Electronic Supplementary Information

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

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1. FL and UV-vis spectra of PMI-N-2CHO in $CHCl_3$ and $CHCl_3$/TFA = 9:1

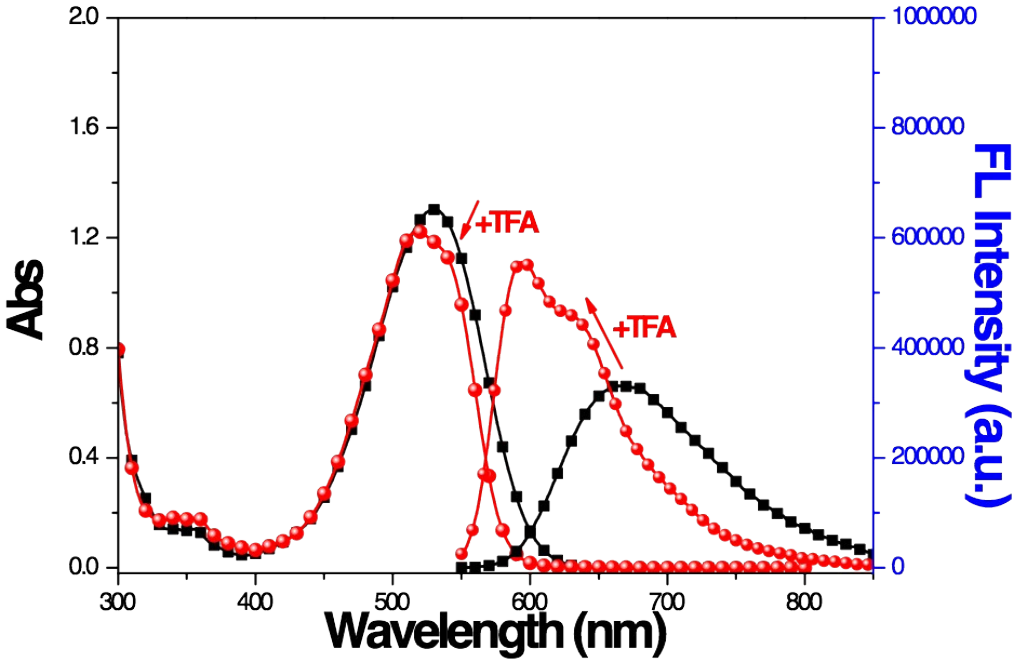


Figure S1. FL and UV-vis spectra of PMI-N-2CHO (**1d**) in $CHCl_3$ (**black line**) and $CHCl_3$/TFA = 9:1 (**red line**) with concentration equals to 1.8×10^{-5} mol/L.

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

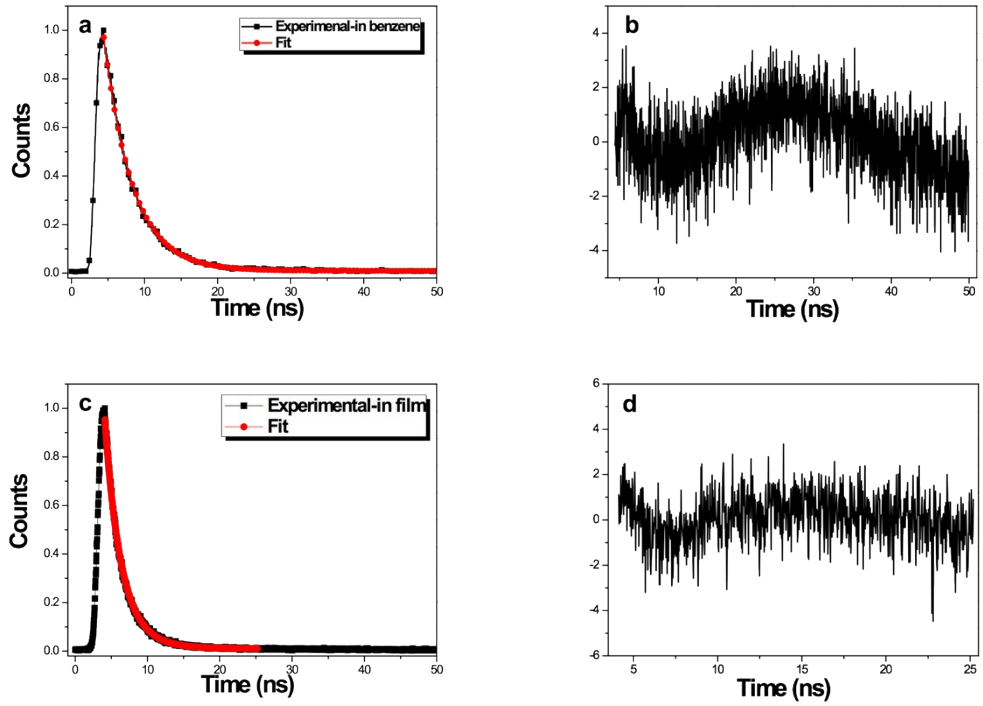


Figure S2. (**a**) fluorescence lifetime spectra of PMI-N-HABI in benzene and (**b**) the corresponding residuals curves between fit and experimental, (**c**) fluorescence lifetime spectra of PMI-N-HABI in film and (**d**) the corresponding residuals curves between fit and experimental; the fluorescence 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_8H_{17}-O-TPIR in benzene and PMI-N-2O-TPIR in solid state

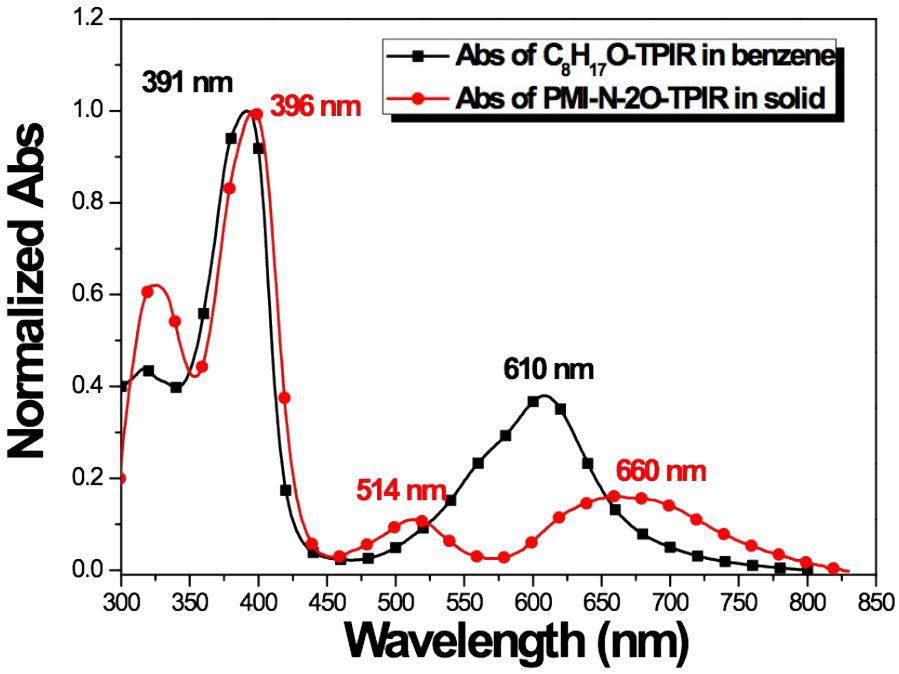


Figure S3. UV-vis spectra of C_8H_{17}-O-TPIR in benzene (black line) and PMI-N-2O-TPIR in solid state (red line);

4. EPR spectra of TPIR, C_8H_{17}-O-TPIR and PMI-N-2O-TPIR in benzene at 283 K;

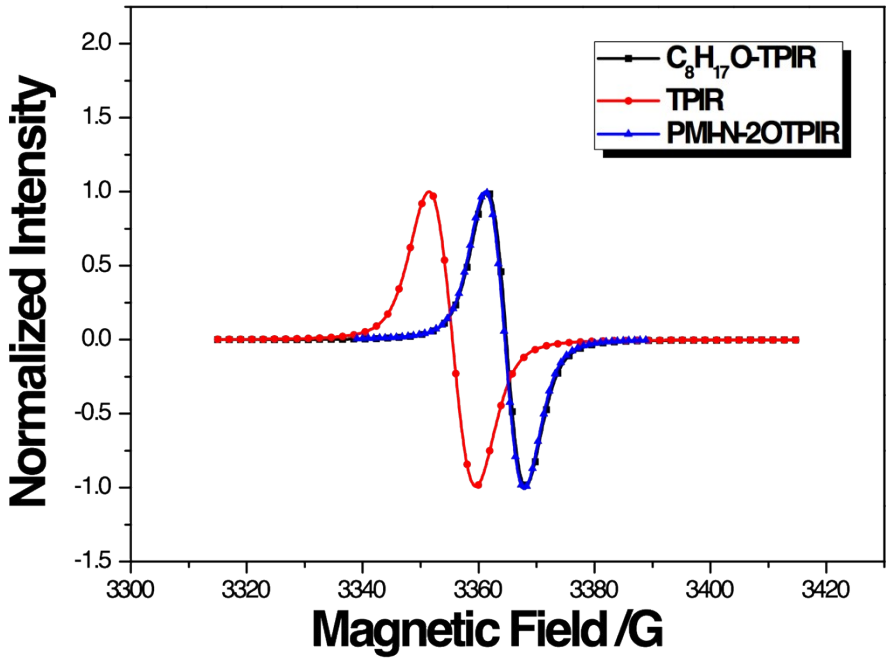


Figure S4. EPR spectra of TPIR (red line), C_8H_{17}-O-TPIR (black line) and PMI-N-2O-TPIR (blue line) in benzene at 283 K;

5. the variation of EPR spectra of $C_8H_{17}O$-HABI at 293 K upon different irradiation time of a 405 nm laser

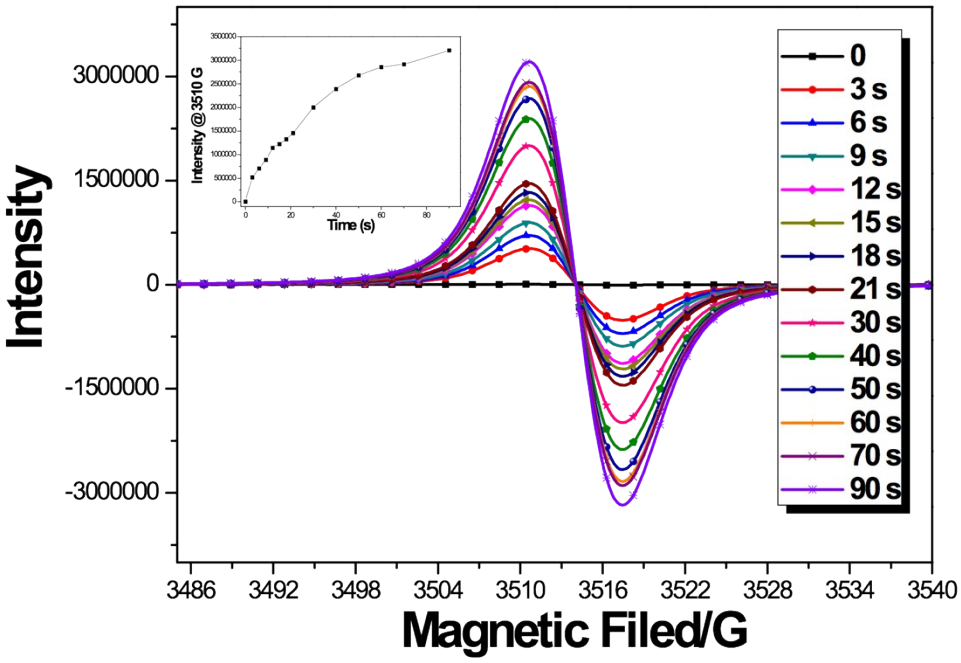


Figure S5. The variation of EPR spectra of $C_8H_{17}O$-HABI at 293 K upon different irradiation time of a 405 nm laser;

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;**

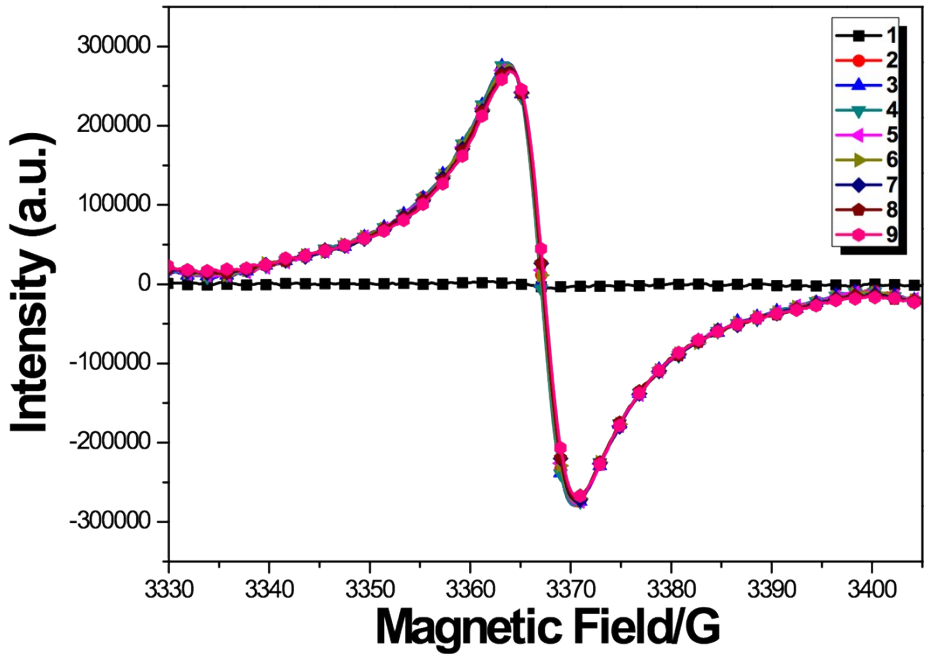


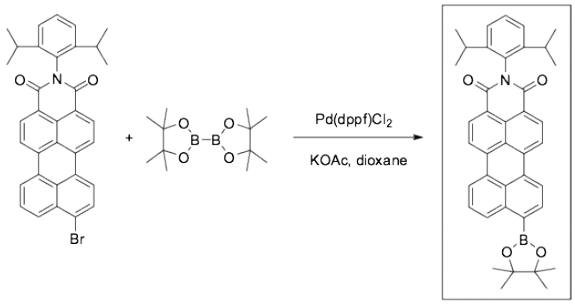
Figure S6. The variation of EPR spectra of PMI-N-HABI at 110 K after 10 s irradiation of a 405 nm laser with continuous scanning; the intervals of each scan is 2 mins;

7. The detail Synthetic procedures for the intermediate products and PMI-N-HABI

Synthetic procedure of **PMI** and **9-Br-PMI**

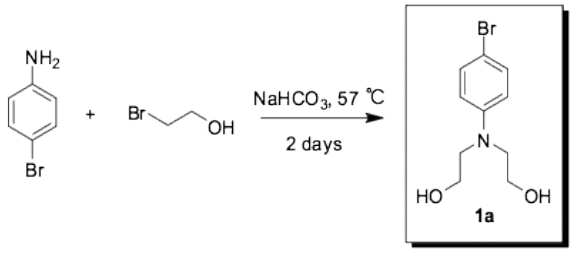
The preparation of PMI and 9-Br-PMI has been reported previously according to Leonhard Feiler et al and we follow this article precisely in synthesizing PMI and 9-Br-PMI in this paper.[1]

Synthetic procedure of **PMI-borate**



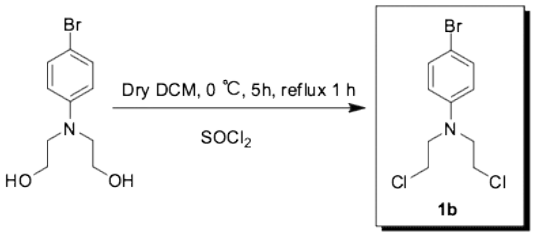
Into a 50 ml flask, 9-Bromo-PMI (0.56 g, 1.0 mmol), bis(pinacolate)diboron (0.30 g, 1.2 mmol), dry potassium acetate (0.29 g, 3.0 mmol) and Pd(dppf)Cl_2 (0.081 g, 0.1 mmol) were added and dispersed in 20 ml distilled dioxane. The system was vacuumized by an oil pump and then filled with N_2 for three times. Then the red colored solution was stirred and heated to 90 ℃ 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 δ_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**:



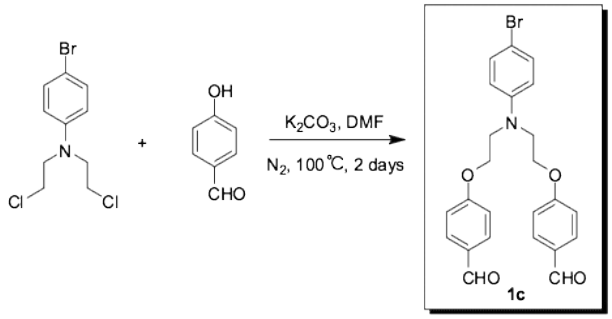
The mixture of 4-Bromoaniline (8.6 g, 0.05 mol), 2-bromoethanol (31.3 g, 0.25 mol) and $NaHCO_3$ (8.4 g, 0.1 mol) were stirred and heated to 57 ℃ for 2 days in a 250 ml two-neck flask. After the reaction finished, the mixture was poured into water, extracted with $CHCl_3$ (250 ml) and then washed with brine (3×200 ml). The organic layer was collected, dried over anhydrous $MgSO_4$, filtered and the solvent was evaperated 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 δ_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**:



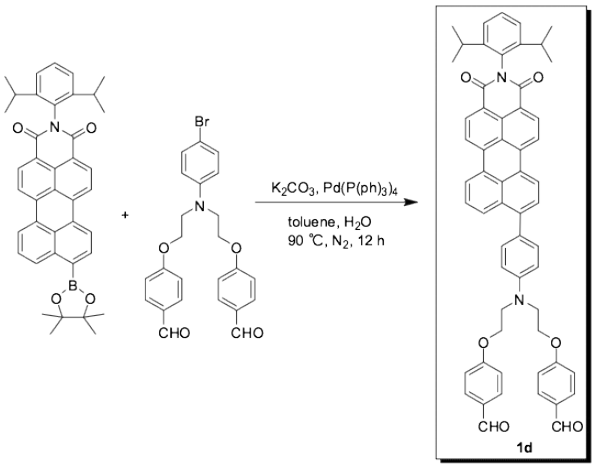
1a (2.6 g, 0.01 mol) was dissolved in 100 ml distilled DCM in a 250 ml two-neck flusk under an ice-water bath. When **1a** was completely dissolved, $SOCl_2$ (1.7 ml, 25 mmol) was added into this stirring solution by a 5 ml syringe gradually in 5 mins. Soon a large amount of white precipitates formed 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 mixtrue 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%;
^{1}H NMR δ_H ($CDCl_3$, 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**:



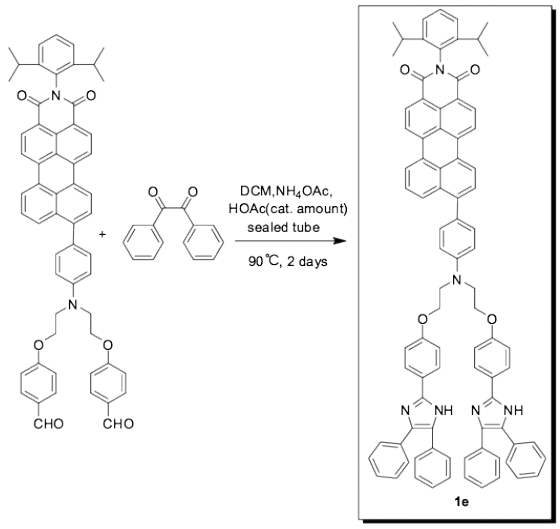
1b (1.0 g, 3.4 mmol), p-Hydroxybenzaldehyde (0.9 g, 7.4 mmol) and K_2CO_3 (1.4 g, 10.2 mmol) were dispersed in 30 ml distilled DMF in a 100 ml flusk. The system was pumped and then injected N_2 for three cycles to ensure the N_2 reaction atmosphere. Then the mixture was stirred and heated to 100 ℃ for 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 $MgSO_4$, 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%.
^{1}H NMR δ_H ($CDCl_3$, 600MHz): 9.87 (s, 2H, Ar-**CHO**), 7.82 (d, J = 8.4 Hz, 4 H), 7.33 (d, J = 9 Hz, 2 H), 6.96 (d, J = 8.4 Hz, 4 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 flusk, PMI-boronate (0.73 g, 1.2 mmol) and 1c (0.47 g, 1 mmol) were dispered into 20 ml toluene and then 5 ml aqueous K_2CO_3 solution (1 mol/L) was added. The reaction system was pumpped 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 ℃ for 1 day. After the reaction was finished, the organic layer was seperated 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 δ_H ($CDCl_3$, 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(m, 3 H), 7.35 (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^+];

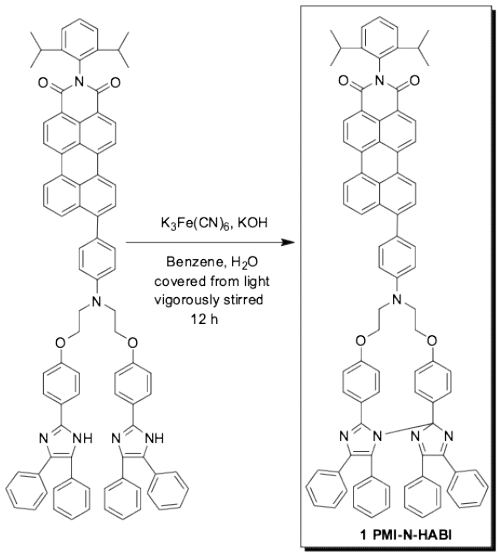
Synthetic procedure of **1e**:



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 ℃ 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 δ_H (^{d}-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); ^{13}C NMR δ_C (^{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; Elemntal 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 $K_3Fe(CN)_6$ (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 $MgSO_4$ and filtered. The resulting solution was then evaporated under reduced pressure for purification by column chromatography on Al_2O_3 (200 - 300) using DCM and Ethyl Acetate as eluent (500 ml – 20 ml). 140 mg black solid was obtained, yield 70%.
^{1}H NMR δ_H (CD_2Cl_2, 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; ^{13}C NMR δ_C (^{d}-DMSO, 600MHz):160.55, 145.87, 135.46, 131.75, 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; Elemntal 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}H NMR and ^{13}C NMR spectra

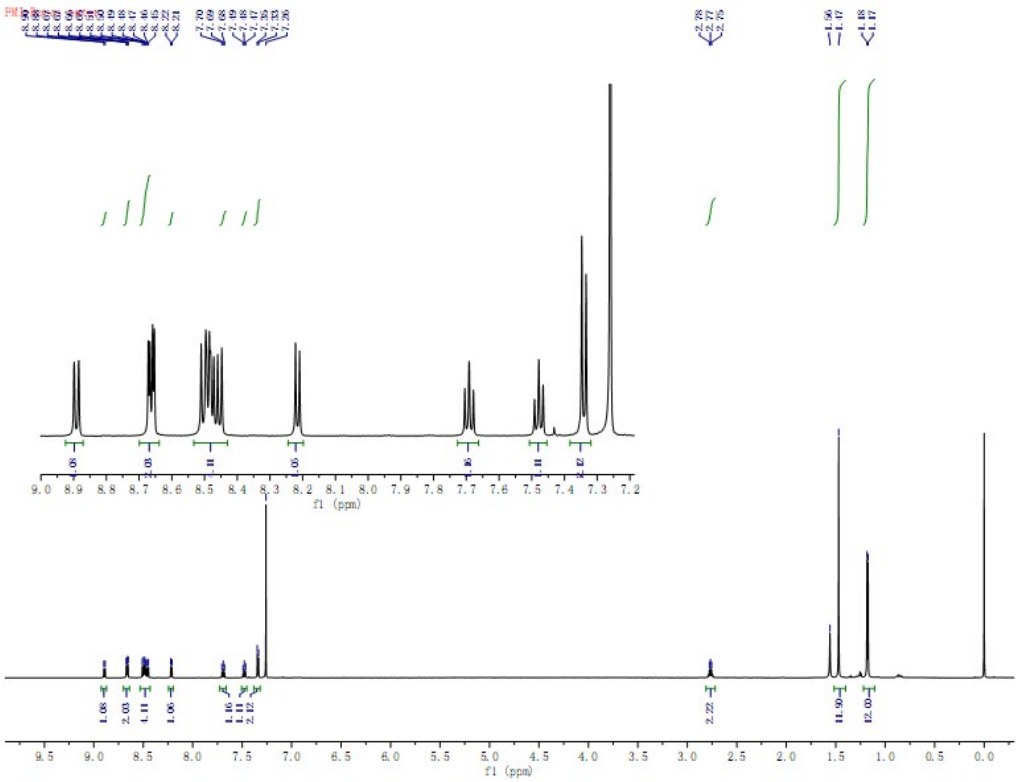


Figure S7. ^{1}H NMR spectrum of PMI-borate in $CDCl_3$

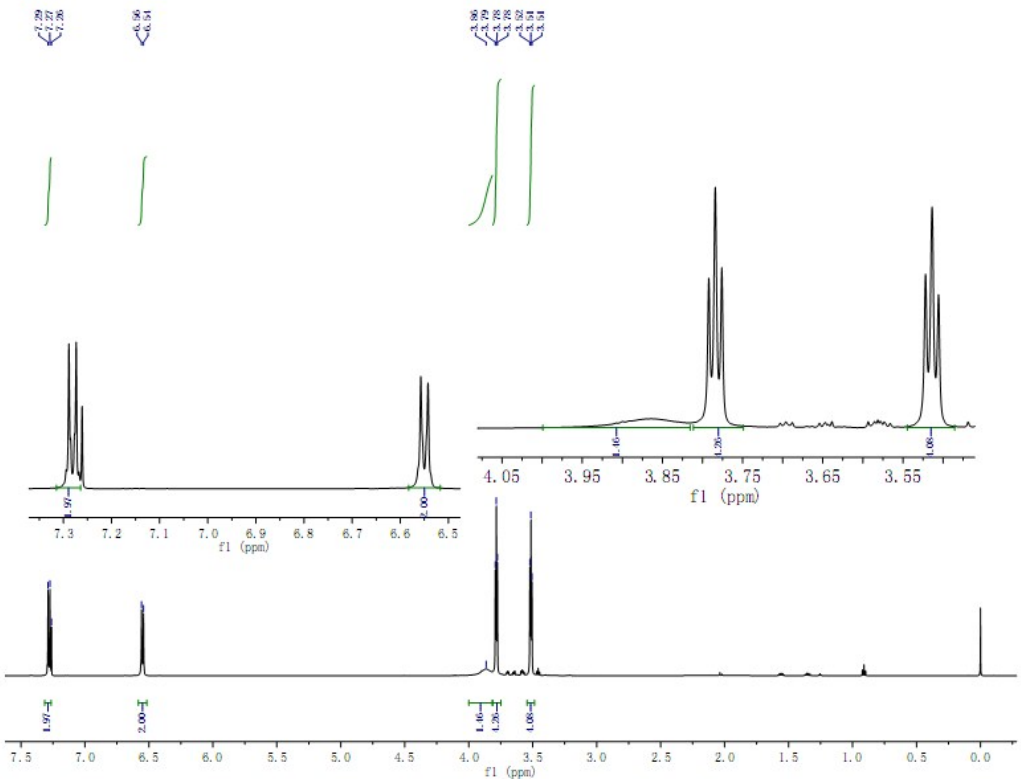


Figure S8. ^{1}H NMR spectrum of **1a** in $CDCl_3$

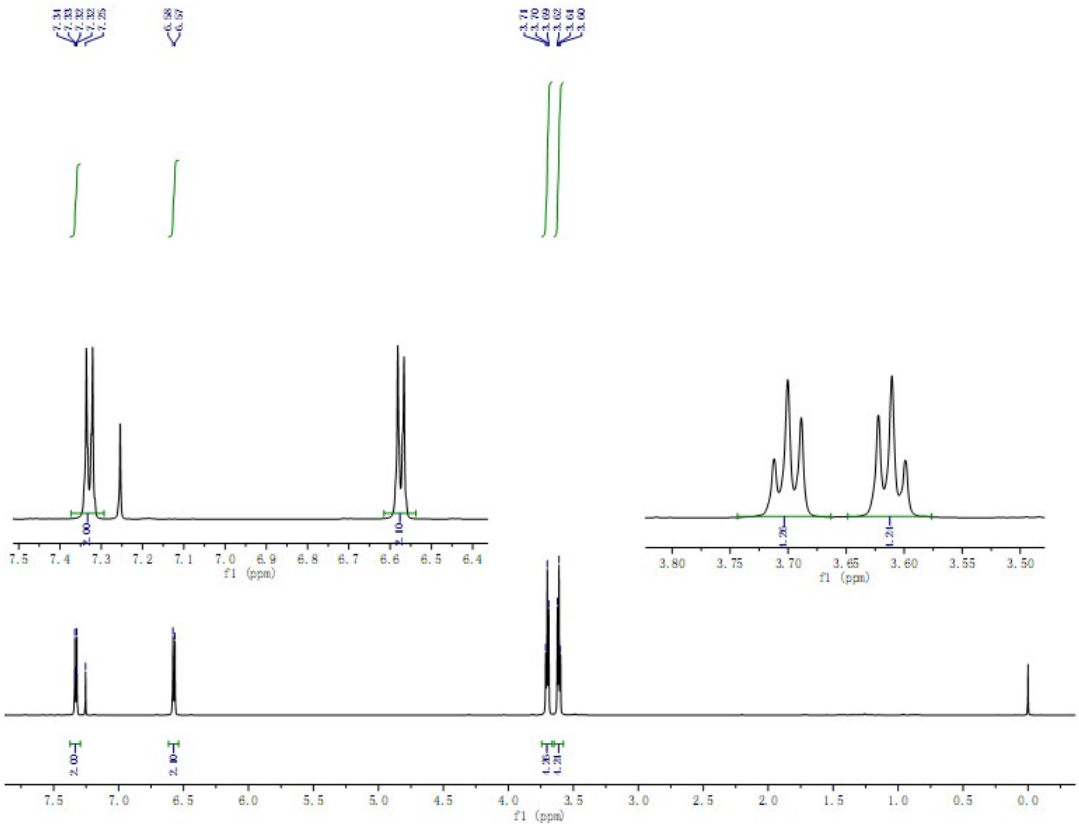


Figure S9. ^{1}H NMR spectrum of **1b** in $CDCl_3$

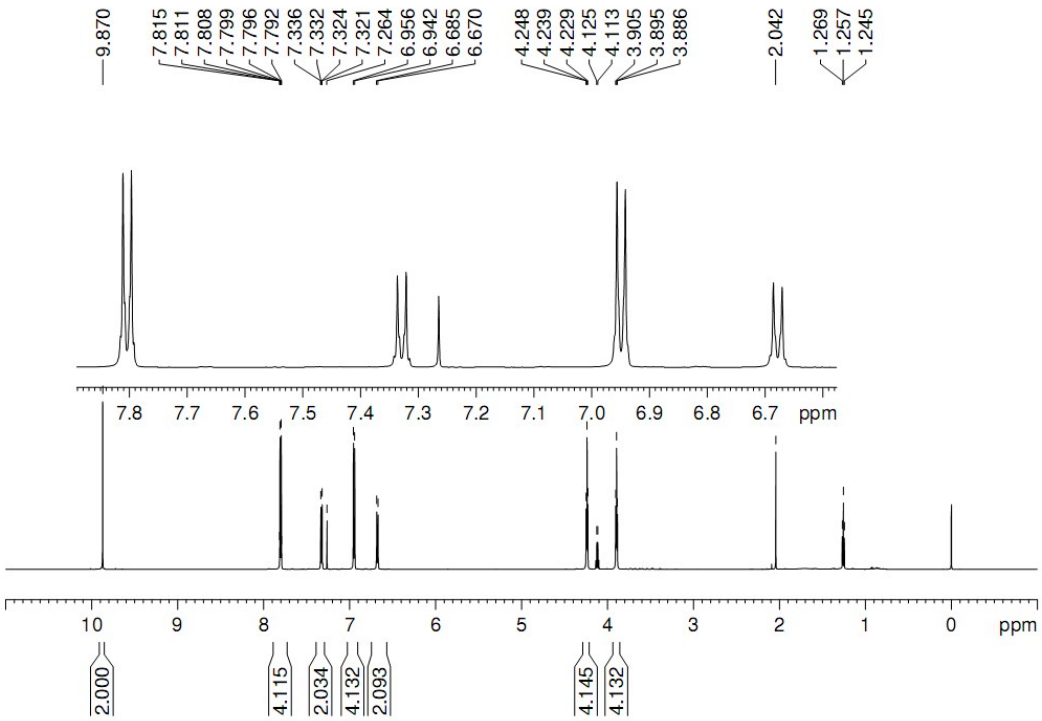


Figure S10. ^{1}H NMR spectrum of **1c** in $CDCl_3$

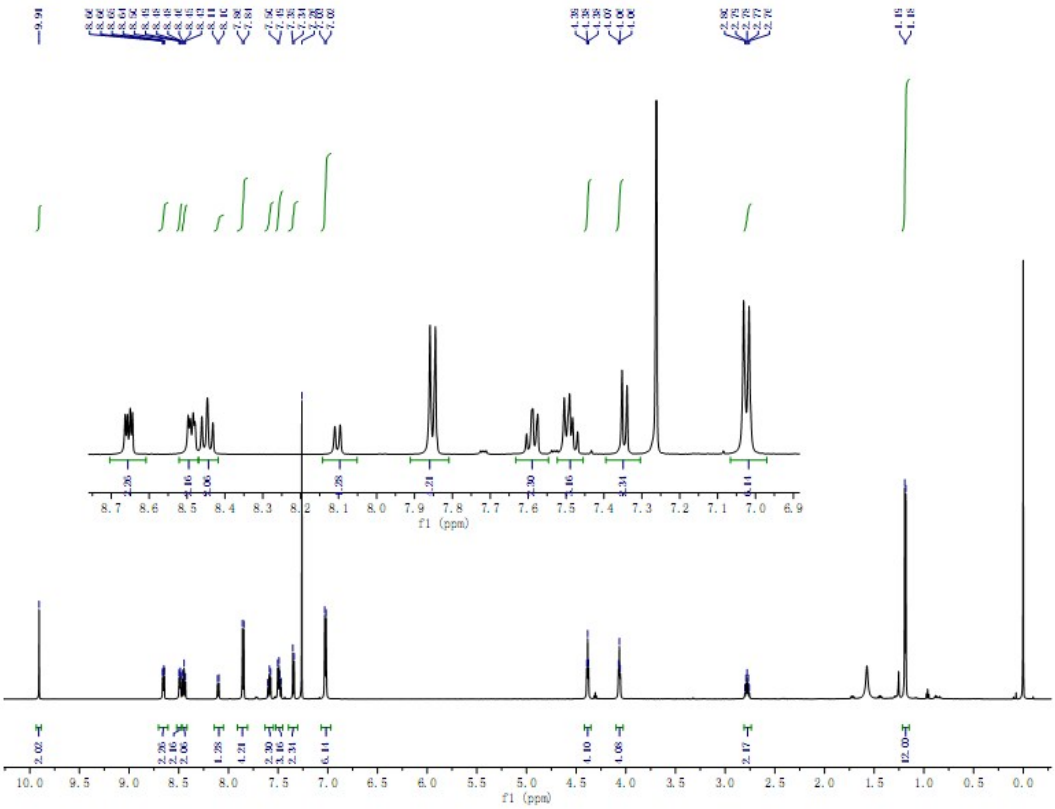


Figure S11. ^{1}H NMR spectrum of **1d** in $CDCl_3$

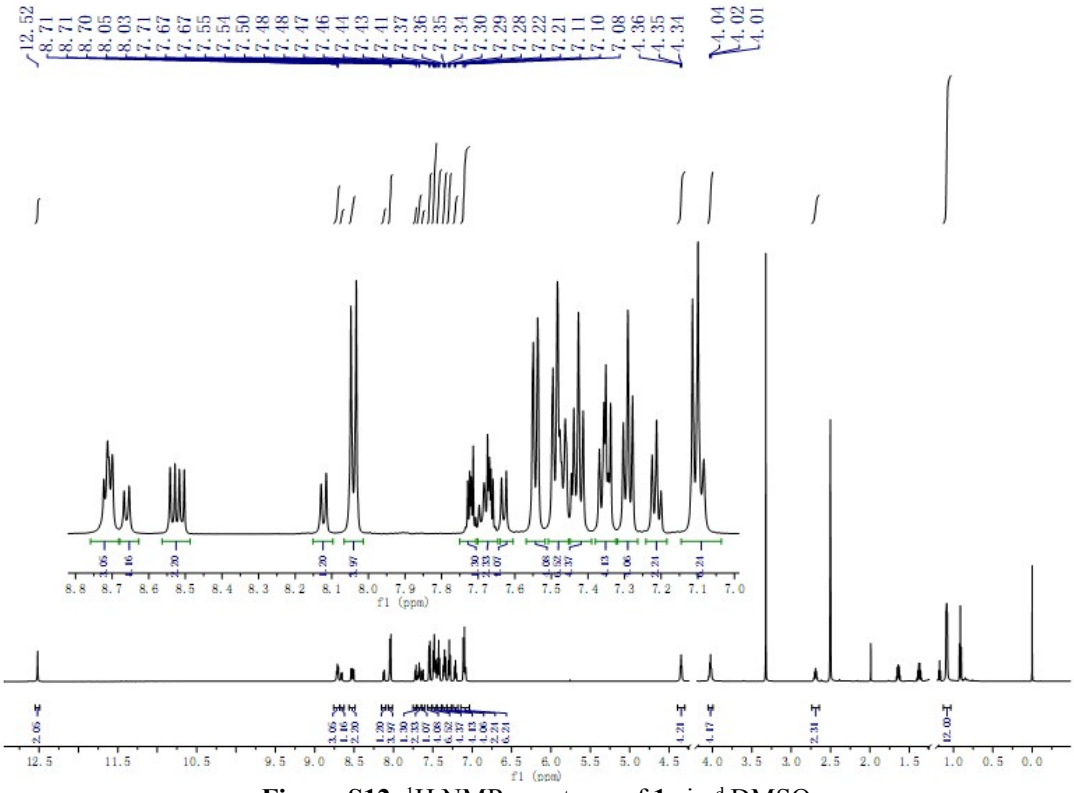


Figure S12. ^{1}H NMR spectrum of **1e** in ^{d}-DMSO

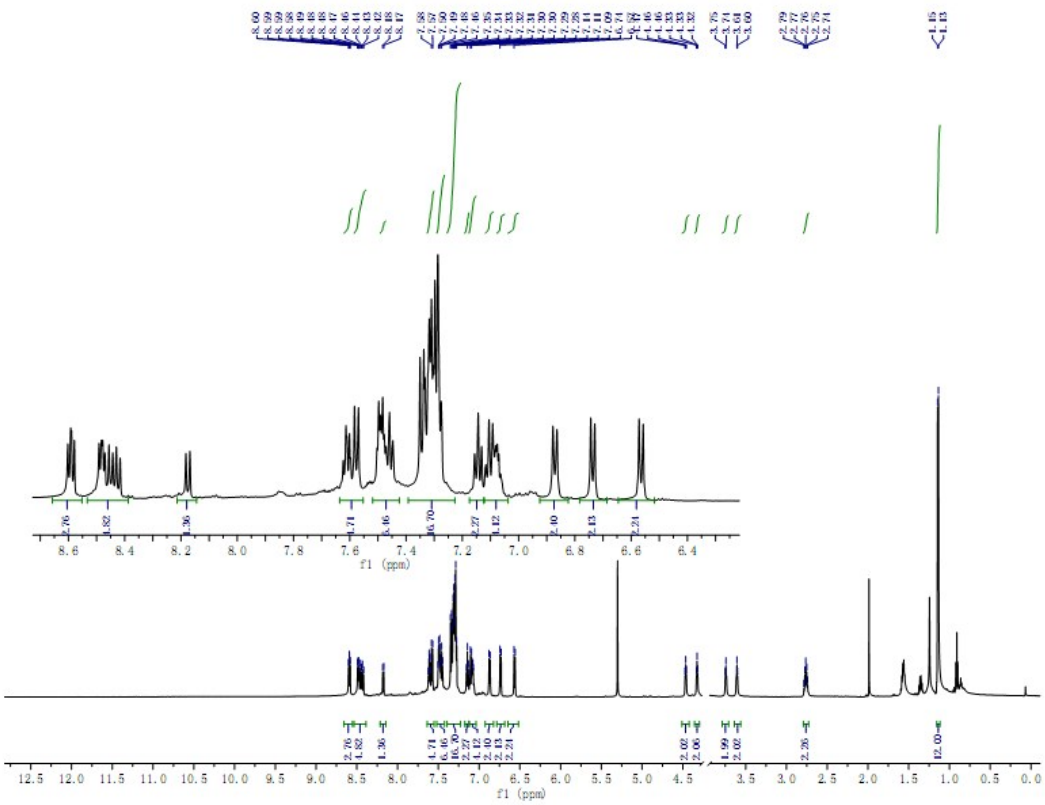


Figure S13. ^{1}H NMR spectrum of **PMI-N-HABI** in CD_2Cl_2

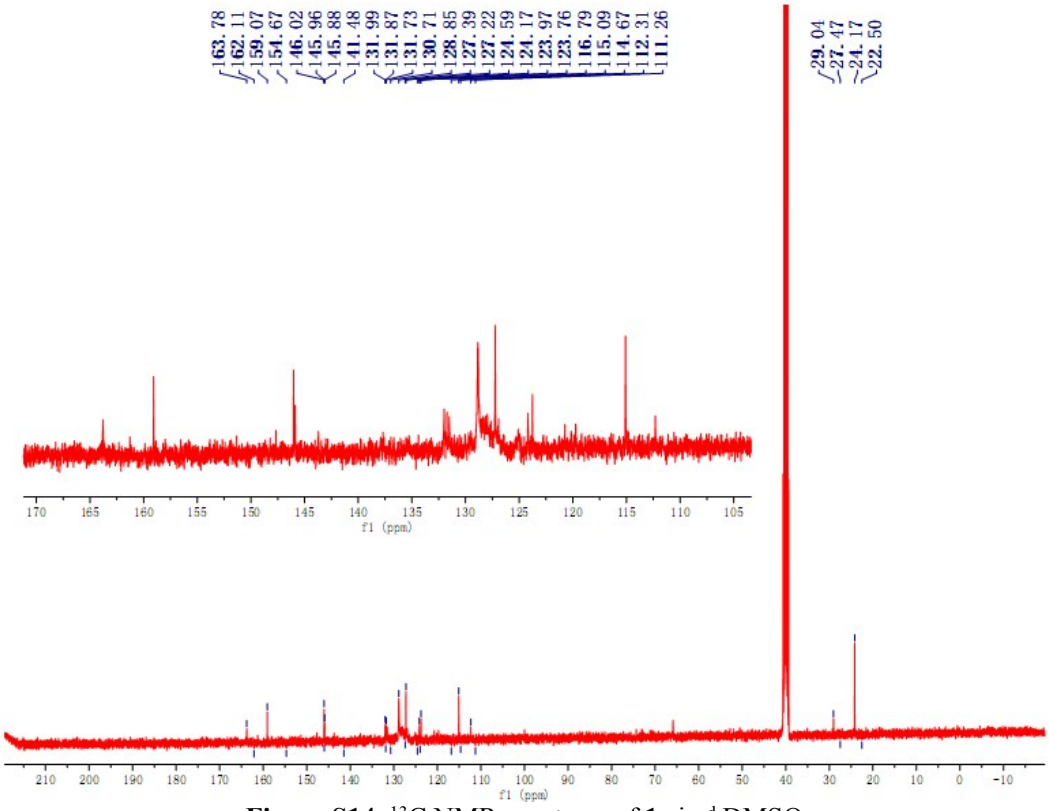


Figure S14. ^{13}C NMR spectrum of **1e** in ^{d}-DMSO

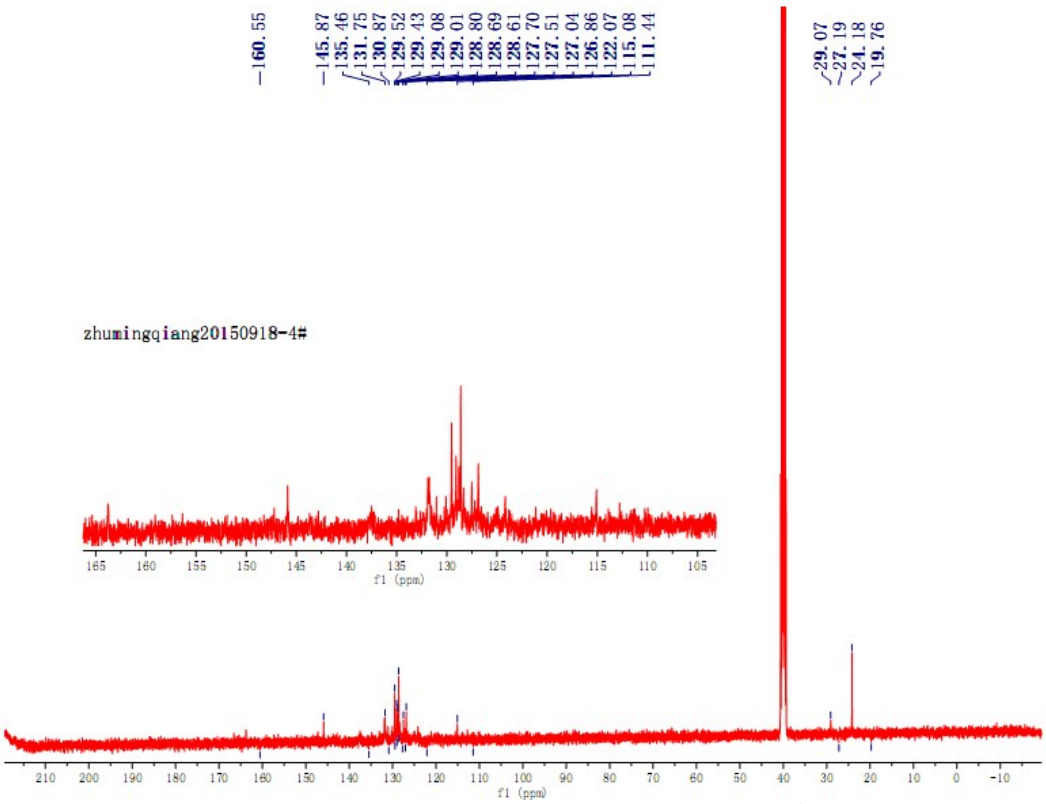


Figure S15. ^{13}C NMR spectrum of **PMI-N-HABI** in ^{d}-DMSO

MALDI-TOF **spectra of PMI-N-2TPI and PMI-N-HABI**

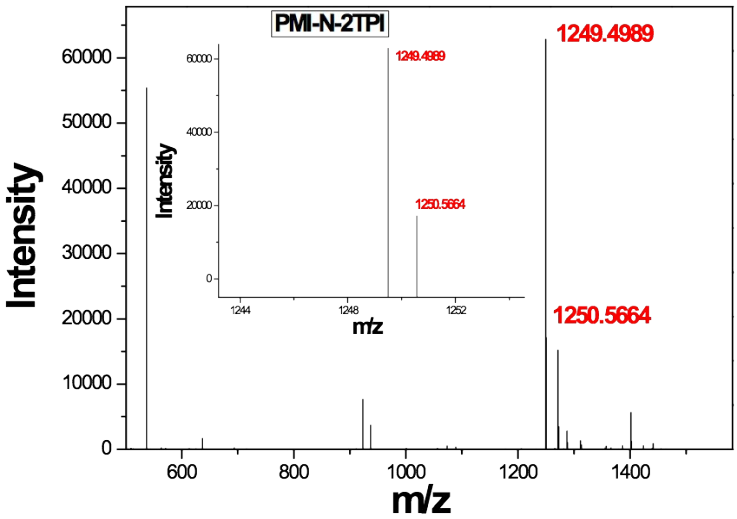


Figure S16. [1]Malti-tof spectrum of **1e**

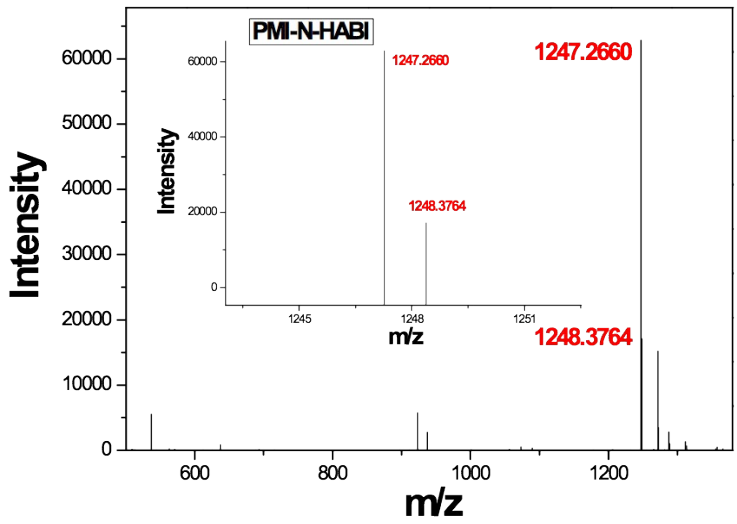


Figure S17. [1]Malti-tof spectrum of **PMI-N-HABI**

8. References

1. Feiler, L.; Langhals, H.; Polborn, K.; *Liebigs Ann.* **1995**, 1229- 1244;