

Electronic Supplementary Information (ESI)

Design, Synthesis and Photoswitching of Broad-Spectrum Fluorescent Hexaarylbiimidazoles

Wen-Liang Gong, Zu-Jing Xiong, Chong Li, Ming-Qiang Zhu*

Table of Contents

1. Experimental
2. Fluorescence spectra measurements
3. Decay profile of C₈H₁₇-O-HABI, Cz-O-HABI, NI-O-HABI and PMI-O-HABI in PMMA film
4. Fluorescent lifetime spectra of Cz-O-HABI, NI-O-HABI and PMI-O-HABI in benzene and PMMA films
5. ¹H NMR and ¹³C NMR spectra
6. Mass spectra
7. **References**

1. Experimental

Materials

All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were purchased from Aladdin, Acros Organics and Pu yang Hui cheng Chemical Co. All reactions were carried out under a dry nitrogen atmosphere unless water was used as a solvent or reagent and the temperatures were measured externally. Benzene was dried over CaH₂ with stirring overnight followed by distillation under reduced pressure. Reported yields are isolated yields. Purification of most intermediates and all final products was accomplished in most cases by gravity column chromatography, using silica gel. For qualitative purity tests of all intermediates and final products, a single spot is visualized using UV-light at 254 nm and 365 nm was obtained.

Characterization

¹H NMR spectra (Bruker AV400) were reported in parts per million (PPM) relative to tetramethylsilane as an internal standard. Elemental analysis (Elementar Vario Micro-cube) was used for quantitative purity analysis of all final products. The mass spectra were recorded at an ESI Ion-Trap mass spectrometer (Agilent 1100 series SL LC/MSD (Trap) CA, USA). MALDI TOF mass spectra were recorded with a MALDI-TOF (Bruker ultrafleXtreme). UV absorbance spectra were recorded with an UV-3600 UV-VIS-NIR spectrophotometer (Shimadzu) at a wavelength scan rate of 4 nm/s. The absorbance changes from photochromism of HABI into 2, 4, 5-triphenylimidazolyl radicals (TPIR) were obtained after subtraction of the absorbance spectra between final TPIR and original HABI. Fluorescence spectra of HABIs were recorded with a FLS920 spectrophotometer (Edinburg) at a wavelength scan rate of 2 nm/s. The emission intensity changes from photochromism of HABIs into TPIRs were obtained upon continuous irradiation (excitation). The 302 nm UV irradiation for the photochromic reaction was performed by using an ultraviolet transmission platform (with 4 ultraviolet tubes, each 8W and 220 V, the measured power is about 0.85 mW/cm²).

Synthetic procedures

4-octyloxy-benzaldehyde (1a): 4-hydroxy-benzaldehyde (5.0g, 0.041mol), n-octyl bromide (8.7g, 0.045mol) and potassium carbonate (17.0g, 0.123mol) were dispersed in 150ml dry DMF in a two-neck flask. The mixture was stirred and heated to 90°C under nitrogen atmosphere for 12h. After the reaction finished, the organic was washed with water and extracted with dichloromethane (3×100ml). Then the organic was concentrated and purified by column chromatography on silica gel with 50%DCM-50%PE as eluent. 9.2g colorless oil was obtained, yield 96%. ¹H NMR (CDCl₃): δ 9.71 (s, 1H), 7.64 (d, 2H, J = 8.4Hz), 6.81 (d, 2H, J = 8.56Hz), 3.85 (t, 2H, J=6.52Hz), 1.63 (m, 2H), 1.0-1.4 (m, 10H), 0.77 (t, 3H, J = 7Hz), MS (APCI) calcd 234.33, found 234.35.

2-(4-octyloxy)-4,5-triphenyl-imidazole (1b): 4-octyloxy-benzaldehyde (2.0g, 0.0085mol), benzil (2.1g, 0.01mol) and ammonium acetate (13.1g, 0.17mol) were dispersed in 50ml acetic acid. The mixture was stirred and heated to 90°C for 12h. After the reaction finished, the organic was washed with water and extracted with dichloromethane (3×100ml). Then the organic was concentrated and purified by column chromatography on silica gel with 50%DCM-50%PE (v-v) as eluent. 3.2g white solid was obtained, yield 88%. ¹H NMR (d⁶-DMSO): δ 12.47 (s, 1H), 8.0 (d, 2H, J = 8.8Hz), 7.56 (d, 2H, J = 8.4Hz), 7.50 (d, 2H, J = 8.56Hz), 7.44 (t, 2H, J = 7.24Hz), 7.37 (m, 1H), 7.31 (t, 2H, J = 7.72Hz), 7.22 (m, 1H), 7.03 (d, 2H, J = 8.8Hz), 4.02 (t, 2H, J=6.52Hz), 1.76 (m, 2H), 1.44 (m, 2H), 1.2-1.34 (m, 8H), 0.88 (t, 3H, J = 7Hz). MS (APCI) calcd 424.58, found 424.36.

C₈H₁₇-O-HABI (1): All manipulations were carried out with exclusion of UV light. Under N₂, 2-(4-octyloxy)-4, 5-triphenyl-imidazole (2.9g, 0.0068mol) was dissolved in 100mL benzene. An aqueous solution of 22.4g K₃Fe(CN)₆ and 7.6g KOH in 100mL distilled water was added into dropwise in 30min. Soon the solution changed from colorless to deep blue green. The mixture was stirred at room temperature for 1 day. After the reaction finished, the organic layer was washed with distilled water. The water layer was extracted by benzene (3×50mL), and then combined. Then dried in MgSO₄, filtered, evaporated the solvents, blue green solid was obtained. This solid was recrystallized from mixture of toluene and acetonitrile, 1.8g yellow needles formed, yield 62%. ¹H NMR (d²-dichloromethane): δ 8.29 (d, 2H, J = 8.8Hz), 7.71 (d, 2H, J = 7.32Hz), 7.50 (d, 2H, J = 8.12Hz), 7.34 (m, 3H), 7.22 (t, 2H, J = 7.84Hz), 6.9-7.17 (m, 10H), 6.76 (t, 4H, J = 7.8Hz), 6.61 (m, 1H), 6.44 (d, 2H, J = 8.72Hz), 4.04 (t, 2H, J = 6.56Hz), 3.79 (m, 2H), 1.81 (m, 2H), 1.64 (m, 2H), 1.47 (m, 2H), 1.1-1.37 (m, 18H), 0.84 (m, 6H). ¹³C NMR (CDCl₃): δ 191.20, 173.42, 162.59, 158.86, 149.67, 138.71, 134.56, 133.80, 132.75, 132.20, 131.62, 131.51, 131.17, 130.52, 130.03, 129.94, 128.48, 128.32, 127.96, 127.86, 127.27, 126.39, 123.75, 114.54, 113.47, 113.35, 99.47, 68.30, 67.95, 31.85, 29.38, 29.27, 29.09, 26.10, 25.96, 22.71, 22.69, 14.14; MS (APCI) calcd 847.14, found 848.52; Elemental analysis (expected, %) C, 82.23; H, 7.38; N, 6.61; O, 3.78; (obtained, %) C, 82.33; H, 7.32; N, 6.59; O, 3.8;

2a: The synthesis procedure of **2a** is according to the former report literature.¹

2b: 2a (1.5 g, 4.5 mmol), 4-hydroxybenzaldehyde (1.1 g, 9 mmol) and potassium carbonate (2.5 g, 18 mmol) were dispersed in 50 ml distilled DMF in a two-neck 100ml flask. The system is extracted and pumped into N₂ for few times and then stirred and heated to 100°C for 1 day. After the reaction finished, the solution was poured into distilled water and extracted by dichloromethane (3×50 mL). After that, dried in MgSO₄, filtered, evaporated the solvents and further purified by simple column chromatography on silica gel with dichloromethane-petroleum=70%-30% (v-v) as eluent. 1.5g white solid was obtained, yield 90%. ¹H NMR (CDCl₃): δ 9.84 (s, 1H), 8.10 (d, 2H, J = 7.72 Hz), 7.78 (d, 2H, J = 8.76 Hz), 7.46 (m, 2H), 7.39 (d, 2H, J = 8.16 Hz), 7.24 (m, 2H), 6.89 (d, 2H, J=8.72 Hz), 4.30 (t, 2H, J=7.04 Hz), 3.91 (m, 2H), 1.92 (m, 2H), 1.75 (m, 2H), 1.50 (m, 4H). MS (APCI) calcd 371.47, found 371.23.

2c: 2b (1.0 g, 2.7 mmol), benzil (1.1 g, 5.4 mmol) and ammonia acetate (4.1 g, 54 mmol) were dispersed in 30mL acetic acid in a 50ml two-neck flask. The mixture was heated to 90°C and stirred for 1day. After the reaction finished, the liquid was poured into 100mL saturated salt water, white precipitate formed. Then filtered, washed with distilled water, dried and further purified by

simple column chromatography on silica gel with dichloromethane as eluent. 1.3g white solid was obtained, yield 86%. ¹H NMR(^d-DMSO): δ12.49 (s, 1H), 8.16 (d, 2H, J = 7.72 Hz), 8.00 (d, 2H, J = 8.8 Hz), 7.62 (d, 2H, J = 8.2 Hz), 7.55 (d, 2H, J = 7.28 Hz), 7.4-7.51 (m, 6H), 7.38 (m, 1H), 7.32 (t, 2H, J = 7.28 Hz), 7.23 (m, 3H), 6.98 (d, 2H, J = 8.88 Hz), 4.43 (t, 2H, J = 6.96 Hz), 3.97 (t, 2H, J = 6.28 Hz), 1.85 (m, 2H), 1.71 (m, 2H), 1.3-1.5 (m, 4H). MS (APCI) calcd 561.71, found 562.31.

Cz-O-HABI (2): All manipulations were carried out with exclusion of UV light. Under N₂, **2c** (0.6 g, 1 mmol) was dissolved in 100mL benzene. An aqueous solution of 8.2 g K₃Fe(CN)₆ and 2.8 g KOH in 50 mL distilled water was added into dropwise in 30 min. Soon the solution changed from colorless to deep blue. The mixture was vigorously stirred at room temperature for 1 day. After the reaction finished, the organic layer was washed with distilled water. The water layer was extracted by benzene (3×50 mL), and combined. Then dried in MgSO₄, filtered, evaporated the solvents, 0.48 g light blue solid was obtained, yield 80%. ¹H NMR (^d-DMSO): δ8.16 (d, 4H, J = 7.72 Hz), 8.00 (d, 4H, J = 8.8 Hz), 7.62 (d, 4H, J = 8.2 Hz), 7.55 (d, 4H, J = 7.28 Hz), 7.4-7.51 (m, 12H), 7.38 (m, 2H), 7.32 (t, 4H, J = 7.28 Hz), 7.23 (m, 6H), 6.98 (d, 4H, J = 8.88 Hz), 4.43 (t, 4H, J = 6.96 Hz), 3.97 (t, 4H, J = 6.28 Hz), 1.85 (m, 4H), 1.71 (m, 4H), 1.3-1.5 (m, 8H); ¹³C NMR (CDCl₃): δ140.43, 131.41, 129.32, 127.97, 127.77, 125.67, 122.84, 120.43, 120.36, 118.78, 114.52, 108.64, 42.95, 28.94, 27.06, 25.91; MS (MALDI-TOF) calcd 1121.41, found 1121.52; Elemental analysis (expected, %) C, 83.54; H, 6.11; N, 7.49; O, 2.85; (obtained, %) C, 83.42; H, 6.09; N, 7.51; O, 2.84;

The synthetic procedures of **4a** and **4b** are according to previously reported literature.²

4c: 4b (1.3 g, 2.3 mmol) and N-(2-hydroxyethyl)-piperazine (21.0 g, 161 mmol) are dispersed in 20ml DMSO. The mixture was stirred and heated to 150 °C for 6 h under N₂. Then the mixture was cooled to room temperature. The deep purple liquid was added into 200 ml distilled water dropwise and extracted by ethyl acetate (200 ml×3). The solution was dried over MgSO₄, filtered and after removing the solvent, dark purple solid was obtained. This solid was washed with 5% KOH (aq) and double distilled water to remove excess solvent and piperazine. The solid residue was dried under vacuum overnight. The dried solid was then dissolved in CH₂Cl₂, purified by column chromatography over silica gel by eluent of 4% methanol in CH₂Cl₂, and 0.94 g dark purple solid was obtained, yield 66%. ¹H NMR (CDCl₃, 400 MHz): δ 8.67 (m, 2H), 8.52 (d, 1H, J = 7.4 Hz), 8.46 (d, 2H, J = 8.2 Hz), 8.39 (d, 1H, J = 8 Hz), 8.28 (d, 1H, J = 8.36 Hz), 7.70 (t, 1H, J = 7.8 Hz), 7.51 (t, 1H, J = 8 Hz), 7.37 (d, 2H, J = 7.6 Hz), 7.2-7.3 (m, 1H, covered by solvent peak at δ 7.26), 3.82 (m, 2H), 3.38 (m, 4H), 3.01 (m, 4H), 2.7-2.9 (m, 4H), 1.21 (d, 12H, J = 6.64 Hz). Mass (APCI) calcd 609.78 found 609.82.

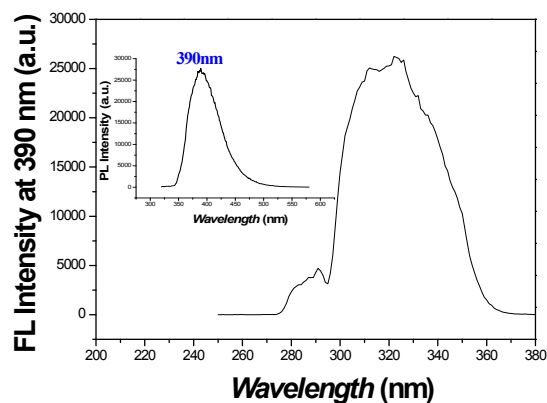
4d: 4c (0.6 g, 1 mmol) is dissolved in 10mL distilled chloroform in atmosphere of ice water (0-5 °C). Phosphorus (III) bromide (PBr₃) (0.14 mL, 1.5 mmol) is added into this solution dropwise in 10min. The mixture is stirred at 0-5 °C for another 30 min, then heated to reflux for 6 h. After the reaction is finished, silica gel is added. After the solvent is removed, the residue was directly used for purification by silica gel column chromatography with 6% methanol in dichloromethane as eluent (v/v). 0.58 g dark purple solid was obtained, yield 87%. ¹H NMR(CDCl₃, 400 MHz): δ 8.64 (t, 2H, J = 7.88 Hz), 8.48 (d, 1H, J = 7.72 Hz), 8.42 (m, 2H), 8.34 (d, 1H, J = 8.28 Hz), 8.24 (d, 1H, J = 8.32 Hz), 7.66 (t, 1H, J = 7.88 Hz), 7.49 (t, 1H, J = 7.72 Hz), 7.34 (d, 2H, J = 7.8 Hz), 7.2-7.3(m, 1H, covered by solvent peak δ 7.26), 3.58(m, 2H), δ 3.33(m, 4H), 2.85-3.15 (m, 6H), 2.28 (m, 2H), 1.19 (d, 12H, J = 6.64 Hz). Mass (APCI) 672.65 found 673.12.

4e: 4d (0.4g, 0.6mmol), 4-hydroxybenzaldehyde (0.7g, 6mmol) and potassium carbonate (0.5g, 3.6mmol) are dissolved in 10mL distilled DMF (N,N-dimethylformamide). The system is extracted and pumped into N₂ for few times and then stirred and heated to 100 °C for 1 day. After the reaction is finished, the solvent is removed by reduced pressure distillation and followed by column chromatography on silica gel with 6% methanol in dichloromethane (v/v) as eluent, 0.40g dark purple solid was obtained, yield 93%. This solid is directly used for next step.

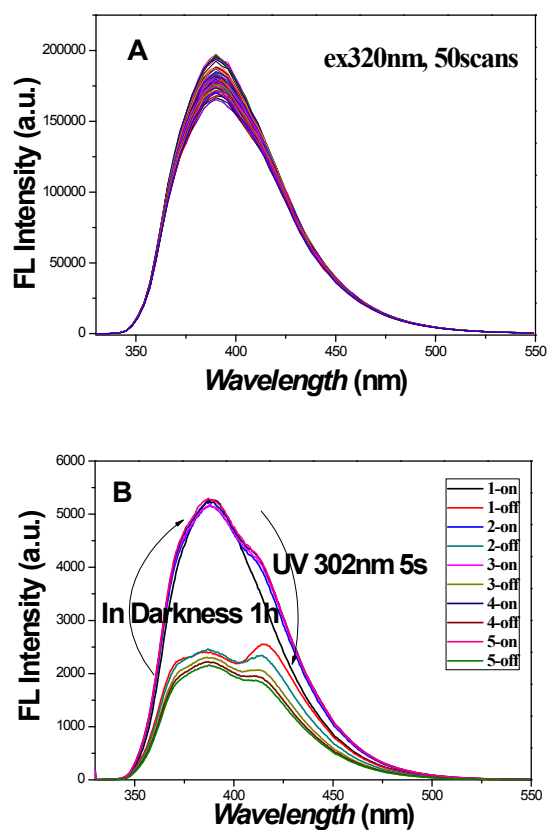
4f: 4e (0.4 g, 0.56 mmol), benzyl (0.47 g, 2.2 mmol) and ammonium acetate (0.86 g, 11.2 mmol) are dissolved in 40 mL acetic acid. The reaction mixture is stirred and heated to 90 °C for 1 day. After the reaction is finished, the mixture is dropped into saturated NaHCO₃ aqueous (100 mL) solution and then extracted by dichloromethane (3×100 mL). The organic phase was washed with water (3×100 mL) and dried over MgSO₄. After the solvent was removed, the residue was purified by column chromatography on silica gel, with 6% methanol in dichloromethane (v/v) as eluent. After the solvent was removed under reduced pressure, compound **6** was obtained as a dark purple powder (0.44 g, 88%). ¹H NMR(^d-DMSO, 400 MHz): δ 12.49 (s, 1H), 8.77 (m, 2H), 8.69 (d, 1H, J = 8.4 Hz), 8.64 (d, 1H, J = 8.36 Hz), 8.55 (m, 2H), 8.28 (d, 1H, J = 8.52 Hz), 8.04 (d, 2H, J = 8.84 Hz), 7.79 (t, 1H, J = 7.84 Hz), 7.56 (d, 2H, J = 7.36 Hz), 7.51 (m, 2H), 7.46 (t, 2H, J = 7.44 Hz), 7.26-7.4 (m, 6H), 7.23 (m, 1H), 7.12 (d, 2H, J = 8.84 Hz), 4.26 (m, 2H), 3.25 (m, 4H), 2.8-3.0 (m, 6H), 2.69 (m, 2H), 1.09 (d, 12H, J = 6.84 Hz). Mass (MALDI-TOF): calcd 904.11 found 904.76.

PMI-O-HABI (4): 4f (0.40 g, 0.44 mmol), potassium ferricyanide (6.2 g, 18.8 mmol) and potassium hydroxide (3.1 g, 55.3 mmol) are dispersed in 40 mL benzene and 20 mL distilled water. The bottle is covered by aluminum foil and vigorously stirred at room temperature for 12 h. After the reaction is finished, the water layer is removed and the organic layer is washed with large amount of distilled water. Then it is dried, filtrated. After remove the solvent, 0.35 g dark purple solid is obtained, yield 88%. ¹H NMR (^d-dichloromethane, 400 MHz): δ 8.77 (m, 4H), 8.69 (d, 2H, J = 8.4 Hz), 8.64 (d, 2H, J = 8.36 Hz), 8.55 (m, 4H), 8.28 (d, 2H, J = 8.52 Hz), 8.04 (d, 4H, J = 8.84 Hz), 7.79 (t, 2H, J = 7.84 Hz), 7.56 (d, 4H, J = 7.36 Hz), 7.51 (m, 4H), 7.46 (t, 4H, J = 7.44 Hz), 7.26-7.4 (m, 12H), 7.23 (m, 2H), 7.12 (d, 4H, J = 8.84 Hz), 4.26 (m, 4H), 3.25 (m, 8H), 2.8-3.0 (m, 12H), 2.69 (m, 4H), 1.09 (d, 24H, J = 6.84 Hz); ¹³C NMR (CDCl₃): δ164.08, 145.71, 131.95, 129.67, 128.60, 124.04, 120.75, 119.87, 119.17, 29.20, 29.09, 24.08, 24.02; Mass (MALDI-TOF): calcd 1806.19 found 1806.019; Elemental analysis (expected, %) C, 81.13; H, 5.80; N, 7.75; O, 5.31; (obtained, %) C, 81.10; H, 5.82; N, 7.71; O, 5.34;

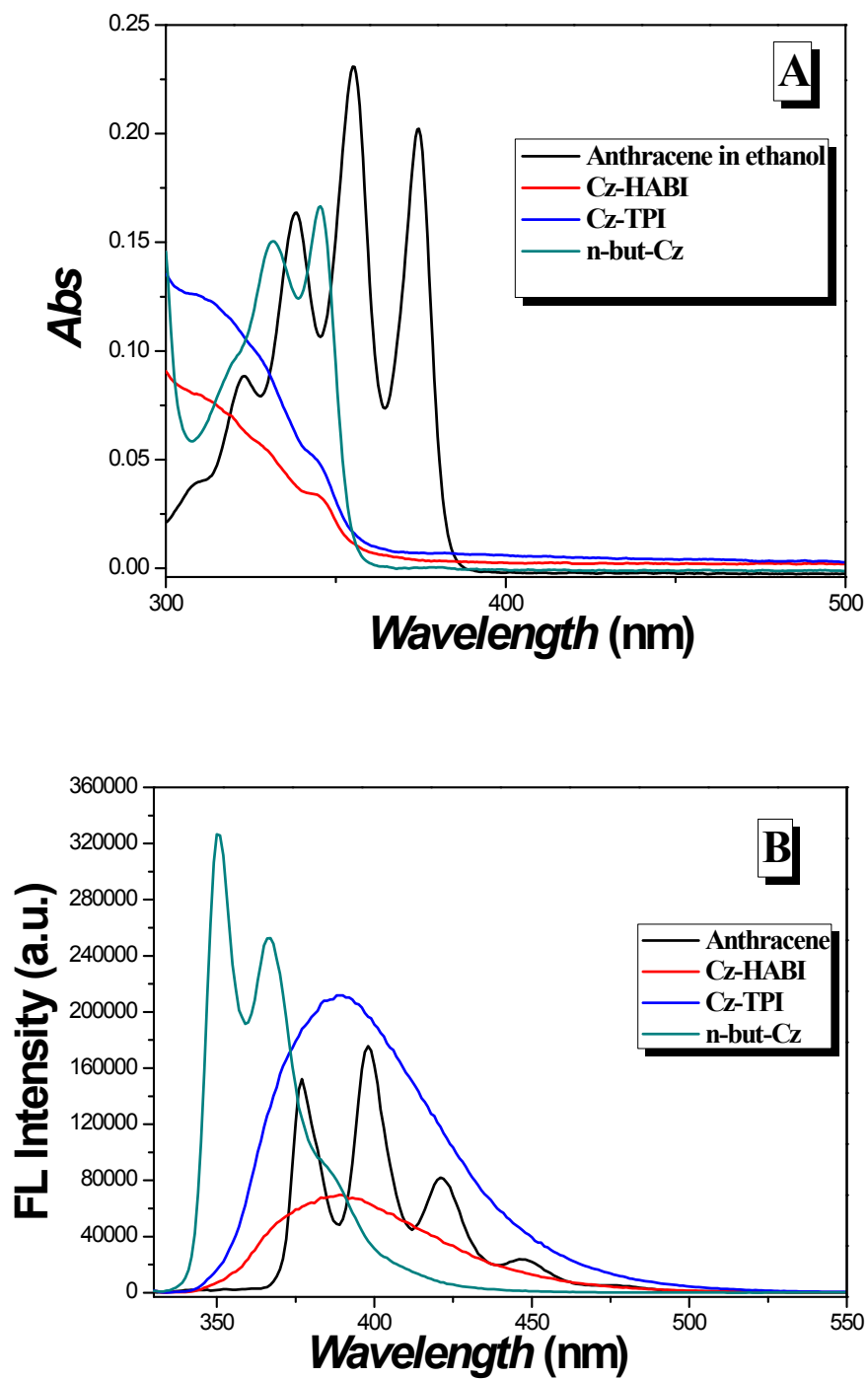
2. Fluorescent spectra measurements



FigureS1. Excitation spectrum of Cz-O-HABI (5×10^{-5} mol/L) in benzene, inset the FL spectra of Cz-O-HABI, $\lambda_{\text{ex}} = 300$ nm, excitation bandwidth and emission bandwidth 1 and 1.



FigureS2. (A) Fluorescent spectra of Cz-O-HABI (5×10^{-5} mol/L) in benzene under $\lambda_{\text{ex}} = 320$ nm for 50 continuous scans, the excitation bandwidth and emission bandwidth 1 and 1; (B) FL spectra of Cz-O-HABI (5×10^{-5} mol/L) in benzene for reversibility, first irradiated under 302 nm for 5 s and then put in darkness for 1 h as a cycle, 5 cycles in total;



FigureS3. (A) FL and (B) UV-Vis spectra of Cz-O-TPI, Cz-O-HABI and n-but-Cz in benzene and Anthracene in ethanol for quantum yield calculation.

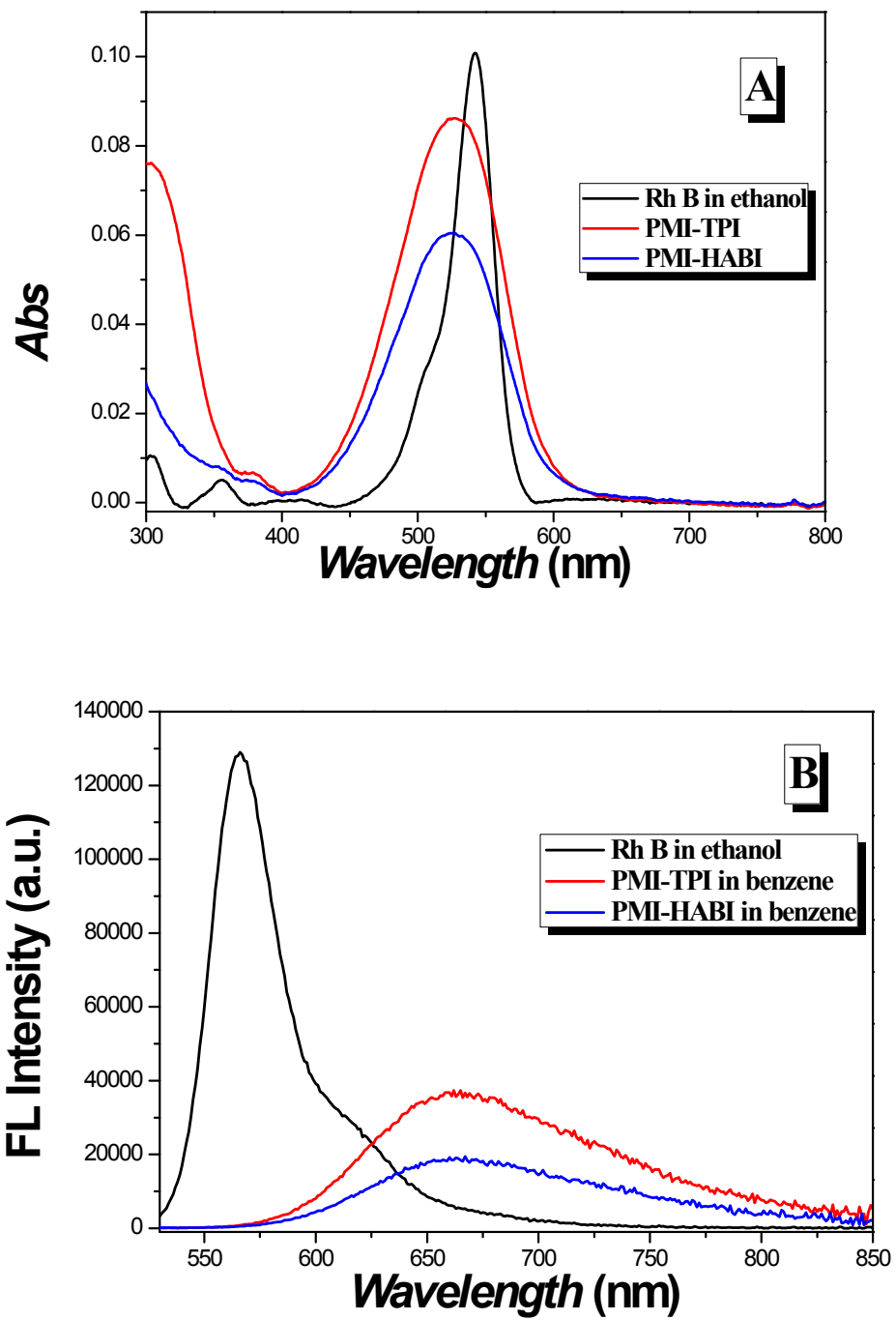


Figure S4. (A) FL spectra and (B) UV-Vis spectra of PMI-O-TPI, PMI-O-HABI in benzene and RhB in ethanol for quantum yield calculation.

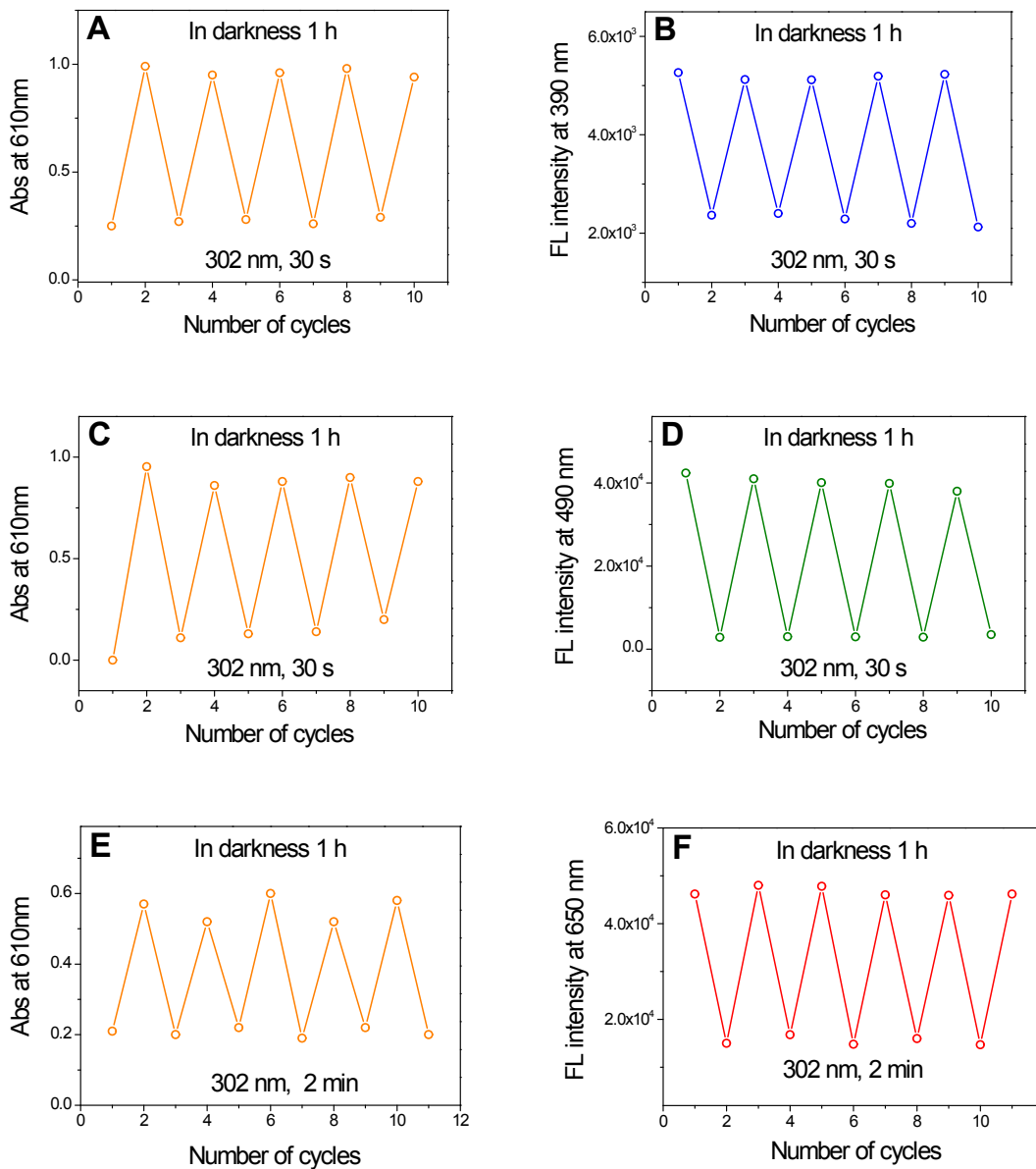


Figure S5. Cycling photochromism and fluorescence switching of Cz-O-HABI, NI-O-HABI and PMI-O-HABI in degassed benzene (5×10^{-5} mol/L). The measurements were performed at room temperature (25°C). Cz-O-HABI, the absorbance at 610 nm (**A**) the emission intensity at 390 nm (**B**); NI-O-HABI, the absorbance at 610 nm (**C**) the emission intensity at 490 nm (**D**); PMI-O-HABI, the absorbance at 610 nm (**E**) the emission intensity at 650 nm (**F**).

3. Decay profile of C₈H₁₇-O-HABI, Cz-O-HABI, NI-O-HABI and PMI-O-HABI in PMMA film

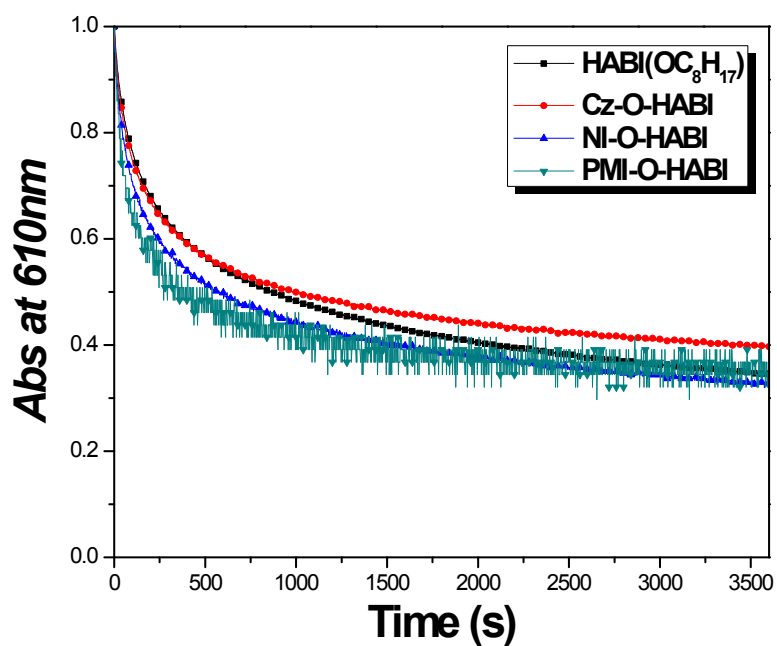


Figure S6. Decay profiles of the colored species generated from C₈H₁₇-O-HABI, Cz-O-HABI, NI-O-HABI and PMI-O-HABI, monitored at 610nm in PMMA films. The measurements were performed at room temperature (25 °C).

4. Fluorescent lifetime spectra of Cz-O-HABI, NI-O-HABI and PMI-O-HABI in benzene and PMMA films

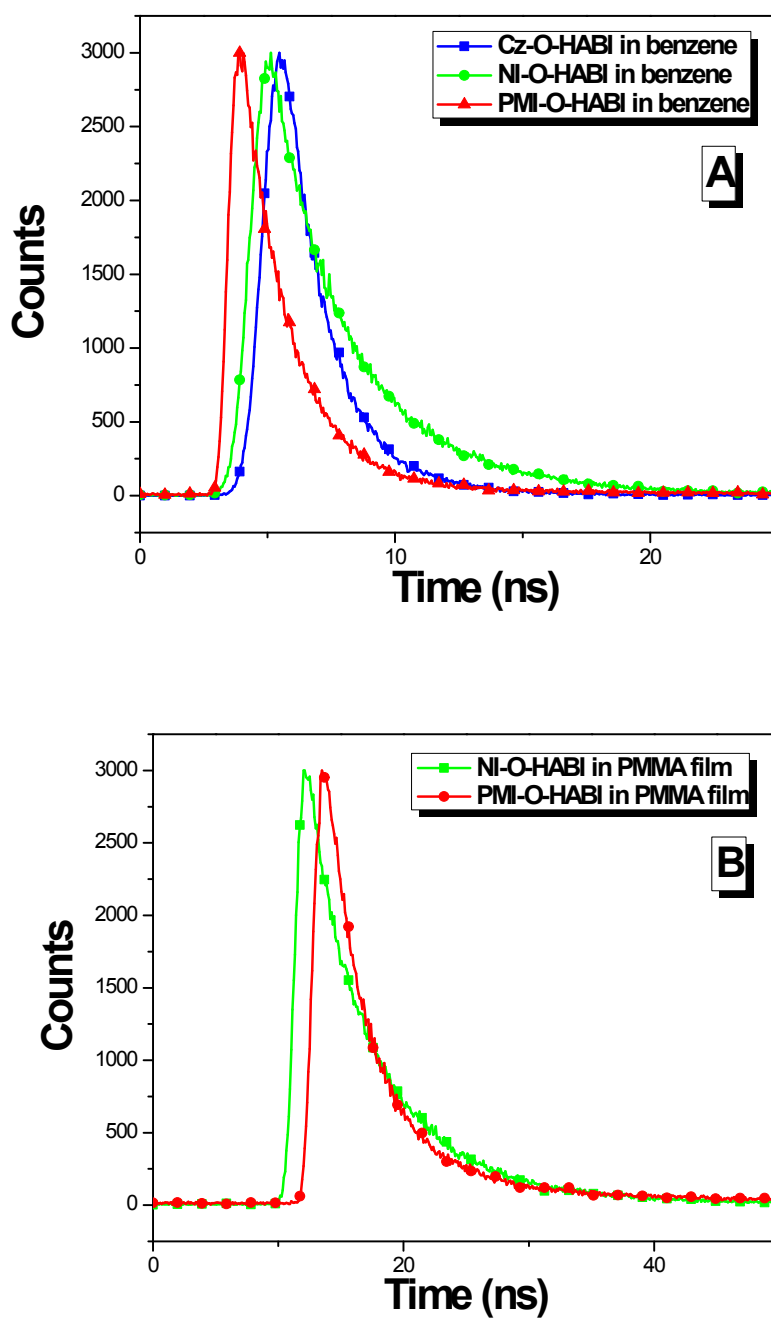
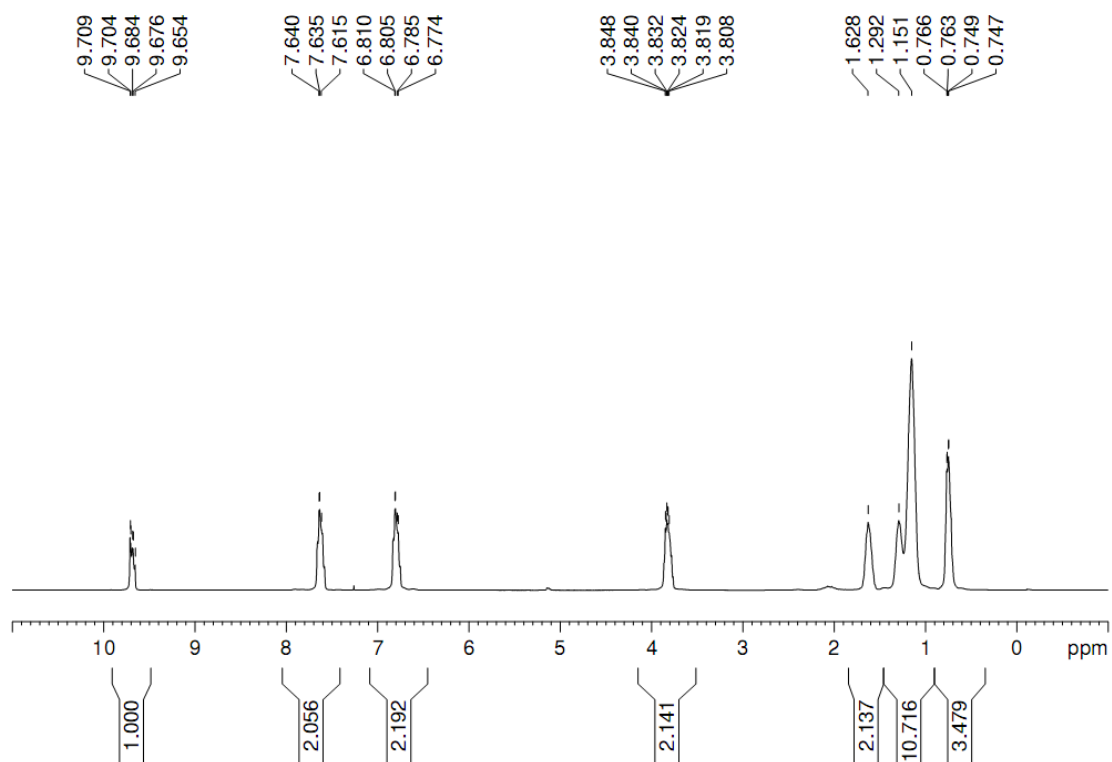
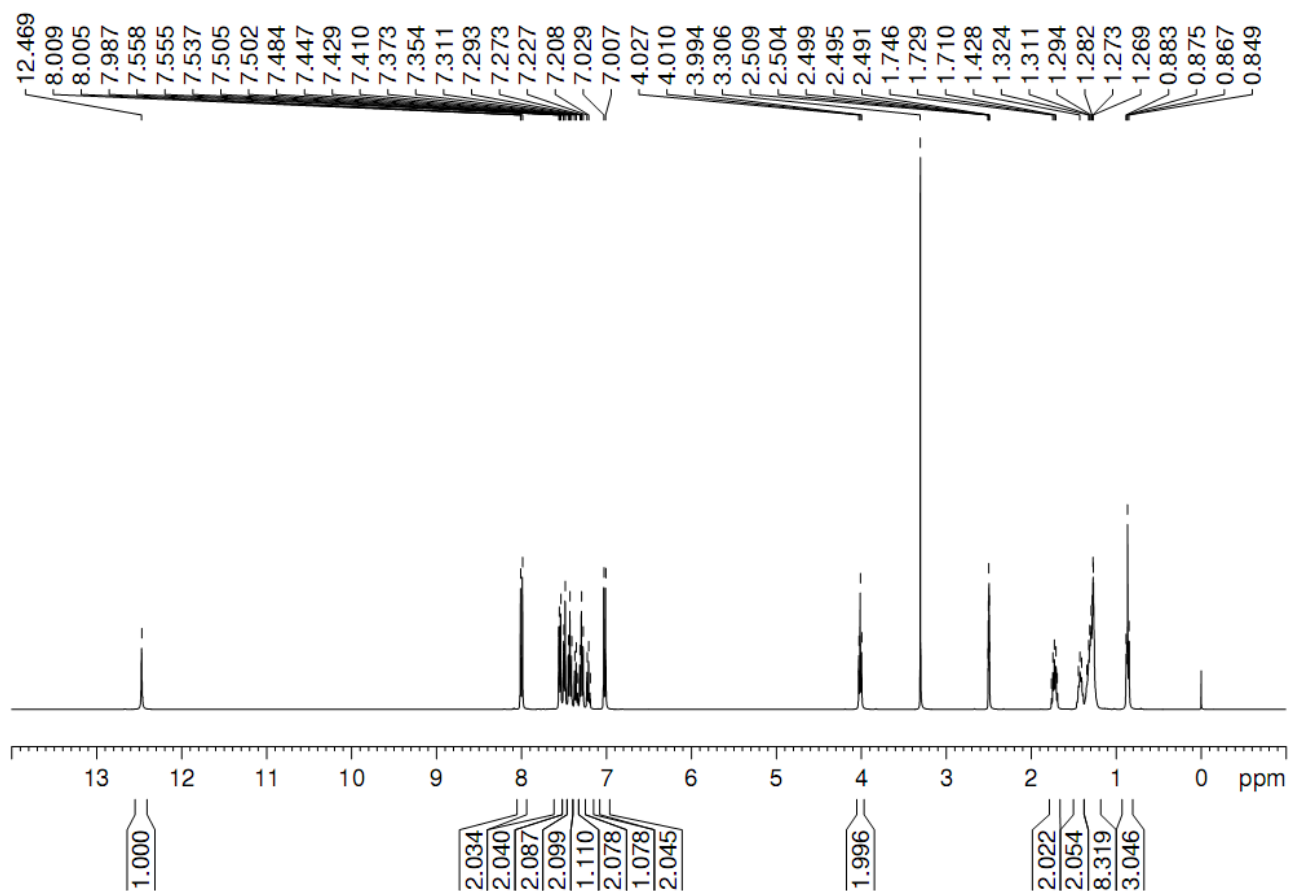


Figure S7. (A) Fluorescent lifetime spectra of Cz-O-HABI ($\tau = 1.87\text{ns}$, $\chi^2 = 1.828$), NI-O-HABI ($\tau = 3.33\text{ns}$, $\chi^2 = 1.886$) and PMI-O-HABI ($\tau_1 = 3.67\text{ns}$, $\tau_2 = 23.58\text{ns}$, $\chi^2 = 1.107$) in benzene solution; and (B) NI-O-HABI ($\tau = 6.11\text{ns}$, $\chi^2 = 2.208$) and PMI-O-HABI ($\tau_1 = 3.52\text{ns}$, $\tau_2 = 16.86\text{ns}$, $\chi^2 = 1.103$) in PMMA film.

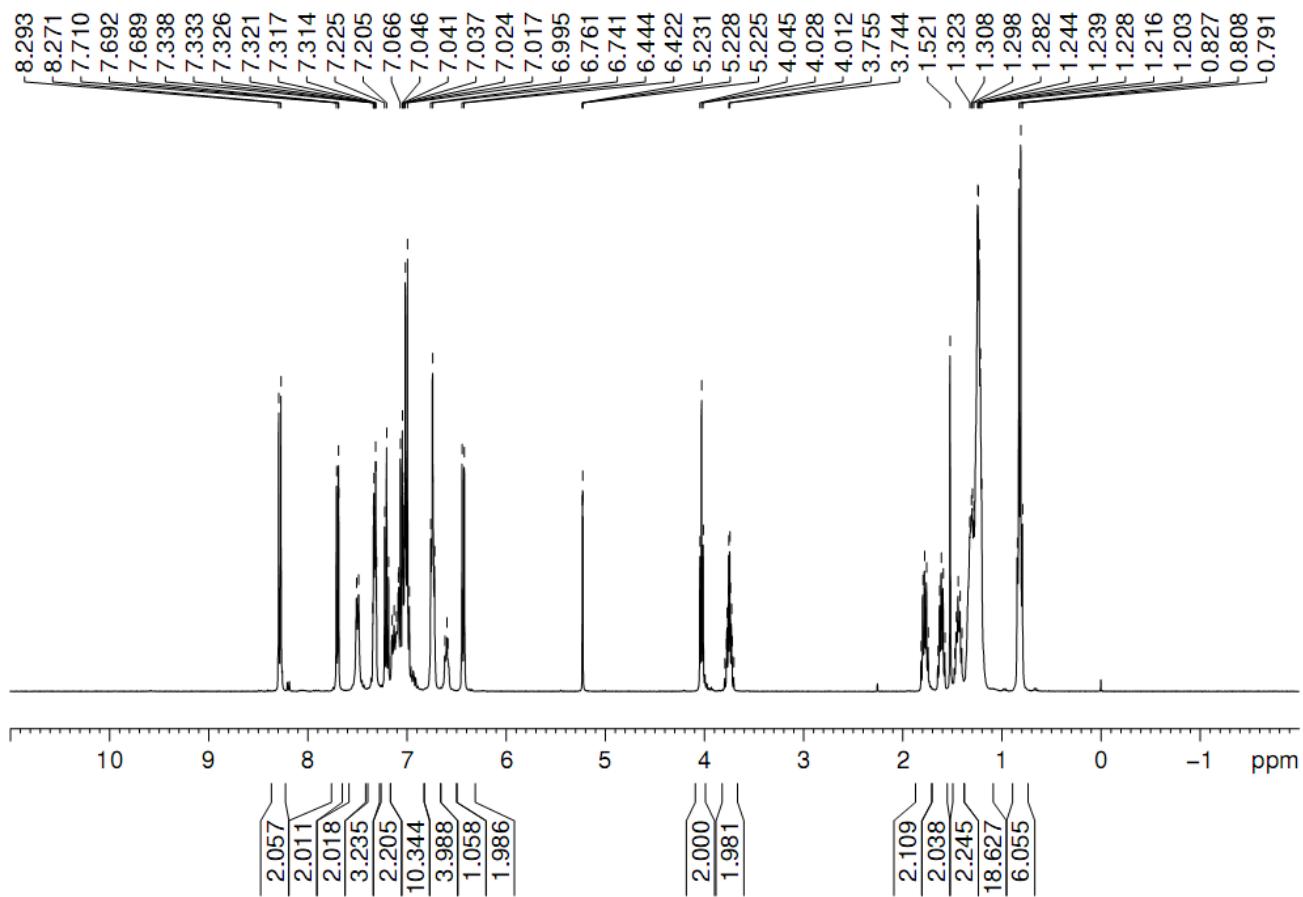
5. $^1\text{H-NMR}$ spectra



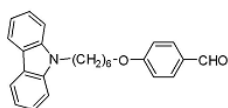
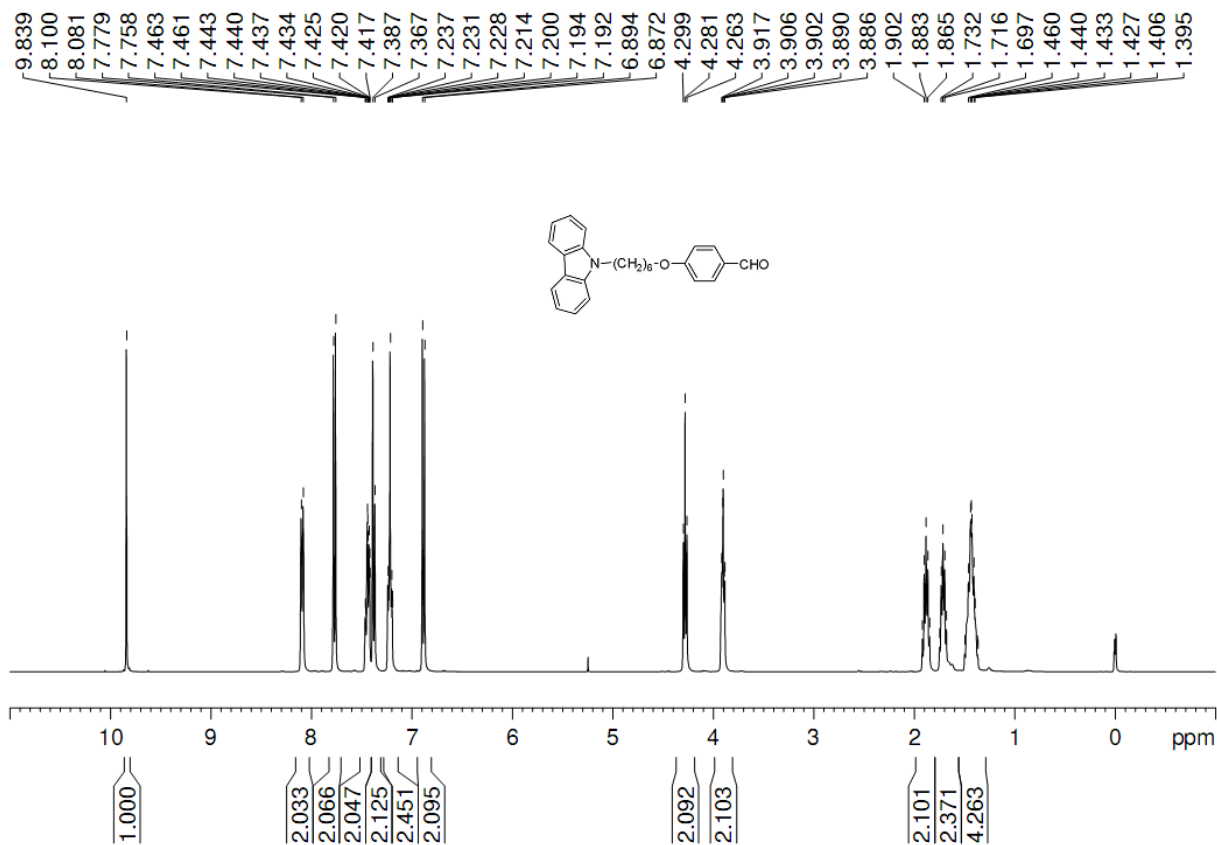
FigureS8. $^1\text{H-NMR}$ spectrum of 4-octyloxy-benzaldehyde in CDCl_3



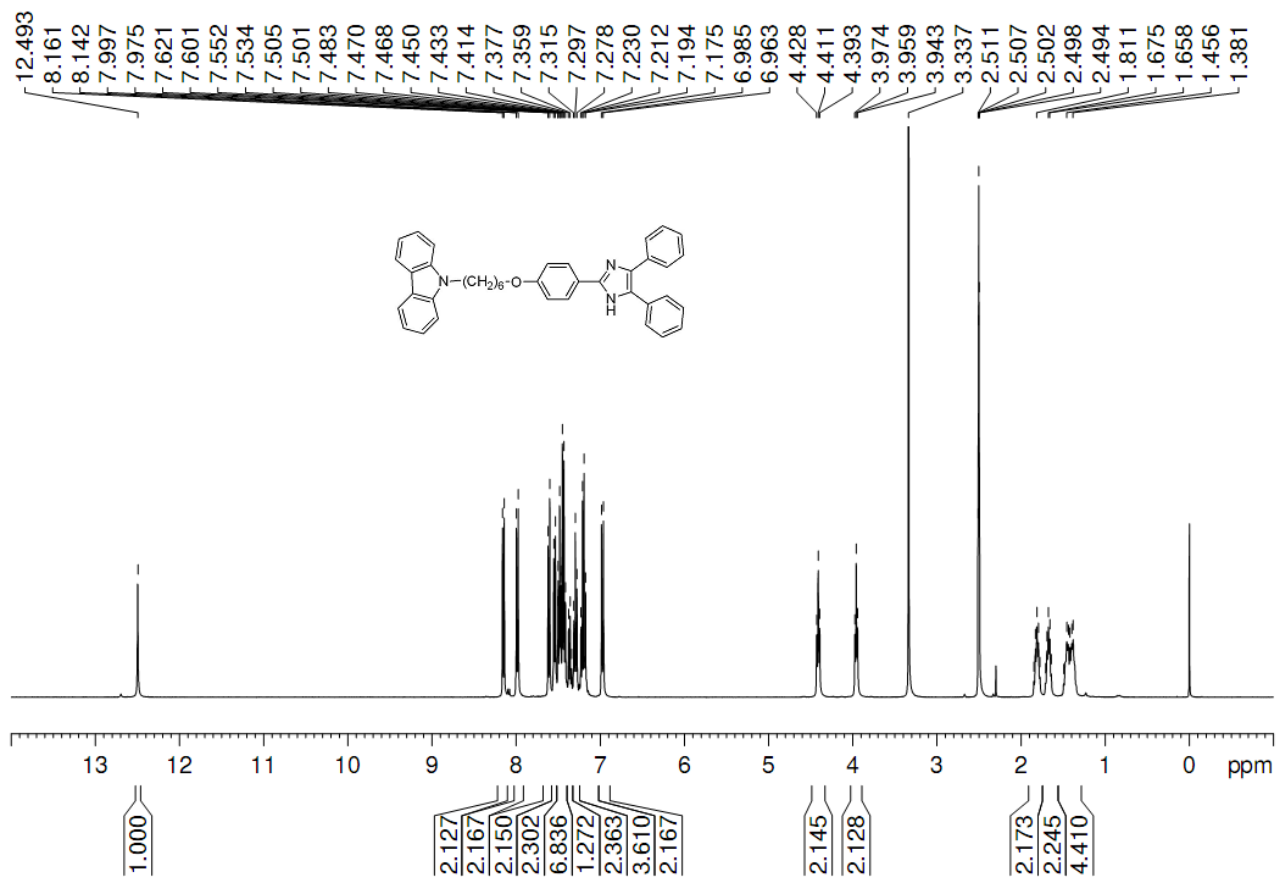
FigureS9. $^1\text{H-NMR}$ spectrum of 2-(4-octyloxy), 4, 5-triphenyl-imidazole in $d\text{-DMSO}$



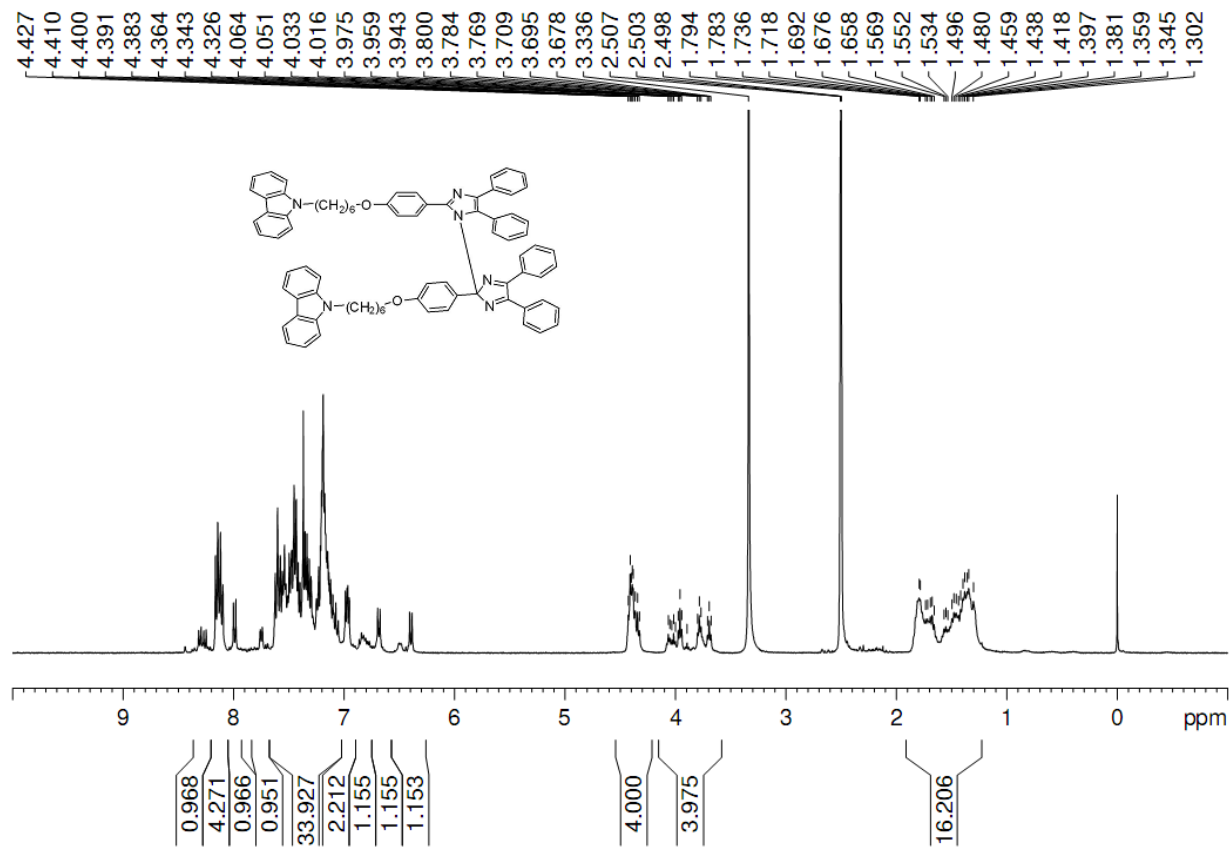
FigureS10. ^1H NMR spectrum of 1 $\text{C}_8\text{H}_{17}\text{-O-HABI}$ in d_4 -dichloromethane



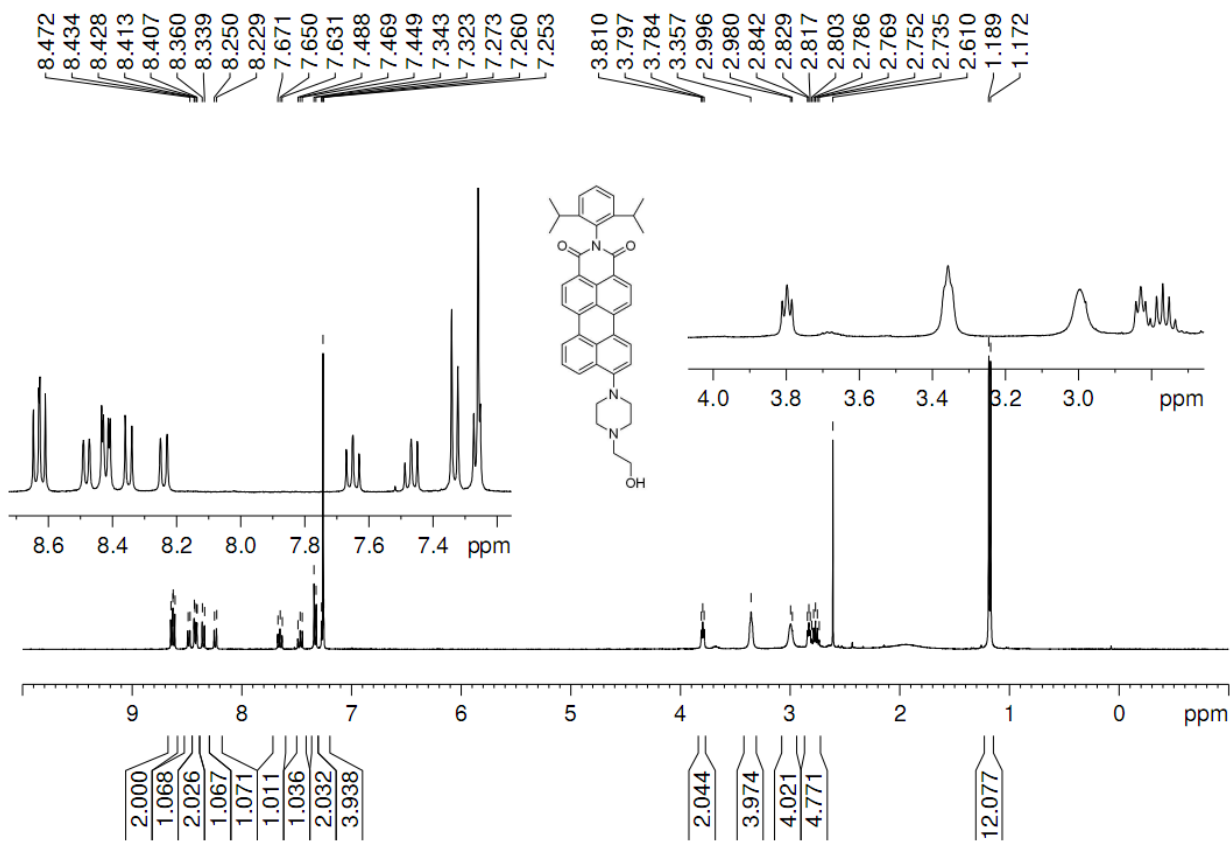
FigureS11. ^1H NMR spectrum of 2b in d_4 - CDCl_3



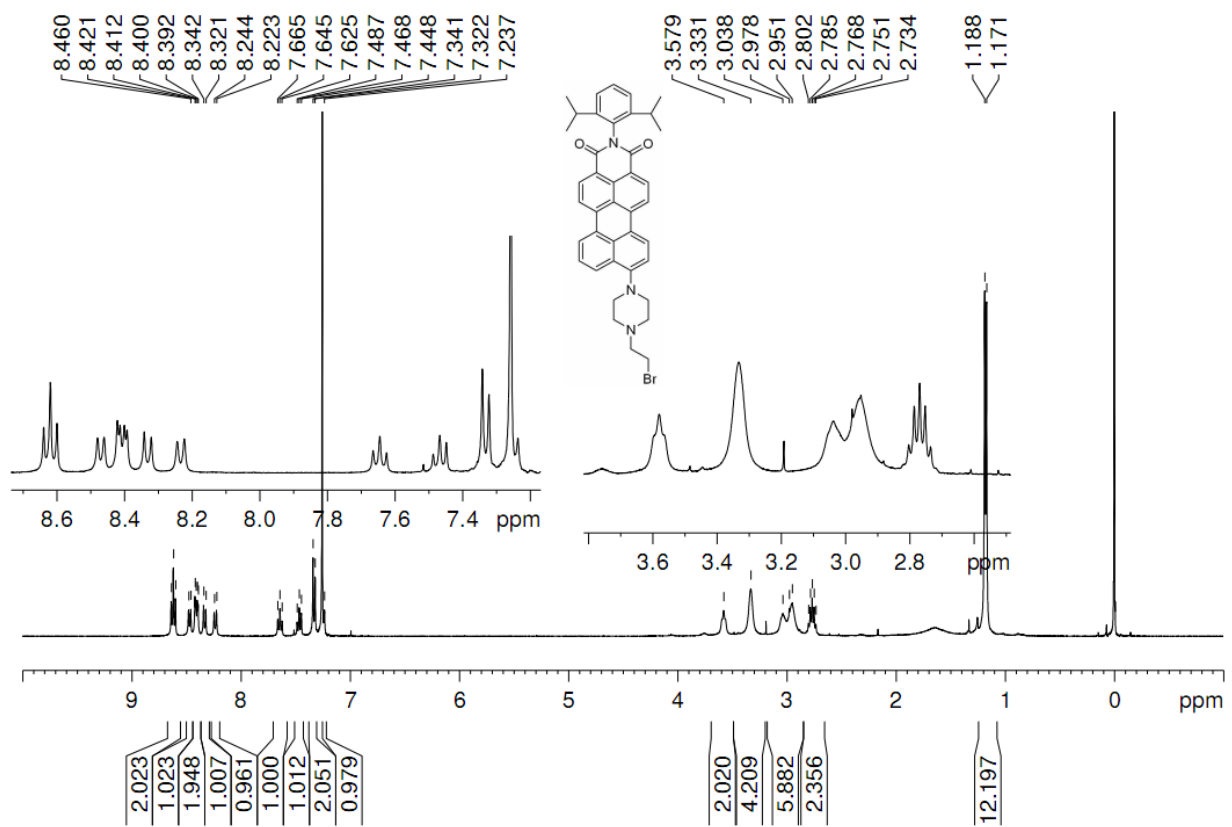
FigureS12. ¹H NMR spectrum of 2c in ^d4-DMSO



FigureS13. ¹H NMR spectrum of Cz-O-HABI in ^d4-DMSO



FigureS14. ¹H NMR spectrum of 4c in ^dCDCl₃



FigureS15. ¹H NMR spectrum of 4d in ^dCDCl₃

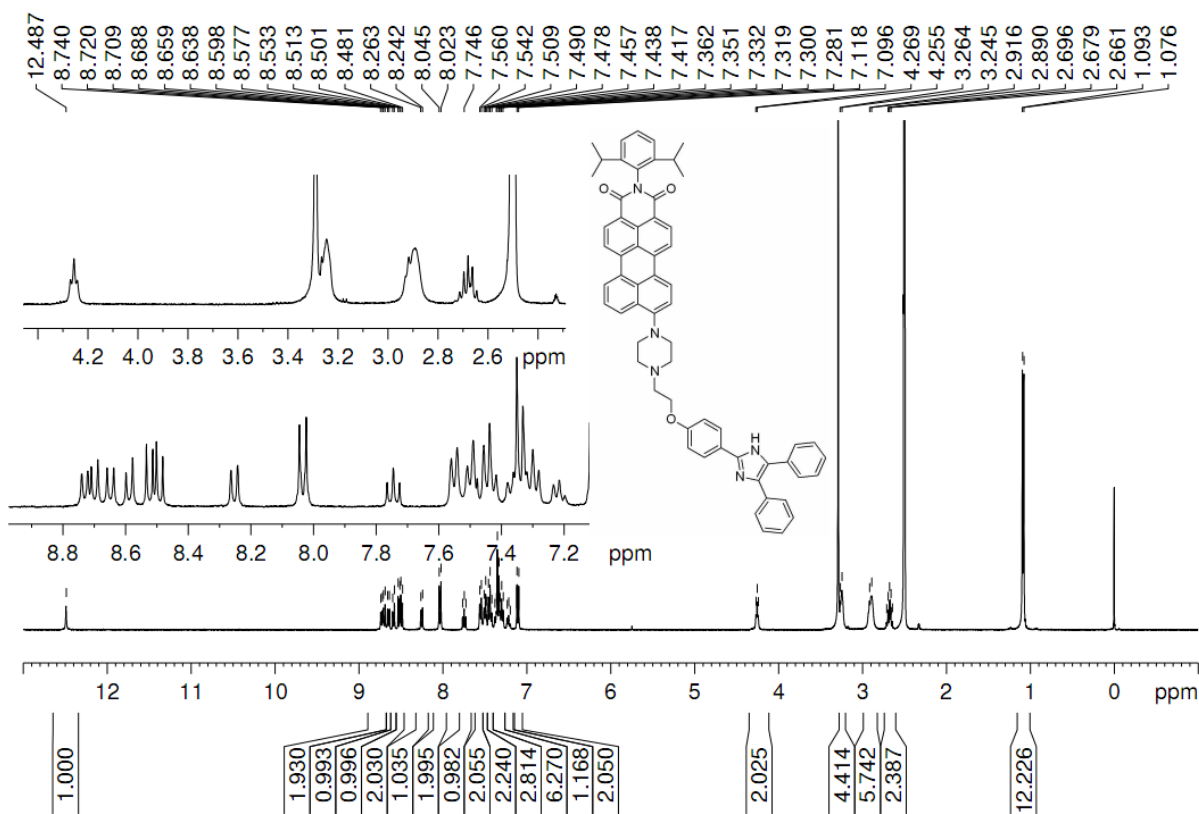


Figure S16. ¹H NMR spectrum of 4f in ^d-DMSO

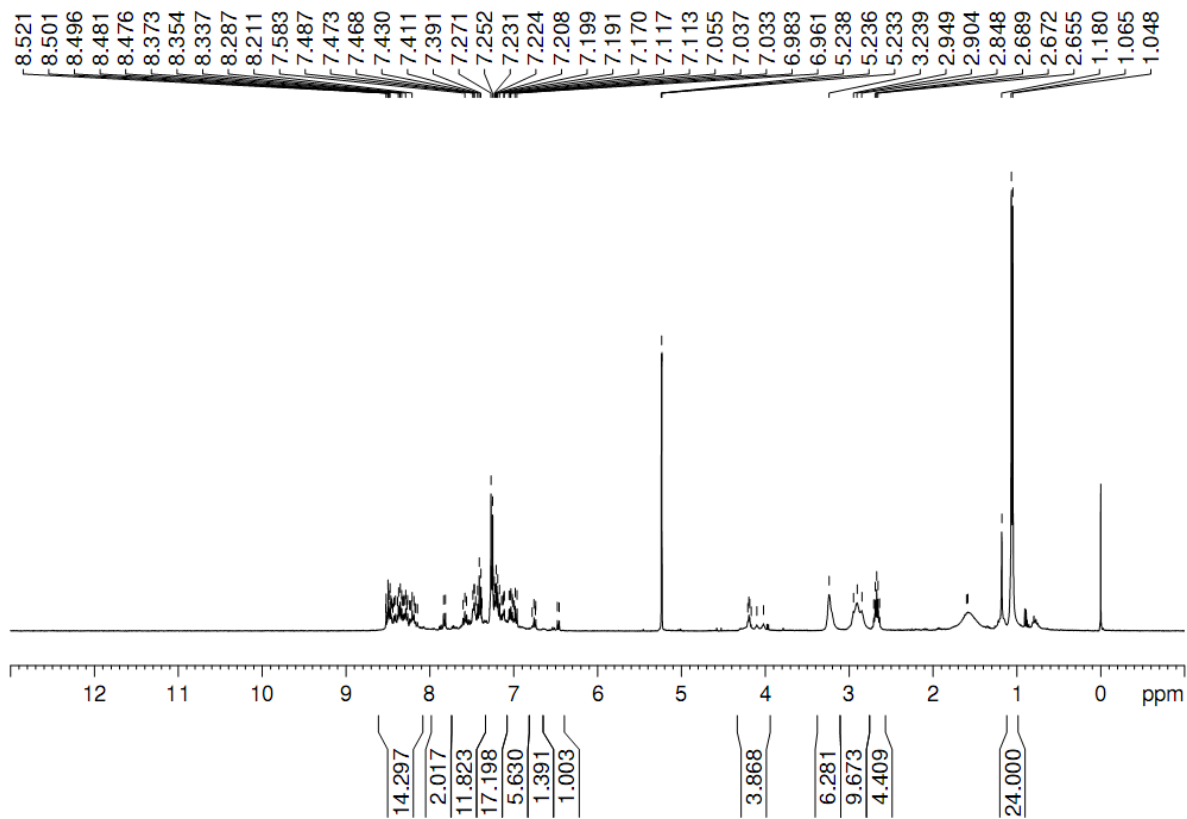
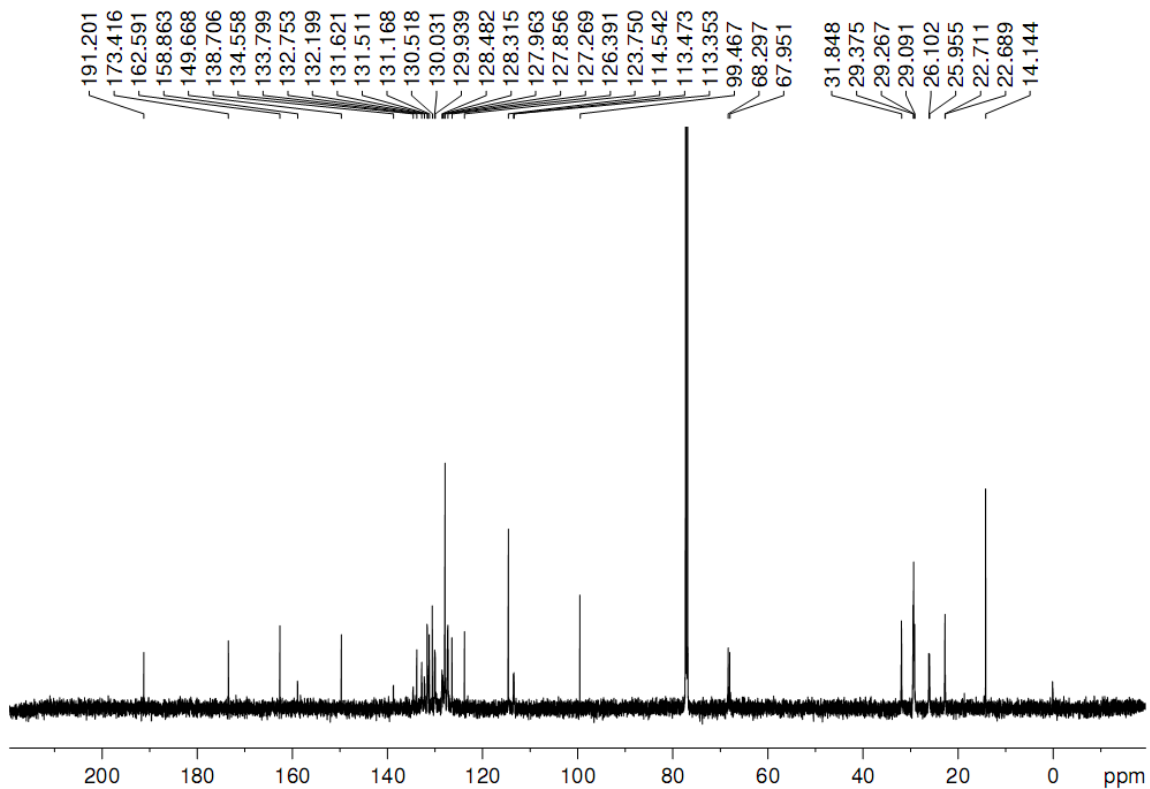
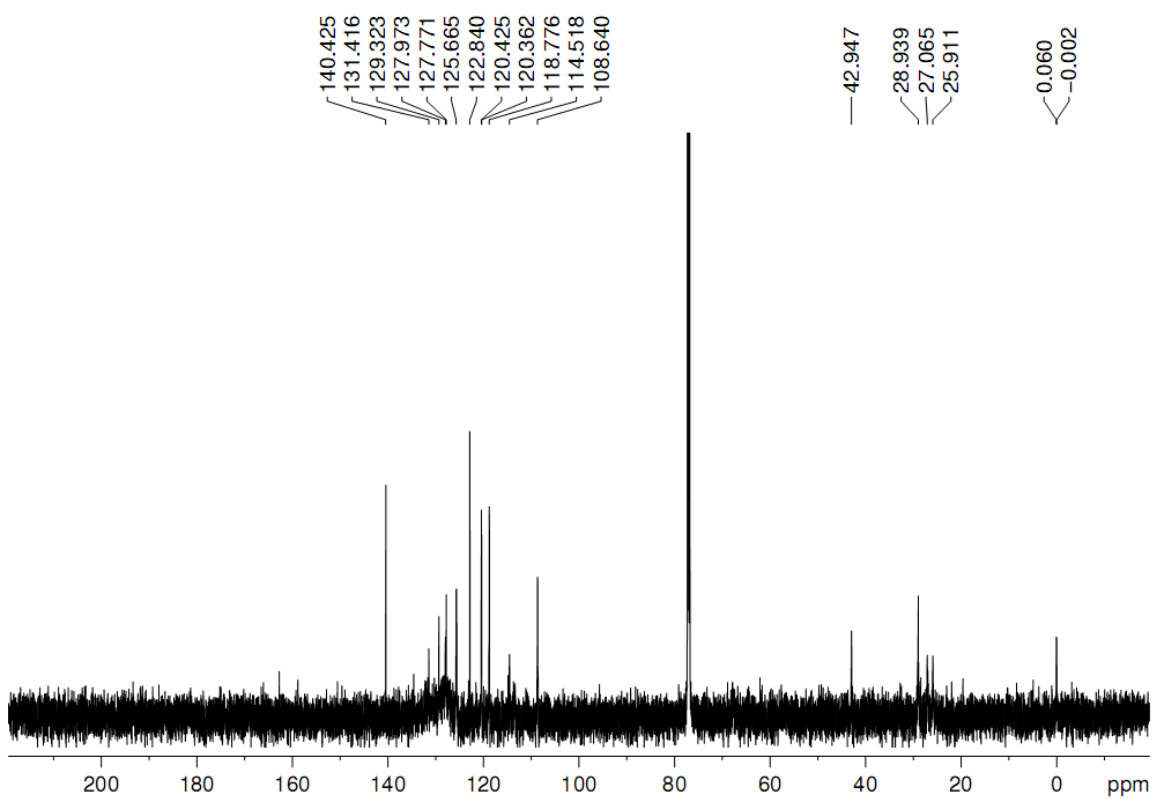


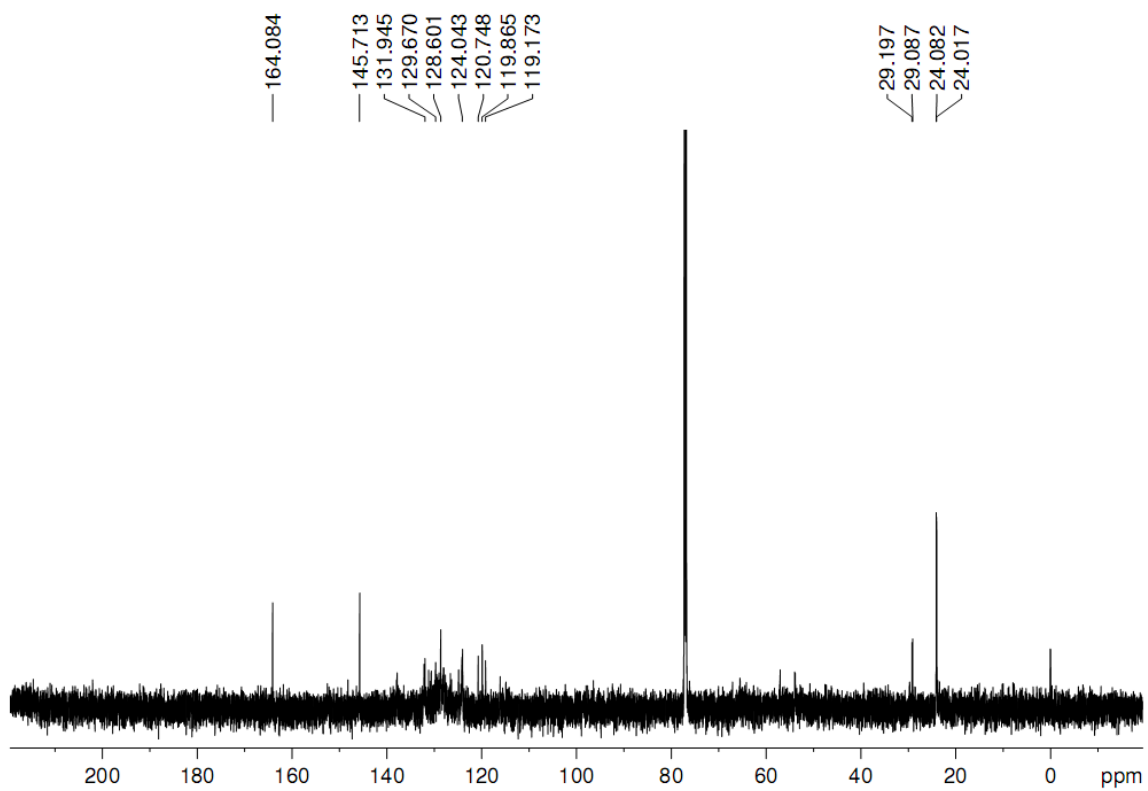
Figure S17. ¹H NMR spectrum of 4 in ^d-DMSO



FigureS18. ^{13}C NMR spectrum of $\text{C}_8\text{H}_{17}\text{-O-HABI}$ in CDCl_3



FigureS19. ^{13}C NMR spectrum of $\text{C}_2\text{-O-HABI}$ in CDCl_3



FigureS20. ^{13}C NMR spectrum of PMI-O-HABI in CDCl_3

6. Mass Spectra

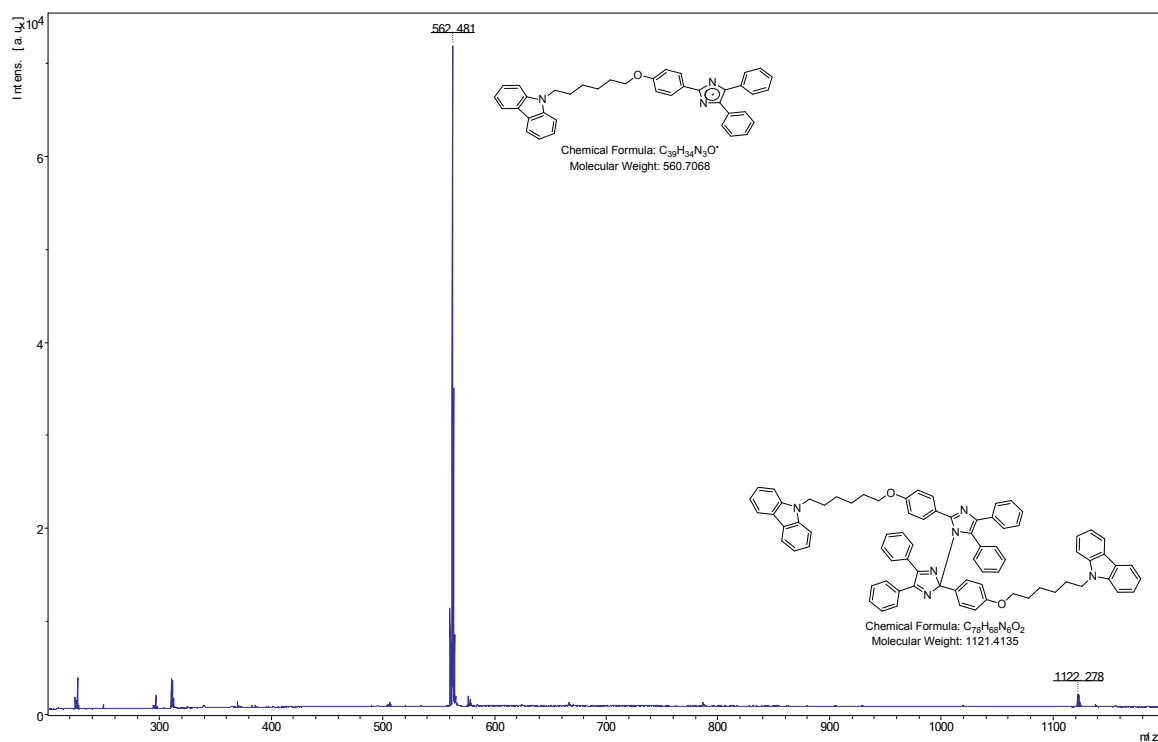


Figure S21. HR-Mass spectrum of Cz-O-HABI

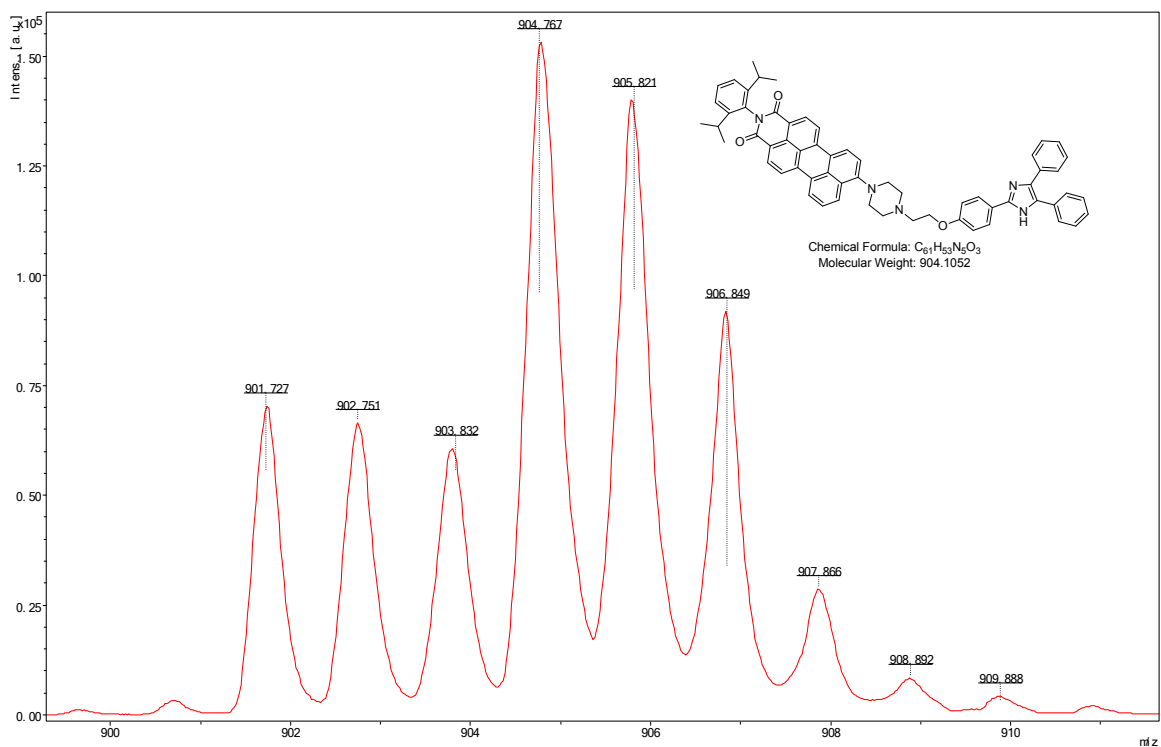
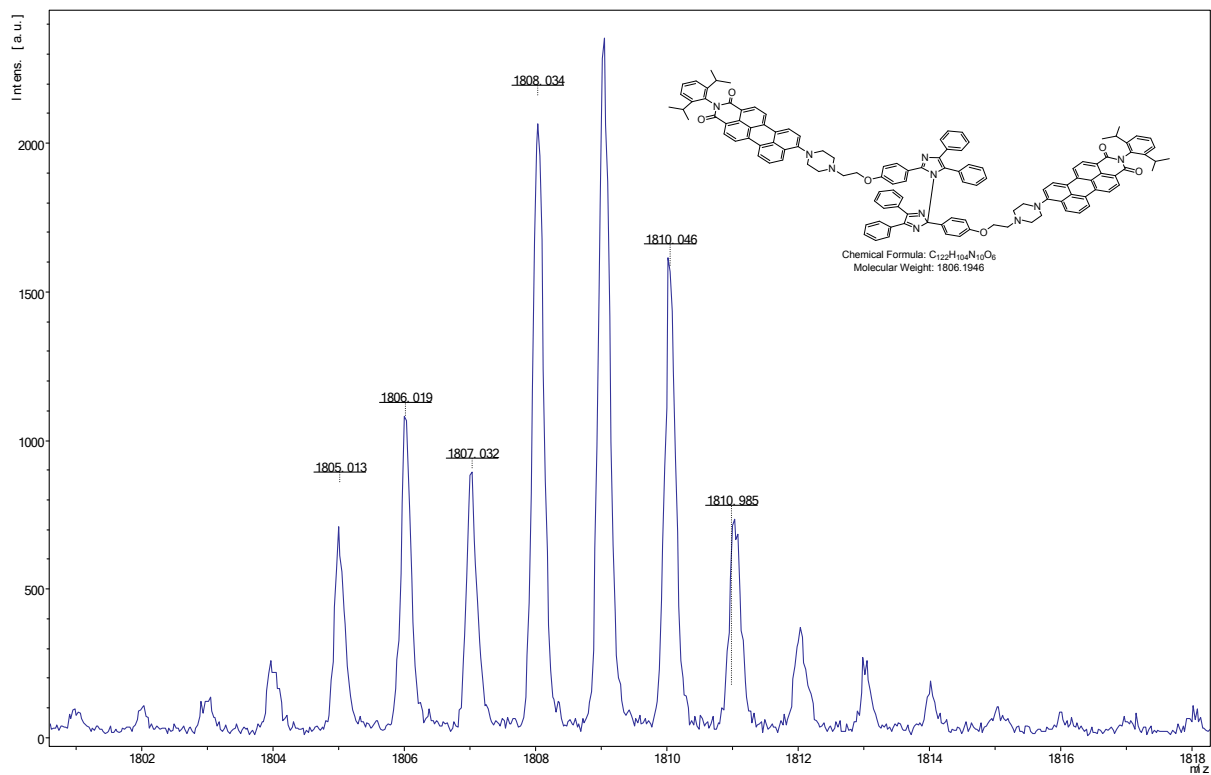


Figure S22. HR-Mass spectrum of 4f (PMI-O-TPI)



FigureS23. HR-Mass spectrum of 4 (PMI-O-HABI)

7. References

1. L. Fu, M. Pan, Y. H. Li, H. B. Wu, H. P. Wang, C. Yan, K. Li, S. C. Wei, Z. Wang, C. Y. Su, *J. Mater. Chem.* 2012, **22**, 22496-22500.
2. L. Feiler, H. Langhals, K. Polborn, *Liebigs Ann.* **1995**, 1229-1244.”