A novel windmill-shaped AIE-active pyrrolopyrrole *aza*-cyanine: design, synthesis and efficient hydrazine detection

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1 Experimental

1.1. Experimental procedure for hydrazine detection

A stock solution of **PPCy-TBE** (0.5 mM) was prepared in dioxane, and a dilute solution (10 μM) was placed in 3 mL cuvettes for all measurements. For the titration experiments, hydrazine solutions were also prepared in water. The **PPCy-TBE** was incubated with different concentrations of hydrazine at 25 °C for desired time. Individual samples for absorption and fluorescence spectral analysis data were recorded.

2.2. Detection of hydrazine vapor based on PPCy-TBE loaded PMMA film

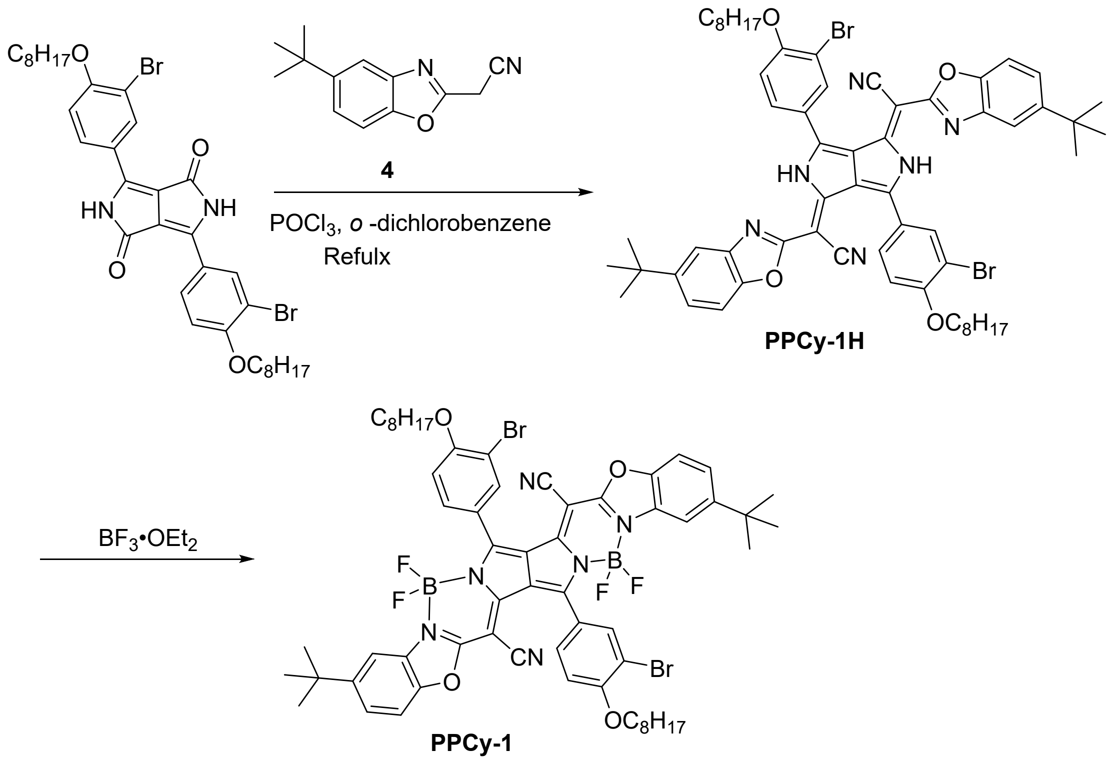
For sensing of the hydrazine vapors, the 1 wt% **PPCy-TBE** -loaded PMMA film was kept in a 50 mL airtight container with 2 mL hydrazine solution for 5 min. Then, the color change at daylight and fluorescence change under 365 nm irradiation were measured with a camera.

2.3. Scanning electron microscopy (SEM)

PPCy-TBE (2.5 mM) in dioxane was mixed with 20 mM hydrazine at room temperature for 10 min. After drying completely, the sample was observed using a Hitachi S-5000H field emission scanning electron microscope.

2.4. Absolute fluorescence quantum yield measurement

Absolute fluorescence quantum yield was measured by Hamamatsu spectrometer C11347, which consisted of an excitation light source based on a xenon arc lamp and a high-sensitivity multichannel detector. The emitted light was collected by the integrating spheres.



Scheme S1 Synthetic routes of **PPCy-1**.

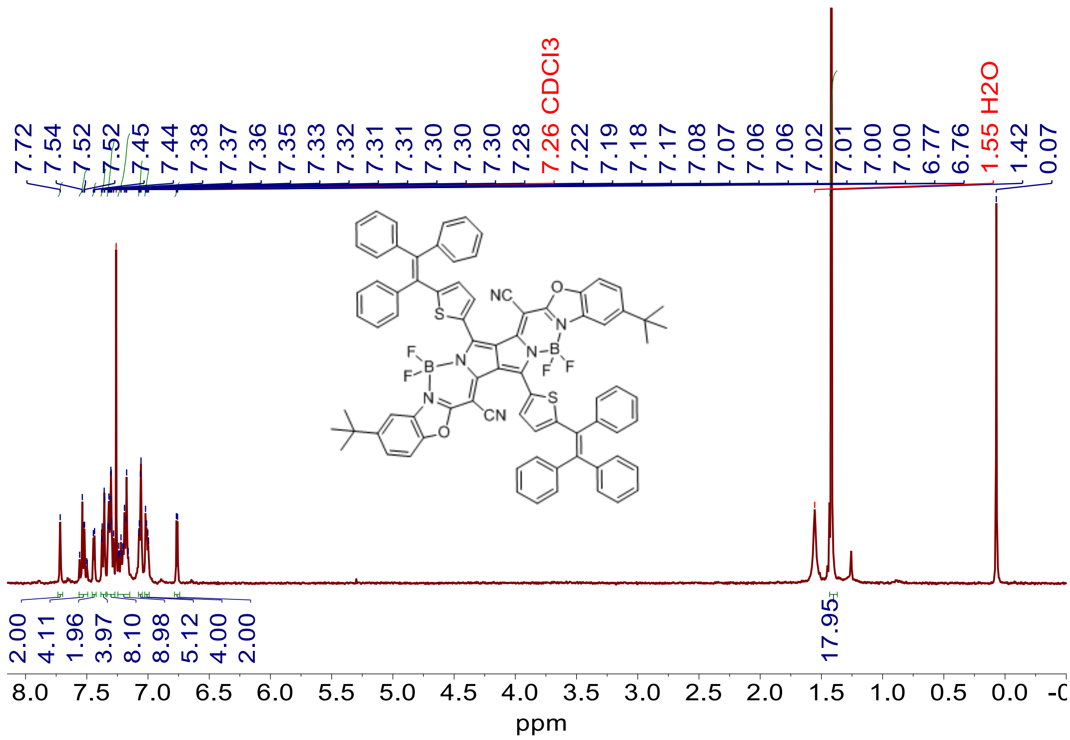


Figure S1 The ^{1}H NMR spectrum of **PPCy-TBE** in $CDCl_3$.

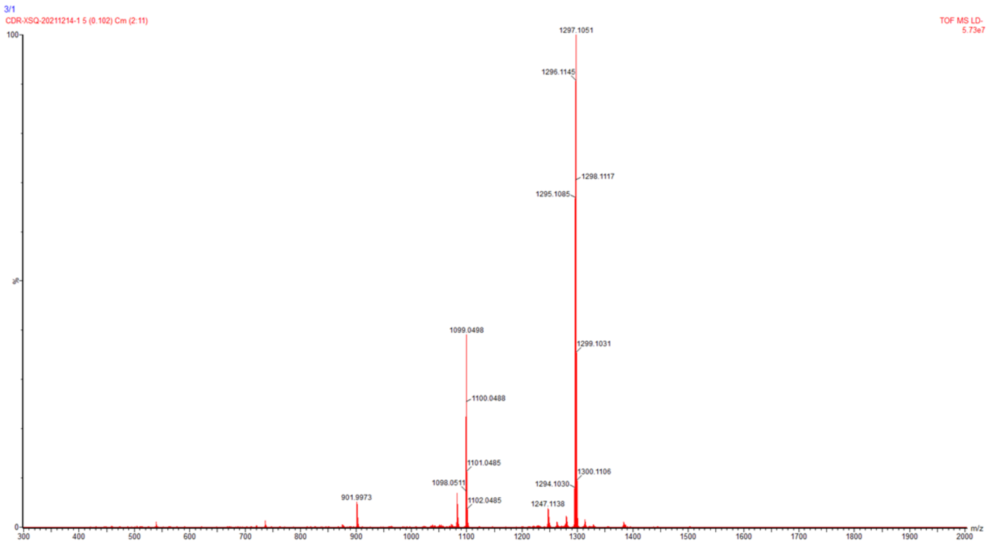


Figure S2 The MALDI-TOF spectrum of **PPCy-TBE**.

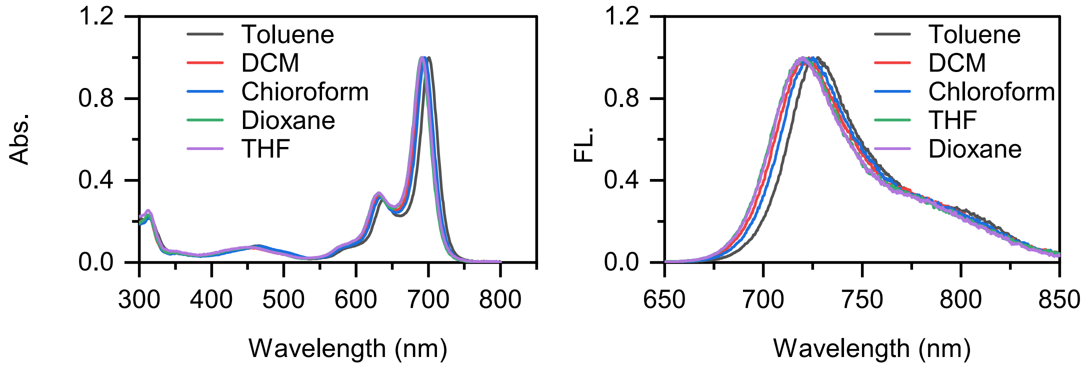


Figure S3 (a) Normalized UV-vis and (b) emission spectra of **PPCy-1** (10 μM) in different solvents.

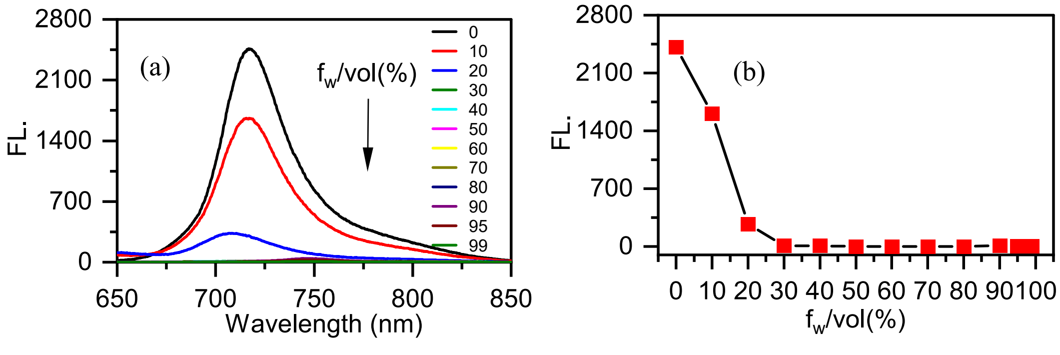


Figure S4 The (a) emission PL spectra and fluorescence intensity of **PPCy-1** (10 μM) in dioxane/water mixtures with different water fractions (f_w).

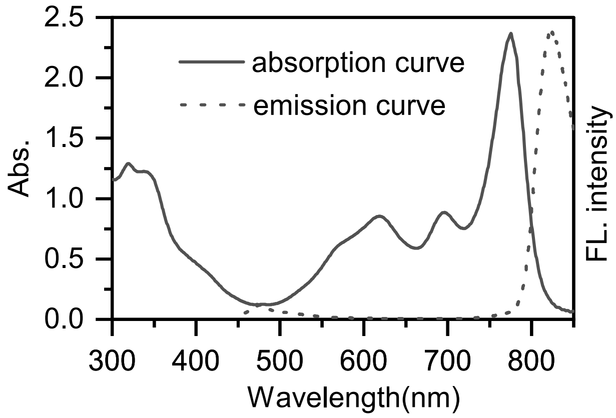


Figure S5 The normalized UV-vis and FL spectra of **PPCy-TBE** NPs.

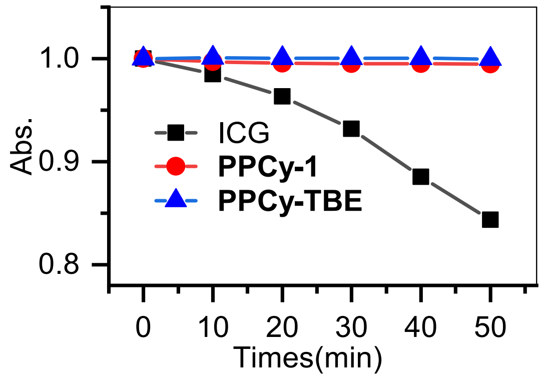


Figure S6 The photo-stability of **PPCy-TBE**, **PPCy-1** and ICG. The corresponding solution (10 μM) was measured after exposure under continuous 365 nm irradiation by Hand-held UV lamp for different time.

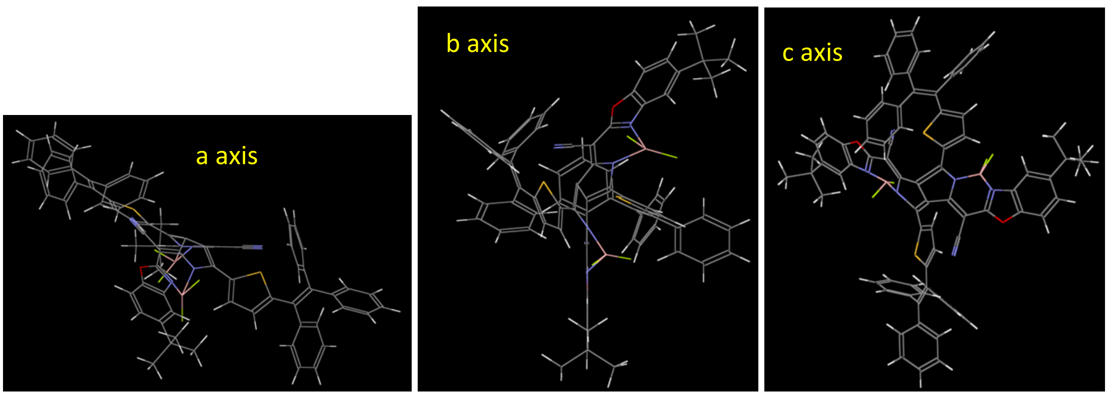


Figure S7 The geometries of **PPCy-TBE** from a, b, c axis view by DFT calculation, respectively.

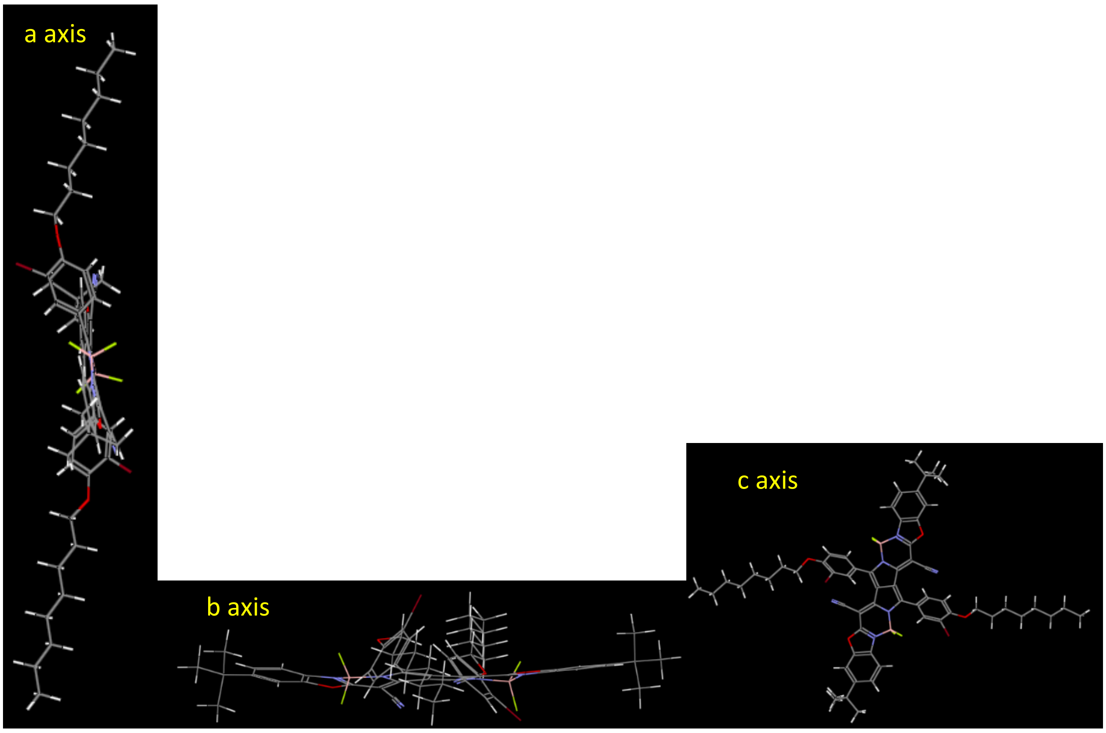


Figure S8 The a, b, c axis view of geometries of **PPCy-1** by DFT calculation.

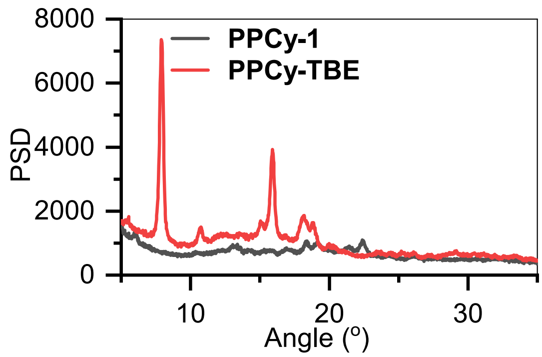
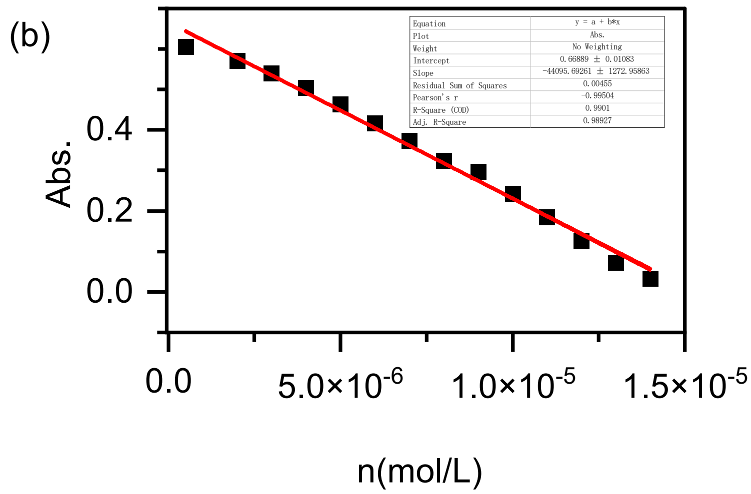


Figure S9 The XRD spectra of **PPCy-TBE** and **PPCy-1**.



Linear Equation: $Y=-44095X+0.67$ $R^2 = 0.99$

$S = 44095$ $\delta = \sqrt{\frac{\sum (A_0 - A_1)^2}{N-1}} = 0.0011023$ (N = 11)

LOD = 3 × δ / S = 3 ×0.0011023/ 44095 =0.075 μM

Figure S10 The linear plot between absorption at 738 nm of **PPCy-TBE** (10 μM) in presence of different content of N_2H_4.

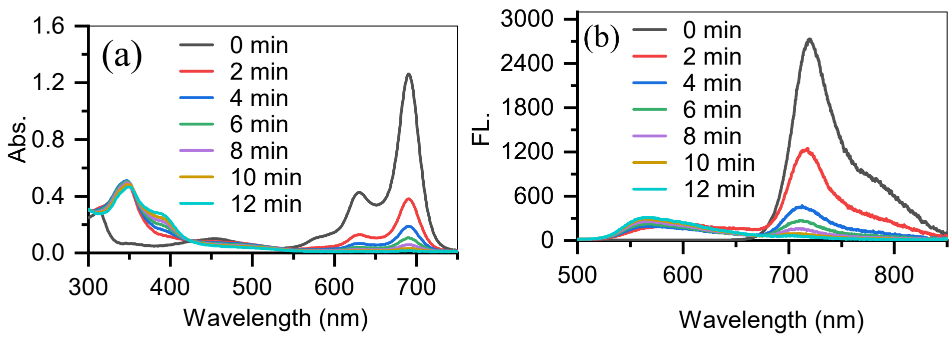


Figure S11 Time-dependent (a) UV-vis absorption and (b) emission spectra of **PPCy-1** (10 μM) in presence of hydrazine (25 μM).

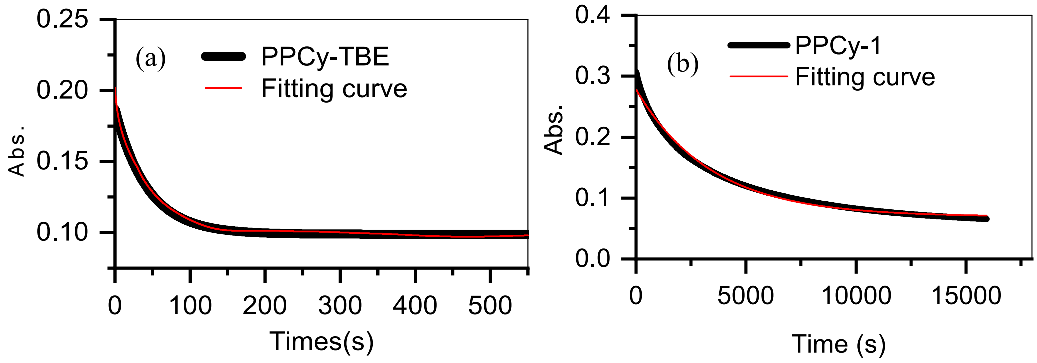


Figure S12 The pseudo-first-order kinetic curves of (a) **PPCy-TBE** (2.5 μM) and (b) **PPCy-1** (2.5 μM) in presence of hydrazine (5 μM) at room temperature.

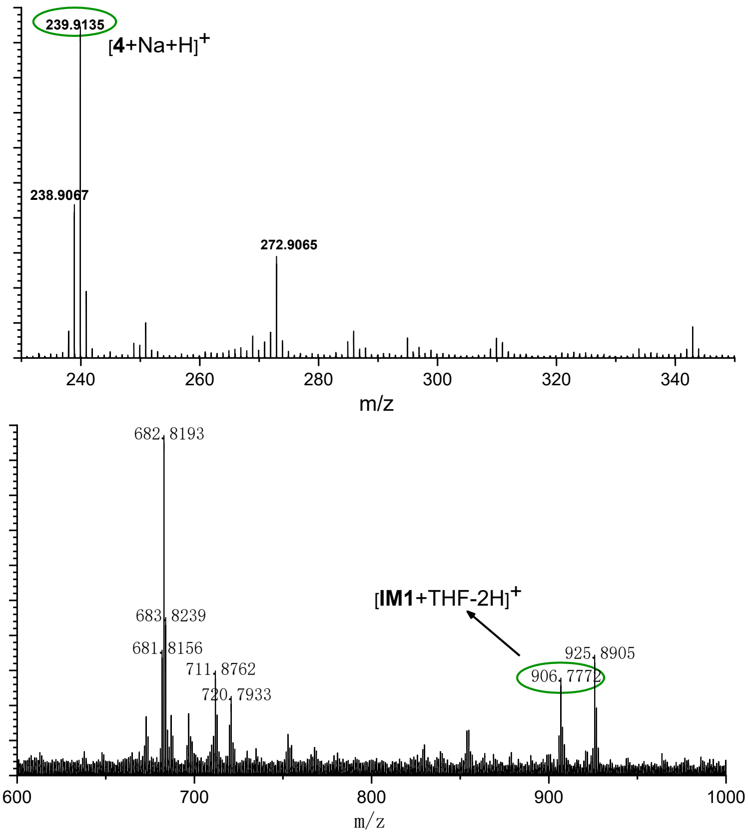


Figure S13 The MALDI-TOF spectra of **PPCy-TBE** with hydrazine.

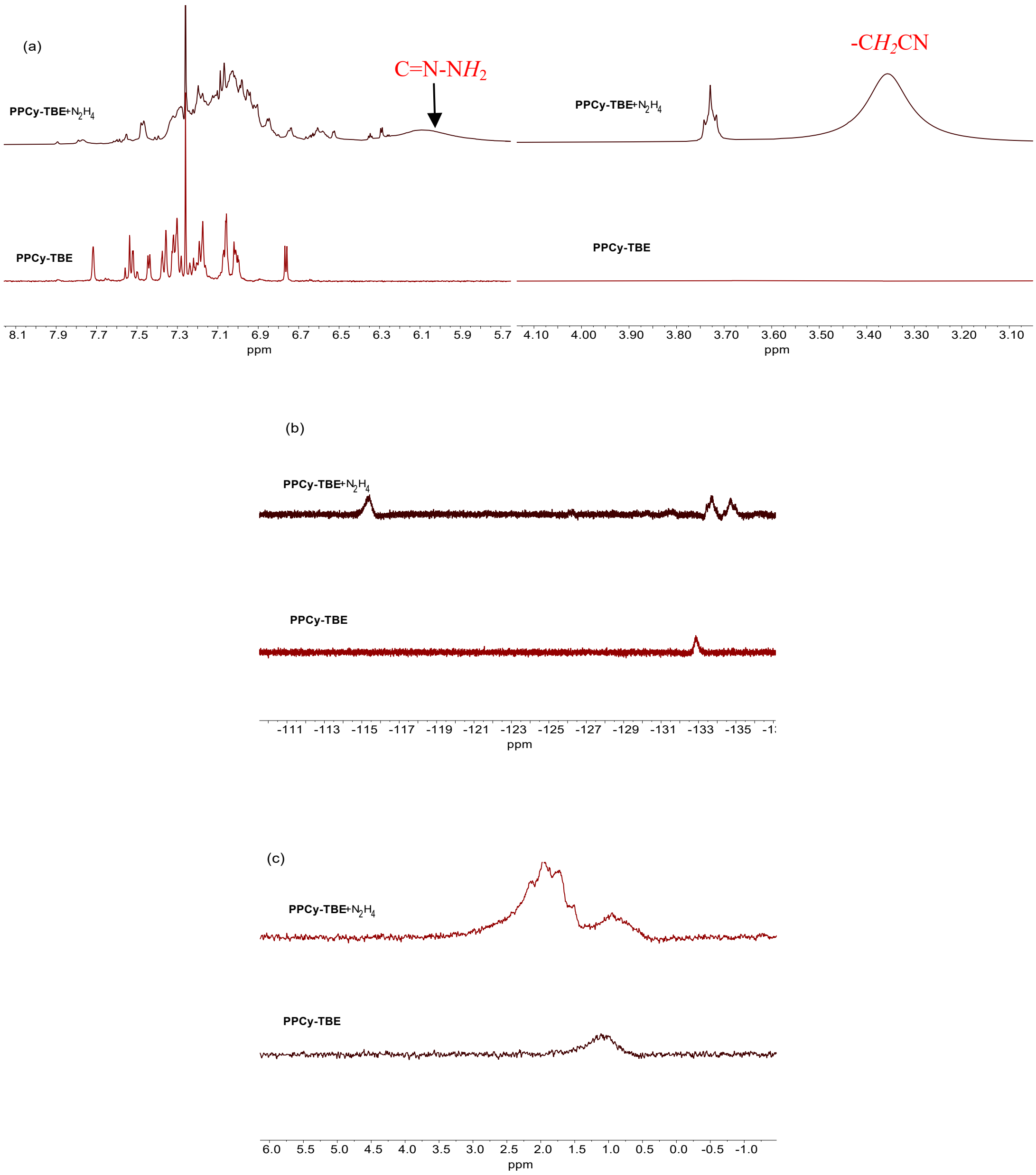


Figure S14 (a) partial ^{1}H NMR, (b) ^{19}F NMR and (c) ^{11}B NMR spectra of **PPCy-TBE** in absence and presence of 2 equiv. hydrazine in $CDCl_3$.

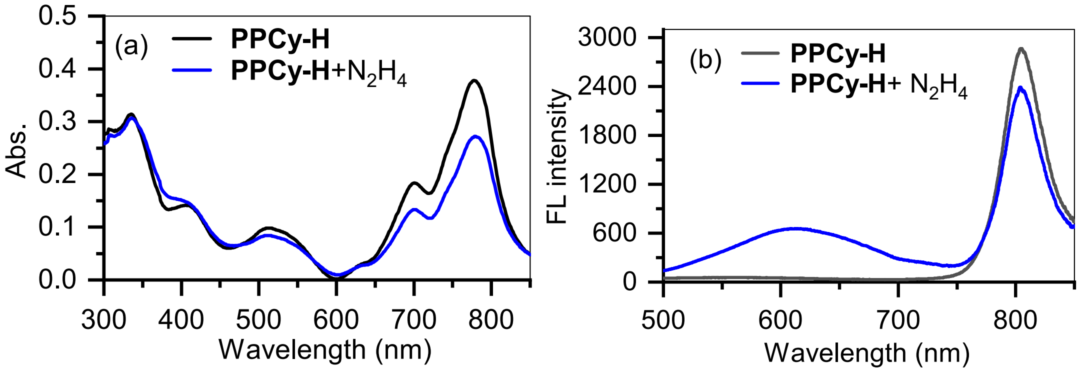


Figure S15 Time-dependent (a) UV-vis absorption and (b) emission spectra of **PPCy-1** (10 μM) in presence of hydrazine (500 μM).

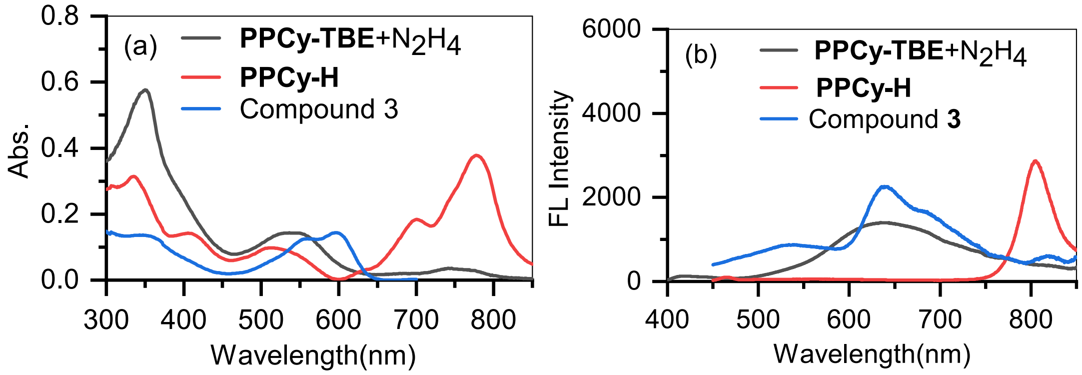


Figure S16 (a) The UV-vis absorption and (b) emission spectra of **PPCy-TBE** + N_2H_4, **3** and **PPCy-H**.

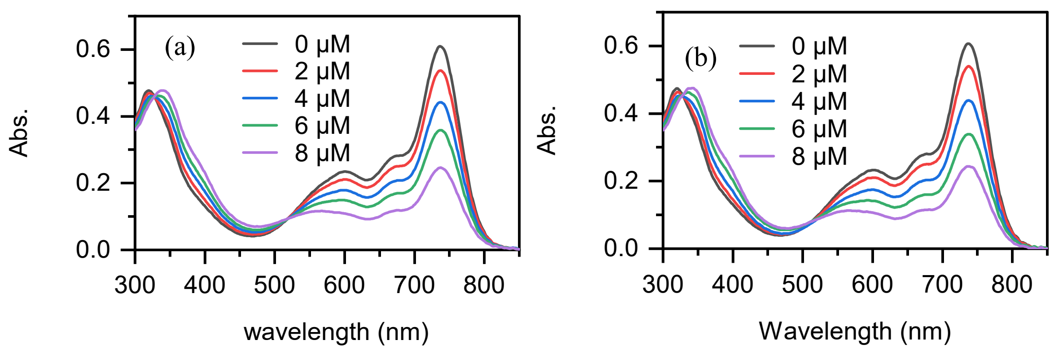


Figure S17 The UV-vis spectra of **PPCy-TBE** (10 μM) in presence of N_2H_4 in real water samples. (a) lake water and (b) tap water.

Table S1 Spectroscopic data of **PPCy-TBE** and control compound **PPCy-1** (10 μM) in different organic solvents.

Compound	Solvent	$\lambda_{max, abs}$ (nm)	$\lambda_{max, em}$ (nm)	Stokes shift (nm)	ε (M^{-1} cm^{-1})	Absolute quantum yield
PPCy-TBE	Toluene	746	812	66	7.0*10^4	-
	CH_2Cl_2	742	821	79	4.7*10^4	-
	Chloroform	751	825	74	5.9*10^4	-
	THF	738	813	75	6.3*10^4	-
	Dioxane	738	803	65	5.7*10^4	0.008
PPCy-1 (control compound)	Toluene	701	725	24	1.5*10^5	-
	CH_2Cl_2	692	723	31	1.3*10^5	-
	Chloroform	695	725	30	1.4*10^5	-
	THF	691	720	29	9.8*10^4	-
	Dioxane	690	720	30	1.2*10^5	0.585

Table S2. Frontier molecular orbital profiles of **PPCy-TBE** and **PPCy-1**.

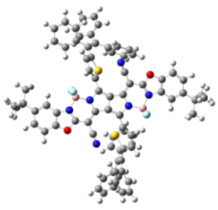
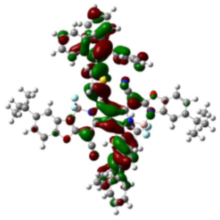
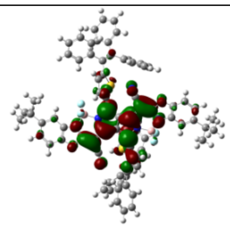
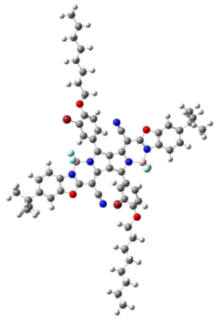
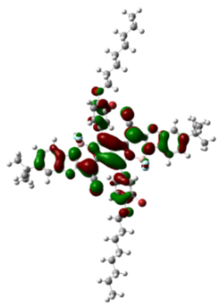
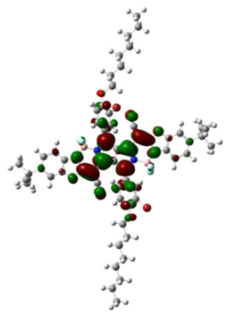
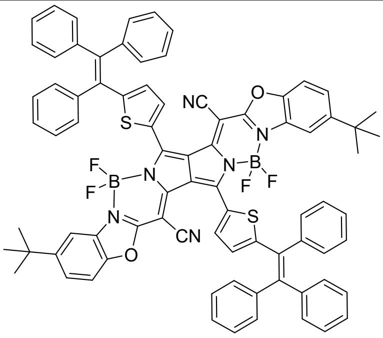
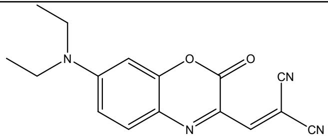
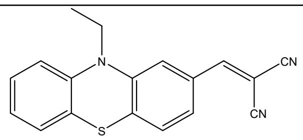
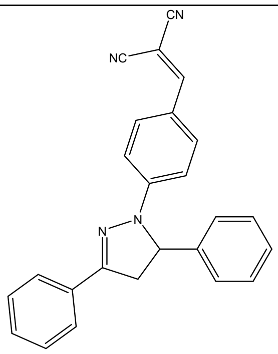
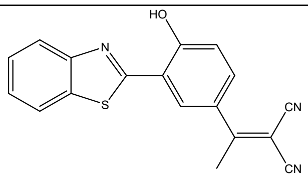
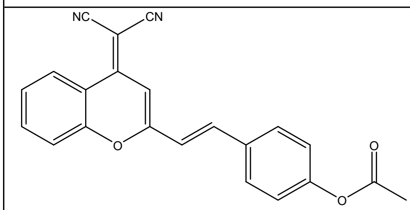
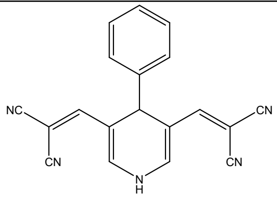
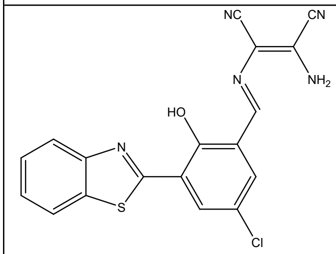
	Optimal structure	HOMO	LUMO	E_g （eV）
PPCy-TBE				1.788
PPCy-1				2.025

Table S3 The comparison of dihedral angle and bond length for **PPCy-TBE** and **PPCy-1**.

	PPCy-TBE	**PPCy-1**
Dihedral angle (°)		
α_{AB}	130.02	179.31
α_{BC}	-147.77	-178.89
α_{CD}	-179.47	177.08
α_{DE}	179.85	179.21
α_{FB}	-102.85	-131.51
Bond length (Å)		
B-F	1.539	1.419
B-F	1.540	1.436
B-N	1.495	1.546
B-N	1.770	1.558

Table S4 Summary of hydrazine fluorescence probes based on acrylonitrile recognition group.

Structure	Remark	Application	Ref.
	colorimetric and ratiometric fluorescent Turn on ($\Delta\lambda_{ab}$ = 198 nm, $\Delta\lambda_{em}$=173 nm), LOD = 0.075μM, response time: 30 s	Hydrazine gas detection, real water sample detection	This work
	Ratiometric signal, LOD = 0.43 μM, response time: 20 min	Cell bioimaging	Chem. Commun., 2012, 48, 8117–8119
	Ratiometric signal, LOD = 121.9 μM	Cell imaging, zebra fish imaging, Paper strip	RSC Adv., 2013, 3,18872-18877
	Off-on signal, LOD = 6.16 μM, response time: 30 min	Not reported	J. Mater. Chem. B, 2014, 2,1846-1851
	Off-on signal, LOD = 29 μM, response time: 55 min	Silica gel plate test, Cell imaging	RSC Adv., 2016, 6, 94959–94966
	Off-on signal, LOD = 570 μM, response time: 1 min	Cell imaging, Paper strip	Analyst, 2018, 143, 4298–4305

	ON-off signal, LOD = 1.1 nM, response time: 60 min	Paper strip	Luminescence. 2022;37:177–185
	Ratiometric signal, LOD = 0.31 μM, response time: 39 min	Cell and mouse imaging, Paper strip	Spectrochim. Acta A: 2022, 268, 120639