Electronic Supplementary Information (ESI)

A novel aggregation-induced emission platform from 2,3-diphenylbenzo[b]thiophene S,S-dioxide

Jingjing Guo,[a] Shimin Hu,[a] Wenwen Luo,[a] Rongrong Hu,[a] Anjun Qin,[a] Zujin Zhao,*[a] and Ben Zhong Tang*[ab]

[a] *State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China. E-mail: mszjzhao@scut.edu.cn*.

[b] *Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk.*

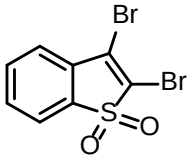
1. General Information

THF was distilled from sodium benzophenone ketyl under dry nitrogen immediately prior to use. All other chemicals and reagents were purchased from commercial sources and used as received without further purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 500 spectrometer in appropriated deuterated solution at room temperature. High resolution mass spectra (HRMS) were recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Single crystal X-ray diffraction intensity data were collected at 100 K on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated MoKα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer. Photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer. Solution fluorescence quantum yields were

measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. Fluorescence lifetimes were determined with a Hamamatsu C11367-11 Quantaurus-Tau time-resolved spectrometer. The ground-state geometries were optimized using the density function theory (DFT) method with B3LYP hybrid functional at the basis set level of 6-31G(d, p). All the calculations were performed using Gaussian 09 package.

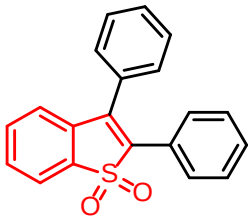
2. Synthesis and Characterization

2,3-Dibromobenzo[b]thiophene S,S-dioxide (DBr-BTO): A solution of 2,3-dibromobenzo[b]thiophene (5.80 g, 20 mmol) in CH_2Cl_2 (150 mL), was treated with *m*CPBA (13.81 g, 80 mmol) and stirred for 4 h at room temperature. After the mixture was cooled, it was washed with saturated $NaHCO_3$, and the aqueous layer was separated from the organic layer. Then the aquatic phase was further extracted with dichloromethane for several times, dried over anhydrous $MgSO_4$. After filtration and solvent evaporation under reduced pressure, the residue was purified by silica-gel column chromatography using dichloromethane/petroleum as eluent. DBr-BTO was obtained as a white solid in 80% yield. ^{1}H NMR (500 MHz, DMSO), δ (ppm): 8.09 (dd, J = 7.6, 0.4 Hz, 1H), 7.87–7.83 (m, 1H), 7.78–7.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 135.67, 134.19, 131.42, 130.98, 128.62, 124.43, 123.31, 121.70. HRMS ($C_8H_4Br_2O_2S$): *m/z* 324.8362 [M^+, calcd 321.8299].

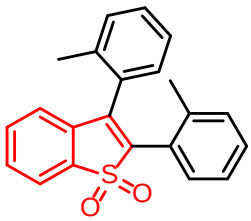


2,3-Diphenylbenzo[b]thiophene S,S-dioxide (DP-BTO): A solution of DBr-BTO (0.64 g, 2 mmol), phenylboronic acid (0.59 g, 4.8 mmol), $Pd(PPh_3)_4$ (231 mg, 0.2 mmol), and potassium carbonate (2.8 g, 20 mmol) in 100 mL of a degassed toluene/ethanol/water mixture (8:1:1 v/v/v) was heated to

reflux for 6 h under nitrogen. After the mixture was cooled to room temperature, the toluene layer was separated from the aqueous layer. The organic layer was washed successively with dichloromethane and dried over anhydrous $MgSO_4$. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography. DP-BTO was obtained as a white solid in 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.88–7.84 (m, 1H), 7.56–7.53 (m, 2H), 7.49–7.43 (m, 5H), 7.36–7.27 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 138.02, 137.45, 136.35, 133.48, 133.21, 130.90, 130.03, 129.65, 129.49, 129.31, 129.19, 129.07, 128.75, 127.03, 124.18, 121.57. HRMS ($C_{20}H_{14}O_2S$): *m/z* 319.0779 [M + H^+, calcd 319.0793].

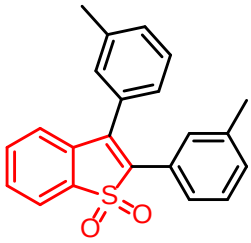


2,3-Di-*o*-tolylbenzo[b]thiophene S,S-dioxide (*o*-DMP-BTO): The procedure was analogous to that described for DP-BTO. Yellow solid, yield 60%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.88–7.85 (m, 1H), 7.57–7.47 (m, 3H), 7.29–7.11 (m, 7H), 7.04–7.01 (m, 1H), 2.23 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 140.20, 139.14, 138.65, 136.41, 136.10, 133.45, 133.14, 130.93, 130.79, 130.58, 130.17, 130.00, 129.82, 129.27, 128.96, 126.07, 125.84, 125.64, 124.19, 121.67, 20.22, 20.15. HRMS ($C_{22}H_{18}O_2S$): *m/z* 347.1105 [M + H^+, calcd 347.1106].

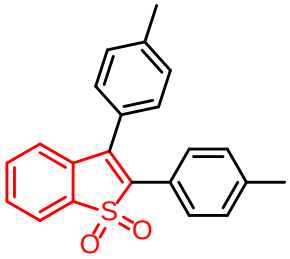


2,3-Di-*m*-tolylbenzo[b]thiophene S,S-dioxide (*m*-DMP-BTO): The procedure was analogous to that described for DP-BTO. Pale yellow solid, yield 66%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm):

7.83–7.80 (m, 1H), 7.59–7.55 (m, 2H), 7.35–7.30 (m, 3H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.20–7.16 (m, 4H), 7.11 (d, *J* = 7.5 Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), *δ* (ppm): 140.34, 139.93, 139.59, 138.61, 137.67, 134.82, 134.62, 132.14, 131.71, 131.45, 131.33, 130.89, 130.77, 130.23, 129.79, 128.45, 127.86, 127.47, 125.64, 122.47, 22.46, 22.43. HRMS ($C_{22}H_{18}O_2S$): *m/z* 346.1033 [M^+, calcd 346.1028].

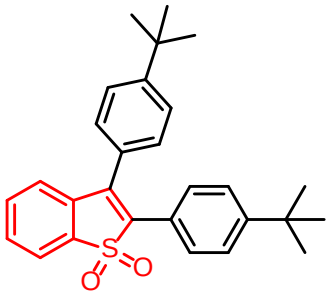


2,3-Di-*p*-tolylbenzo[b]thiophene S,S-dioxide (*p*-DMP-BTO): The procedure was analogous to that described for DP-BTO. Greenish yellow, yield 71%. ^{1}H NMR (500 MHz, $CDCl_3$), *δ* (ppm): 7.84–7.82 (m, 1H), 7.52–7.49 (m, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.31–7.28 (m, 1H), 7.25–7.21 (m, 4H), 7.11–7.10 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), *δ* (ppm): 139.80, 139.50, 137.37, 137.06, 136.32, 133.49, 133.39, 129.86, 129.76, 129.49, 129.10, 128.99, 127.97, 124.18, 124.06, 121.45, 21.45. HRMS ($C_{22}H_{18}O_2S$): *m/z* 346.1026 [M^+, calcd 346.1028].

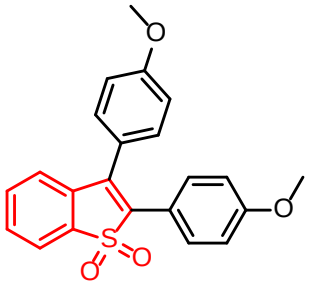


2,3-Bis(4-(*tert*-butyl)phenyl)benzo[b]thiophene S,S-dioxide (DTBP-BTO): The procedure was analogous to that described for DP-BTO. White solid, yield 91%. ^{1}H NMR (500 MHz, $CDCl_3$), *δ* (ppm): 7.85–7.82 (m, 1H), 7.53–7.49 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.32–7.24 (m, 5H), 1.37 (s, 9H), 1.283 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$), *δ* (ppm): 152.71, 152.61, 137.15, 136.98, 136.24, 133.72, 133.37, 129.69, 128.79, 128.75, 128.07, 126.41, 126.08,

125.72, 124.20, 124.12, 121.38, 34.87, 34.79, 31.27, 31.11. HRMS ($C_{28}H_{30}O_2S$): *m/z* 430.1975 [M^+, calcd 430.1967].

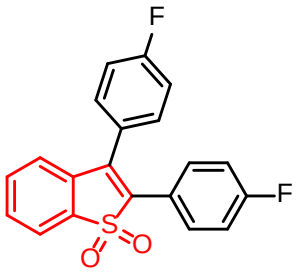


2,3-Bis(4-methoxyphenyl)benzo[b]thiophene S,S-dioxide (DMOP-BTO): The procedure was analogous to that described for DP-BTO. Greenish yellow solid, yield 69%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.82–7.80 (m, 1H), 7.53–7.48 (m, 2H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.32–7.30 (m, 1H), 7.26 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 3.84 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 160.49, 160.38, 136.46, 136.26, 136.25, 133.66, 133.45, 130.72, 130.61, 129.65, 123.92, 123.01, 121.42, 119.47, 114.70, 114.36, 55.36, 55.29. HRMS ($C_{22}H_{18}O_4S$): *m/z* 378.0931 [M^+, calcd 378.0926].

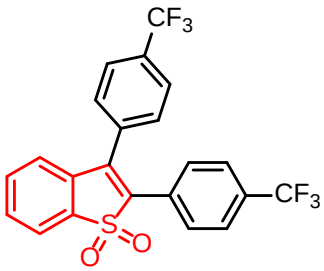


2,3-Bis(4-fluorophenyl)benzo[b]thiophene S,S-dioxide (DFP-BTO): The procedure was analogous to that described for DP-BTO. White solid, yield 82%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.88–7.84 (m, 1H), 7.59–7.54 (m, 2H), 7.48–7.43 (m, 2H), 7.35–7.27 (m, 3H), 7.19–7.13 (m, 2H), 7.05–6.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 164.41, 164.27, 162.40, 162.28, 137.13, 137.12, 136.81, 136.15, 133.64, 132.84, 131.42, 131.35, 131.12, 131.05, 130.28, 126.54, 126.51, 123.98, 122.91, 122.88, 121.74, 116.73, 116.55, 116.31, 116.13. HRMS ($C_{20}H_{12}F_2O_2S$):

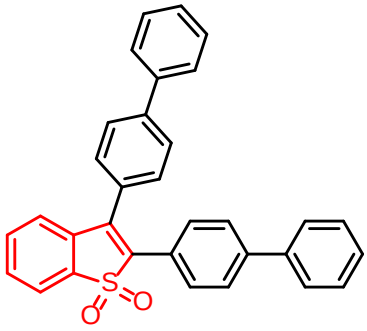
m/z 355.0582 [M + H^+, calcd 355.0604].



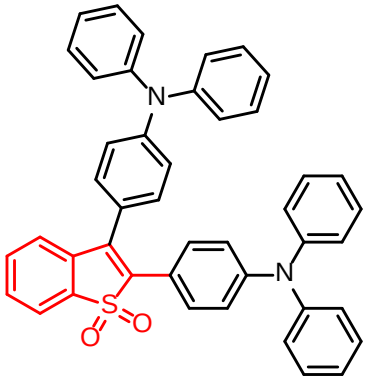
2,3-Bis(4-(trifluoromethyl)phenyl)benzo[b]thiophene S,S-dioxide (DTFMP-BTO): The procedure was analogous to that described for DP-BTO. White solid, yield 77%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.91–7.89 (m, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.64–7.57 (m, 6H), 7.48 (d, J = 8.0 Hz, 2H), 7.27–7.25 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 138.22, 137.28, 136.15, 134.17, 133.88, 132.08, 130.91, 130.24, 129.64, 129.52, 126.50, 126.47, 125.99, 125.96, 124.68, 124.22, 122.51, 122.02. HRMS ($C_{22}H_{12}F_6O_2S$): *m/z* 455.0544 [M + H^+, calcd 455.0540].



2,3-Di([1,1'-biphenyl]-4-yl)benzo[b]thiophene S,S-dioxide (DBP-BTO): The procedure was analogous to that described for DP-BTO. Green solid, yield 74%. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.90–7.86 (m, 1H), 7.73–7.69 (m, 2H), 7.67–7.53 (m, 10H), 7.50–7.32 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 142.35, 142.32, 140.08, 139.92, 137.53, 137.11, 136.36, 133.55, 133.25, 130.05, 129.83, 129.63, 128.98, 128.85, 127.98, 127.86, 127.81, 127.46, 127.07, 127.07, 125.98, 124.20, 121.62. HRMS ($C_{32}H_{22}O_2S$): *m/z* 470.1362 [M^+, calcd 470.1341].



2,3-Bis(4-(diphenylamino)phenyl)benzo[b]thiophene S,S-dioxide (DTPA-BTO): The procedure was analogous to that described for DP-BTO. Orange solid, yield 62%. ^{1}H NMR (500 MHz, CD_2Cl_2), δ (ppm): 7.80–7.78 (m, 1H), 7.59–7.51 (m, 2H), 7.42–7.40 (m, 1H), 7.37–7.34 (m, 2H), 7.32–7.28 (m, 8H), 7.23–7.21 (m, 2H), 7.15–7.06 (m, 14H), 6.94–6.93 (m, 2H). ^{13}C NMR (125 MHz, CD_2Cl_2), δ (ppm): 150.19, 148.40, 137.61, 134.97, 134.79, 131.43, 130.77, 126.57, 125.27, 125.16, 125.03, 123.33, 122.32. HRMS ($C_{44}H_{32}N_2O_2S$): *m/z* 652.2184 [M^+, calcd 652.2217]



3. X-Ray Crystallography

Crystal data for DP-BTO (CCDC 1501903): $C_{20}H_{14}O_2S$, *MW* = 318.37, monoclinic, Cc, *a* = 8.7763(9) Å, *b* = 18.341(2) Å, *c* = 19.844(2) Å, β = 100.092(4)°, *V* = 3144.8(6) Å^3, *Z* = 8, *Dc* = 1.345 g cm^{-3}, μ = 0.213 mm^{-1} (MoKα, λ = 0.71073), *F*(000) = 1328, *T* = 172(2) K, $2\theta_{max}$ = 25.39° (98.7%), 9091 measured reflections, 5181 independent reflections (R_{int} = 0.0571), GOF on F^2 = 1.007, R_1 = 0.0842, wR_2 = 0.0861 (all data), Δe 0.227 and –0.269 eÅ^{-3}.

Crystal data for *o*-DMP-BTO (CCDC 1501899): $C_{22}H_{18}O_2S$, *MW* = 346.42, monoclinic, P2(1)/n, *a*

= 9.9496(11) Å, b = 12.5896(12) Å, c = 14.3507(13) Å, β = 99.202(4)°, V = 1774.5(3) Å^3, Z = 4, Dc = 1.297 g cm^{-3}, μ = 0.194 mm^{-1} (MoKα, λ = 0.71073), F(000) = 728, T = 173(2) K, $2\theta_{max}$ = 25.39° (99.3%), 11820 measured reflections, 3237 independent reflections (R_{int} = 0.0656), GOF on F^2 = 1.024, R_1 = 0.0895, wR_2 = 0.0980 (all data), Δe 0.354 and –0.211 eÅ^{-3}.

Crystal data for *p*-DMP-BTO (CCDC 1501900): $C_{22}H_{18}O_2S$, MW = 346.42, triclinic, P-1, a = 10.1340(5) Å, b = 10.9037(6) Å, c = 17.7060(9) Å, α = 90.049(2)°, β = 92.799(2)°, γ = 114.437(2)°, V = 1778.61(16) Å^3, Z = 4, Dc = 1.294 g cm^{-3}, μ = 0.194 mm^{-1} (MoKα, λ = 0.71073), F(000) = 728, T = 173(2) K, $2\theta_{max}$ = 25.41° (98.4%), 17607 measured reflections, 6446 independent reflections (R_{int} = 0.0733), GOF on F^2 = 1.058, R_1 = 0.1079, wR_2 = 0.1215 (all data), Δe 0.273 and –0.345 eÅ^{-3}.

Crystal data for DTBP-BTO (CCDC 1501894): $C_{28}H_{30}O_2S$, MW = 430.58, monoclinic, P2(1)/c, a = 16.9872(11) Å, b = 11.0288(9) Å, c = 12.9726(11) Å, β = 101.237(2)°, V = 2383.8(3) Å^3, Z = 4, Dc = 1.200 g cm^{-3}, μ = 0.157 mm^{-1} (MoKα, λ = 0.71073), F(000) = 920, T = 173(2) K, $2\theta_{max}$ = 25.36° (98.7%), 13303 measured reflections, 4318 independent reflections (R_{int} = 0.0962), GOF on F^2 = 1.061, R_1 = 0.1276, wR_2 = 0.1322 (all data), Δe 0.262 and –0.355 eÅ^{-3}.

Crystal data for DMOP-BTO (CCDC 1501892): $C_{22}H_{18}O_4S$, MW = 378.42, triclinic, P-1, a = 9.6225(9) Å, b = 10.5635(9) Å, c = 10.9316(9) Å, α = 63.981(2)°, β = 64.608(3)°, γ = 78.743(3)°, V = 902.05(14) Å^3, Z = 2, Dc = 1.393 g cm^{-3}, μ = 0.205 mm^{-1} (MoKα, λ = 0.71073), F(000) = 396, T = 172(2) K, $2\theta_{max}$ = 25.34° (98.4%), 8404 measured reflections, 3248 independent reflections (R_{int} = 0.0822), GOF on F^2 = 1.012, R_1 = 0.1146, wR_2 = 0.1054 (all data), Δe 0.252 and –0.337 eÅ^{-3}.

Crystal data for DFP-BTO (CCDC 1511289): $C_{22}H_{12}F_2O_2S$, MW = 354.36, monoclinic, P2(1)/c, a = 10.3524(5) Å, b = 10.3346(6) Å, c = 15.3392(9) Å, β = 90.826(2)°, V = 1639.80(16) Å^3, Z = 4, Dc = 1.435 g cm^{-3}, μ = 0.229 mm^{-1} (MoKα, λ = 0.71073), F(000) = 728, T = 174(2) K, $2\theta_{max}$ = 25.10°

(98.0%), 8942 measured reflections, 2869 independent reflections (R_{int} = 0.0365), GOF on F^2 = 1.066, R_1 = 0.0589, wR_2 = 0.1213 (all data), Δe 0.302 and –0.366 eÅ^{-3}.

Crystal data for DTFMP-BTO (CCDC 1501897): $C_{22}H_{12}F_6O_2S$, MW = 454.38, triclinic, P-1, a = 7.5333(4) Å, b = 10.9876(7) Å, c = 11.6354(8) Å, α = 91.853(3)°, β = 90.826(2)°, γ = 95.099(2)°, V = 958.64(10) Å^3, Z = 2, Dc = 1.574 g cm^{-3}, μ = 0.243 mm^{-1} (MoKα, λ = 0.71073), F(000) = 460, T = 174(2) K, 2θ_{max} = 25.38° (98.2%), 8525 measured reflections, 3458 independent reflections (R_{int} = 0.0613), GOF on F^2 = 1.040, R_1 = 0.0953, wR_2 = 0.0994 (all data), Δe 0.274 and –0.297 eÅ^{-3}.

Crystal data for DBP-BTO (CCDC 1501891): $C_{32}H_{22}O_2S$, MW = 470.56, monoclinic, P2(1)/c, a = 11.3812(9) Å, b = 9.0240(7) Å, c = 23.553(2) Å, β = 100.181(3)°, V = 2380.9(3) Å^3, Z = 4, Dc = 1.313 g cm^{-3}, μ = 0.164 mm^{-1} (MoKα, λ = 0.71073), F(000) = 984, T = 173(2) K, 2θ_{max} = 25.35° (98.6%), 13366 measured reflections, 4304 independent reflections (R_{int} = 0.0696), GOF on F^2 = 1.041, R_1 = 0.0964, wR_2 = 0.1039 (all data), Δe 0.237 and –0.372 eÅ^{-3}.

4. Additional Data

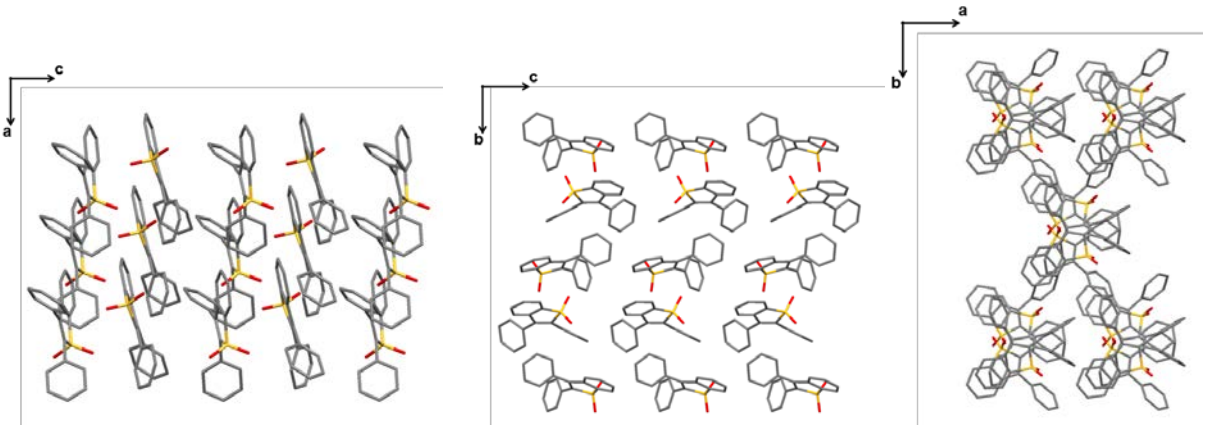


Fig S1. The packing pattern of DP-BTO in crystals.

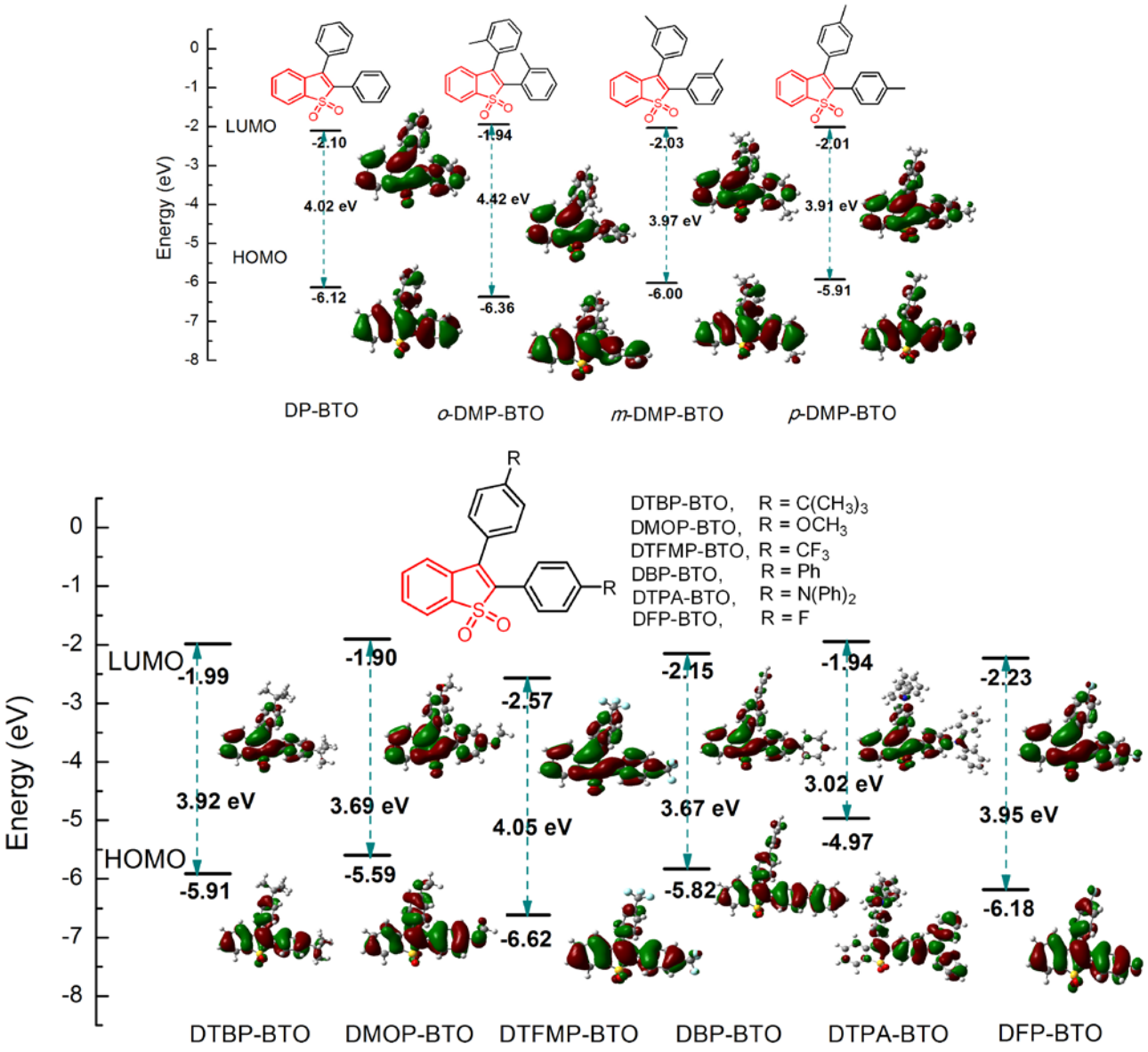


Fig. S2 The HOMOs and LUMOs of the new luminogens at the B3LYP/6-31G (d, p) level in the gas phase based on the ground-state geometries.

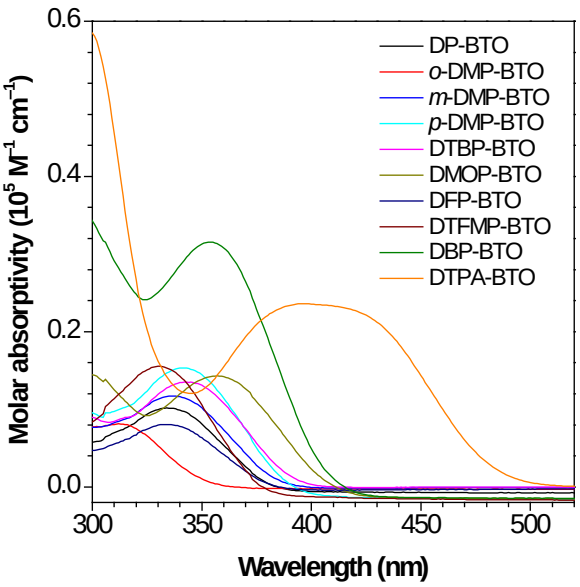


Fig. S3 Absorption spectra of the new luminogens in THF solutions.

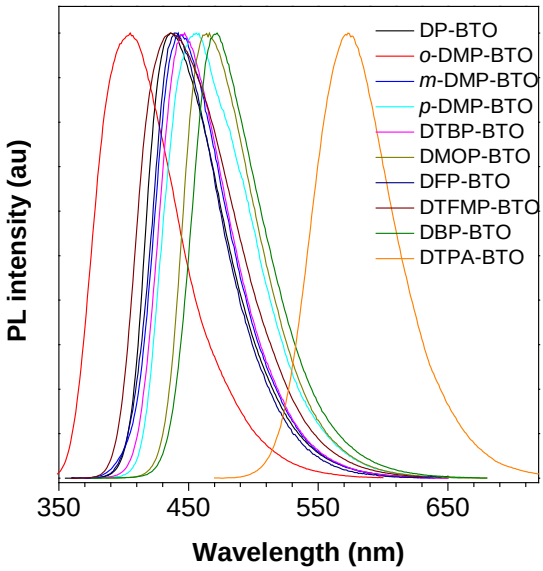


Fig. S4 Photoluminescence (PL) spectra of the powders of the new luminogens.

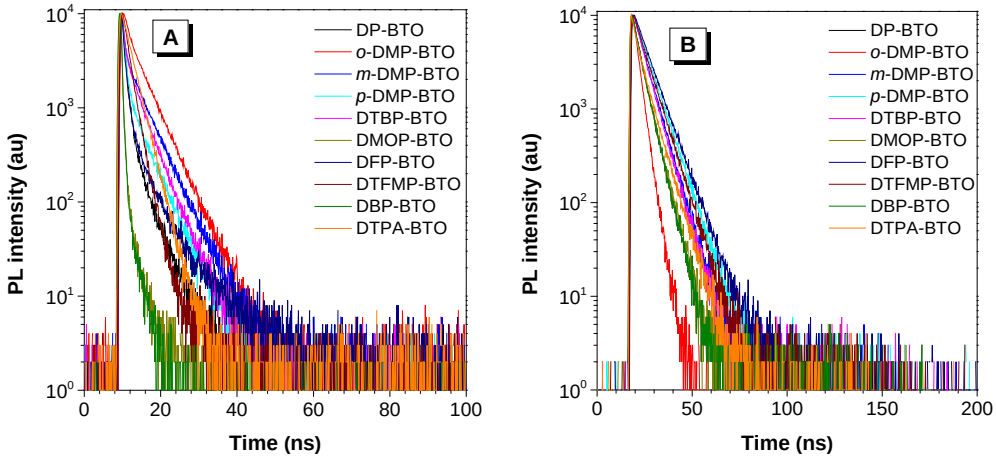


Fig. S5 Transient PL spectra of the new luminogens in (A) THF solutions and (B) powders.