Electronic Supplementary Information *for*

Photoinduced Fluorescence Modulation through Controllable Intramolecular [2+2] Photocycloaddition in Single Molecules and Molecular Aggregates

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1. Experimental Section

Materials and Reagents. 2-Bromobenzothiophene, *m*-chloroperbenzoic acid and 1,2bis(bromomethyl)benzene were purchased from Aladdin Company. The purity of mchloroperbenzoic acid was 70-80%, and the others were of analytical grade.

Synthesis of 2-Bromobenzo[b]thiophene 1,1-dioxide (Br-BTO). A certain amount of 3chloroperbenzoic acid (m-CPBA) (13.80 g, 80 mmol) was added into a solution of 2bromobenzo[b]thiophene (4.26 g, 20 mmol) in dichloromethane (200 mL), and then the solution was stirred for 12 h at 0 °C. After that, it was washed with saturated NaHCO₃, and the aqueous layer was separated from the organic layer. The aquatic phase was further extracted with dichloromethane several times, and the organic solution was dried over anhydrous Na₂SO₄. After filtration and solvent evaporation under reduced pressure, the residue was purified by silica-gel column chromatography using dichloromethane/petroleum as eluent. Br-BTO was obtained as a white solid 75% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.97 (d, J = 7.7 Hz, 1H), 7.92 (s, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.64 – 7.58 (m, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 135.25, 135.15, 132.49, 131.60, 131.03, 126.09, 122.63, 121.98. HRMS (ESI) m/z: [M+H]⁺ 244.9266 (calcd. for C₈H₅BrO₂S, 243.9194).

Synthesis of 2-(4-hydroxyphenyl)benzo[b]thiophene 1,1-dioxide (P-BTO-OH). A solution of Br-BTO (0.98 g, 4.0 mmol), (4-hydroxyphenyl)boronic acid (0.83 g, 6 mmol), Pd(PPh₃)₄ (0.23 g, 0.2 mmol), and potassium carbonate (2.21 g, 16 mmol) in 100 mL degassed DMF was heated at 100 °C for 24 h under nitrogen. After the mixture was cooled to room temperature, 50 mL ethyl acetate was added, the organic layer was washed with saturated salt water and then dried over anhydrous Na₂SO₄. Then, the solvent was removed under reduced pressure. The residue was purified by silica-gel column chromatography away from light and then further recrystallized with ethanol. P-BTO-OH was obtained as yellow acicular crystals in 79% yield. ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.19 (s, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.74 – 7.65 (m, 4H), 7.56 (dd, 2H), 6.95 (d, J = 8.7 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 159.92, 141.65, 136.52, 134.80, 131.74, 130.13, 128.46, 125.75, 121.80, 121.64, 118.17, 116.76. HRMS (ESI) m/z: [M+H]⁺ 259.0431 (calcd. for C₁₄H₁₀O₃S, 258.0351).

Synthesis of 2,2'-(((1,2-phenylenebis(methylene))bis(oxy))bis(4,1-phenylene))bis(benzo[b] thiophene 1,1-dioxide) (P-2OBTO). 2-(4-Hydroxyphenyl)benzo[b]thiophene 1,1-dioxide (1.03 g, 4 mmol), 1,2-bis(bromomethyl)benzene (0.46 g, 1.75 mmol), and K_2CO_3 (0.69 g, 5 mmol) were added to a 100 mL two-necked flask, to which 50 mL of acetonitrile was then added. It was 2-(4-hydroxyphenyl)benzo[b]thiophene observed that the 1,1-dioxide 1,2and bis(bromomethyl)benzene were completely dissolved under rapid stirring followed by heating and refluxing for 12 hours. The yellow solid powder was observed to precipitate during the reaction. At the end of the reaction, the reaction system was cooled to room temperature, the yellow powder produced during the reaction was left by filtration and washed several times with acetonitrile and water, and dried to obtain bright yellow solid powder in 78% yield. M.P.: 270°C ∽290°C. ¹H NMR (400 MHz, DMSO-d₆) δ 7.90 (d, J = 7.6 Hz, 2H), 7.83 – 7.77 (m, 6H), 7.68 (t, J = 7.5 Hz, 2H), 7.57 (t, J = 7.0 Hz, 6H), 7.40 (d, J = 7.1, 3.8 Hz, 2H), 7.22 (d, J = 8.8 Hz, 4H), 5.35 (s, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.18, 141.14, 136.55, 135.31, 134.85, 131.52, 130.40, 129.25, 128.78, 128.30, 125.94, 123.10, 121.69, 120.06, 116.26, 67.88. HRMS (ESI) m/z: [M+Na]+ 641.1055 (calcd. for C₃₆H₂₆O₆S₂, 618.1171).

Synthesis of 2,2'-(((1,3-phenylenebis(methylene))bis(oxy))bis(4,1-phenylene))bis(benzo[b] thiophene 1,1-dioxide) (P-2MBTO). The procedure was analogous to that described for 2P-BTO. The product was obtained as a white solid in a yield of 81%. M.P.: $217^{\circ}C \sim 227^{\circ}C$. 1H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (d, J = 7.1 Hz, 2H), 7.81 (d, J = 7.6 Hz, 5H), 7.73 – 7.67 (m, 2H), 7.59 (d, J = 5.8 Hz, 5H), 7.45 (s, 3H), 7.22 (d, J = 8.1 Hz, 4H), 5.23 (s, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 160.25, 141.16, 137.40, 136.56, 134.87, 131.55, 130.42, 128.31, 127.89, 127.49, 125.96, 123.08, 121.71, 120.00, 116.27, 69.78. HRMS (ESI) m/z: [M+Na]⁺ 641.1046 (calcd. for C₃₆H₂₆O₆S₂, 618.1171).

Synthesis of 2,2'-(((1,4-phenylenebis(methylene))bis(oxy))bis(4,1-phenylene))bis(benzo[b] thiophene 1,1-dioxide) (P-2PBTO). The procedure was analogous to that described for P-2OBTO. The product was obtained as a white solid in a yield of 76%. M.P.: $248^{\circ}C \sim 260^{\circ}C$. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.90 (d, J = 7.5 Hz, 2H), 7.86 – 7.77 (m, 5H), 7.71 (t, J = 7.5 Hz, 2H), 7.59 (dd, J = 13.3, 7.2 Hz, 4H), 7.51 (s, 3H), 7.22 (d, J = 8.7 Hz, 3H), 5.22 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ

160.22, 141.11, 136.83, 136.52, 134.92, 131.54, 130.45, 128.43, 128.31, 125.99, 123.09, 121.73, 119.94, 116.28, 69.61. HRMS (ESI) m/z: [M+Na]⁺ 641.1025 (calcd. for C₃₆H₂₆O₆S₂, 618.1171).

Synthesis of 2P-2OBTO. P-2OBTO (0.62 g, 1 mmol) was taken in a clean 50 mL beaker, and 10 mL of petroleum ether was added and then placed on a stirrer with rapid stirring so that the P-2MBTO powder could be dispersed and suspended in the solvent. Then the suspension was continuously irradiated with a 365 nm ultraviolet lamp (8 W) for 2 hours. After the reaction was completed, the suspension was filtered to leave a solid powder and washed with hot acetonitrile reagent several times and then dried to obtain the pure white powder with a yield of 93%. M.P.: >300°C. HRMS (ESI) m/z: $[M+H]^+$ 619.1265 (calcd. for C₃₆H₂₆O₆S₂, 618.1171).

Synthesis of *trans*-2P-BTO-OH. 2P-2OBTO (0.3 g, 1 mmol) was placed in a 50 mL roundbottomed flask and 25 mL of dichloromethane was added for stirring to produce a suspension solution of 2P-2OBTO uniformly dispersed in dichloromethane. to which An excess of boron tribromide was slowly added dropwise at 0 °C, and then stirring was continued for 72 hours at 0 °C. At the end of the reaction, 2P-2OBTO was observed to dissolve completely to form a red solution. The reaction was then quenched by the slow addition of ice water to the continuously stirred reaction system, followed by the addition of saturated aqueous sodium bicarbonate solution dropwise. After the pH of the reaction system was adjusted to reach neutrality, it was washed with dichloromethane and saturated saline several times and distilled under reduced pressure to obtain the crude product, and then the crude product was washed with dichloromethane three times to obtain the pure white product with a yield of 25%. ¹H NMR (400 MHz, DMSO-d₆) δ 7.77 (d, J = 7.8 Hz, 2H), 7.70 (d, J = 7.7 Hz, 2H), 7.61 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 4H), 6.58 (d, J = 8.8 Hz, 4H), 5.77 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 157.90, 139.70, 133.83, 132.97, 131.09, 130.79, 122.50, 119.62, 115.28, 70.30, 47.81. HRMS (ESI) m/z: [M+H]+ 517.0758 (calcd. for C₂₈H₂₀O₆S₂, 516.0701).

Characterization of UV-Visible and Fluorescence Properties of All Samples. UV-vis absorption spectra of the compounds in solid state were recorded by Agilent Cary 5000 UV-Vis-NIR spectrophotometer with a calibrating sphere. The absorbance of these compounds in solid state was measured after UV irradiation at 365 nm with different irradiation time from 0 s to 300 s. Steady PL spectra of all samples were performed on an Edinburgh Instruments model FLS980 fluorescence spectrophotometer equipped with a xenon arc lamp using a front face sample holder.

Time-resolved fluorescence measurements were conducted with EPL-series lasers. The solid of the compounds were placed in the solid sample holder, and then each of the sample was excited using a EPLED laser at 380 nm. Time-decayed PL curves can be obtained and then the lifetimes were calculated. The absolute PL quantum yields of all samples were determined `using an integrating sphere equipped with FLS980 spectrophotometer at least three times. The solids of these compounds were placed in the solid sample holder after irradiated at 365 nm with different irradiation time from 0 s to 300 s respectively, and then their PL spectra in solid state were recorded using FLS980 fluorescence spectrophotometer with the excitation light at 405 nm. The time-depending PL spectra of these compounds were obtained in this way.

2. Supplementary Schemes and Figures



Scheme S1. Synthesis routes of P-2OBTO, P-2MBTO and P-2PBTO.



Scheme S2. Synthesis routes of 2P-2OBTO and trans-2P-BTO-OH.



Figure S1. The UV-vis absorption spectra of P-2OBTO, P-2MBTO and P-2PBTO in DMSO at a concentration of 100.0 μ M.



Figure S2. PL spectra of P-2OBTO, P-2MBTO and P-2PBTO in DMSO at a concentration of 10.0μ M upon on excitation at 395 nm.



Figure S3. Time-resolved PL decay curves of P-2OBTO (a), P-2MBTO (b) and P-2PBTO (c) in DMSO after 380 nm excitation at a concentration of 100.0 μ M. The emission wavelengths of P-2OBTO (a), P-2MBTO (b) and P-2PBTO (c) are 470 nm, 473 nm and 465 nm, respectively.



Figure S4. The changes of PL intensity versus irradiation time for P-2OBTO and P-2MBTO in solution, and the corresponding linear fitting curves.



Figure S5. XRD spectrum of P-2OBTO powder.



Figure S6. Time-resolved PL decay curves of P-2MBTO (a) and P-2PBTO (b) after 380 nm excitation in solid state at room temperature. The emission wavelengths of P-2MBTO (a) and P-2PBTO (b) are 474 nm and 473 nm, respectively.



Figure S8. ¹³C NMR spectra of P-2OBTO and 2P-BTO-OH in DMSO-*d*₆.



Figure S9. High-resolution mass spectrum of 2P-2MBTO.



Figure S10. (a) UV-visible spectra of P-2OBTO and 2P-2OBTO in DMSO (100 μ M). (b) Normalized PL emission spectra of 2P-2OBTO in DMSO (100 μ M) and in solid upon excitation at 405 nm.



Figure S11. Time-resolved spotlight decay curves of 2P-2OBTO in DMSO at a concentration of 100.0 μ M (a) and in the solid state (b) after excitation at 380 nm respectively. The emission wavelengths of 2P-2OBTO in liquid (a) and solid (b) are 466 nm and 465 nm respectively.



Figure S12. (a) Aggregation-caused fluorescence quenching behavior of P-2OBTO in DMSO/water mixtures with varying contents of water (fw) upon excitation at 360 nm. (b) Aggregation-induced emission enhancement behavior of 2P-2OBTO in DMSO/DCM mixtures (100.0 μ M) with varying DCM fractions (fw) upon excitation at 360 nm.



Figure S13. Changes in PL intensity of P-2OBTO in solid (a) and in solution (b) versus UV irradiation time.

Table S1. UV-visible absorption wavelengths and molar absorption coefficients of thecompounds P-2OBTO, P-2MBTO and P-2PBTO in DMSO.

Compounds	$\lambda_{ab}\left(nm ight)$	c (mol·L ⁻¹)	€ (L·mol⁻¹·cm⁻¹)
P-2OBTO	360	1.0×10 ⁻⁴	28780
P-2MBTO	360	1.0×10 ⁻⁴	16476
P-2PBTO	360	1.0×10 ⁻⁴	19282

3. NMR and HRMS Spectra of Compounds



Figure S14. ¹H NMR spectrum of Br-BTO in DMSO-d₆



Figure S15. ¹³C NMR spectrum of Br-BTO in DMSO-*d*₆



Figure S17. ¹³C NMR spectrum of P-BTO-OH in DMSO-d₆



δ (ppm)

Figure S19. ¹³C NMR spectrum of P-2OBTO in DMSO- d_6





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 δ (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 $\delta~(ppm)$

Figure S23. ¹³C NMR spectrum of P-2PBTO in DMSO-*d*₆



Figure S25. ¹³C NMR spectrum of trans-2P-BTO-OH in DMSO-d₆







Figure S27. High-resolution mass spectrum of P-BTO-OH.







Figure S29. High-resolution mass spectrum of P-2MBTO.







Figure S31. High-resolution mass spectrum of trans-2P-BTO-OH.