, 4H) 1.83 (br, 4H) 1.70-1.67 (m, 4H) 1.54 (br, 4H) 1.40-1.22 (m, 36H) 0.80-0.78 (m, 12H) ^{13}CNMR (75 MHz, THF-*d8*) δ 156.79, 153.24, 151.07, 146.38, 143.91, 142.51, 142.23, 141.06, 135.75, 134.14, 132.44, 131.48, 131.09, 130.58, 129.29, 128.18, 127.16, 126.30, 125.32, 125.22, 124.23, 123.14, 122.08, 120.27, 113.60, 112.52, 112.02, 111.49, 89.84, 86.82, 71.94, 65.61, 29.91, 29.07, 28.59, 27.40, 25.78, 24.14, 20.65, 11.53. MS (ESI): Calcd. for $C_{87}H_{97}N_3O_6S_3$, 1376.93; found 1375.08.

Synthesis of the dye ZHG4

A mixture of compound 7 (0.25 g, 0.31 mmol), compound 10 (0.31 g, 0.46 mmol), $Pd_2(dba)_3$ (0.056 g, 0.06mmol) and $AsPh_3$ (0.190 g, 0.62 mmol) in 52 ml mixed solution of THF/Et_3N (25/1, V/V) was heated at 70°C overnight under N_2. The reaction solution was removed under vacuum and water was added. The water phase was then extracted with DCM. Combined organic phase was dried by Na_2SO_4. Column chromatography over silica gel with petroleum ether/DCM (1/1) gave corresponding ester and then was dissolved in MeOH/THF/H_2O (1/1/1) mixed solution, NaOH (1 g, 250 mmol) was added and stirred overnight at room temperature. The solution pH was neutralized to 3 with 1M HCl and the precipitation was filtered to give the **ZHG4** dye (0.11 g, 0.09 mmol, 26%) as rufous solid. ^{1}HNMR (THF-*d8*, 300Hz) δ_H 7.96 (d, J = 6.6 Hz, 2H), 7.86 (d, J = 6.6 Hz, 1H) 7.77 (d, J = 5.6 Hz, 1H) 7.74 (s, 1H) 7.67 (s, 1H) 7.60 (d, J = 2.9 Hz, 1H) 7.46-7.43 (m, 8H) 7.35 (d, J = 2.9 Hz, 1H) 7.15 (d, J = 2.2 Hz, 3H) 7.13 (dd, J = 6.6 2.2 Hz, 3H) 6.85 (d, J = 6.6 Hz, 4H) 4.25 (q, J = 9.4 4.8 Hz 4H) 3.89 (t, J = 4.8 4H) 1.87-1.79 (m, 4H) 1.70-1.65 (m, 4H) 1.55-1.51 (m, 4H) 1.42-1.22 (m, 36H) 0.81-0.80 (m, 12H) ^{13}CNMR (75 MHz, THF-*d8*) δ 161.83, 158.77, 155.23, 153.08, 148.39, 145.89, 144.35, 144.19, 142.91, 136.36, 136.14, 134.56, 134.46, 133.73, 133.10, 132.92, 132.57, 131.50, 130.73, 130.18, 130.14, 129.56, 127.29, 127.19, 126.28, 125.95, 125.75, 125.10, 122.60, 122.26, 117.52, 114.50, 113.93, 91.97, 88.68, 74.04, 73.92, 67.59, 67.01, 31.90, 31.87, 30.52, 29.47, 29.46, 29.42, 29.36, 29.31, 26.10, 26.07, 26.03, 22.63, 22.60, 13.53, 13.49. MS (ESI): Calcd. for $C_{85}H_{95}N_3O_6S_4$, 1382.95; found 1381.75.

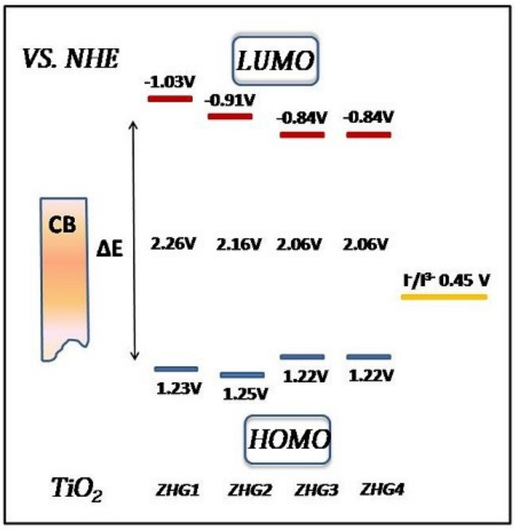


Fig S1 Schematic diagram of the energy levels of the TiO_2 conduction band, dyes and I^-/I_3^- redox couples.

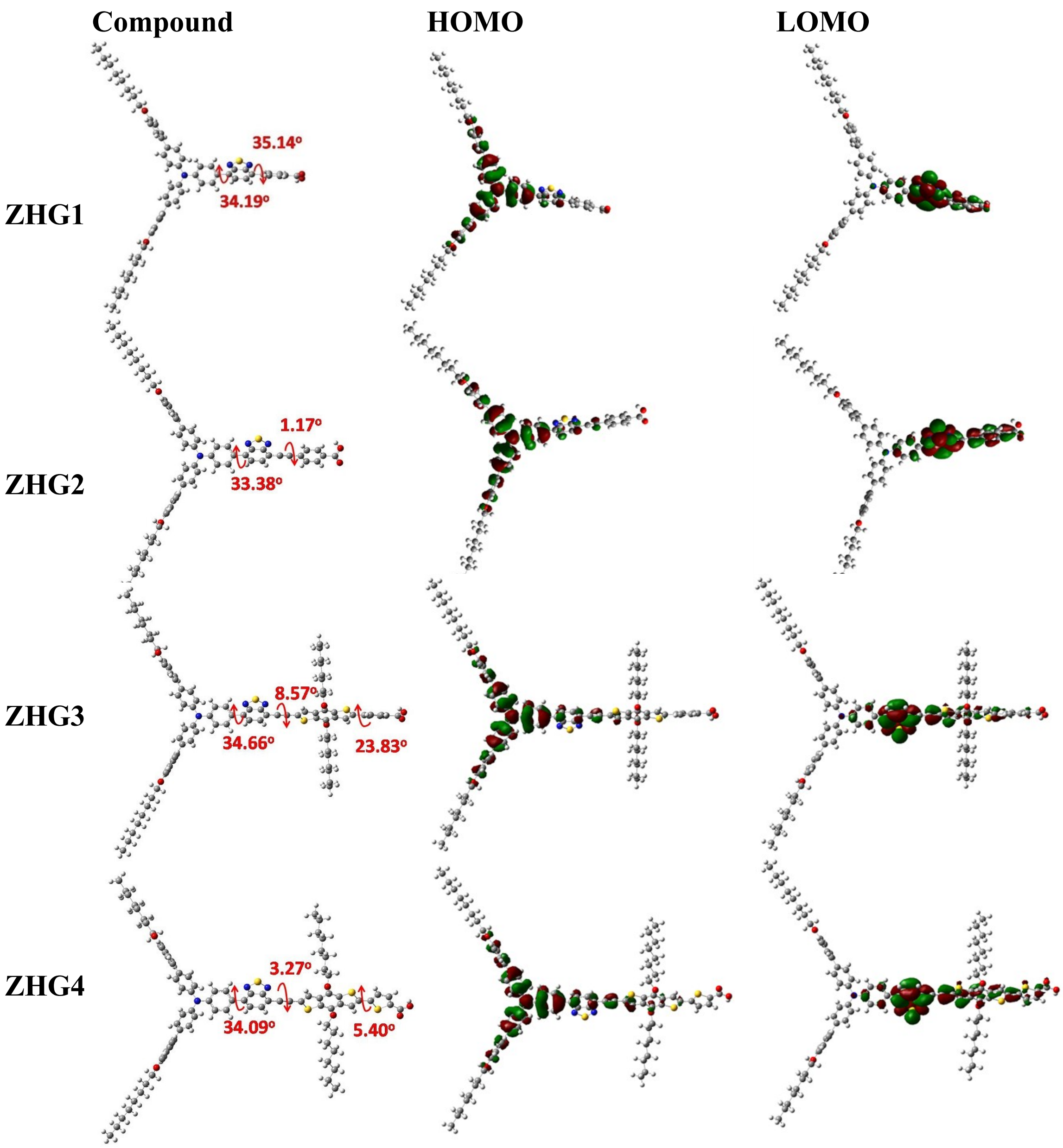


Fig. S2 HOMO and LUMO frontier molecular orbitals of ZHG dyes calculated by density-functional theory (DFT) at the DFT-B3LYP/6-31G(d,p) level with Gaussian 09 suite of programs.[1]

Table S1 The intensities (I) of Ti2$p_{3/2}$ signal originating from samples of TiO_2, ZHG1/TiO_2, ZHG2/TiO_2, ZHG3/TiO_2 and ZHG4/TiO_2

Sample	I/a.u	d^a/Å
TiO_2	15138	
ZHG1	7132	16
ZHG2	6474	18
ZHG3	4171	27
ZHG4	4660	24

[a] The mean thickness of organic coatings on titania surface.

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