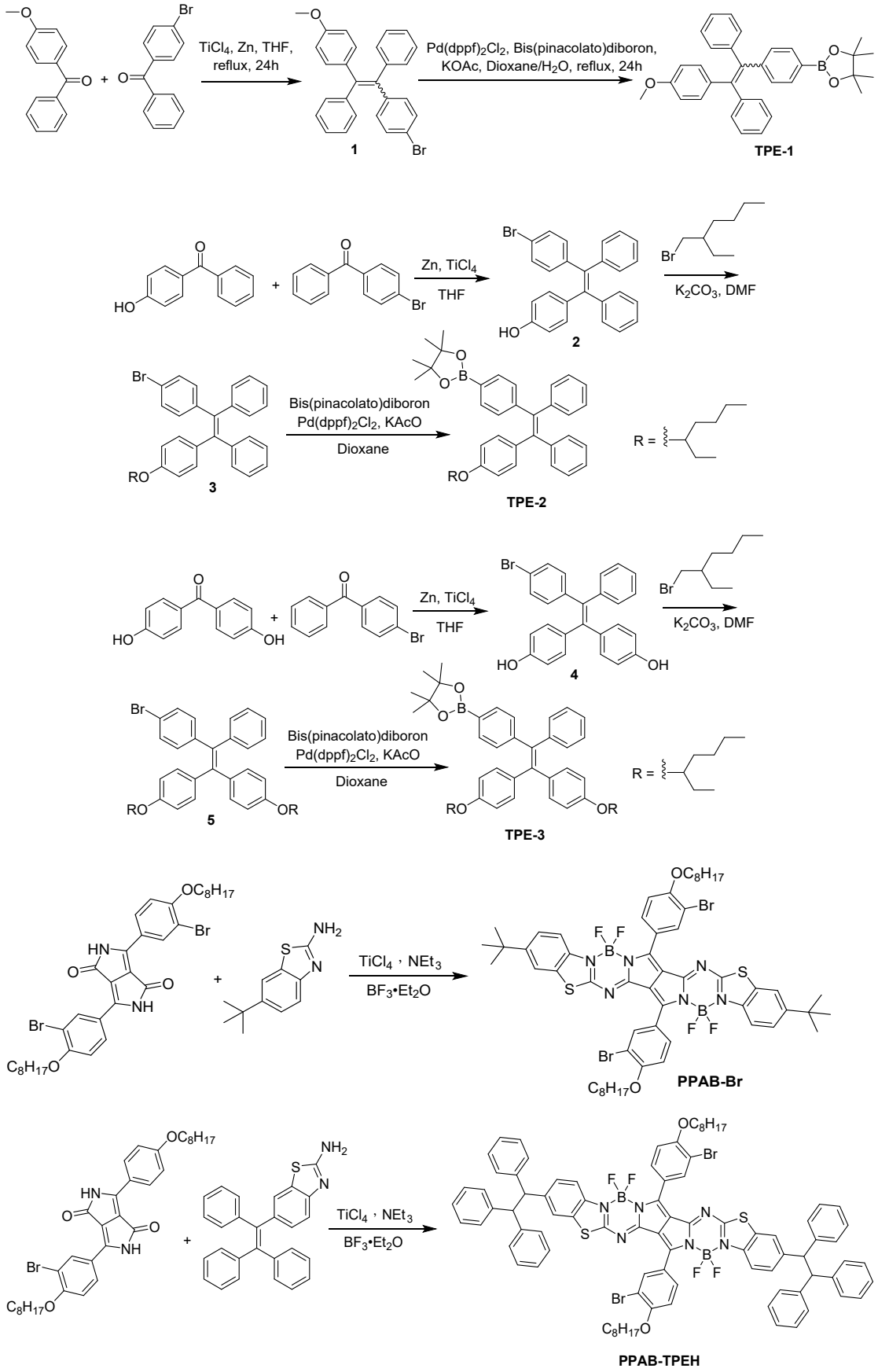
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Novel butterfly-shaped AIE-active pyrrolopyrrole *aza*-BODIPYs: synthesis, bioimaging and diamine / polyamine detection

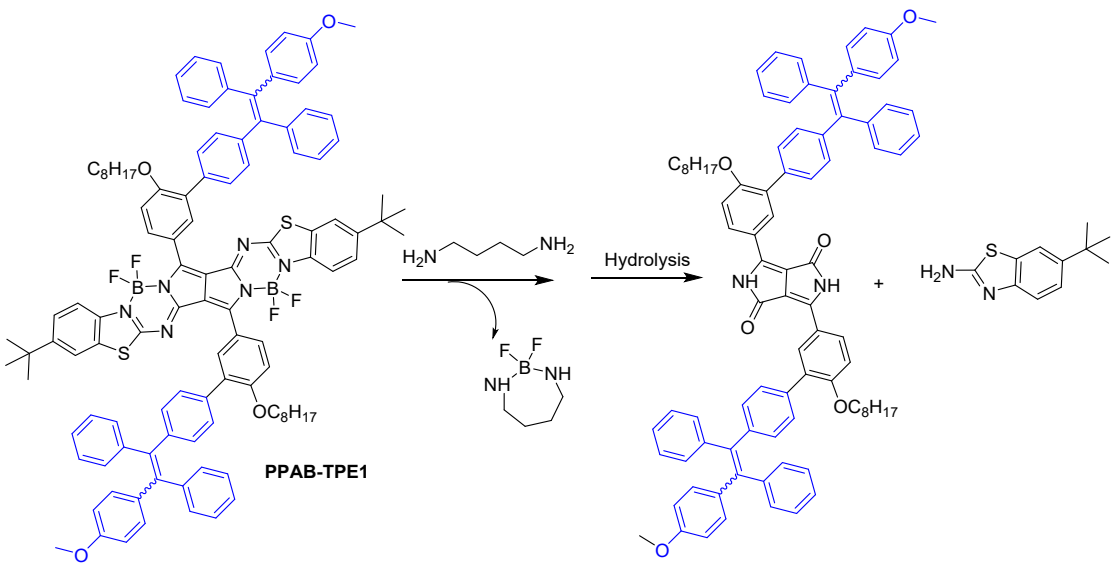
Wenting Li [a], Lingyun Wang [a*], Chufeng Zhang [a], Xueguang Ran [b], Hao Tang [a], Derong Cao [a]

[a] Key Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, 381 Wushan Road, Guangzhou, China, 510641. E-mail: lingyun@scut.edu.cn

[b] Institute of Animal Science, Guangdong Academy of Agricultural Sciences, Ministry of Agriculture Key Laboratory of Animal Nutrition and Feed Science in South China, State Key Laboratory of Livestock and Poultry Breeding, Guangzhou, 510641, China.



Scheme S1 Synthetic routes of **TPE1**~ **TPE3**, **PPAB-Br** and **PPAB-TPEH**.



Scheme S2 The proposed reaction mechanism between **PPAB-TPE1** and putrescine.

1.1 Preparation and determination of putrescine vapor concentration

A volume of 5 mL of putrescine solution with various concentrations was placed at the bottoms of sealed 100 mL bottles. After putrescine vapor reached equilibrium, **PPAB-TPE1**-loaded PMMA film was left for 10 s at room temperature. After being taken out from the bottle, the resulting film was taken photos as soon as possible.

1.2 Putrescine solution as ink for writing on **PPAB-TPE1** coated filter paper

A volume of 20 μL of dioxane stock solution of the **PPAB-TPE1** (10 mM) was drop-casted onto the Whatman filter paper followed by evaporation to dry. A volume of 400 μL of putrescine solution (1 mM) was prepared and used as ink for writing.

1.3 Measurement of detection limit

The detection limit was gained from the UV–vis titration data. On the basis of the results of the UV–vis titrating experiment, a good linear relationship between the absorption at 667 nm of **PPAB-TPE1** and diamine /polyamine concentration ranging from 0 to 5 μM was obtained. A limit of detection (LOD) was calculated by means of Eq. (1):

$$\text{Detection limit} = (3\times\sigma) / k \qquad (1)$$

Where σ is the standard deviation of blank measurements, k is the slope between absorption at 667 nm versus diamine /polyamine concentration.

1.4 Cell culture

Cells were cultured in high-glucose Dulbecco's Modified Eagle's Medium (H-DMEM) containing 10% fetal bovine serum (FBS) and 1% penicillin streptomycin at 37oC in a humidified environment containing 5% CO_2. Before the experiment, the cells were pre-cultured until confluence was reached.

1.5 Cytotoxicity

Cell viability was evaluated using the Cell Counting Kit-8 (CCK-8) assay. CCK-8 was just as WST-8 to produce formazan in the presence of an electron mediator, and

the amount of the formazan generated in cells was directly proportional to the number of living cells. The HeLa cells were seeded in 96-well plates at a density of 3000 cells per well. **PPAB-TPE1** NPs at 10, 50, 100 μM was added into a 96-well plate. Meanwhile, cells culture with complete medium (H-DME with 10% FBS) were evaluated as a control. The HeLa cells were incubated in the medium under 5% CO2 in an incubator maintained at 37 °C for 1, 2 and 4 days, respectively. Then, 10 μL of the CCK-8 was added to each well of a 96-well plate incubated for additional 2 h. The absorbance was measured at 450 nm using a microplate reader (Varioskan Flash, Thermo Scientific). The assay was repeated three times.

1.6 Cell imaging

HeLa cells were seeded in the 12-well plate and cultured in H-DMEM with 10% FBS at 37 0C in a humidified environment containing 5% CO_2. After 80% confluence, the medium was removed and the adherent cells were rinsed twice with 1 × PBS. **PPAB-TPE1** NPs in DMEM medium with FBS at 50 μM was then added to the culture plate. After incubation for 2 hours, the cells were washed three times with 1 × PBS buffer. The nuclei were stained by 4',6-diamidino-2-phenylindole (DAPI) for 10 min. The cell monolayer was then washed twice with 1 × PBS buffer and imaged using a confocal laser scanning microscope (Japan Olympus Co., Ltd) with an objective lens (× 60). Excitation of HeLa cells at 635 nm was carried out with a HeNe laser and the emission was collected from 700 nm to 800 nm.

1.8 The standard for the determination of quantum yields

We used Hamamatsu absolute PL quantum yield spectrometer C11347 to measure absolute fluorescence quantum yields of PPAB dyes, this instrument consists of an excitation light source based on a xenon arc lamp and a high-sensitivity multichannel detector. The emitted light are collected by the integrating spheres. The use of integrating spheres has usually required a laser as the excitation source in combination with a fibre coupled CCD camera or a calibrated photodiode as the luminescence detectors.

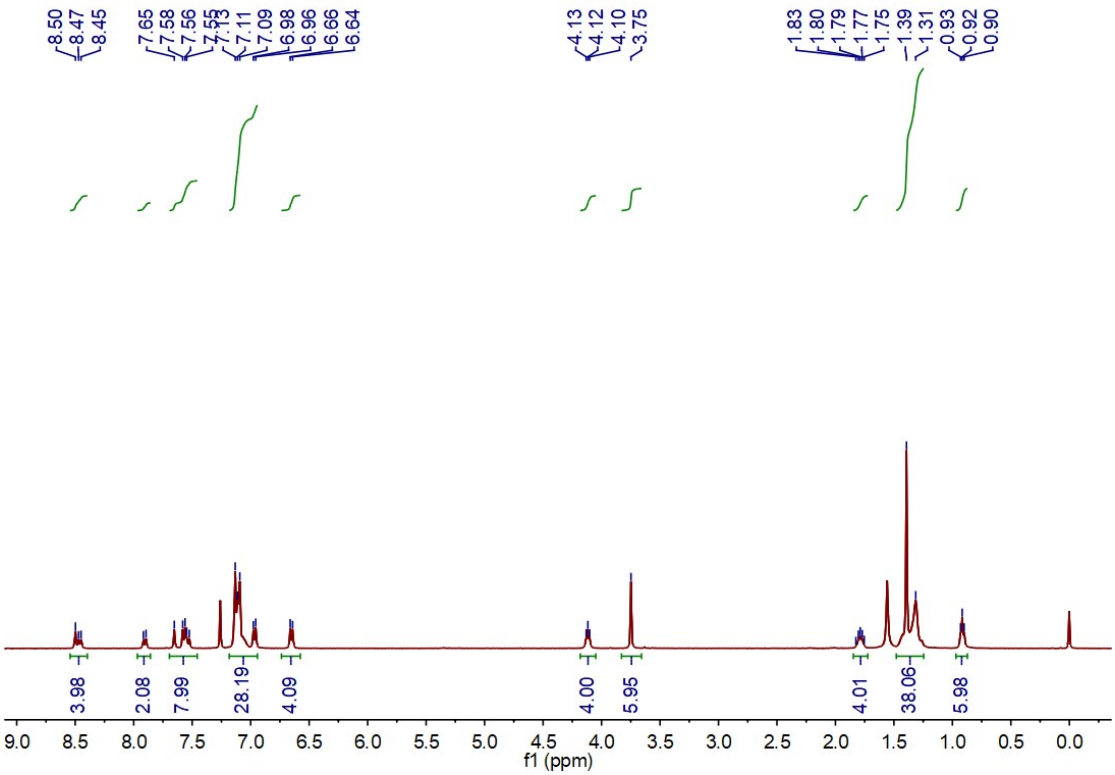


Figure S1 ^{1}H NMR spectrum of **PPAB-TPE1** in $CDCl_3$.

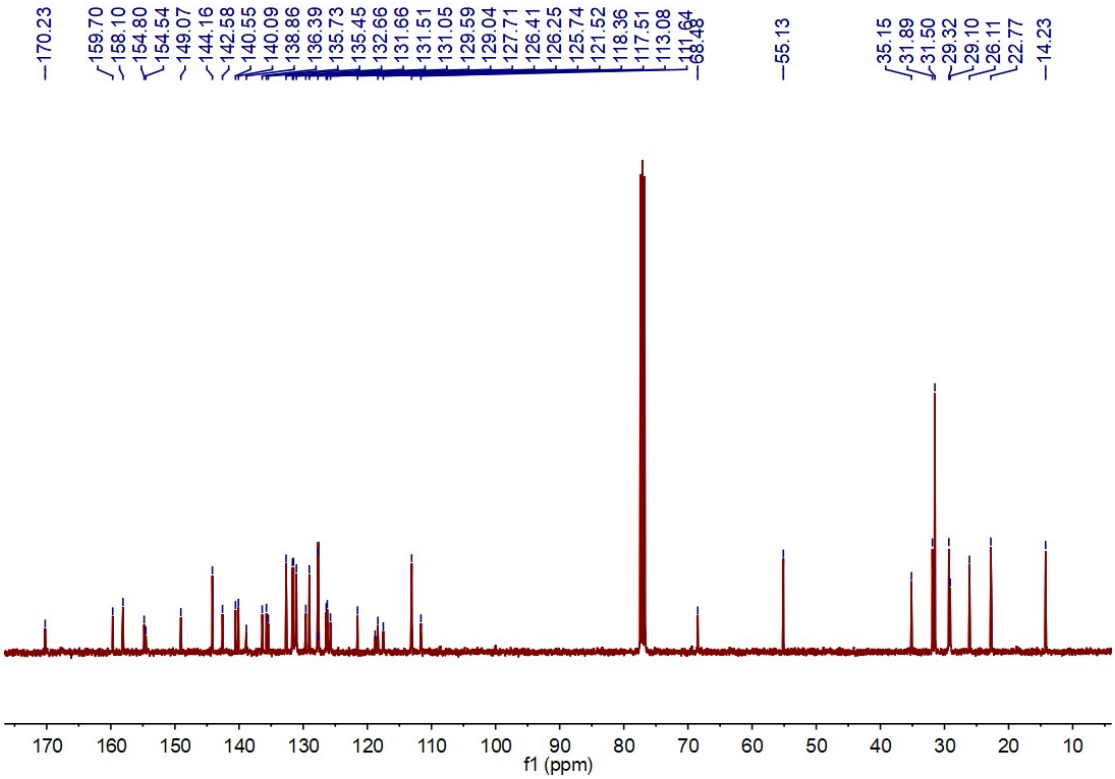


Figure S2 ^{13}C NMR spectrum of **PPAB-TPE1** in $CDCl_3$.

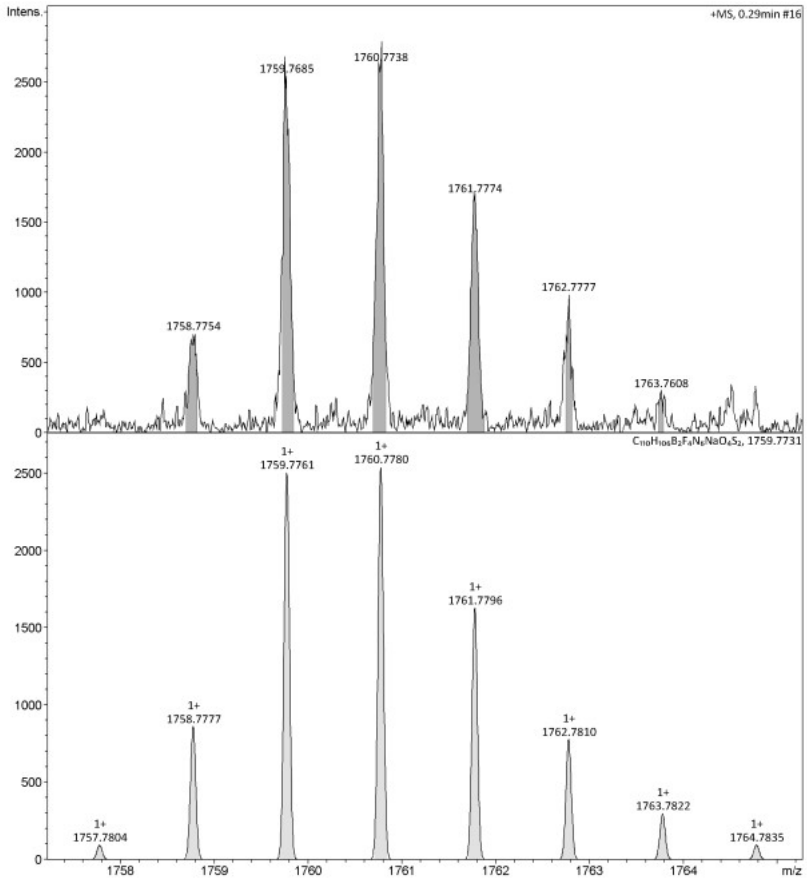


Figure S3 HRMS spectra of **PPAB-TPE1**.

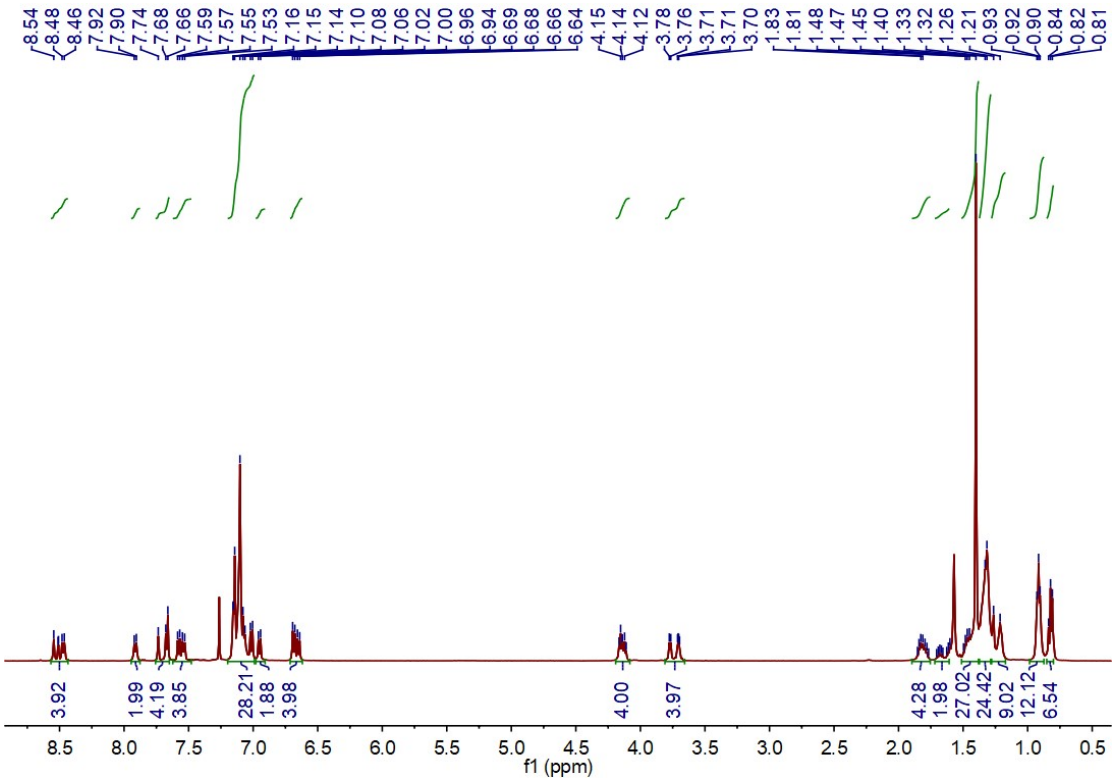


Figure S4 ^{1}H NMR spectrum of **PPAB-TPE2** in $CDCl_3$.

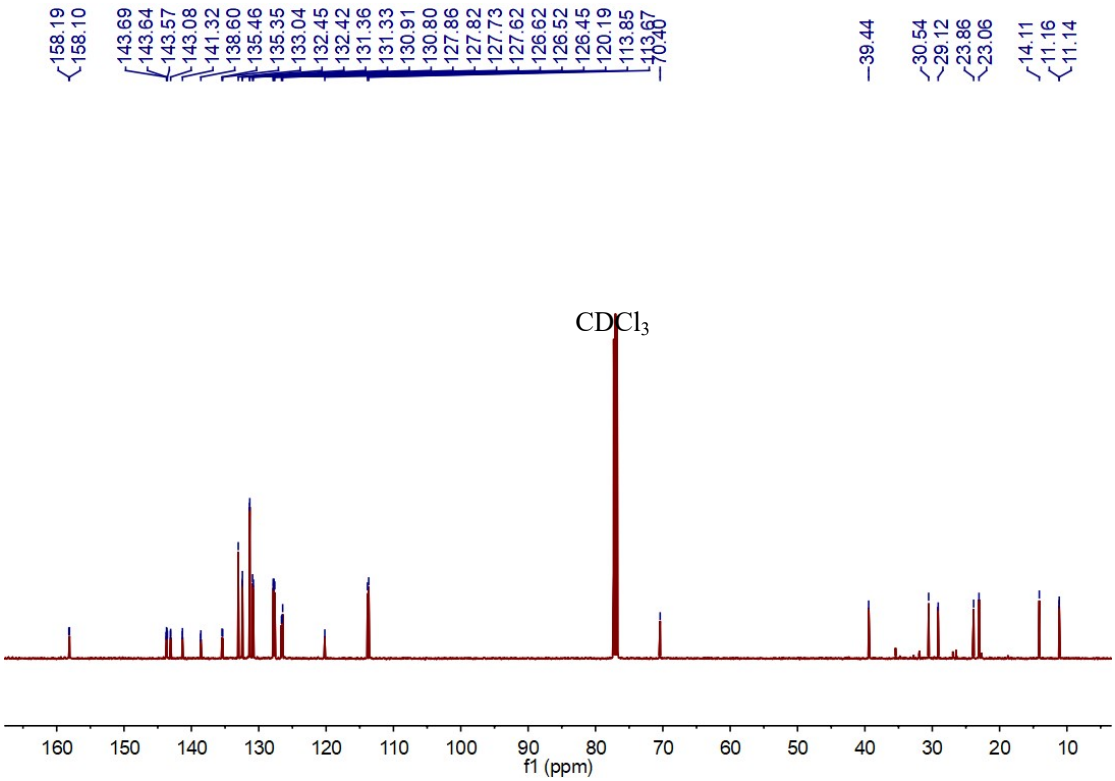


Figure S5 ^{13}C NMR spectrum of **PPAB-TPE2** in $CDCl_3$.

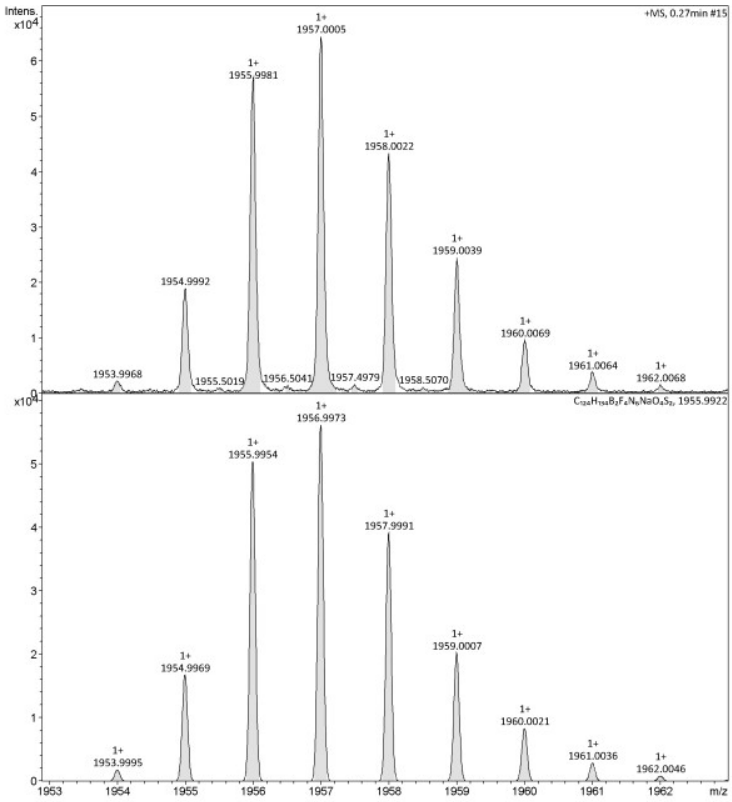


Figure S6 HRMS spectrum of **PPAB-TPE2**.

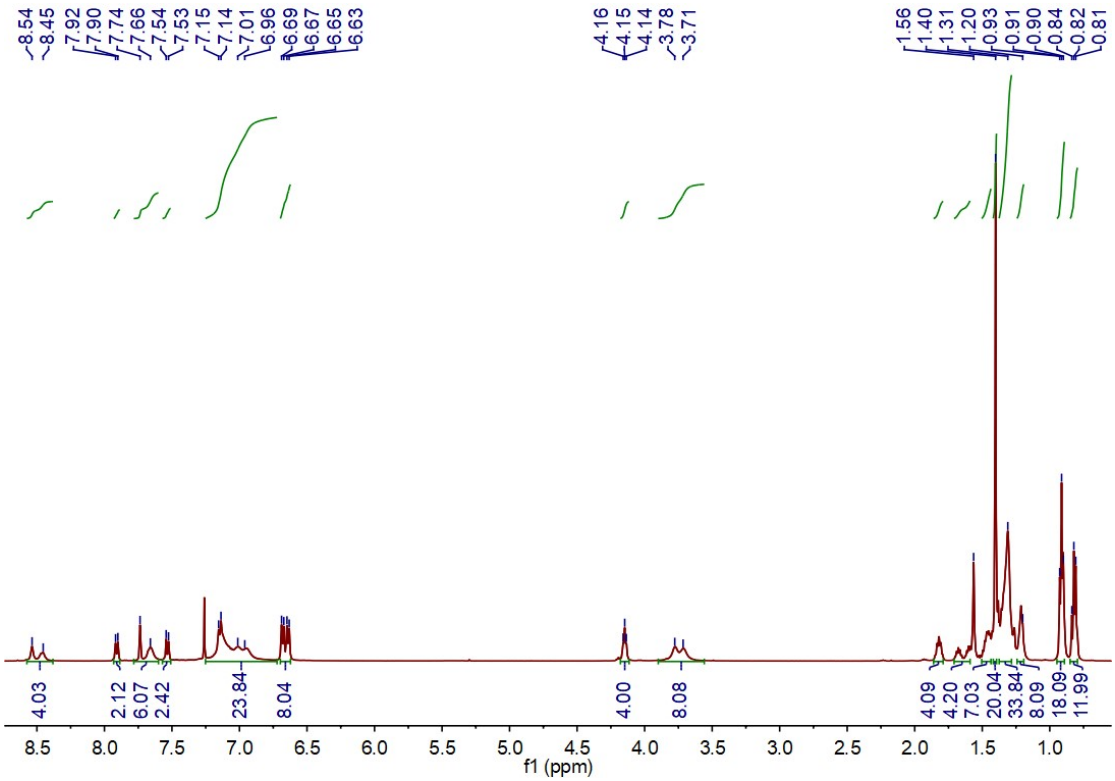


Figure S7 ^{1}H NMR spectrum of **PPAB-TPE3** in $CDCl_3$.

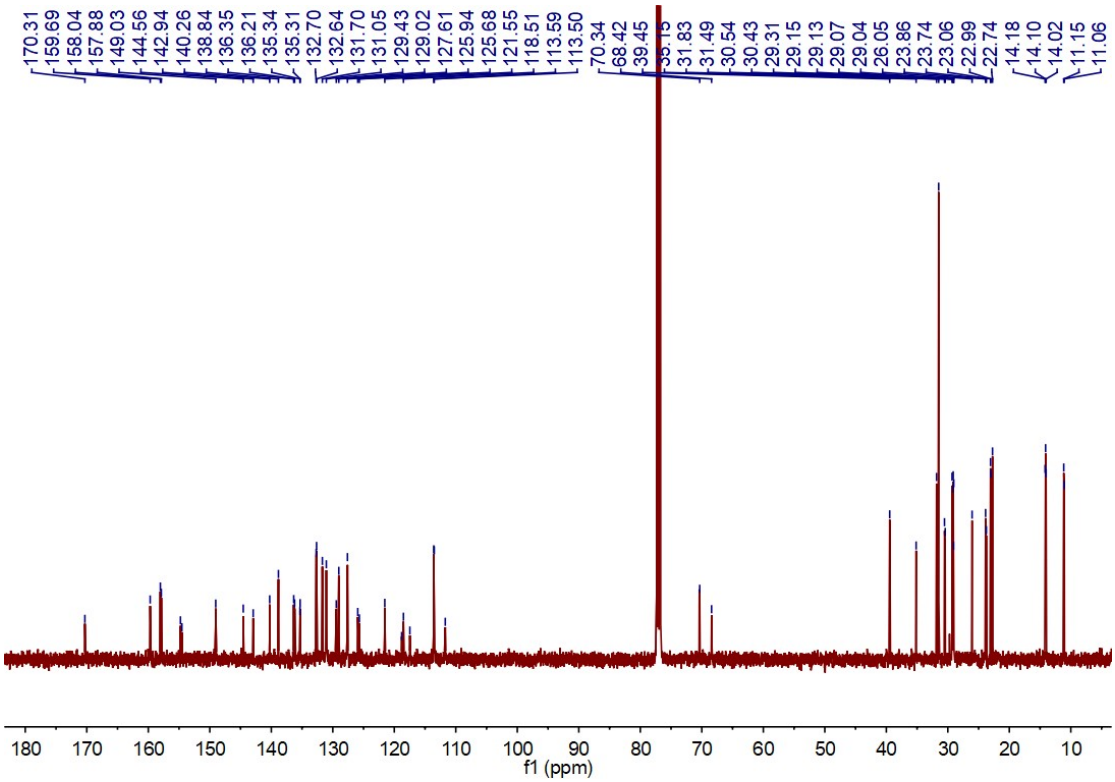


Figure S8 ^{13}C NMR spectrum of **PPAB-TPE3** in $CDCl_3$.

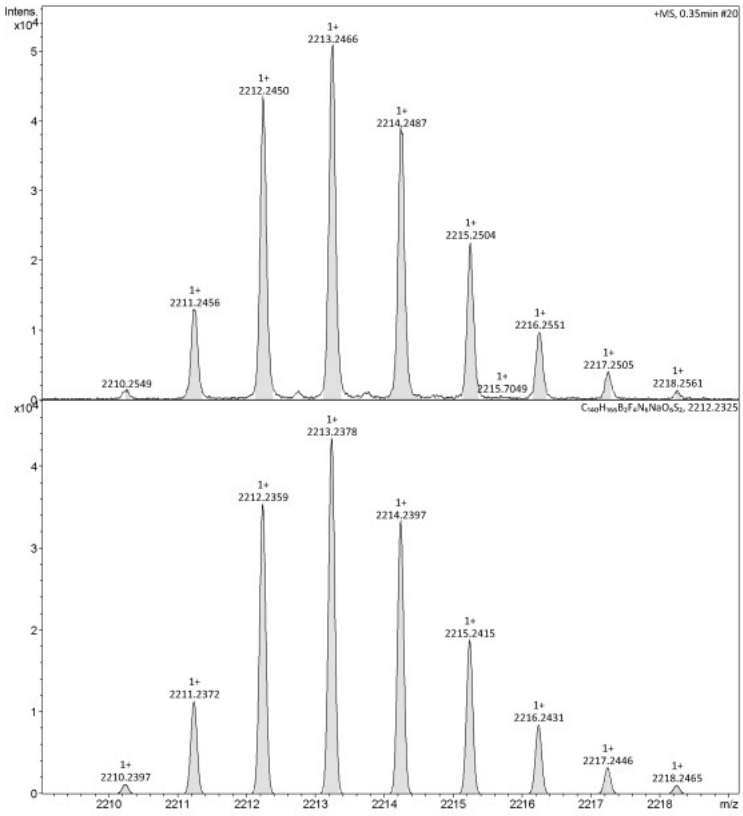
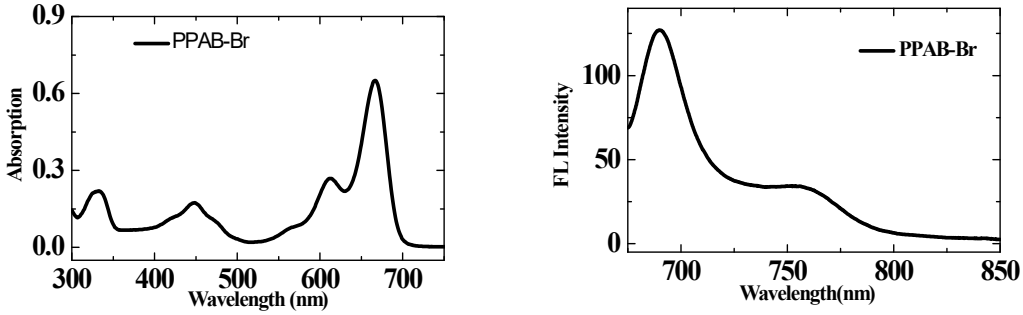


Figure S9 HRMS spectrum of **PPAB-TPE3**.



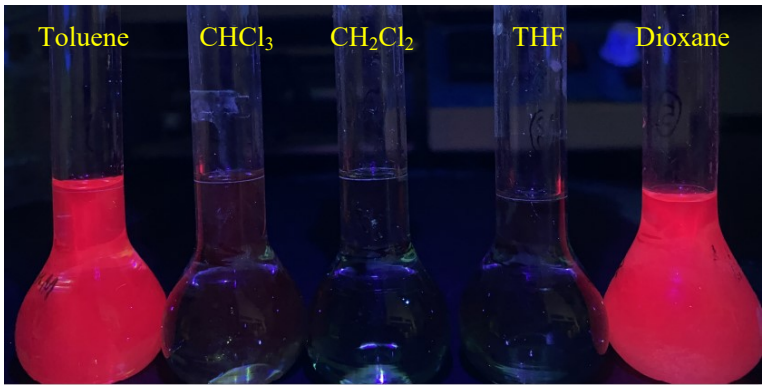


Figure S10 (a) UV-vis and (b) emission spectra of **PPAB-Br** (10 μM) in CH_2Cl_2. (c) The photographs of **PPAB-TPE1** in different solvents under 365 nm UV light.

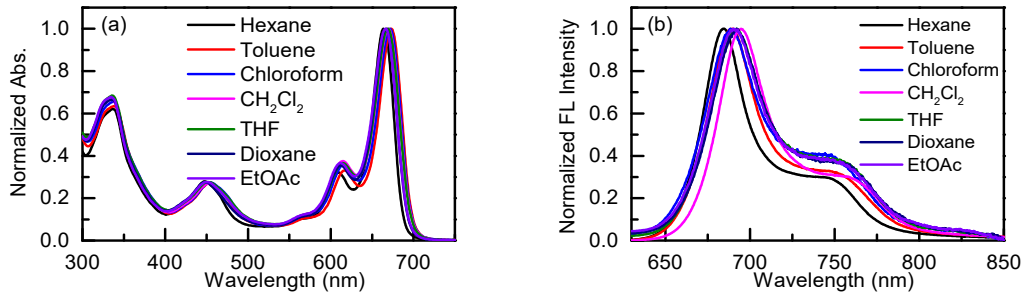


Figure S11 (a) UV-vis and (b) emission spectra of **PPAB-TPE2** (10 μM) in various solvents.

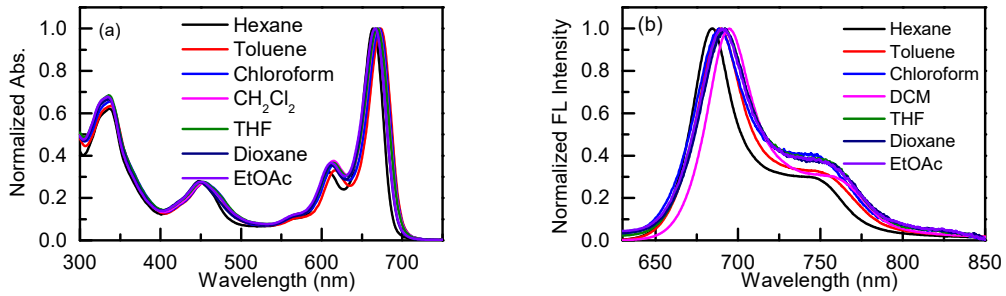


Figure S12 (a) UV-vis and (b) emission spectra of **PPAB-TPE3** (10 μM) in different solvents.

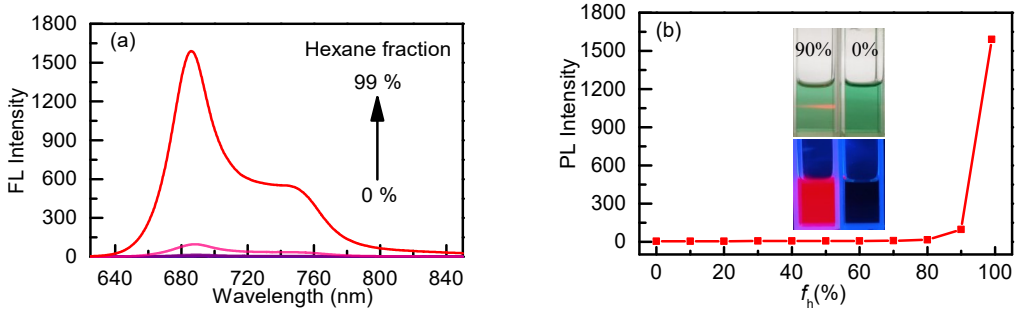


Figure S13 (a) PL spectra of **PPAB-TPE2** (10 μM) in CH_2Cl_2/hexane mixtures with different hexane fractions (f_h); (b) Plot of the emission intensity versus f_h (Inset: the fluorescent photos in absence and presence of 99% hexane taken under 365 nm UV irradiation).

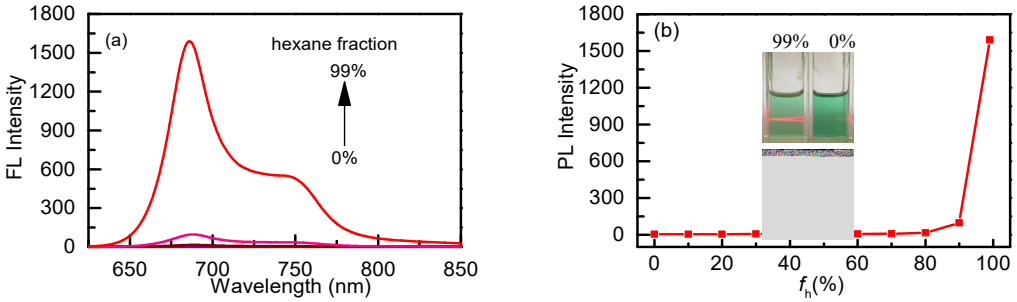


Figure S14 (a) PL spectra of **PPAB-TPE3** (10 μM) in CH_2Cl_2/hexane mixtures with different hexane fractions (f_h); (b) Plot of the emission intensity versus f_h (Inset: the fluorescent photos in absence and presence of 99% hexane taken under 365 nm UV irradiation).

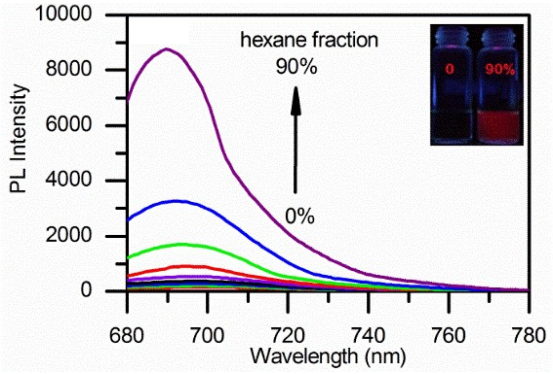


Figure S15 PL spectra of **PPAB-TPEH** (10 μM) in various hexane fractions of CH_2Cl_2-hexane mixtures. Inset: the fluorescent photos in absence and presence of 90% hexane taken under 365 nm UV irradiation.

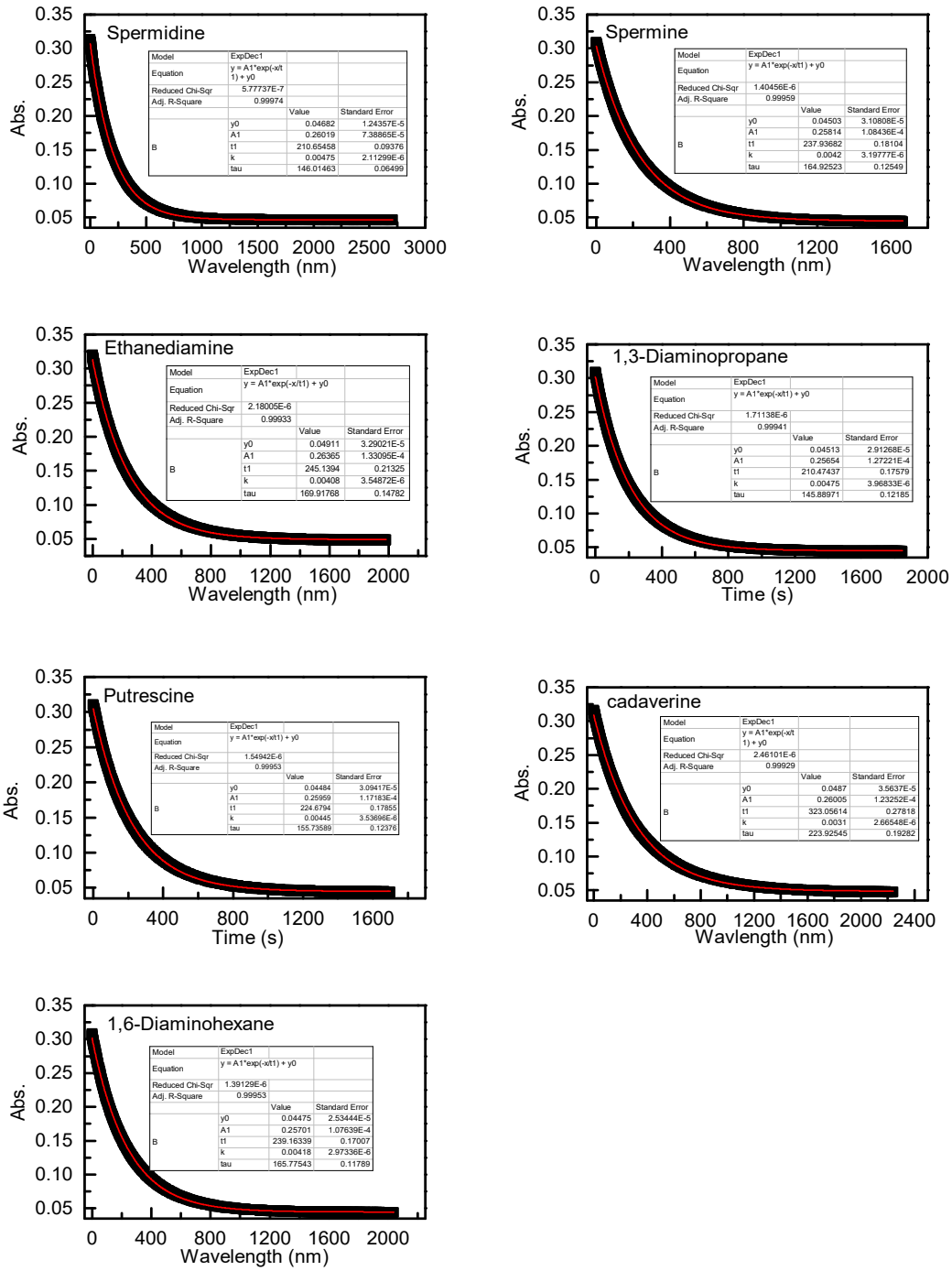


Figure S16 The kinetics reaction of **PPAB-TPE-1** (2.5 μM) in THF in presence of 12.5 μM spermidine, spermine, ethanediamine, 1,3-diaminopropane, putrescine, cadaverine, 1,6-diaminohexane at 22 ºC.

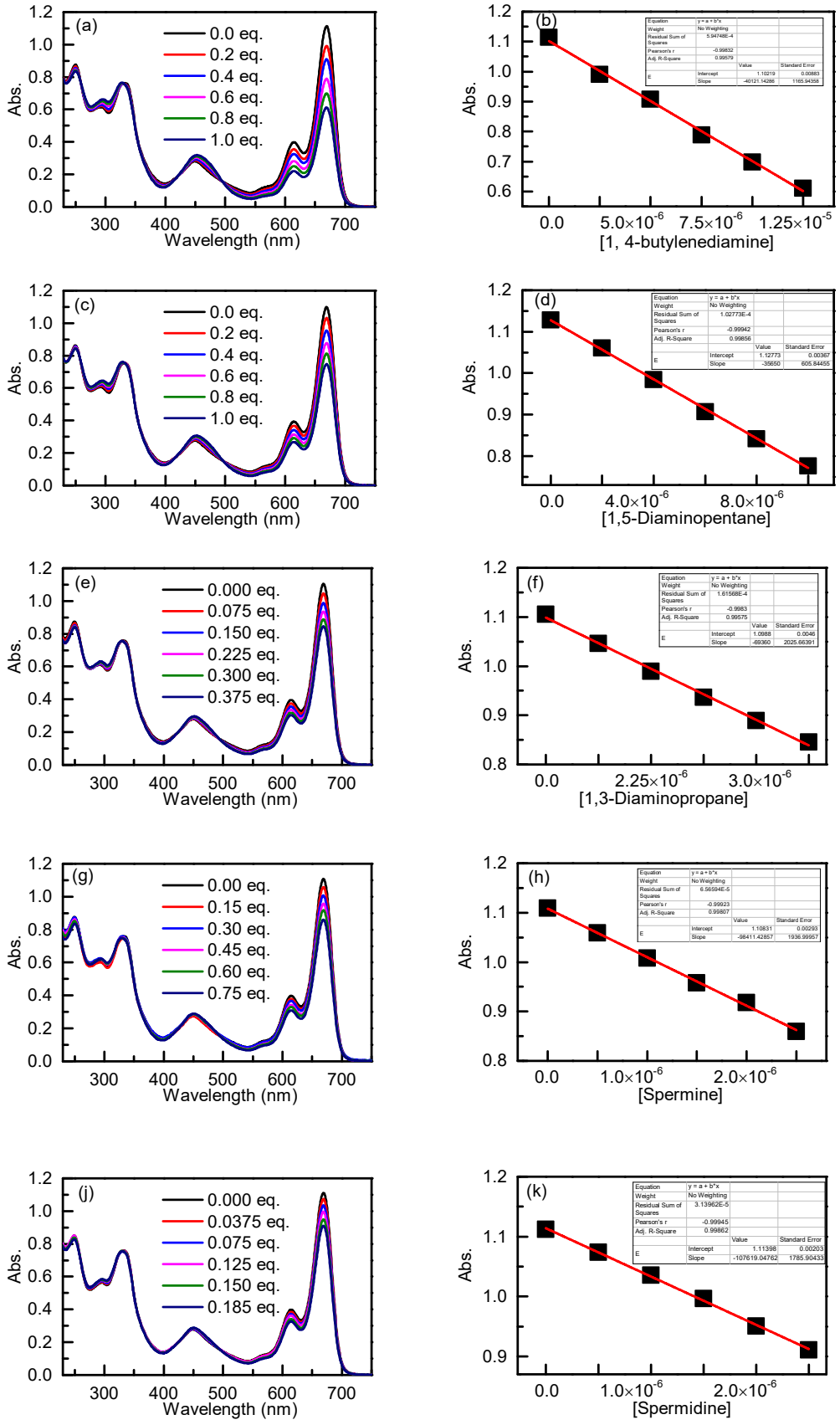
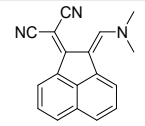
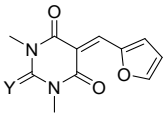
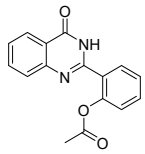
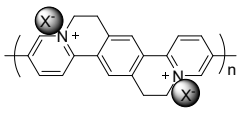
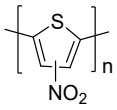
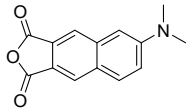
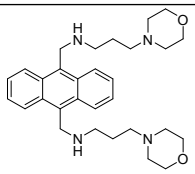
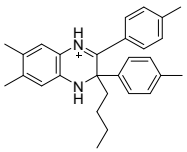
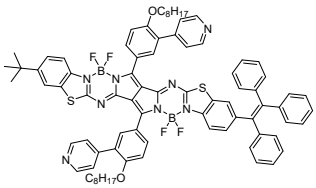
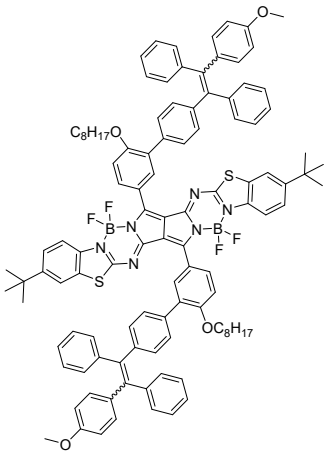


Figure S17 (a-k) Concentration-dependent UV-vis spectra of **PPAB-TPE1** (10 μM) in THF in presence of (a) putrescine (c) cadaverine (e) 1,3-propanediamine (g) spermidine

(j) spermidine at 22 ^{o}C, each solution was mixed and left for 5 min. The linear relationship between (b) putrescine (d) cadaverine (f) 1,3-propanediamine (h) spermidine (k) spermidine absorption of 669 nm of **PPAB-TPE1**.

Table S1 The comparison of amine detection based on **PPAB-TPE1** with other probes.

Probes	LOD	Remark	Reference
	No data	“turn-on”; primary amines: 5 min	J. Am. Chem. Soc. 2014, 136, 15493-15496
	dimethylamine: 0.4 ppm Ammonia: 0.5 ppm	Colorimetric; 5 min	Chem. Eur. J. 2017, 23, 3562-3566
	Ammonia vapor: 8.4 ppm	“turn-on”; 5 min	ACS Sens. 2016, 1, 179-184
	volatile amines: low ppm range	Fluorescence quenching;	Angew. Chem. Int. Ed. 2014, 53, 9792-9796
	BAs: ppm level	absorption response; putrescine: 20 min cadaverine: 60 min	Sensors & Actuators: B. Chemical, 2018, 271, 183-188
	BAs: 0.2 μM	Ratiometric fluorescence; 5 min	Analyst, 2016, 141, 827-831
	Put: 0.78 μM; Cad:1.20 μM	“turn-off”	Sensors & Actuators: B. Chemical, 2018, 254, 842-854
	Ammonia vapor: 690 ppb	colorimetric and fluorescence; 5 min	Chem. Eur. J. 2017, 23, 14911-14917
	BAs: ppb level	colorimetric and fluorescent, rapid (30 s), high sensitivity, high selectivity	Sens. Actuators B Chem. 2020; 312: 127953

	Put: 0.143 μM, Cad: 0.161 μM, DPA: 0.083 μM, Spm: 0.058 μM Spd: 0.053 μM	colorimetric and fluorescent, rapid (5 min), high selectivity, visual Put vapor detection	This work