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

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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 MoK\(\alpha\) 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 CH₂Cl₂ (150 mL), was treated with mCPBA (13.81 g, 80 mmol) and stirred for 4 h at room temperature. After the mixture was cooled, it was washed with saturated NaHCO₃, 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 MgSO₄. 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. ¹H 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); ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 135.67, 134.19, 131.42, 130.98, 128.62, 124.43, 123.31, 121.70. HRMS (C₈H₄Br₂O₂S): 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(PPh₃)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 MgSO₄. 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. ¹H NMR (500 MHz, CDCl₃), 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); ¹³C NMR (125 MHz, CDCl₃), 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 (C₂₀H₁₄O₂S): 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\%. ¹H NMR (500 MHz, CDCl₃), 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); ¹³C NMR (125 MHz, CDCl₃), 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 (C₂₂H₁₈O₂S): 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\%. ¹H NMR (500 MHz, CDCl₃), 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$_3$), $\delta$ (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$_2$S): $m/z$ 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$_3$), $\delta$ (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$_3$), $\delta$ (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$_2$S): $m/z$ 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$_3$), $\delta$ (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$_3$), $\delta$ (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,
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$_3$), $\delta$ (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$_3$), $\delta$ (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$_4$S): $m/z$ 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$_3$), $\delta$ (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$_3$), $\delta$ (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$_2$O$_2$S):
2,3-Bis(4-(trifluoromethyl)phenyl)benzo[\textit{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$_3$), $\delta$ (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$_3$), $\delta$ (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$_6$O$_2$S): $m/z$ 455.0544 [M + H$^+$, calcd 455.0540].

2,3-Di(\textit{\textbf{1,1'-biphenyl}}\textit{-4-yl})benzo[\textit{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$_3$), $\delta$ (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$_3$), $\delta$ (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$_2$S): $m/z$ 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$_2$Cl$_2$), $\delta$ (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$_2$Cl$_2$), $\delta$ (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$_2$O$_2$S): m/z 652.2184 [M$,^+$, calcd 652.2217]

3. X-Ray Crystallography

Crystal data for DP-BTO (CCDC 1501903): C$_{20}$H$_{14}$O$_2$S, $MW = 318.37$, monoclinic, Cc, $a = 8.7763(9)$ Å, $b = 18.341(2)$ Å, $c = 19.844(2)$ Å, $\beta = 100.092(4)^0$, $V = 3144.8(6)$ Å$^3$, $Z = 8$, $Dc = 1.345$ g cm$^{-3}$, $\mu = 0.213$ mm$^{-1}$ (MoK$\alpha$, $\lambda = 0.71073$), $F(000) = 1328$, $T = 172(2)$ K, $2\theta_{\text{max}} = 25.39^0$ (98.7%), 9091 measured reflections, 5181 independent reflections ($R_{\text{int}} = 0.0571$), GOF on $F^2 = 1.007$, $R_1 = 0.0842$, $wR_2 = 0.0861$ (all data), $\Delta e$ 0.227 and $-0.269$ eÅ$^{-3}$.

Crystal data for $\alpha$-DMP-BTO (CCDC 1501899): C$_{22}$H$_{18}$O$_2$S, $MW = 346.42$, monoclinic, P2(1)/n, $a$
\[a = 9.9496(11) \text{ Å}, b = 12.5896(12) \text{ Å}, c = 14.3507(13) \text{ Å}, \beta = 99.202(4)^\circ, V = 1774.5(3) \text{ Å}^3, Z = 4, Dc = 1.297 \text{ g cm}^{-3}, \mu = 0.194 \text{ mm}^{-1} (\text{MoK}_\alpha, \lambda = 0.71073), F(000) = 728, T = 173(2) \text{ K}, 2\theta_{\text{max}} = 25.39^\circ (99.3\%), 11820 \text{ measured reflections, 3237 independent reflections (}R_{\text{int}} = 0.0656), \text{GOF on } F^2 = 1.024, R_1 = 0.0895, wR_2 = 0.0980 \text{ (all data), } \Delta e 0.354 \text{ and } -0.211 \text{ eÅ}^{-3}.

Crystal data for \textit{p}-DMP-BTO (CCDC 1501900): C\textsubscript{22}H\textsubscript{18}O\textsubscript{2}S, \textit{MW} = 346.42, triclinic, P-1, \(a = 10.1340(5) \text{ Å}, b = 10.9037(6) \text{ Å}, c = 17.7060(9) \text{ Å}, \alpha = 90.049(2)^\circ, \beta = 92.799(2)^\circ, \gamma = 114.437(2)^\circ, V = 1778.61(16) \text{ Å}^3, Z = 4, Dc = 1.294 \text{ g cm}^{-3}, \mu = 0.194 \text{ mm}^{-1} (\text{MoK}_\alpha, \lambda = 0.71073), F(000) = 728, T = 173(2) \text{ K}, 2\theta_{\text{max}} = 25.41^\circ (98.4\%), 17607 \text{ measured reflections, 6446 independent reflections (}R_{\text{int}} = 0.0733), \text{GOF on } F^2 = 1.058, R_1 = 0.1079, wR_2 = 0.1215 \text{ (all data), } \Delta e 0.273 \text{ and } -0.345 \text{ eÅ}^{-3}.

Crystal data for DTBP-BTO (CCDC 1501894): C\textsubscript{28}H\textsubscript{30}O\textsubscript{2}S, \textit{MW} = 430.58, monoclinic, P2(1)/c, \(a = 16.9872(11) \text{ Å}, b = 11.0288(9) \text{ Å}, c = 12.9726(11) \text{ Å}, \alpha = 90.826(2)^\circ, \beta = 92.799(2)^\circ, \gamma = 114.437(2)^\circ, V = 2383.8(3) \text{ Å}^3, Z = 4, Dc = 1.200 \text{ g cm}^{-3}, \mu = 0.157 \text{ mm}^{-1} (\text{MoK}_\alpha, \lambda = 0.71073), F(000) = 920, T = 173(2) \text{ K}, 2\theta_{\text{max}} = 25.36^\circ (98.7\%), 13303 \text{ measured reflections, 4318 independent reflections (}R_{\text{int}} = 0.0962), \text{GOF on } F^2 = 1.061, R_1 = 0.1276, wR_2 = 0.1322 \text{ (all data), } \Delta e 0.262 \text{ and } -0.355 \text{ eÅ}^{-3}.

Crystal data for DMOP-BTO (CCDC 1501892): C\textsubscript{22}H\textsubscript{18}O\textsubscript{4}S, \textit{MW} = 378.42, triclinic, P-1, \(a = 9.6225(9) \text{ Å}, b = 10.5635(9) \text{ Å}, c = 10.9316(9) \text{ Å}, \alpha = 63.981(2)^\circ, \beta = 64.608(3)^\circ, \gamma = 78.743(3)^\circ, V = 902.05(14) \text{ Å}^3, Z = 2, Dc = 1.393 \text{ g cm}^{-3}, \mu = 0.205 \text{ mm}^{-1} (\text{MoK}_\alpha, \lambda = 0.71073), F(000) = 396, T = 172(2) \text{ K}, 2\theta_{\text{max}} = 25.34^\circ (98.4\%), 8404 \text{ measured reflections, 3248 independent reflections (}R_{\text{int}} = 0.0822), \text{GOF on } F^2 = 1.012, R_1 = 0.1146, wR_2 = 0.1054 \text{ (all data), } \Delta e 0.252 \text{ and } -0.337 \text{ eÅ}^{-3}.

Crystal data for DFP-BTO (CCDC 1511289): C\textsubscript{22}H\textsubscript{12}F\textsubscript{2}O\textsubscript{2}S, \textit{MW} = 354.36, monoclinic, P2(1)/c, \(a = 10.3524(5) \text{ Å}, b = 10.3346(6) \text{ Å}, c = 15.3392(9) \text{ Å}, \beta = 90.826(2)^\circ, V = 1639.80(16) \text{ Å}^3, Z = 4, Dc = 1.435 \text{ g cm}^{-3}, \mu = 0.229 \text{ mm}^{-1} (\text{MoK}_\alpha, \lambda = 0.71073), F(000) = 728, T = 174(2) \text{ K}, 2\theta_{\text{max}} = 25.10^\circ\)
(98.0%), 8942 measured reflections, 2869 independent reflections ($R_{\text{int}} = 0.0365$), GOF on $F^2 = 1.066$, $R_1 = 0.0589$, $wR_2 = 0.1213$ (all data), $\Delta e$ 0.302 and $-0.366$ eÅ$^{-3}$.

Crystal data for DTFMP-BTO (CCDC 1501897): $\text{C}_{22}\text{H}_{12}\text{F}_6\text{O}_2\text{S}$, $MW = 454.38$, triclinic, P-1, $a = 7.5333(4)$ Å, $b = 10.9876(7)$ Å, $c = 11.6354(8)$ Å, $\alpha = 91.853(3)^{\circ}$, $\beta = 90.826(2)^{\circ}$, $\gamma = 95.099(2)^{\circ}$, $V = 958.64(10)$ Å$^3$, $Z = 2$, $Dc = 1.574$ g cm$^{-3}$, $\mu = 0.243$ mm$^{-1}$ (MoKα, $\lambda = 0.71073$), $F(000) = 460$, $T = 174(2)$ K, $2\theta_{\text{max}} = 25.38^\circ$ (98.2%), 8525 measured reflections, 3458 independent reflections ($R_{\text{int}} = 0.0613$), GOF on $F^2 = 1.040$, $R_1 = 0.0953$, $wR_2 = 0.0994$ (all data), $\Delta e$ 0.274 and $-0.297$ eÅ$^{-3}$.

Crystal data for DBP-BTO (CCDC 1501891): $\text{C}_{32}\text{H}_{22}\text{O}_2\text{S}$, $MW = 470.56$, monoclinic, $P2(1)/c$, $a = 11.3812(9)$ Å, $b = 9.0240(7)$ Å, $c = 23.553(2)$ Å, $\beta = 100.181(3)^{\circ}$, $V = 2380.9(3)$ Å$^3$, $Z = 4$, $Dc = 1.313$ g cm$^{-3}$, $\mu = 0.164$ mm$^{-1}$ (MoKα, $\lambda = 0.71073$), $F(000) = 984$, $T = 173(2)$ K, $2\theta_{\text{max}} = 25.35^\circ$ (98.6%), 13366 measured reflections, 4304 independent reflections ($R_{\text{int}} = 0.0696$), GOF on $F^2 = 1.041$, $R_1 = 0.0964$, $wR_2 = 0.1039$ (all data), $\Delta e$ 0.237 and $-0.372$ eÅ$^{-3}$.

4. Additional Data

![Fig S1](image). 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.