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Supporting Information

Tunable Phosphorescence Supramolecular Switch by Anthracene Photoreaction in Aqueous Solution

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Experimental Procedures



Scheme S1. Synthesis pathway of compounds BPA and BPA_{EPO}.

Materials

Unless otherwise specified, all reagents and solvents were purchased from commercial sources and used without further purification. The compound **1** and **3** was synthesized according to reported literature.^{1, 2} NMR spectra were recorded on a Bruker AVANCE III HD 400. Chemical shifts (δ) for ¹H NMR spectra are reported in parts per million (ppm) and are reported relative to the solvent residual peak. Low-resolution mass (LRMS) spectra were performed on a Bruker Autoflex III TOF/TOF200 and Thermo-Finnigan LCQ-Advantage. High-resolution mass (HRMS) spectra were acquired using a Varian 7.0T FTMS. UV-Vis absorption spectrum was measured by Shimadzu UV-3600. The photo-induced endoperoxidation experiments were carried out using a photochemical reaction apparatus with a 365 nm LED flashlight. Fluorescence and phosphorescence spectra were performed on a Varian Cary Eclipse spectrofluorometer equipped with a plotter unit and a quartz cell (1 cm × 1 cm) at 25 °C. Quantum yield and phosphorescence lifetimes were recorded in a conventional quartz cell (10 × 10 × 45 mm) at 25 °C on an Edinburgh Analytical Instruments FLS920 spectrometer employing the single photon counting technique.

Synthesis of 2

9,10-bis(4-aminophenyl)anthracene 1 (720.9 mg, 2.0 mmol, 1 equiv.) was dissolved with 20 ml tetrahydrofuran (THF) and placed in a 100 ml round-bottomed flask fitted with pressure-equalized dropping funnel. N, N-diisopropylethylamine (1292.5 mg, 10.0 mmol, 5 equiv.) were added into the flask at 0 °C. Then 4-bromobutyryl chloride (1483.6 mg, 8.0 mmol, 4 equiv.) dissolved in 10 ml THF was added dropwise with dropping funnel over 0.5 h. This mixture was stirred at 0 °C under an argon atmosphere for further 12 h. Subsequently, the mixture was filtrated to removed ammonium salt. The exceed THF in the filtrate was removed in vacuum. And the residue was recrystallized from THF/dichloromethane and the solid was washed with dichloromethane and 1

M hydrochloric acid solution. Ivory solid 1093.7 mg (83 %) was gotten after dried in vacuum dryer overnight.

¹H NMR (400 MHz, d_6 -DMSO): δ = 10.26 (s, 2H), 7.87 (d, J=8.3, 4H), 7.62 (dd, J=6.8, 3.2, 4H), 7.45 – 7.35 (m, 8H), 3.66 (t, J=6.5, 4H), 2.59 (t, J=7.2, 4H), 2.19 (dt, J=14.0, 6.9, 4H).

¹³C NMR (100 MHz, d_6 -DMSO): $\delta = 177.85$, 132.40, 131.26, 129.46, 129.20, 126.50, 125.77, 125.41, 119.18, 34.73, 27.42, 21.75.

LRMS (m/z): $[M]^+$ calculated for $C_{34}H_{30}Br_2N_2O_2^+$: 658.065; found: 658.010.



Figure S1. ¹H NMR spectrum (400 MHz, 298 K, d_6 -DMSO) of the compound 2.



Figure S2. ¹³C NMR spectrum (100 MHz, 298 K) of the compound 2.



Figure S3. The MALDI-TOF mass spectra of compound 2.

Synthesis of BPA

2 (658.4 mg, 1.0 mmol, 1 equiv.), 4-(4-bromophenyl)pyridine (1170.5 mg, 5.0 mmol, 5 equiv.) was added into a 250 ml flask and dissolved with 50 ml acetonitrile. The mixture was heated to 85 °C and condensed under the protection of nitrogen for 48 h. Subsequently, the mixture was filtered and the residue is washed with acetonitrile and diethyl ether respectively. Yellow solid 822.7 mg (73%) was obtained after dried in vacuum dryer overnight.

¹H NMR (400 MHz, d_6 -DMSO): $\delta = 10.27$ (s, 2H), 9.20 (d, J = 6.4 Hz, 4H), 8.59 (d, J = 6.6 Hz, 4H), 8.05 (d, J = 8.6 Hz, 4H), 7.83 (dd, J = 17.7, 8.4 Hz, 8H), 7.58 (dd, J = 6.8, 3.2 Hz, 4H), 7.41 (dd, J = 6.8, 3.2 Hz, 4H), 7.35 (d, J = 8.4 Hz, 4H), 4.73 (t, J = 6.9 Hz, 4H), 2.55 (d, J = 7.4 Hz, 4H), 2.42 – 2.33 (m, 4H).

¹³C NMR (100 MHz, d_6 -DMSO): δ = 169.98, 153.65, 145.14, 138.54, 136.25, 132.75, 132.68, 132.64, 131.22, 130.12, 129.40, 126.40, 126.22, 125.38, 124.49, 119.18, 59.74, 32.64, 26.24.

HRMS (m/z): $[M-2Br]^{2+}$ calculated for $C_{56}H_{46}Br_2N_4O_2^{2+}$: 483.0978; found: 483.0978.



Figure S5. ¹³C NMR spectrum (100 MHz, 298 K) of the compound BPA.



Figure S6. HRMS spectrum of compound BPA.

Synthesis of BPA_{EPO}

Weigh 100 mg of **BPA** in a 100 ml beaker and add 4 ml of ultra-dry DMSO. At this time, 0.6 mg of 5,10,15,20-tetraphenylporphyrin was added as a photosensitive singlet oxygen generator. While stirring, a 365 nm flashlight was used to irradiate it overnight to make the photo-oxidation reaction take place. After the reaction 80 ml acetone was poured into the bottle to precipitate the product. Solid are centrifuged and washed with acetone 3 times. Finally the product (more than 30 mg) was gotten after vacuum drying overnight.

¹H NMR (400 MHz, DMSO): δ = 10.28 (s, 2H), 9.18 (d, *J* = 6.3 Hz, 4H), 8.57 (d, *J* = 6.3 Hz, 4H), 8.04 (d, *J* = 8.5 Hz, 4H), 7.85 (d, *J* = 8.0 Hz, 8H), 7.52 (d, *J* = 8.4 Hz, 4H), 7.29 (s, 4H), 7.10 – 6.98 (m, 4H), 4.72 (t, *J* = 6.5 Hz, 4H), 2.55 (s, 4H), 2.40 – 2.32 (m, 4H).

¹³C NMR (100 MHz, DMSO): δ = 170.12, 153.67, 145.15, 139.94, 139.07, 132.76, 132.70, 130.15, 127.79, 127.55, 126.73, 126.30, 124.51, 122.96, 118.95, 83.18, 59.73, 32.62, 26.22.

HRMS (m/z): $[M-2Br]^{2+}$ calculated for $C_{56}H_{46}Br_2N_4O_4^{2+}$: 499.0927; found: 499.0935.



Figure S8. ¹³C NMR spectrum (100 MHz, 298 K) of the compound BPA_{EPO}.



Figure S9. HRMS spectrum of compound BPA_{EPO}.



Scheme S2. Synthesis route of reference molecule BPB.

Synthesis of BPB

3 (484.2 mg, 2.0 mmol, 1 equiv.), 4-(4-bromophenyl)pyridine (936.4 mg, 4.0 mmol, 2 equiv.) was added into a 100 ml flask and dissolved with 50 ml acetonitrile. The mixture was heated to 95 °C and condensed under the protection of nitrogen for 48 h. Subsequently, the mixture was filtered and the residue is washed with acetonitrile and diethyl ether respectively. Light brown solid 714.3 mg (75%) was obtained after dried in vacuum dryer overnight.

¹H NMR (400 MHz, DMSO): δ = 10.02 (s, 1H), 9.15 (d, *J* = 6.7 Hz, 2H), 8.53 (d, *J* = 6.7 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.01 (t, *J* = 7.3 Hz, 1H), 4.67 (t, *J* = 6.9 Hz, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.35 – 2.24 (m, 2H).

¹³C NMR (100 MHz, DMSO): δ = 169.74, 153.56, 145.08, 139.06, 132.75, 132.60, 130.11, 128.59, 124.94, 124.43, 123.08, 119.05, 59.65, 32.51, 26.23.

LRMS (m/z): [M-Br]⁺ calculated for C₂₁H₂₀BrN₂O⁺: 395.075; found: 395.081



Figure S11. ¹³C NMR spectrum (100 MHz, 298 K) of the compound BPB.



Figure S13. Job's plots of BPA with (a) CB[7] and (b) CB[8] measured by (c) fluorescence spectra and (d) UV-Vis absorption spectra respectively.



Figure S14. Titration experiment of BPA with (a) CB[7] and (b) CB[8] by UV-Vis absorption spectra and (c), (d) fitting of their apparent bonding constants.



Figure S15. Figure 12. ¹H NMR spectra (400 MHz, d_6 -DMSO: $D_2O = 1:1$, 298 K) of BPA, CB[7]/BPA and CB[8]/BPA ([BPA] = 0.5 mM).



Figure S16. ¹H NMR spectra (400 MHz, d_6 -DMSO: D₂O = 1:1, 298 K) of **BPA** with the addition of gradient concentration **CB**[7].



Figure S17. ¹H NMR spectra (400 MHz, d_6 -DMSO: $D_2O = 1:4$, 298 K) of **BPA** with the addition of gradient concentration **CB[8]**.



Figure S18. ¹H NMR spectra (400 MHz, d_6 -DMSO: $D_2O = 1:4$, 298 K) of gradient concentration of **BPA/CB[8]** (**BPA:CB[8]=1:1**).



Figure S19. 2D ROSEY spectrum (400 MHz, d_6 -DMSO: $D_2O = 1:4$, 298 K) of **BPA** in presence of 1 equiv. of **CB[8]**.



Figure S20. 2D DOSY spectrum (400 MHz, d_6 -DMSO: $D_2O = 1:4$, 298 K) of BPA and BPA in presence of 1 equiv. of CB[8].



Figure S21. (a), (b) Job's plot measured by UV-Vis absorption spectra between **BPB** and **CB**[7] and (c) titration experiment for (d) fitting of their bonding constants.



Figure S22. Comparison chart of ¹H NMR spectra (400 MHz, D_2O , 298 K) of BPB, CB[7]/BPB and CB[8]/BPB ([BPA] = 0.5 mM, CB[7] is 2 equivalent and CB[8] is 1 equivalent).





Figure S23. (a) ¹H NMR spectra (400 MHz, D_2O , 298 K) of BPB (1 mM), with the gradient concentration addition of CB[7] (from 0 to 2.5 equiv.), and (b) its partial enlargement of hydrogen peaks in aromatic region.



Figure S24. The MALDI-TOF mass spectra of one BPB binding two CB[7].



Figure S25. (a) ¹H NMR spectra (400 MHz, D_2O , 298 K) of **BPB** (1 mM), with the gradient concentration addition of **CB[8]** (from 0 to 0.6 equiv.), and (b) its partial enlargement of hydrogen peaks in aromatic region.



Figure S26. Scanning electronic microscopy image of (a) **BPA**, (b) **BPA/CB[7]**, (c) **BPA/CB[8]** and (d) local amplification of rhombic particles. (The droplets are dried on the silicon wafer, the composition of the solution is MeOH : water = 1 : 4)



Figure S27. The excitation and emission spectra of BPA aqueous solution were studied by adding the host macrocycle gradually. (a) and (b) are for CB[7], while (c) and (d) are for CB[8].



Figure S28. The UV-vis absorption spectra used to monitor the photo-induced internal peroxycyclization of **BPA**. Variation of UV-vis absorption spectra with exposure time under 365 nm LED flashlight for (a) **BPA**, (c) **CB[7]/BPA**, (e) **CB[8]/BPA**, and (g) **CB[7,8]/BPA**. The change of absorption at 375.5nm with irradiation time and the first-order kinetics fitting curve of (b) **BPA**, (d) **CB[7]/BPA**, (f) **CB[8]/BPA**, (h) **CB[7,8]/BPA** ([**BPA**] : [**CB[7]**] : [**CB[8]**] = 1 : 2 : 1) in water (containing 2.5% of DMSO) at 298 K.



Figure S29. BPA combined with singlet oxygen to form internal peroxycyclization product **BPA**_{EPO} under 365nm UV irradiation, and there was no damage on the molecular skeleton.



Figure S30. The fluorescence spectra of the process of photo-oxidation.



Figure S31. Comparison of FT-IR spectra of BPA and BPA_{EPO}.



Figure S32. (a) The high-resolution mass spectrometry of the oxidation specie, the comparison of (b) UV-Vis absorption spectrum, (c) photoluminescence spectrum between the oxidation specie and **BPA**_{EPO}, and (d) comparison of photo reaction rate constant under deoxygen conditions (fitted by quasi first order rate equation y=a+b*exp(-kx)).



Figure S33. Job's plots of BPA_{EPO} with (a) CB[7] and (b) CB[8] measured by (c) fluorescence spectra and (d) UV-Vis absorption spectra respectively.



Figure S34. The total quantum yield of photoluminescence of (a) $CB[8]/BPA_{EPO}$ and (b) $CB[7,8]/BPA_{EPO}$

References

- 1. T. K. Ronson, W. Meng and J. R. Nitschke, J. Am. Chem. Soc., 2017, 139, 9698-9707.
- 2. A. I. D. Alanine, C. W. G. Fishwick and C. Szantay, *Tetrahedron Lett.*, 1989, **30**, 6571-6572.