

ESI to accompany

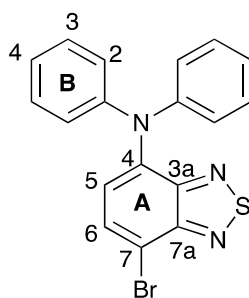
DSCs with hole-stabilizing surfaces: “Inorganic” versus “organic” strategies

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Syntheses of precursors

Abbreviation: Bis(dibenzylideneacetone)palladium(0) = [Pd(dba)₂]

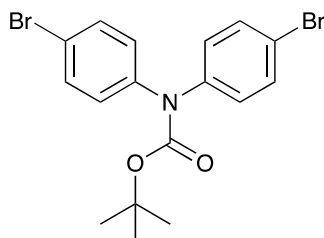
7-Bromo-*N,N*-diphenylbenzo[*c*][1,2,5]thiadiazol-4-amine



4,7-Dibromo-2,1,3-benzothiadiazole (5.00 g, 17.0 mmol) and Ph₂NH (2.88 g, 17 mmol) were dissolved in dry toluene (40 mL) under N₂; NaO^tBu (2.12 g, 22.1 mmol) was then added. Catalytic amounts of [Pd(dba)₂] (0.196 g, 0.340 mmol) and P^tBu₃ (0.279 g, 0.340 mmol) were added to the dark red solution and the reaction mixture was stirred overnight at room temperature. The solvent was then removed under reduced pressure and the residue purified by column chromatography (SiO₂, hexane:CH₂Cl₂ 1:0 changing to 1:2). The product was obtained as a red oil. Ultrasonic treatment in hexane yielded an orange solid (1.62 g, 4.22 mmol, 24.8%). ¹H NMR (500 MHz, CD₂Cl₂) δ / ppm 7.70 (d, *J* = 8.0 Hz, 1H, H^{A6}), 7.26 (m, 4H, H^{B3}), 7.12–7.06 (m, 2H, H^{B4}), 7.03 (m, 4H, H^{B2}), 7.02 (d, *J* = 8.0 Hz, 1H, H^{A5}). ¹³C NMR (126 MHz, CD₂Cl₂) δ / ppm 155.2 (C^{A7a}), 151.2

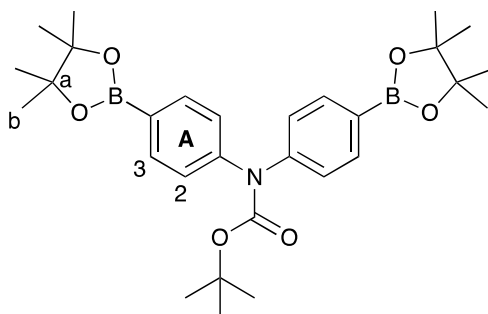
(C^{A3a}), 148.1 (C^{B1}), 140.4 (C^{A4}), 133.1 (C^{A6}), 129.8 (C^{B3}), 124.8 (C^{B2}), 124.2 (C^{B4}), 124.1 (C^{A5}), 107.9 (C^{A1}).

***tert*-Butyl bis(4-bromophenyl)carbamate**



This compound was prepared as previously reported and spectroscopic data agreed with the literature.^{3,4}

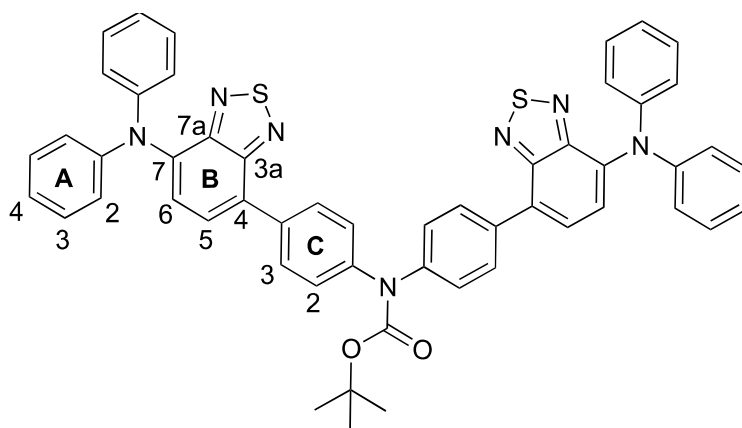
***tert*-Butyl bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate**



tert-Butyl bis(4-bromophenyl)carbamate (5.00 g, 11.7 mmol) was dissolved in dry THF (20 mL) and cooled to -78°C under N_2 . Then a 1.6 M solution of *n*-BuLi in hexane (17.6 mL, 28.1 mmol) was added dropwise over a period of 5 min. The mixture was stirred at -78°C for 2.5 h. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.85 mL, 28.1 mmol) was added in one portion and the mixture allowed to warm up to room temperature during which time it turned cloudy; it was stirred for a further 3 d at room temperature. The precipitate that

formed was removed by filtration and the solvent of the mother liquor evaporated. Column chromatography (SiO₂, hexane:EtOAc = 10:1 changing to 1:1) gave a colourless solid, which was suspended in hexane and then removed by filtration. The product was obtained as a colourless crystalline solid (4.63 g, 8.88 mmol, 75.9%). ¹H NMR (500 MHz, CD₂Cl₂) δ / ppm 7.69 (d, *J* = 8.5 Hz, 4H, H^{A3}), 7.17 (d, *J* = 8.5 Hz, 4H, H^{A2}), 1.44 (s, 9H, H^{tBu}), 1.32 (s, 24H, H^b). ¹³C NMR (126 MHz, CD₂Cl₂) δ / ppm 153.7 (C^{C=O}), 146.2 (C^{A1}), 135.6 (C^{A3}), 126.7 (C^{A2}), 84.4 (C^a), 81.9 (C^{tBu}), 28.5 (C^{tBu}), 25.2 (C^a).

***tert*-Butyl bis(4-(7-(diphenylamino)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)-carbamate**

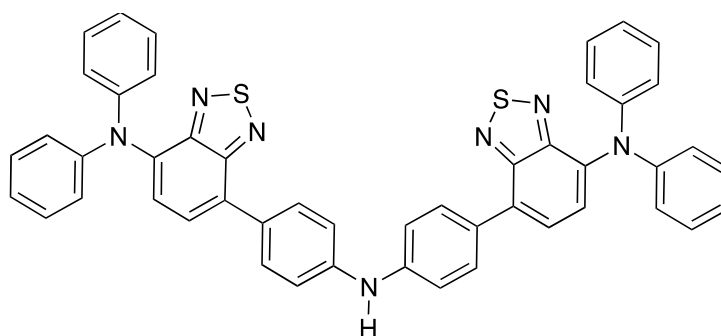


7-Bromo-*N,N*-diphenylbenzo[c][1,2,5]thiadiazol-4-amine (1.20 g, 3.14 mmol), *tert*-butyl bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate (0.779 g, 1.49 mmol) and K₂CO₃ (0.826 g, 5.98 mmol) were combined in a flask under N₂, and then H₂O and THF were added and the mixture degassed with N₂ for 15 min. After the addition of Pd(PPh₃)₄ (0.173 g, 0.149 mmol) the mixture was heated at reflux for 3 d. Then the solvent was removed under reduced pressure and the resulting solid was purified by column chromatography (SiO₂, hexane:EtOAc = 10:1 and SiO₂, CH₂Cl₂:hexane 4:1 changing to 10:1). The product was isolated as a red solid (509 mg, 0.584 mmol, 39.2%). ¹H NMR (500 MHz, CD₂Cl₂) δ / ppm 7.94 (m, 4H, H^{C3}), 7.64 (d, *J* = 7.8 Hz, 2H, H^{B5}), 7.41 (d_{AB}, *J* = 8.6

Hz, 4H, H^{C2}), 7.30–7.25 (m, 8H, H^{A3}), 7.24 (d, *J* = 7.8 Hz, 2H, H^{B6}), 7.11 – 7.02 (m, 12H, H^{A2+A4}), 1.52 (s, 9H, H^{tBu}). ¹³C NMR (126 MHz, CD₂Cl₂) δ / ppm 155.4 (C^{B3a}), 154.0 (C^{C=O}), 152.2 (C^{B7a}), 148.3 (C^{A1}), 143.4 (C^{C1}), 139.6 (C^{B7}), 135.4 (C^{C4}), 129.9 (C^{C3}), 129.7 (C^{A3}), 129.2 (C^{B4}), 129.0 (C^{B5}), 127.6 (C^{C2}), 124.6 (C^{A2}), 124.5 (C^{B6}), 123.9 (C^{A4}), 81.9 (C^{tBu}), 28.6 (C^{tBu}).

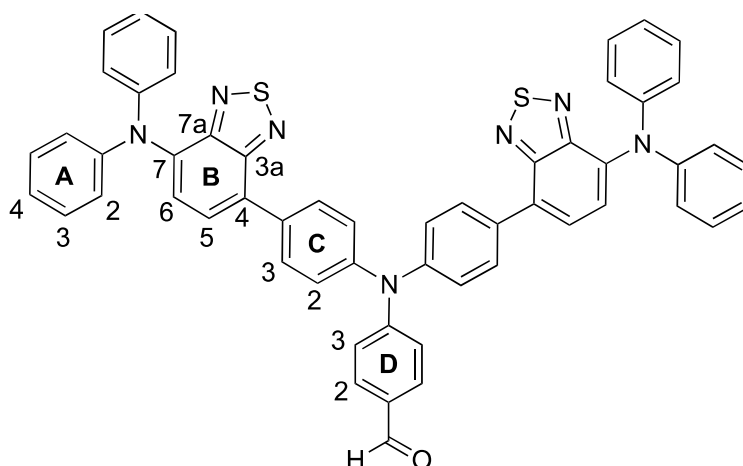
Compound 10a

7-(4-((4-(7-(Diphenylamino)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)amino)phenyl)-*N,N*-diphenylbenzo[c][1,2,5]thiadiazol-4-amine



tert-Butyl-bis(4-(7-(diphenylamino)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)carbamate (113 mg, 0.13 mmol) was heated to 210 °C for 1 h in an oven. It was then used without further purification or analysis.

4-(Bis(4-(7-(diphenylamino)benzo[c][1,2,5]thiadiazol-4-yl)phenyl)amino)benzaldehyde



Compound **10a** (100 mg, 0.130 mmol), 4-bromobenzaldehyde (28.8 mg, 0.155 mmol), NaO^tBu (37.3 mg, 0.389 mmol) and a catalytic amount of [Pd(dba)₂] (1.50 mg, 2.59 μmol) under N₂. Dry, degassed toluene (10 mL) and P^tBu₃ (2.60 μL 1M solution in toluene, 2.60 μmol) were added, and the reaction mixture was stirred overnight at 100 °C. Further amounts of [Pd(dba)₂] (1.50 mg, 2.59 μmol) and P^tBu₃ (2.60 μL 1M solution in toluene, 2.60 μmol) were added and the mixture stirred again overnight. The hot reaction mixture was filtered through a glass frit, which was subsequently rinsed with hot toluene. The solvent was removed under reduced pressure and the solid residue was purified by column chromatography (SiO₂, CH₂Cl₂:hexane 4:1). The red fraction was collected and, after removal of solvent, the red solid was suspended in hexane and sonicated until no more compound was sticking to the wall of the flask. The solid was collected by filtration and dried on the frit. The product was obtained as red solid (101 mg, 0.115 mmol, 88.5%). ¹H NMR (500 MHz, CD₂Cl₂) δ / ppm 9.85 (s, 1H, H^{CHO}), 7.98 (m, 4H, H^{C3}), 7.76 (m, 2H, H^{D2}), 7.65 (d, *J* = 7.8 Hz, 2H, H^{B5}), 7.38 (m, 4H, H^{C2}), 7.31–7.23 (m, 12H, H^{A3+B6+D2}), 7.08 (m, 12H, H^{A2+A4}). ¹³C NMR (126 MHz, CD₂Cl₂) δ / ppm 190.6 (C^{CHO}), 155.2 (C^{B3a}), 153.2 (C^{D4}), 152.0 (C^{B7a}), 148.1 (C^{A1}), 146.2 (C^{C1}), 139.4 (C^{B7}), 134.5 (C^{C4}), 131.5 (C^{D2}), 130.7 (C^{C3}), 130.3 (C^{D1}), 129.6

(C^{A3}), 128.9 (C^{B4}), 128.7 (C^{B5}), 126.3 (C^{C2}), 124.45 (C^{A2}), 124.4 (C^{B6}), 123.7 (C^{A4}), 120.9 (C^{D3}). MALDI-TOF MS: m/z 1078.7 [M]⁺ (calc. 1078.3).

DSC fabrication and measurements

Solaronix test cell kit components were used for all DSC preparation. The TiO₂ electrodes were heated to 450 °C to remove residual volatile organic impurities, then cooled to ca. 80 °C and immersed in a 1 mM DMSO solution of the anchoring ligand **1** or **2** for ca. 24 h. The colourless electrode was removed from the solution, washed with DMSO and EtOH and dried under a stream of N₂. The electrode was then immersed in a 1 mM EtOH solution of ZnCl₂ for ca. 24h. The electrode was removed, washed with EtOH and dried under a stream of N₂. Next, the electrode was immersed in either a 1 mM CH₂Cl₂ solution of **9** or a 1 mM THF solution of **10** for ca. 43 h. The yellow-orange coloured electrodes were removed from the solutions, washed with the corresponding solvent and dried under a stream of N₂. For functionalization of electrodes with **11**, the colourless TiO₂ electrodes were immersed in a 0.5 mM DMSO solution of **11** for 24h. The dark red electrodes were then removed, washed with DMSO and EtOH, and dried under a stream of N₂. Solaronix test cell platinum electrodes were used for the counter electrodes, and residual volatile organic impurities were removed by heating at 450 °C for 30 min.

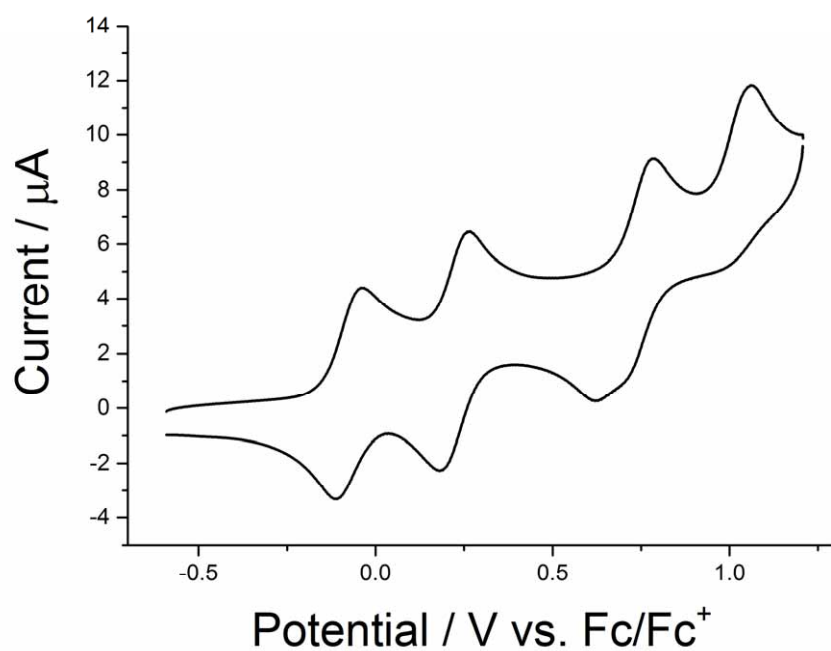
The dye-covered TiO₂ electrode and Pt counter electrode were combined using thermoplast hot-melt sealing foil (Solaronix, Meltonix 1170-25 Series, 25 µm) by heating while pressing them together. The electrolyte comprised LiI (0.1 mol dm⁻³), I₂ (0.05 mol dm⁻³), 1-methylbenzimidazole (0.5 mol dm⁻³) and 1-butyl-3-methylimidazolium iodide (0.6 mol dm⁻³) in 3-methoxypropionitrile, and was introduced into the cell by vacuum backfilling. The hole on the counter electrode was sealed using hot-melt sealing foil and a cover glass. The solar cell measurements and testing protocol was performed using fully masked cells. The area of the aperture in the mask was smaller than the active area of the dye-sensitized TiO₂ (0.288 cm²). Current density-voltage ($J-V$) measurements were made by irradiating the DSC from behind using a SolarSim 150 (100 mW cm⁻² =

1 sun) light source. The power of the simulated light was calibrated using a reference silicon cell.

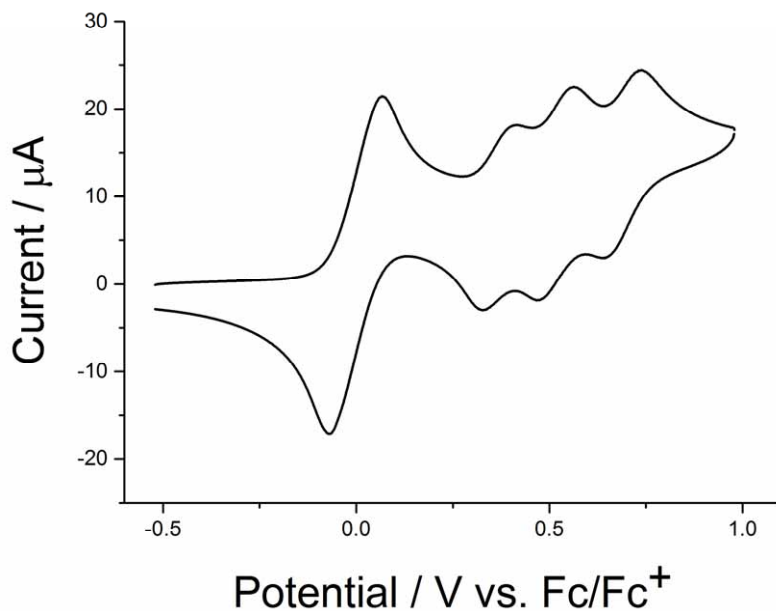
External quantum efficiency (EQE) spectra were recorded using a Spe-Quest quantum efficiency instrument from Rera Systems (Netherlands) equipped with a 100 W halogen lamp (QTH) and a lambda 300 grating monochromator (Lot Oriel). The monochromatic light was modulated to 3Hz using a chopper wheel (ThorLabs). The cell response was amplified with a large dynamic range IV converter (CVI Melles Griot) and then measured with a SR830 DSP Lock-In amplifier (Stanford Research).

References

1. B. Bozic-Weber, E. C. Constable, N. Hostettler, C. E. Housecroft, R. Schmitt, and E. Schönhofer, *Chem. Commun.*, 2012, 48, 5727.
2. F. C. Krebs and M. Biancardo, *Sol. Energy Mater. Sol. Cells*, 2006, **90**, 142.
3. Y. Hirao, H. Ino, A. Ito, K. Tanaka and T. Kato, *J. Phys. Chem. A*, 2006, **110**, 4866.
4. A. G. Bonn, M. Neuburger and O. S. Wenger, *Inorg. Chem.*, 2014, **53**, 11075.



(a)



(b)

Fig. S1. Cyclic voltammograms of CH_2Cl_2 (degassed) solutions of compounds (a) **9** and (b) **10**, versus internal Fc/Fc^+ [$n\text{Bu}_4\text{N}][\text{PF}_6]$ as supporting electrolyte; scan rate = 0.1 V s^{-1} .

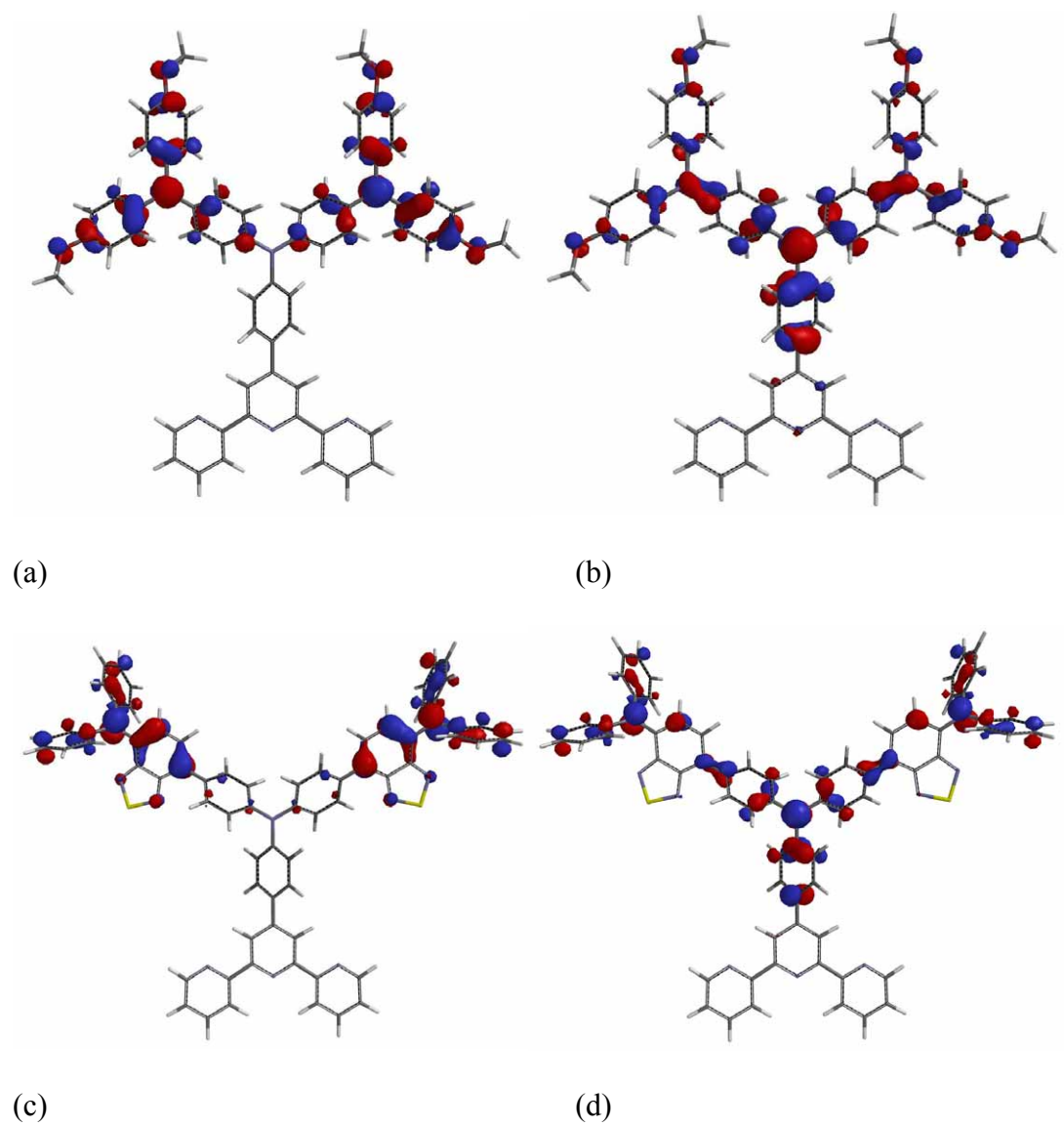


Fig. S2. Molecular orbital compositions: (a) HOMO-1 in **9**, (b) HOMO-2 in **9**, (c) HOMO-1 in **10**, (d) HOMO-2 in **10**.

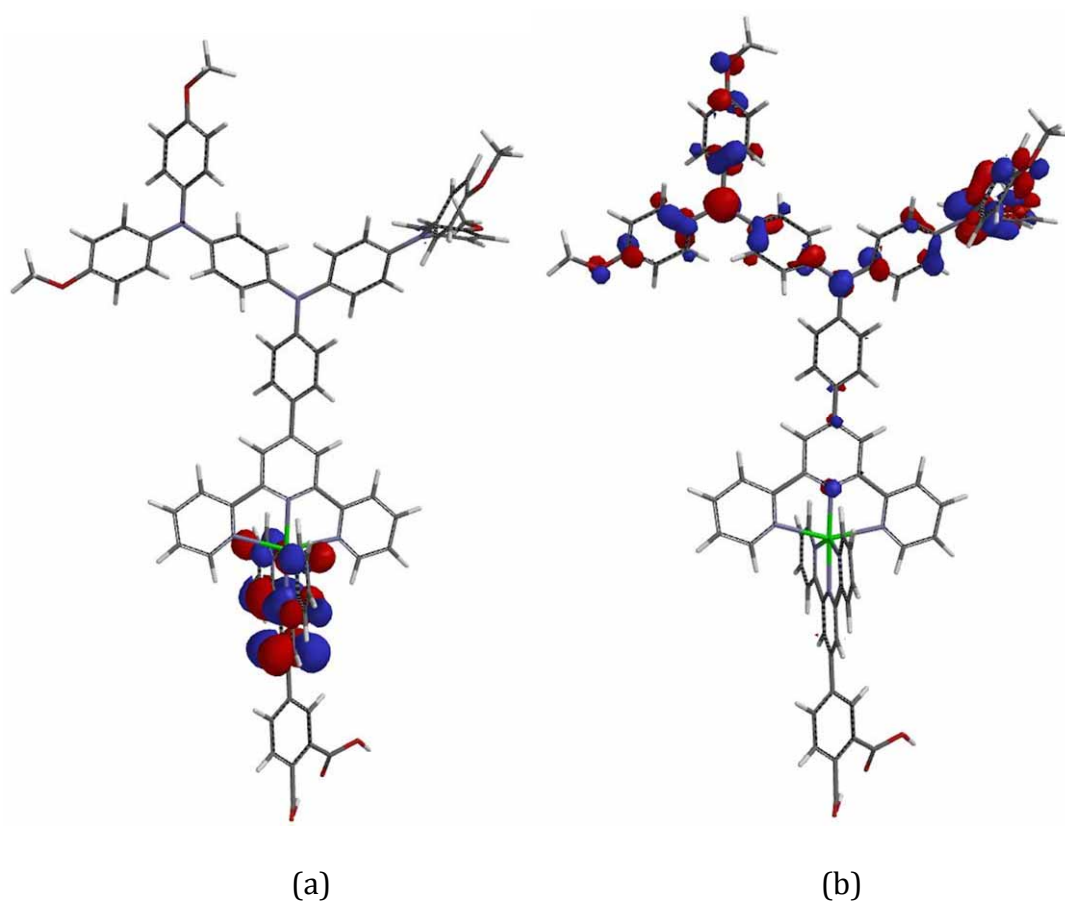


Fig. S3. Molecular orbital compositions: (a) LUMO in [Zn(**1**)(**9**)]²⁺, (b) HOMO in [Zn(**1**)(**9**)]²⁺.

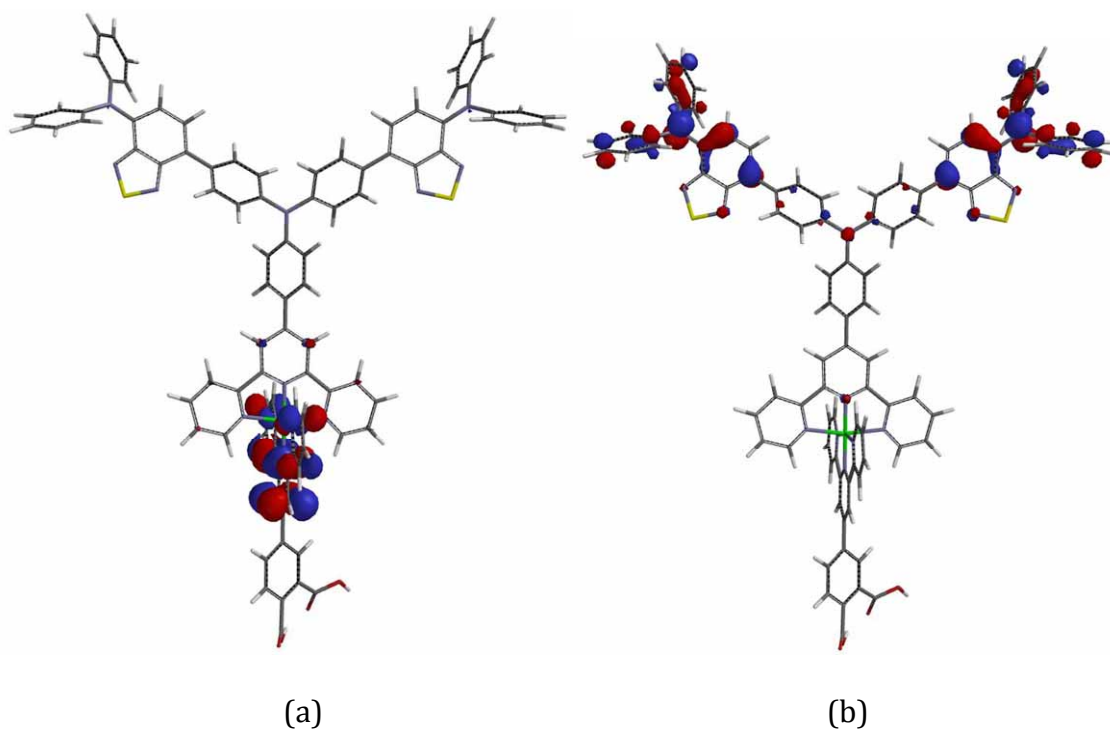


Fig. S4. Molecular orbital compositions: (a) LUMO in $[\text{Zn}(\mathbf{1})(\mathbf{10})]^{2+}$, (b) HOMO in $[\text{Zn}(\mathbf{1})(\mathbf{10})]^{2+}$.

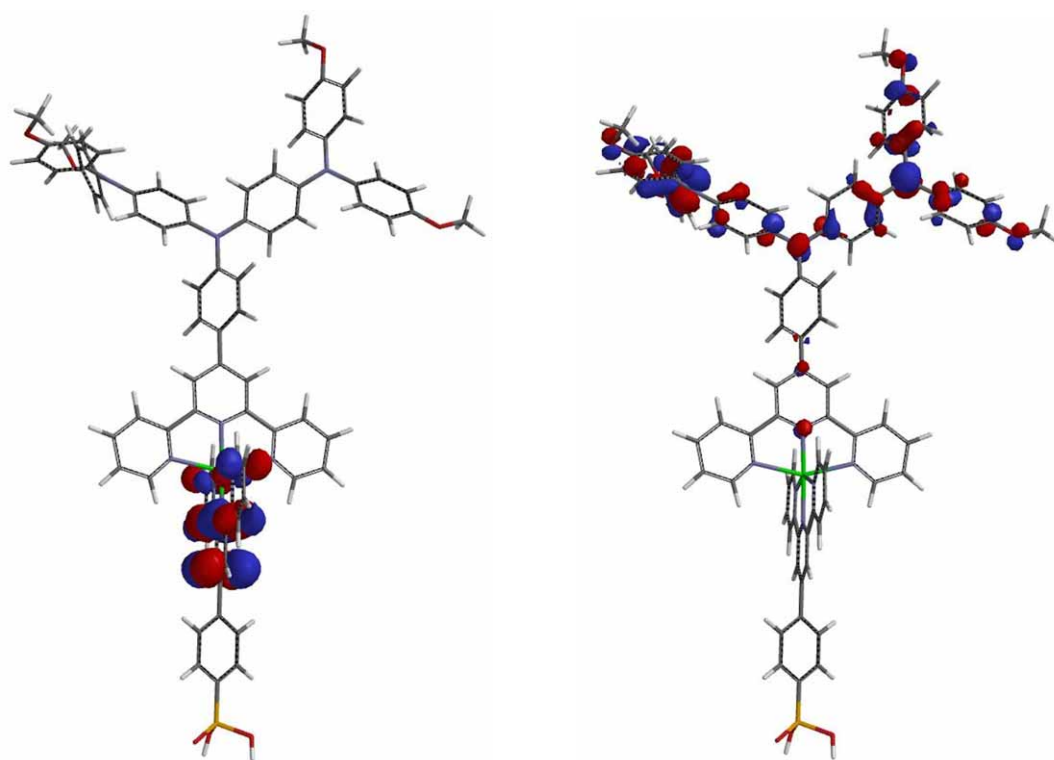


Fig. S5. Molecular orbital compositions: (a) LUMO in $[\text{Zn}(\mathbf{2})(\mathbf{9})]^{2+}$, (b) HOMO in $[\text{Zn}(\mathbf{2})(\mathbf{9})]^{2+}$.

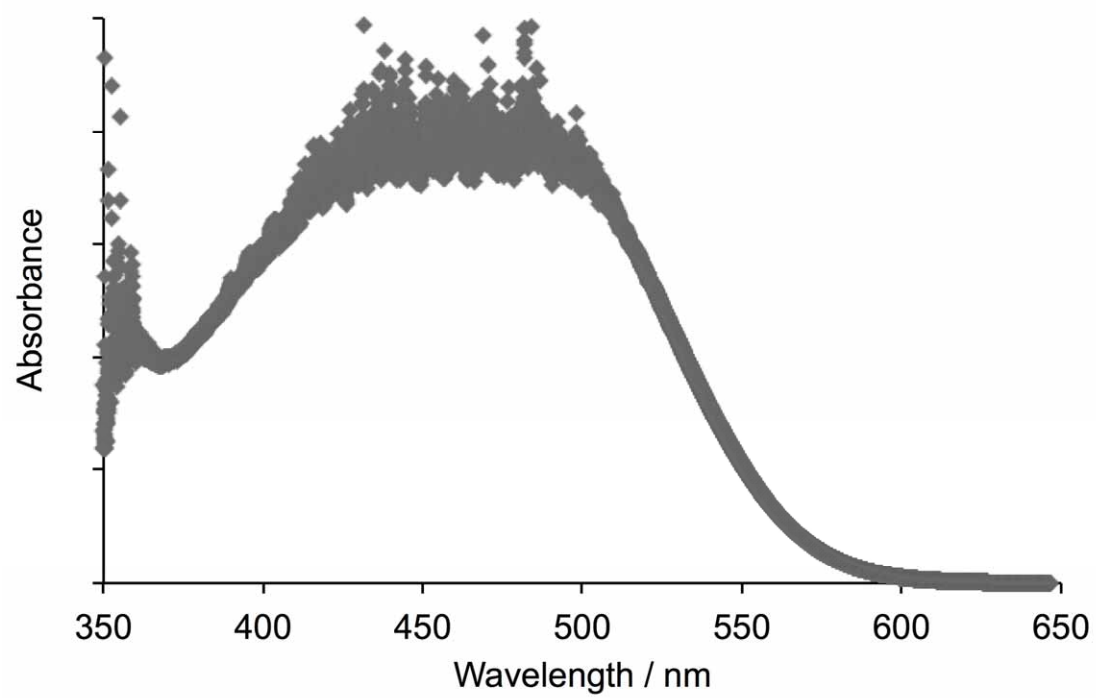


Fig. S6. Solid-state absorption spectrum of an FTO/TiO₂ electrode functionalized with dye **11**.

