Electronic Supplementary Information

Twofold Photoswitching of Near-Infrared Fluorescence and Electron Paramagnetic Resonance Based on Perylenemonoimide-Hexaarylbimidazole Dyad for Optical Nanoimaging of Electrospun Polymer Nanowires

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Table of Contents

1. Figure S1. FL and UV-vis spectra of PMI-N-2CHO (1d) in CHCl₃ and CHCl₃/TFA = 9:1;

2. Figure S2. The fitting results of fluorescence lifetime of PMI-N-HABI in benzene and film;

3. Figure S3. Normalized UV-vis spectra of C₈H₁₇-O-TPIR in benzene and PMI-N-2O-TPIR in solid state;

4. Figure S4. EPR spectra of TPIR, C₈H₁₇-O-TPIR and PMI-N-2O-TPIR in benzene at 283 K;

5. Figure S5. The variation of EPR spectra of C₈H₁₇-O-HABI at 293 K upon different irradiation time of a 405 nm laser;

6. Figure S6. The variation of EPR spectra of PMI-N-HABI at 110 K after 10 s irradiation of a 405 nm laser with continuous scanning;

7. Detail synthetic procedures and characterizations

8. Reference
1. FL and UV-vis spectra of PMI-N-2CHO in CHCl$_3$ and CHCl$_3$/TFA = 9:1

![FL and UV-vis spectra](image)

**Figure S1.** FL and UV-vis spectra of PMI-N-2CHO (1d) in CHCl$_3$ (black line) and CHCl$_3$/TFA = 9:1 (red line) with concentration equals to $1.8 \times 10^{-5}$ mol/L.
2. The fitting results of fluorescence lifetime of PMI-N-HABI in benzene and film

Figure S2. (a) fluorescence lifetime spectra of PMI-N-HABI in benzene and (b) the corresponding residuals curves between fit and experimental, (c) fluorescence lifetime spectra of PMI-N-HABI in film and (d) the corresponding residuals curves between fit and experimental; the fluorescence lifetime of PMI-N-HABI in benzene was calculated to be 3.94 ns, $\chi^2 = 1.713$; in film was calculated to be two lifetimes, which are 2.0 and 3.30 ns, $\chi^2 = 1.229$;
3. Normalized UV-vis spectra of C$_8$H$_{17}$-O-TPIR in benzene and PMI-N-2O-TPIR in solid state

Figure S3. UV-vis spectra of C$_8$H$_{17}$-O-TPIR in benzene (black line) and PMI-N-2O-TPIR in solid state (red line);
4. EPR spectra of TPIR, C₈H₁₇-O-TPIR and PMI-N-2O-TPIR in benzene at 283 K;

Figure S4. EPR spectra of TPIR (red line), C₈H₁₇-O-TPIR (black line) and PMI-N-2O-TPIR (blue line) in benzene at 283 K;
5. the variation of EPR spectra of C₈H₁₇O-HABI at 293 K upon different irradiation time of a 405 nm laser

Figure S5. The variation of EPR spectra of C₈H₁₇O-HABI at 293 K upon different irradiation time of a 405 nm laser;
6. The variation of EPR spectra of PMI-N-HABI at 110 K after 10 s irradiation of a 405 nm laser with continuous scanning;

**Figure S6.** The variation of EPR spectra of PMI-N-HABI at 110 K after 10 s irradiation of a 405 nm laser with continuous scanning; the intervals of each scan is 2 mins;
7. The detail Synthetic procedures for the intermediate products and PMI-N-HABI

Synthetic procedure of PMI and 9-Br-PMI

The preparation of PMI and 9-Br-PMI has been reported previously according to Leonhard Feiler et al and we follow this article precisely in synthesizing PMI and 9-Br-PMI in this paper.1

Synthetic procedure of PMI-borate

Into a 50 ml flask, 9-Bromo-PMI (0.56 g, 1.0 mmol), bis(pinacolate) diboron (0.30 g, 1.2 mmol), dry potassium acetate (0.29 g, 3.0 mmol) and Pd(dpff)Cl$_2$ (0.081 g, 0.1 mmol) were added and dispersed in 20 ml distilled dioxane. The system was vacuumized by an oil pump and then filled with N$_2$ for three times. Then the red colored solution was stirred and heated to 90 °C for 12 h. After the reaction has been finished, about 10 g silica gel (200-300) was added to the residue. The solvents were evaporated under reduced pressure and the remaining red powder was used directly for column chromatography on silica gel (200-300). The eluent was solvent mixture of DCM-Methanol = 500:2 (v-v) and 0.45 g red solid powder was obtained, yield 74%.

$^1$H NMR $\delta_H$(CDCl$_3$, 600MHz): 8.90 (d, J = 12 Hz, 1 H), 8.67 (m, 2 H), 8.51 (m, 4 H), 8.22(d, J = 6 Hz, 1 H), 7.70 (t, J = 6 Hz, 1 H), 7.49 (t, J = 6 Hz, 1 H), 7.35 (d, J = 12 Hz, 2 H), 2.78 (m, 2 H), 1.47 (s, 12 H), 1.18 (d, J = 6 Hz, 12 H);

LC-MS (APCI): calculated: 607.54, found: 608.48, [M$^+$+H$^+$];

Synthetic procedure of 1a:

The mixture of 4-Bromoaniline (8.6 g, 0.05 mol), 2-bromoethanol (31.3 g, 0.25 mol) and NaHCO$_3$ (8.4 g, 0.1 mol) were stirred and heated to 57 °C for 2 days in a 250 ml two-neck flask. After the reaction finished, the mixture was poured into water, extracted with CHCl$_3$ (250 ml) and then washed with brine (3×200 ml). The organic layer was collected, dried over anhydrous MgSO$_4$, filtered and the solvent was evaporated by a reduced pressure. The residue was then purified by column chromatography on silica gel (200-300) using Ethyl Acetate and Hexane (30-70, v-v) as eluent; 9.8 g white solid was obtained, yield 76%.

$^1$H NMR $\delta_H$(CDCl$_3$, 600MHz): 7.31 (d, J = 12 Hz, 2 H), 6.58 (d, J = 12 Hz, 2 H), 3.89 (s, broad, 2H, overlap with N-(CH$_2$-CH$_2$-OH)$_2$), 3.82 (t, J = 6 Hz, 4 H, N-(CH$_2$-CH$_2$-OH)$_2$), 3.55 (t, J = 6 Hz, 4 H, N-(CH$_2$-CH$_2$-OH)$_2$);

LC-MS (APCI): calculated: 260.13, found: 261.21, [M$^+$+H$^+$];
Synthetic procedure of 1b:

1a (2.6 g, 0.01 mol) was dissolved in 100 ml distilled DCM in a 250 ml two-neck flask under an ice-water bath. When 1a was completely dissolved, SOCl₂ (1.7 ml, 25 mmol) was added into this stirring solution by a 5 ml syringe gradually in 5 mins. Soon a large amount of white precipitates formed in the solution and then after 10 mins, the precipitates were totally dissolved again. The solution was then left in the ice-water bath for 5 h, and then heated to reflux for 1 h. After the reaction was finished, ethanol (50 ml) was added into the mixture to quench the excess amount of SOCl₂. 10 g silica gel was then added and the mixture was evaporated under reduced pressure. The residue was purified by column chromatography using Ethyl Acetate and Hexane (10-90, v-v) as eluent; 1.8 g white solid was obtained, yield 59%.

1H NMR δ (CDCl₃, 600MHz): 7.34 (d, J = 6 Hz, 2 H), 7.32 (d, J = 6 Hz, 2 H), 3.71 (t, J = 6 Hz, 4 H), 3.62 (t, J = 6 Hz, 4 H); LC-MS (APCI): calculated: 297.02, found: 297.13, [M⁺];

Synthetic procedure of 1c:

1b (1.0 g, 3.4 mmol), p-Hydroxybenzaldehyde (0.9 g, 7.4 mmol) and K₂CO₃ (1.4 g, 10.2 mmol) were dispersed in 30 ml distilled DMF in a 100 ml flask. The system was pumped and then injected N₂ for three cycles to ensure the N₂ reaction atmosphere. Then the mixture was stirred and heated to 100 °C for 2 days. After the reaction finished, the solution was poured into water and extracted with DCM (200 ml). The organic layer was washed with brine (3×100 ml), dried over MgSO₄, filtered and evaporated. The residue was then purified by column chromatography on silica gel using Ethyl Acetate and Hexane as eluent (40-60, v-v). 1.50 g white solid was obtained, yield 95%.

1H NMR δ (CDCl₃, 600MHz): 9.87 (s, 2H, Ar-CHO), 7.82 (d, J = 8.4 Hz, 4 H), 7.32 (d, J = 6 Hz, 4 H), 7.31 (t, J = 6 Hz, 4 H), 6.96 (d, J = 8.4 Hz, 4 H), 6.69 (d, J = 9 Hz, 2 H), 6.69 (d, J = 9 Hz, 2 H), 4.25 (t, J = 6 Hz, 4 H), 3.91 (t, J = 6 Hz, 4 H); LC-MS (APCI): calculated: 468.34, found: 469.47, [M⁺+H⁺];

Synthetic procedure of 1d:
In a 100 ml two-neck flask, PMI-borane (0.73 g, 1.2 mmol) and 1c (0.47 g, 1 mmol) were dispersed into 20 ml toluene and then 5 ml aqueous K$_2$CO$_3$ solution (1 mol/L) was added. The reaction system was pumped to low pressure and then injected with N$_2$. This process was repeated for 3 times to ensure N$_2$ atmosphere of the system. Then the reaction was stirred and heated to 90 °C for 1 day. After the reaction was finished, the organic layer was separated and washed with brine (3 × 50 ml). Then it was dried over MgSO$_4$, filtered, evaporated under reduced pressure and purified by column chromatography on silica gel (200 - 300) using DCM and Methanol as eluent (500 - 5, v - v), 0.72 g purple solid was obtained, yield 83%.

$^1$H NMR $\delta$ (CDCl$_3$, 600 MHz): 9.91 (s, 2 H), 8.66 (m, 2 H), 8.50 (m, 2 H), 8.46 (t, J = 6 Hz, 2 H), 8.11 (d, J = 6 Hz, 1 H), 7.85 (d, J = 12 Hz, 4 H), 7.60 (t, J = 6 Hz, 2H), 7.50 (d, J = 6 Hz, 2 H), 7.00 (d, J = 6 Hz, 6 H), 4.39 (t, J = 6 Hz, 4 H), 4.08 (t, J = 6 Hz, 4 H), 2.80 (m, 2 H), 1.19 (d, J = 6 Hz, 12 H); LC-MS (APCI): calculated: 869.01, found: 870.05, [M$^+$+H$^+$];

Synthetic procedure of 1e:

Into a sealed tube (50 ml), 1d (0.5 g, 0.58 mmol), benzil (0.48 g, 2.32 mmol) and ammonium acetate (1.12 g, 14.5 mmol) were dissolved in 20 ml DCM with 0.1 ml acetic acid as catalyst. The reaction was stirred and heated to 110 °C for 2 days. After the reaction was finished, the organic layer was mixed with silica gel (5 g) and then directly evaporated under reduced pressure. The resulting residue was used for purification on column chromatography on silica gel (200 - 300) using DCM and Methanol as eluent. The volume of methanol was increased from 1 % to 5 % and finally 0.65 g black purple solid was obtained, yield 90%.

$^1$H NMR $\delta$ (d-$^2$DMSO, 600MHz): 12.52 (s, 2 H), 8.71 (m, 3 H), 8.67 (d, J = 6 Hz, 1 H), 8.54 (m, 2 H), 8.13 (d, J = 6 Hz, 1 H), 8.05 (d, J = 12 Hz, 4 H), 7.73 (m, 1 H), 7.68 (m, 2 H), 7.65 (d, J = 6 Hz,
1 H), 7.55 (d, J = 6 Hz, 4 H), 7.48 (m, 6 H), 7.45 (m, 4 H), 7.37 (m, 4 H), 7.30 (m, 4 H), 7.22 (t, J = 6 Hz, 2 H), 7.10 (t, J = 6 Hz, 6 H), 4.36 (t, J = 6 Hz, 4 H), 4.04 (t, J = 6 Hz, 4 H), 2.80 (m, 2 H), 1.19 (d, J = 6 Hz, 12 H); 13C NMR δC (d-DMSO, 600MHz): 163.78, 162.11, 159.07, 154.67, 146.02, 145.96, 145.88, 141.48, 131.99, 131.87, 131.73, 130.71, 128.85, 127.39, 127.22, 124.59, 124.17, 123.97, 123.76, 116.79, 115.09, 114.67, 112.31, 111.26, 29.04, 24.47, 24.17, 22.50; Malti-tof m/z: (calculated) 1248.5302 (100.0%), 1249.5336 (93.0%), 1250.5369 (42.8%), 1251.5403 (12.9%), 1252.5436 (2.9%), 1249.5272 (2.2%), 1250.5306 (2.1%); found 1249.4989, 1250.5664; Elemental Analysis: required C, 82.80; H, 5.33; N, 6.74; O, 5.13; found C, 82.75; H, 5.34; N, 6.76; O, 5.12;

Synthetic procedure of PMI-N-HABI (1):

Into a 250 ml two-neck flask, 1e (0.2 g, 0.16 mmol) was dispersed in 50 ml benzene. This solution was vigorously stirred and covered from daylight by aluminum foil. Consequently, an aqueous solution (50 ml) of K3Fe(CN)6 (2.63 g, 8 mmol) and KOH (0.90 g, 16 mmol) was added into dropwise in 20 mins. The reaction was detected by TLC plate until the starting material was totally converted. After the reaction was finished, the organic layer was collected, washed with brine (3 × 50 ml), dried over MgSO4 and filtered. The resulting solution was then evaporated under reduced pressure for purification by column chromatography on Al2O3 (200 - 300) using DCM and Ethyl Acetate as eluent (500 ml − 20 ml). 140 mg black solid was obtained, yield 70%.

1H NMR δH (CD2Cl2, 600MHz): 8.60 (t, J = 6 Hz, 2 H), 8.50 (m, 4 H), 8.18 (d, J = 6 Hz, 1 H), 7.60 (m, 4 H), 7.48 (m, 6 H), 7.20-7.40 (m, 17 H), 7.14 (t, J = 18 Hz, 2 H), 7.10 (m, 4 H), 6.88 (d, J = 6 Hz, 2 H), 6.73 (d, J = 6 Hz, 2 H), 6.57 (d, J = 6 Hz, 2 H), 4.47 (t, J = 6 Hz, 2 H), 4.33 (t, J = 6 Hz, 2 H), 3.75 (d, J = 6 Hz, 2 H), 3.61 (d, J = 6 Hz, 2 H), 2.80 (m, 2 H), 1.19 (d, J = 6 Hz, 12 H);

Malti-tof m/z: calculated 1246.5146 (100.0%), 1247.5179 (93.0%), 1248.5213 (42.8%), 1249.5246 (12.9%), 1250.5280 (2.9%), 1247.5116 (2.2%), 1248.5149 (2.1%); found 1247.2260, 1248.3764;

13C NMR δC (d-DMSO, 600MHz): 160.55, 145.87, 135.46, 131.75, 131.51, 130.87, 129.52, 129.43, 129.08, 129.01, 128.80, 128.69, 128.61, 127.70, 127.51, 127.04, 126.86, 122.07, 115.08, 111.44, 29.07, 27.19, 24.18, 19.76; Elemental Analysis: required C, 82.80; H, 5.33; N, 6.74; O, 5.13; found C, 82.75; H, 5.36; N, 6.71; O, 5.10;
\[ ^1\text{H} \text{NMR and } ^{13}\text{C} \text{ NMR spectra} \]

**Figure S7.** $^1$H NMR spectrum of PMI-borate in CDCl$_3$

**Figure S8.** $^1$H NMR spectrum of 1a in CDCl$_3$
Figure S9. $^1$H NMR spectrum of 1b in CDCl$_3$

Figure S10. $^1$H NMR spectrum of 1c in CDCl$_3$
Figure S11. $^1$H NMR spectrum of 1d in CDCl$_3$.

Figure S12. $^1$H NMR spectrum of 1e in $^6$DMSO.
Figure S13. $^1$H NMR spectrum of PMI-N-HABI in CD$_2$Cl$_2$.

Figure S14. $^{13}$C NMR spectrum of 1e in $^6$DMSO.
Figure S15. $^{13}$C NMR spectrum of PMI-N-HABI in $^d$DMSO
MALDI-TOF spectra of PMI-N-2TPI and PMI-N-HABI

**Figure S16.** 1Malti-tof spectrum of 1e

**Figure S17.** 1Malti-tof spectrum of PMI-N-HABI

8. References