Development of a Novel Chromophore Reaction-based Fluorescent Probe for Biogenic Amines Detection

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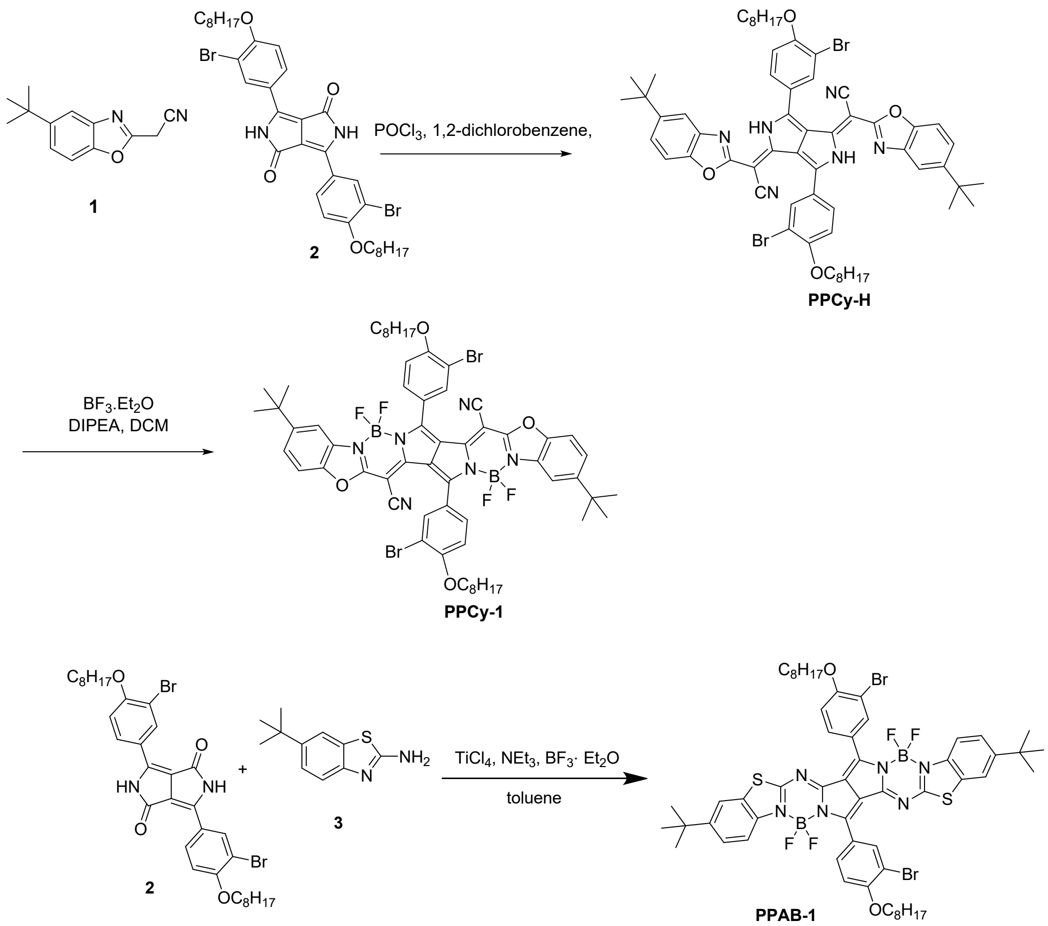
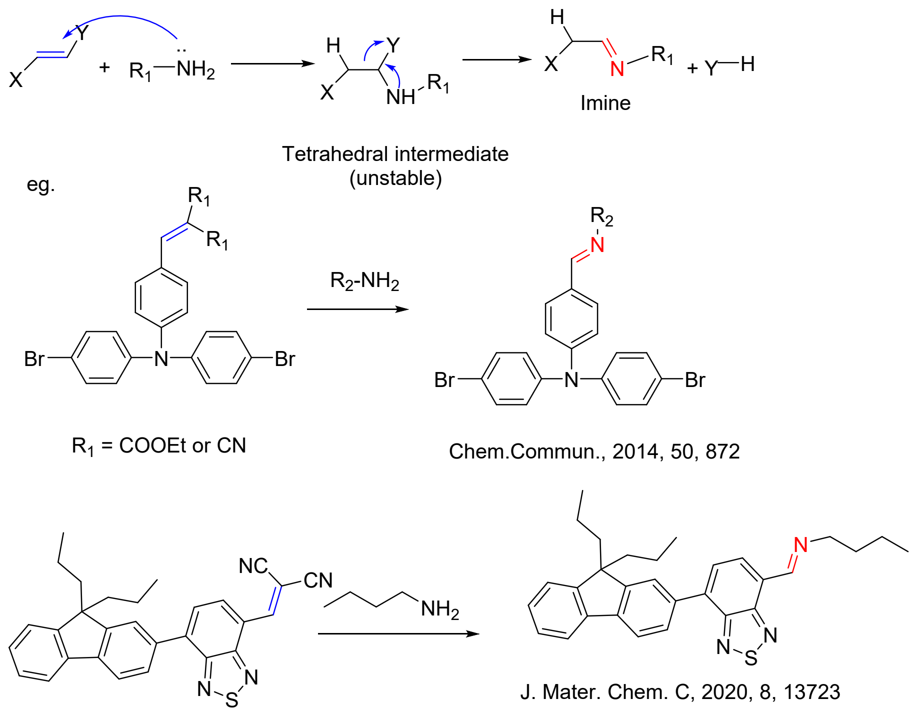
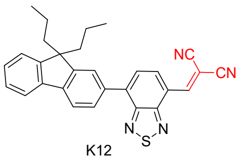
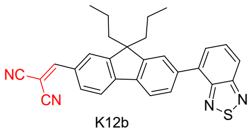
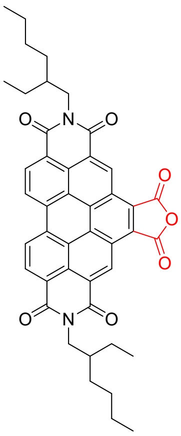
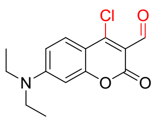
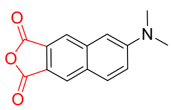


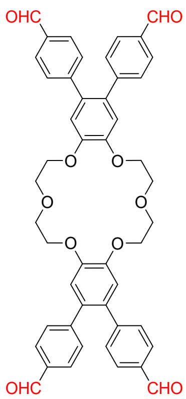
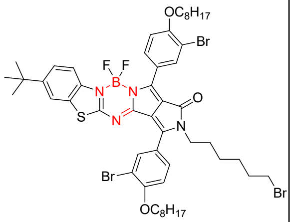
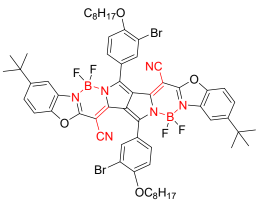
Scheme S1 The synthetic routes of **PPCy-1** and **PPAB-1**.



Scheme S2 The possible reaction process *aza*-Michael addition between amine and electrophile and some examples.

Table S1 The comparison of LOD, sensing characteristics and sensing mechanism with reported methods.

Probes	LOD	Response mechanisms	Remarks	Ref.
 K12  K12b	Cad. vapors: 130 ppb (**K12**) Cad. Vapors: 610 ppb **(K12b)**	Solution: *aza*-Michael addition Films: photoinduced hole transfer	Reaction time: **K12**: >30 min **K12b**: overnight High sensitivity to primary alkyl amines, Practical application: No	J. Mater. Chem. C, 2020, 8, 13723
	Spm.:180 nM Other diamines:180 -400 nM Cad. vapors: 4.3 ppm	Reaction-induced polarity-driven self-aggregation	Difficult to discriminative detection BAs and other amines, small spectral changes, Practical application: detect fish freshness	ACS Appl. Mater. Interfaces, 2019, 11, 47207
	Cad.: 209 nM	Dechlorination and condensation reaction	Reaction time: 40 min, small spectral changes,	Dyes and Pigments, 2021, 186, 108963
	BAs: less than 0.2 μM	Nucleophilic addition	Reaction time: 10 min Practical application: No	Analyst, 2016, 141, 827

	Spd.: 46 nM	Schiff base formation induced aggregation of terphenyl derivative	Reaction time: > 20 min Practical application: detect Spd in artificial urine sample	Sensor Actuat. Chem, 2018, 258, 841
	Spm.: 0.193 μM	Chromophore reaction	Reaction time: 60 s, high selectivity to Spm and Spd, but slow reactivity to Put and Cad Practical application: detect fish freshness	Anal. Chim. Acta 2020, 1135, 38
	Put.: 0.179 μM Cad.: 0.229 μM Spd.: 0.043 μM Spm.: 0.066 μM	Novel chromophore reaction	Reaction time: 1 min, high selectivity and high sensitivity to BAs, Large spectral changes Practical application: detect BAs vapor and shrimp freshness	This work

Abbr: Putrescine (Put), cadaverine (Cad), spermine (Spm), spermidine (Spd)

Table S2 The vapor pressure, pK_a and relative vapor density of different amines.

Amines	Vapor pressure (kPa)	pK_a	Relative vapor density (air = 1)
1,3-Diaminepropane	0.58	10.94, 9.82	2.5
Putrescine	0.31	10.80	No data
Cadaverine	0.13	10.05	No data
Spermidine	0.036	11.56, 10.80, 9.52	No data
Trimethylamine	214.6	9.80	2.04
Triethylamine	7.6	10.78	3.5
Ammonia	48.0	9.23	0.6

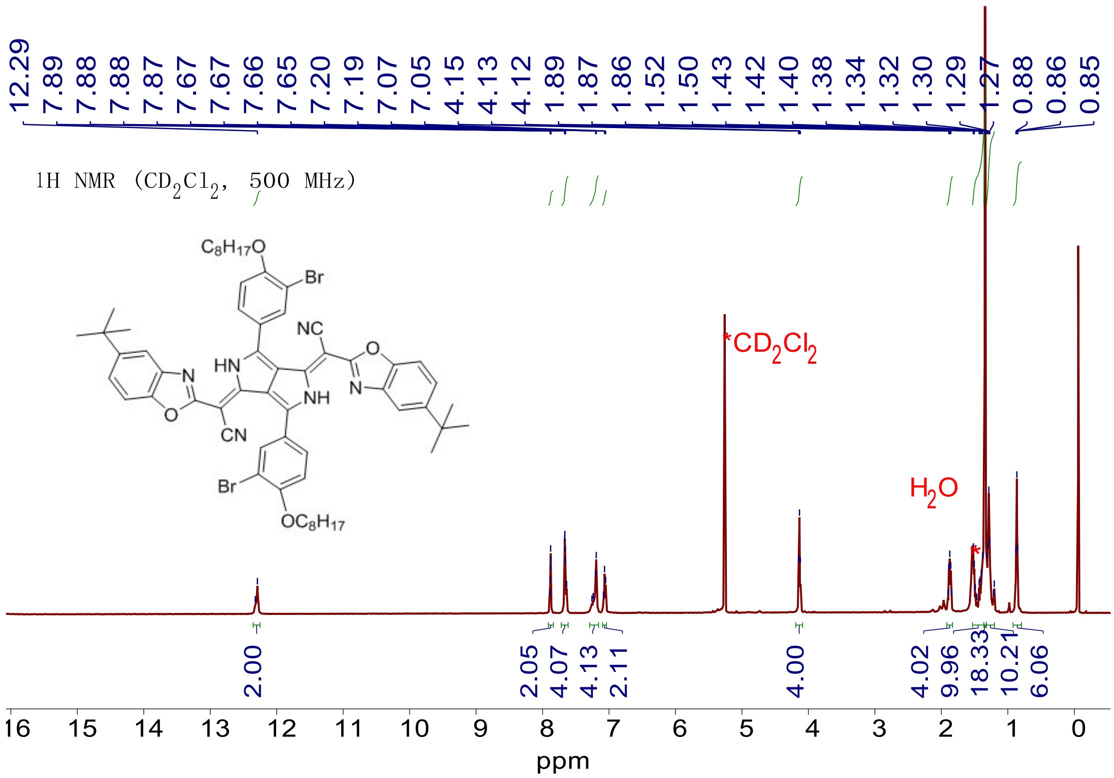


Figure S1 [1]H NMR spectrum of **PPCy-H**

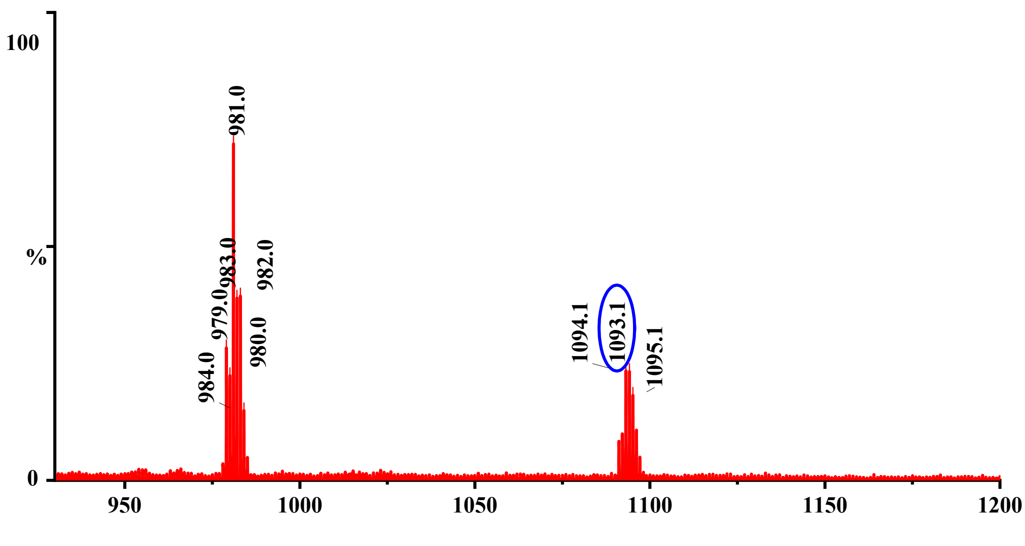


Figure S2 MALDI-TOF spectrum of **PPCy-H**

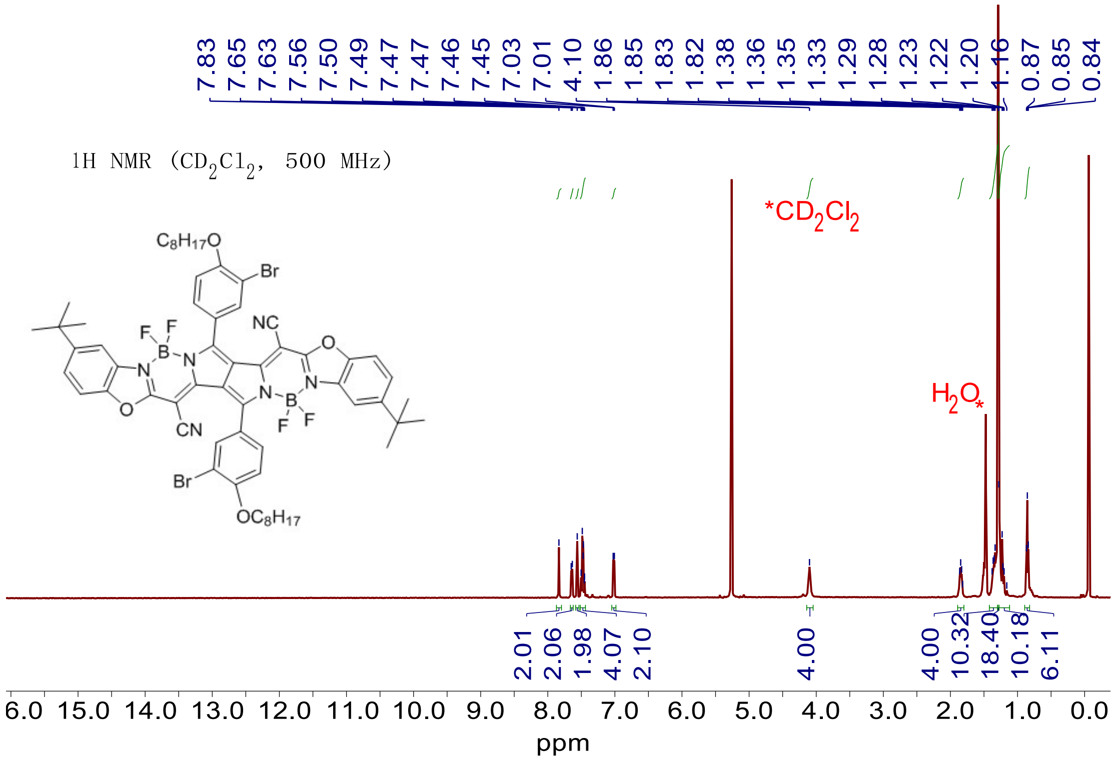


Figure S3 ^{1}H NMR spectrum of **PPCy-1**

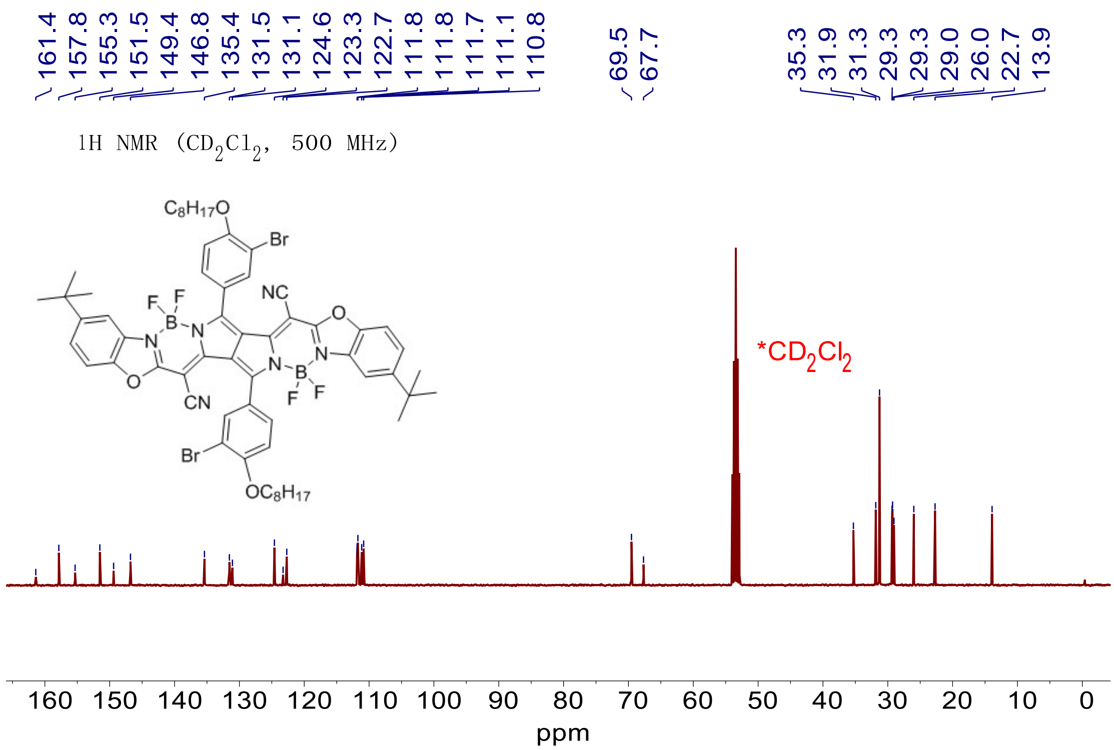


Figure S4 ^{13}C NMR spectrum of **PPCy-H**

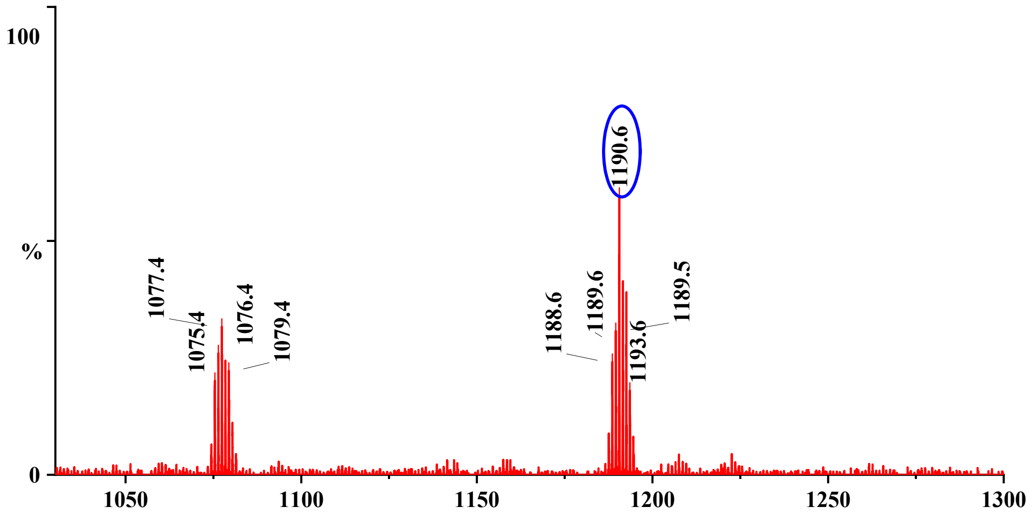


Figure S5 MALDI-TOF spectrum of **PPCy-1**

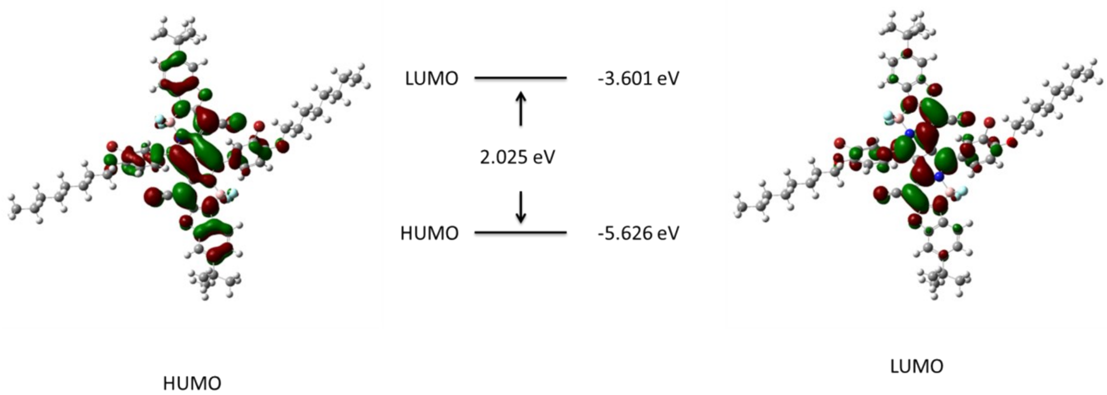


Figure S6 DFT calculation of **PPCy-1**

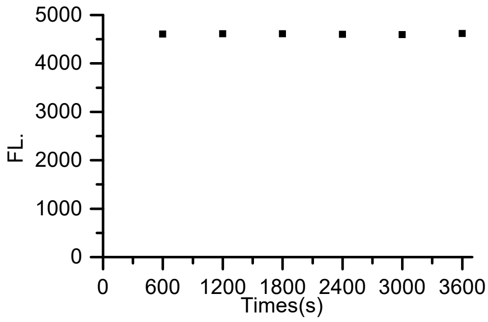
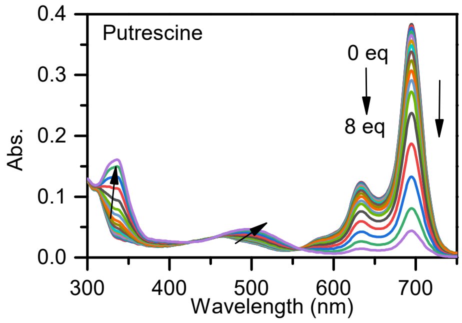
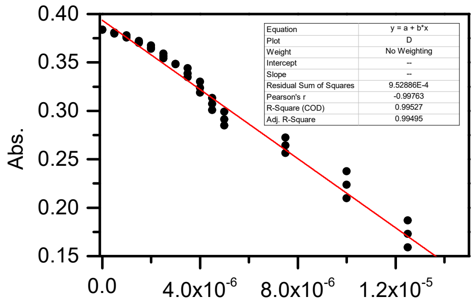


Figure S7 The emission intensity at 720 nm of **PPCy-1** after exposure xenon lamp (150 W) for different time.



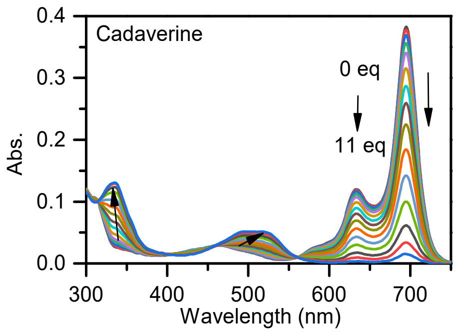


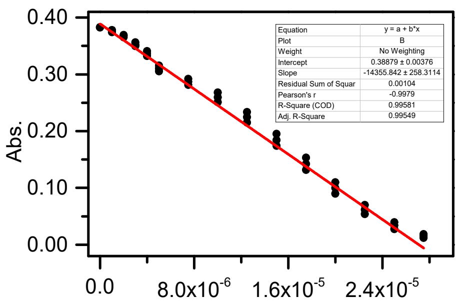
Linear Equation: Y=-18192.8X+0.39761 R = 0.99601

S = 1.82×10^4 $\delta = \sqrt{\frac{\sum (A_0 - A_1)^2}{N-1}}$ = 0.00109068786 (N = 11) K

= 3

LOD = K × δ / S = 3 × 0.00109/ (1.82×10^4) = 0.179 ± 0.00415 μM





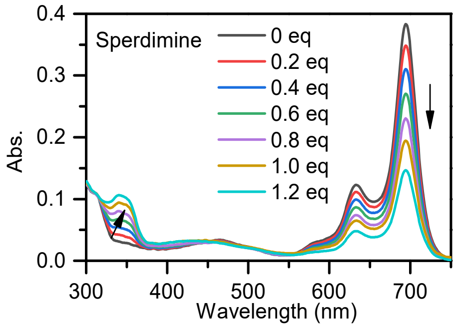
Li

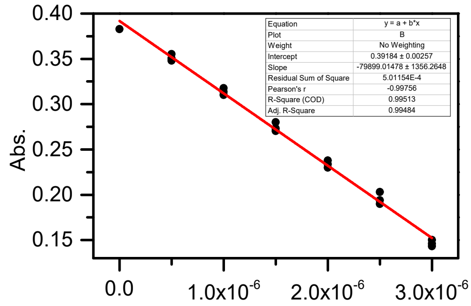
near Equation: Y= -14355.8X+ 0.38879 R = 0.9952

S = 1.43×10^4 $\delta = \sqrt{\frac{\sum (A_0 - A_1)^2}{N-1}}$ = 0.00109068786 (N = 11) K

= 3

LOD = K × δ / S = 3 × 0.00109/ (1.43×10^4) = 0.229 ± 0.00411 μM

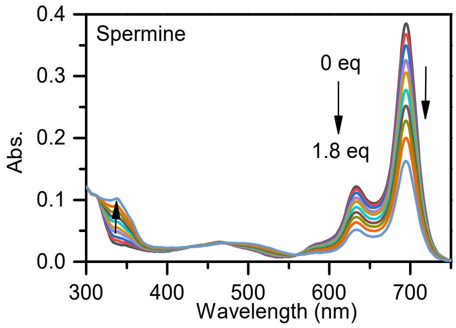


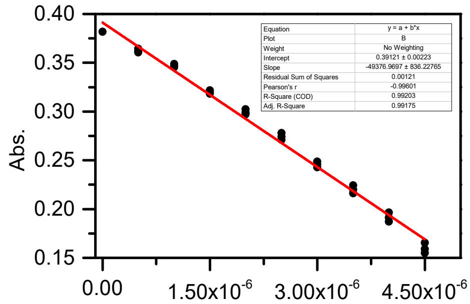


Linear Equation: Y= -76505.18X+ 0.38844 R = 0.99909

S = 7.65 × 10^4 $\delta = \sqrt{\frac{\sum (A_0 - A_1)^2}{N-1}}$ = 0.00109068786 (N = 11) K = 3

LOD = K × δ / S = 3 × 0.00109/ (7.65 × 10^4) = 0.0427±0.00102 μM





Linear Equation: Y= -49377.0X+ 0.39121 R = 0.99907

S = 4.93 × 10^4 $\delta = \sqrt{\frac{\sum (A_0 - A_1)^2}{N-1}}$ = 0.00109068786 (N = 11) K = 3

LOD = K × δ / S = 3 × 0.00109/ (4.93 × 10^4) = 0.0663±0.00112 μM

Figure S8 Concentration-dependent UV-vis spectra and linear relationship of absorption at 695 nm of **PPCy-1** (2.5 μM) in presence of putrescine, cadaverine, spermine, spermidine at 25 ^{o}C, each solution was mixed and left for 2 min.

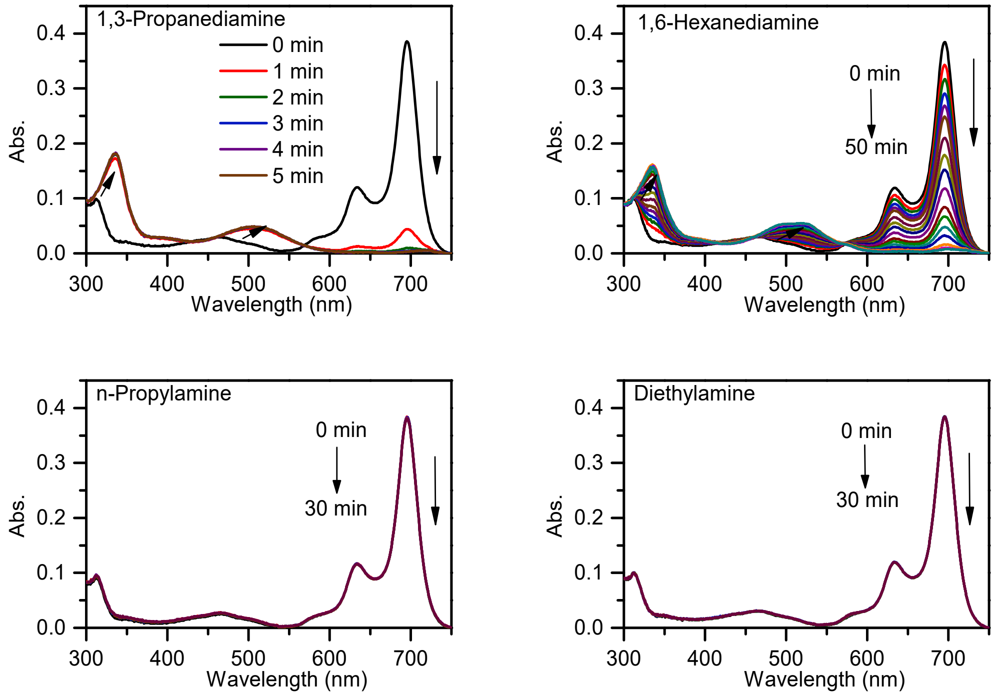


Figure S9 The time-dependent UV-Vis spectra of **PPCy-1** (2.5 μM) in presence of 1,3-propanediamie, 1,6-hexanediamino, n-propylamine and diethylamine (50 μM) at room temperature.

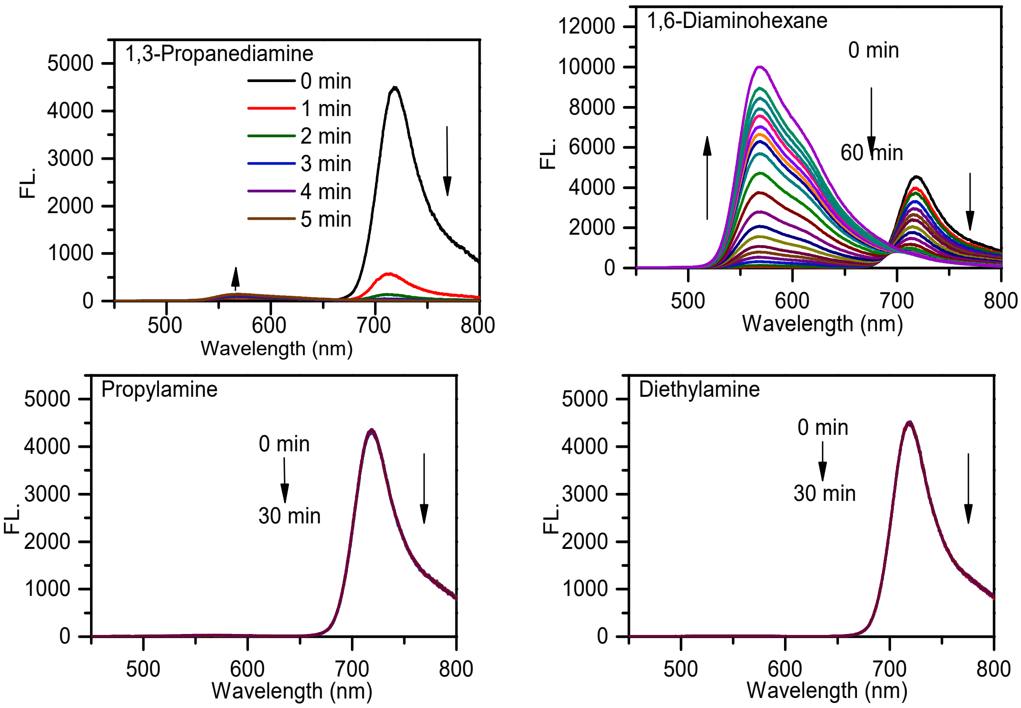


Figure S10 The time-dependent emission spectra of **PPCy-1** (2.5 μM) in presence of 1,3-propanediamie, 1,6-diaminohexane, propylamine and diethylamine (50 μM) at room temperature.

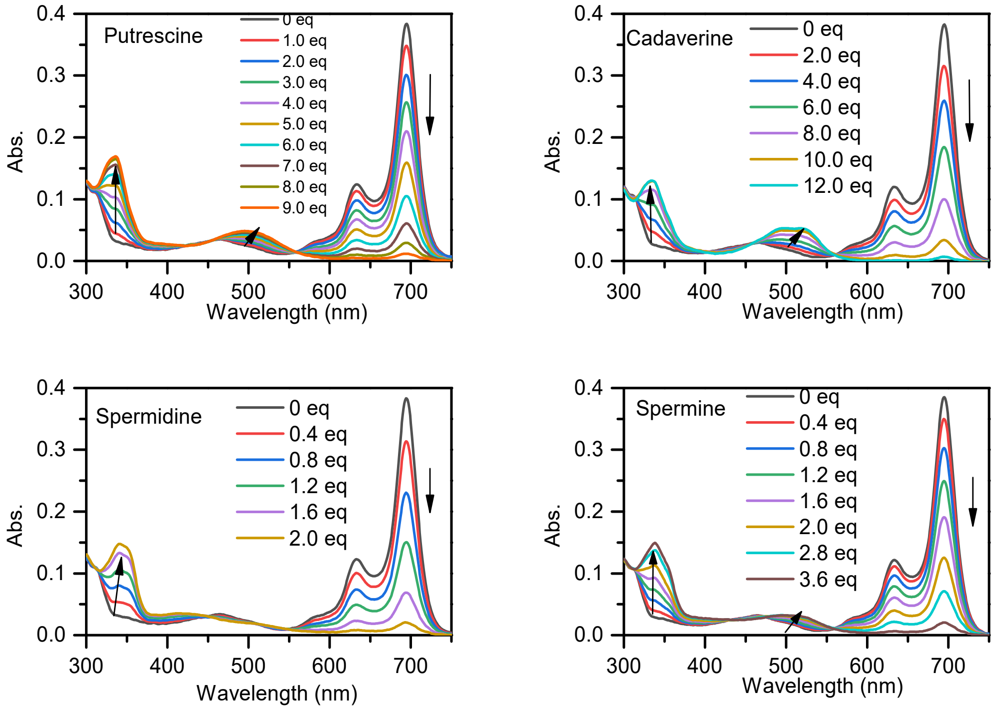


Figure S11 The BAs concentration-dependent UV-vis spectra of **PPCy-1** (2.5 μM) in presence of putrescine, cadaverine, spermidine, and spermine at room temperature for 2 min.

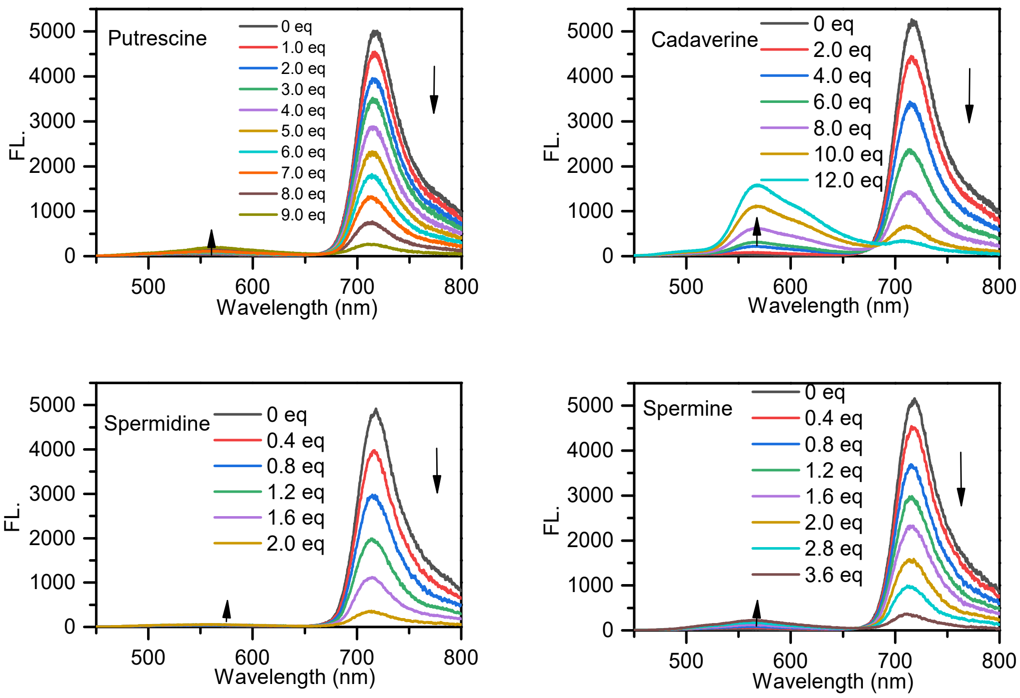
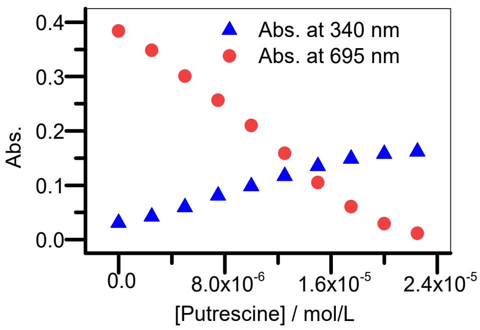
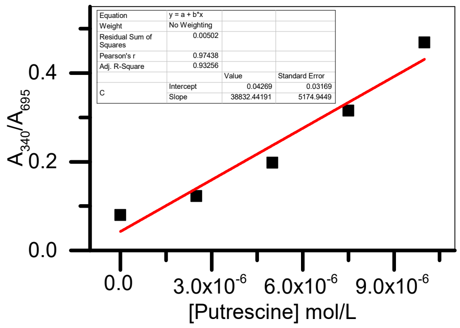
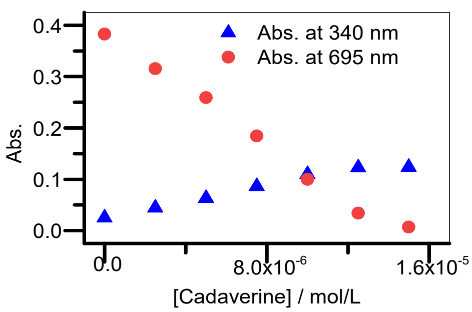
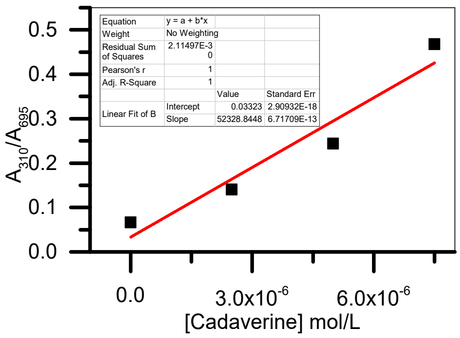


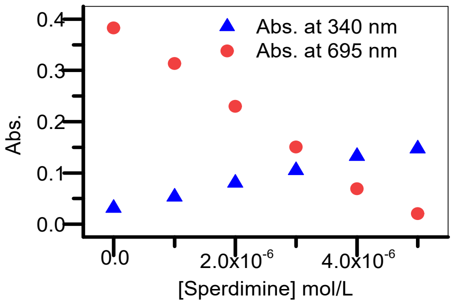
Figure S12 The BAs concentration-dependent emission spectra of **PPCy-1** (2.5 μM) in presence of putrescine, cadaverine, spermidine, and spermine at room temperature for 2 min.

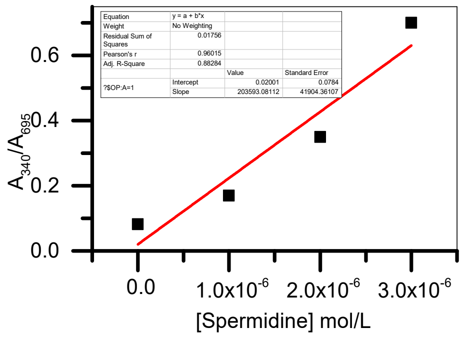


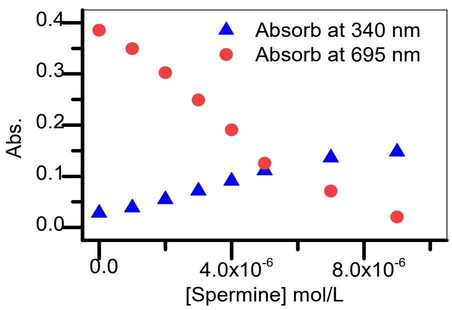


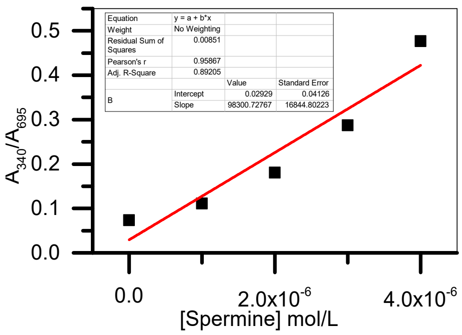












The standard deviation and slope were obtained by plotting ratio of absorption intensities at 340 nm and 695 nm with concentration of amine. Detection limit = 3 σ/K, σ = Standard error = 0.00109, K = Slope = 38832 (putrescine), 52328 (cadaverine), 203593 (spermidine) and 98300 (spermine). Detection Limit = 0.084 (putrescine), 0.063 (cadaverine), 0.016 (spermidine) and 0.033 μM (spermine).

Figure S13 Determination of limit of detection (LOD) using linearly-fitted ratiometric plot using absorption intensities at 340 nm and 695 nm of putrescine, cadaverine, spermidine, and spermine.

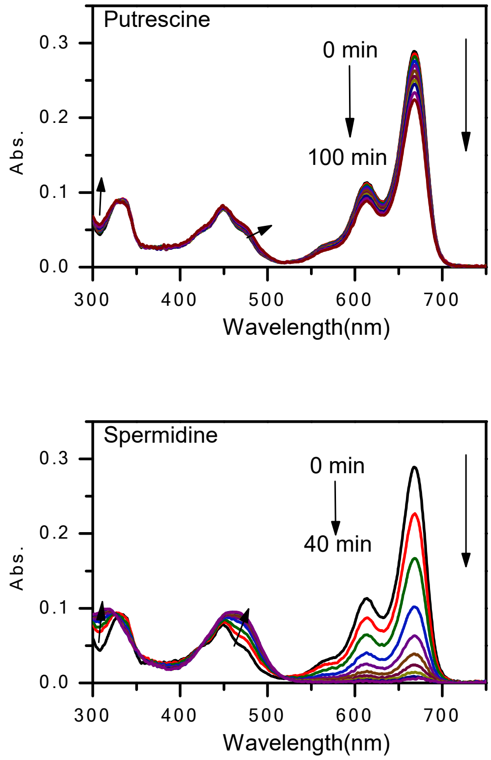


Figure S14 The time-dependent UV-Vis spectra of **PPAB-1** (2.5 μM) in presence of spermidine, cadaverine (50 μM) at room temperature.

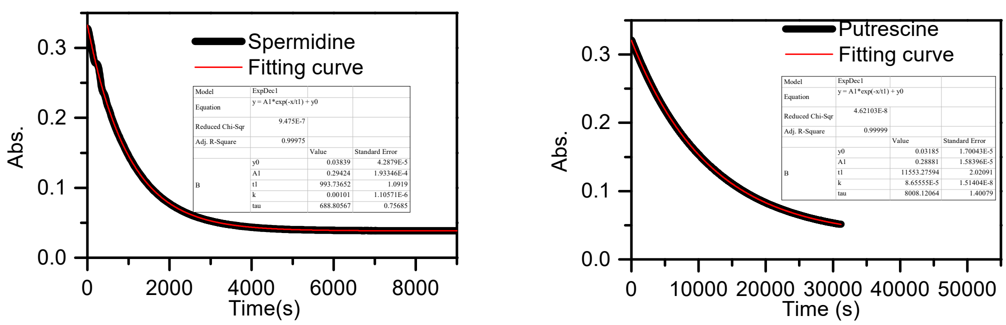
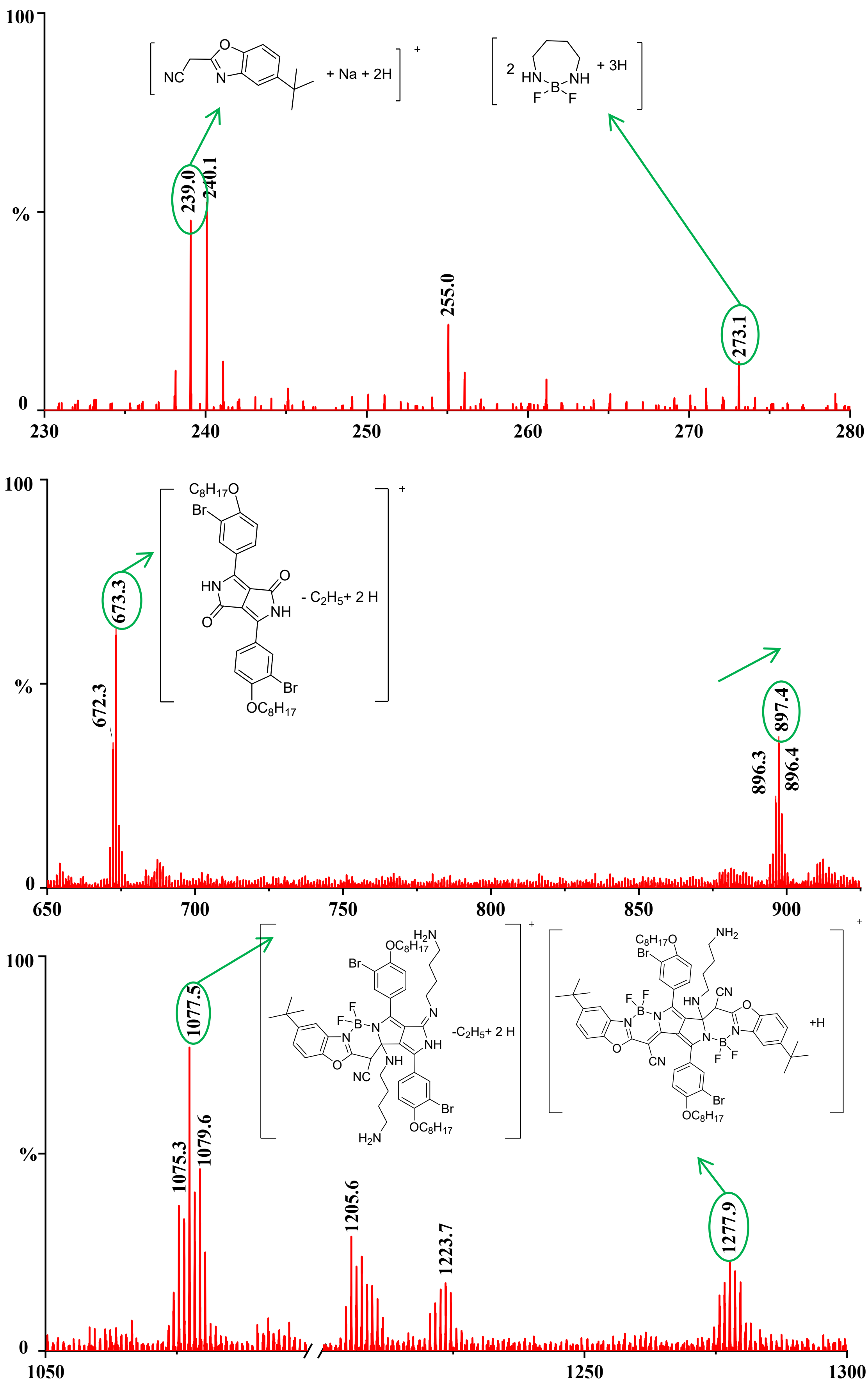


Figure S15 The reaction kinetics of **PPAB-1** (2.5 μM) in presence of spermidine, cadaverine (50 μM) at room temperature.



100
%
0
239.0
240.1
255.0
273.1
+ Na + 2H
+ 3H
230
240
250
260
270
280
672.3
673.3
- C2H5+ 2 H
896.3
896.4
897.4
650
700
750
800
850
900
1075.3
1077.5
1079.6
1205.6
1223.7
1277.9
-C2H5+ 2 H
+H
1050
1250
1300

Figure S16 The HRMS spectra of **PPCy-1** (2.5 μM) in presence of cadaverine (50 μM) at room temperature.

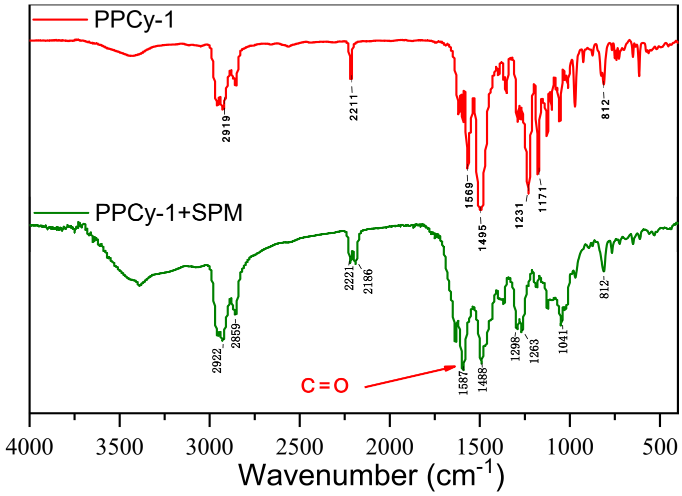


Figure S17 The FTIR spectra of **PPCy-1** in absence and presence of spermidine.

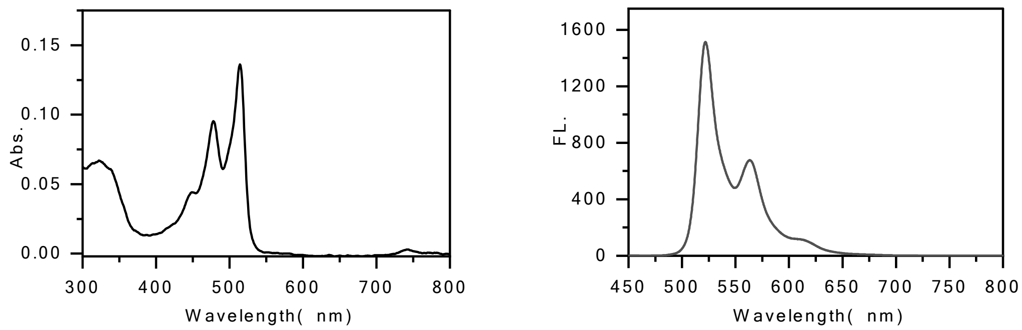


Figure S18 (a) the UV-Vis and (b) emission spectra of DPP compound **2** (2.5 μM).

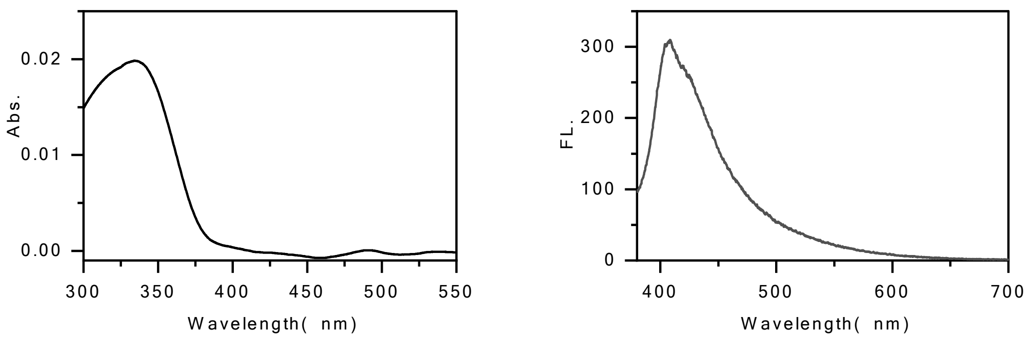


Figure S19 (a) the UV-Vis and emission spectra of heteroaromatic acetonitrile **1** (2.5 μM) in $CHCl_3$.

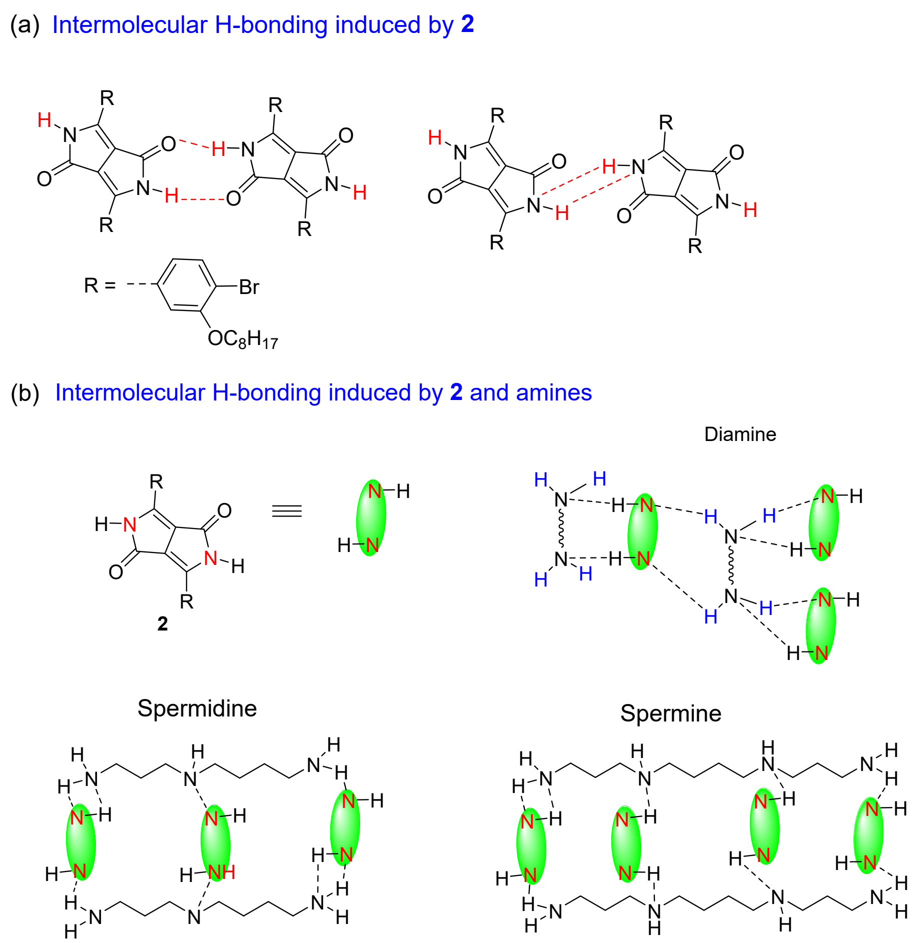


Figure S20 (a) The possible intermolecular H-bonding of diketopyrrolopyrrole (**2**). (b) The possible intermolecular H-bonding of between different amines and diketopyrrolopyrrole (**2**).

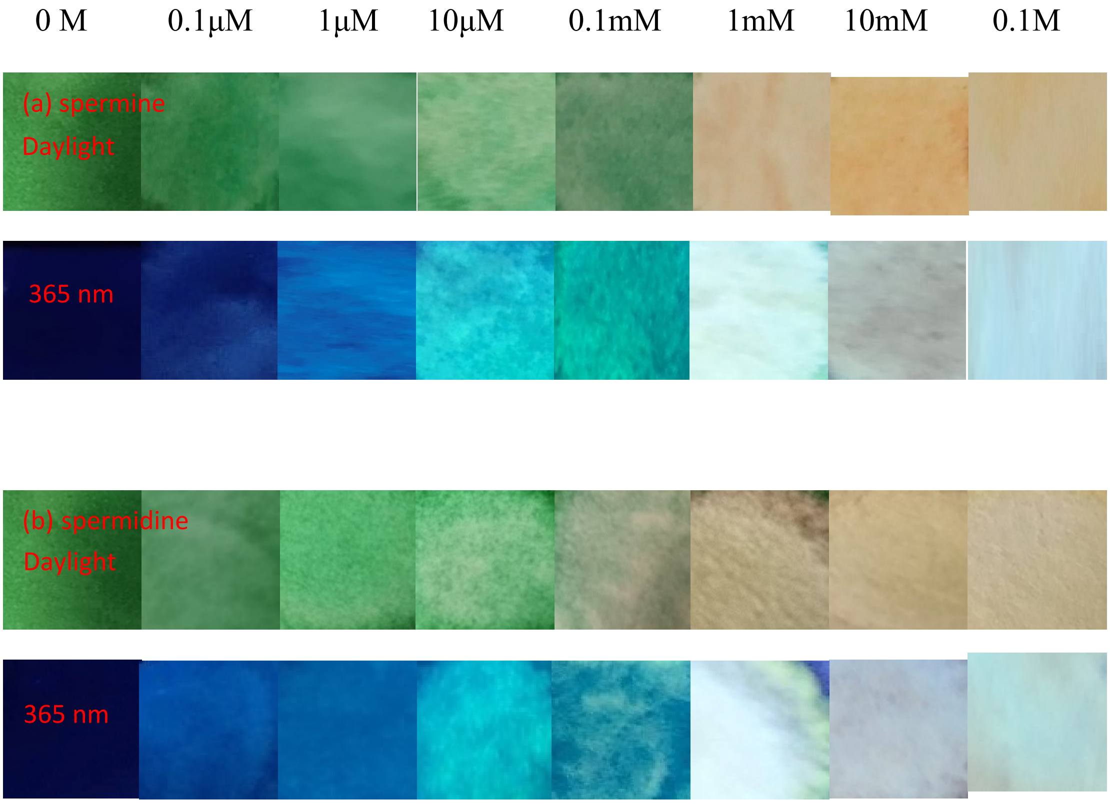


Figure S21. The color and emission changes of **PPCy-1-**loaded filter paper with colorimetric (top) and fluorescent (bottom) dual modes in presence of (a) spermine, and (b) spermidine at 25 ^{o}C.

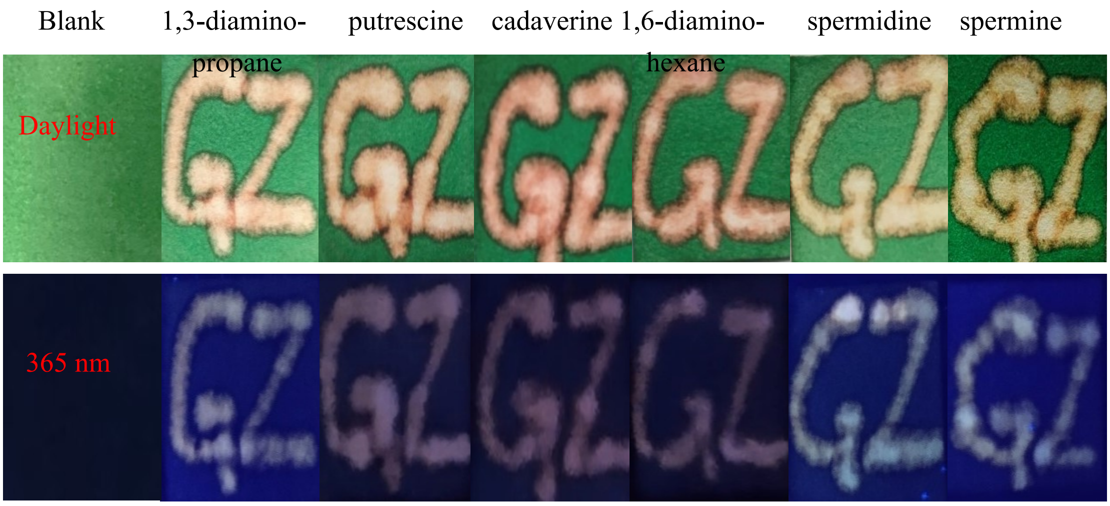


Figure S22. Photos of **PPCy-1**-loaded filter paper written “GZ” letters before and after exposure to amine solution (1 mM) in dioxane under daylight and UV light. From left to right: blank, 1,3-diaminopropane, putrescine, cadaverine, 1,6-diaminohexane, spermidine, spermine.

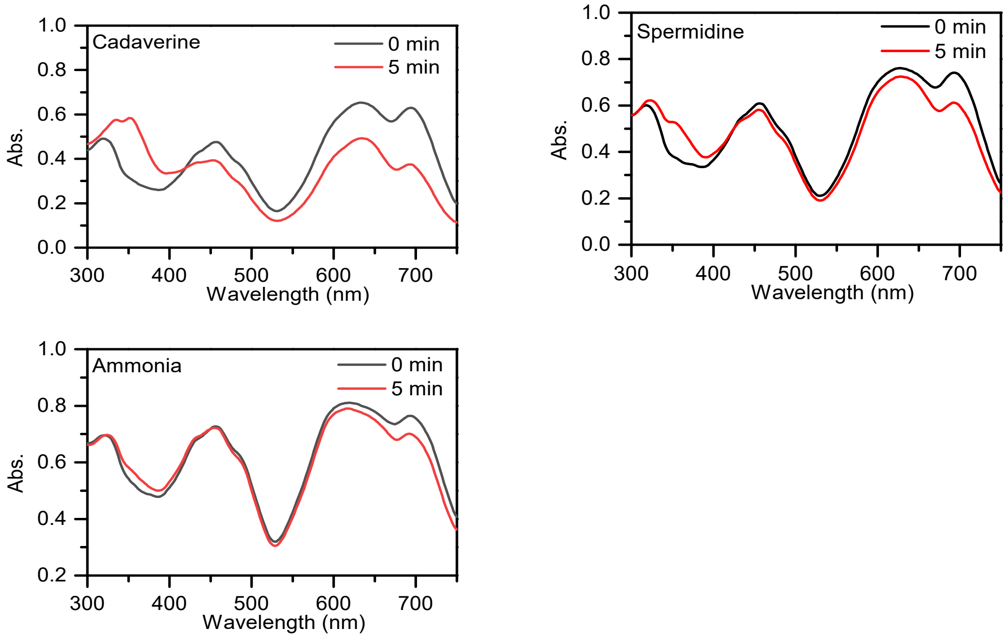


Figure S23. UV-vis spectra and photos of **PPCy-1**-loaded filter paper before and after exposure to spermidine and ammonia vapor.

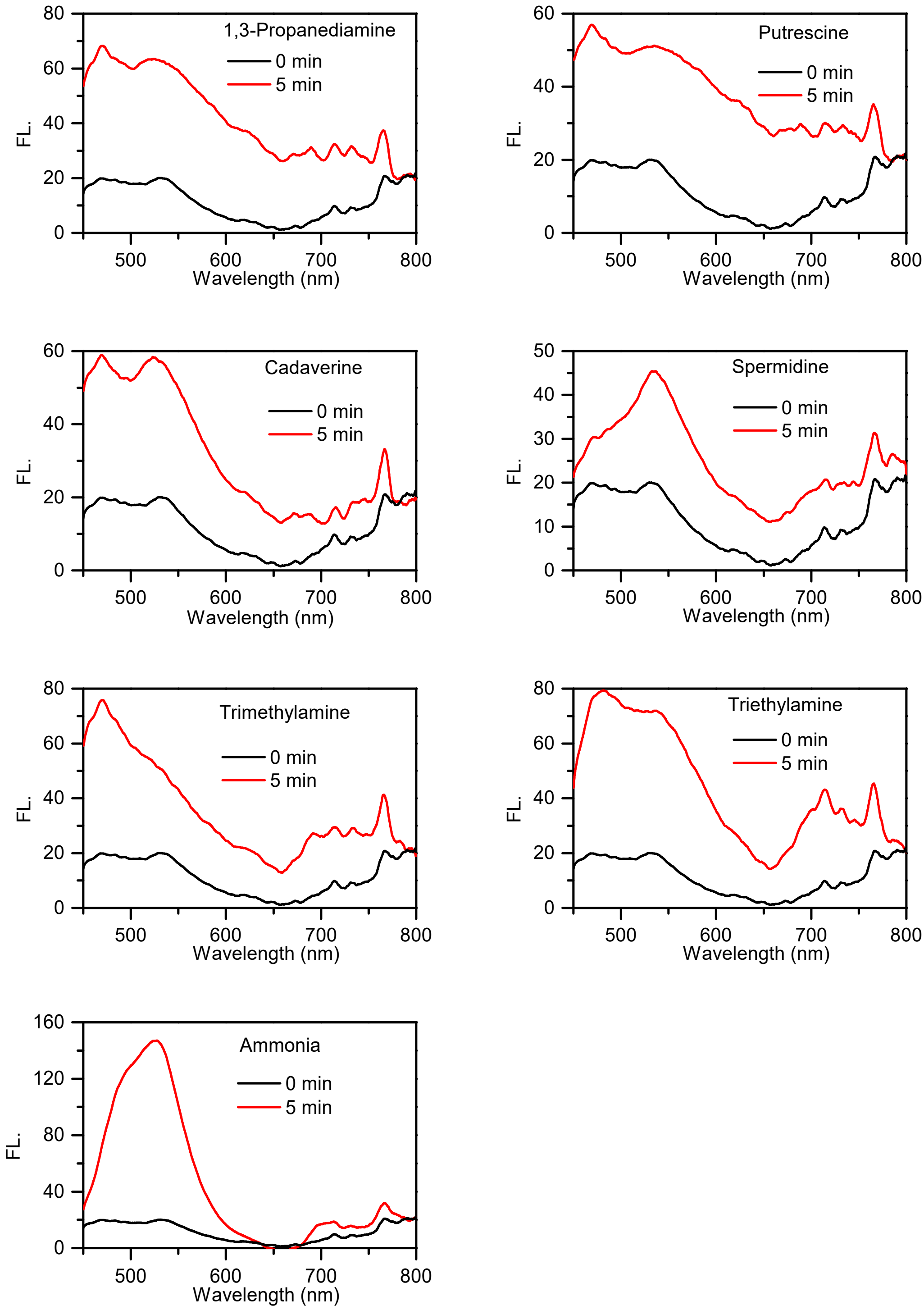


Figure S24. The emission spectra and photos of **PPCy-1**-loaded filter paper before and after exposure to trimethylamine, triethylamine, putrescine, 1,3-diaminepropane, cadaverine, spermidine and ammonia vapor.

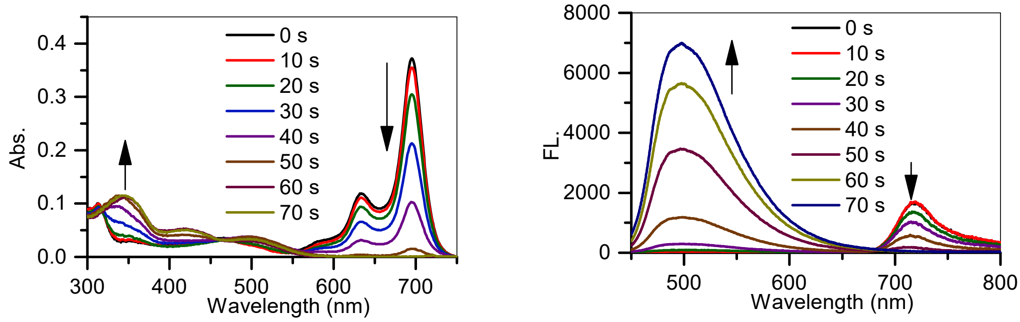


Figure S25 The time-dependent (left) absorption and (right) emission spectra of **PPCy-1** (2.5 μM) solution in presence of ammonia vapor at room temperature.

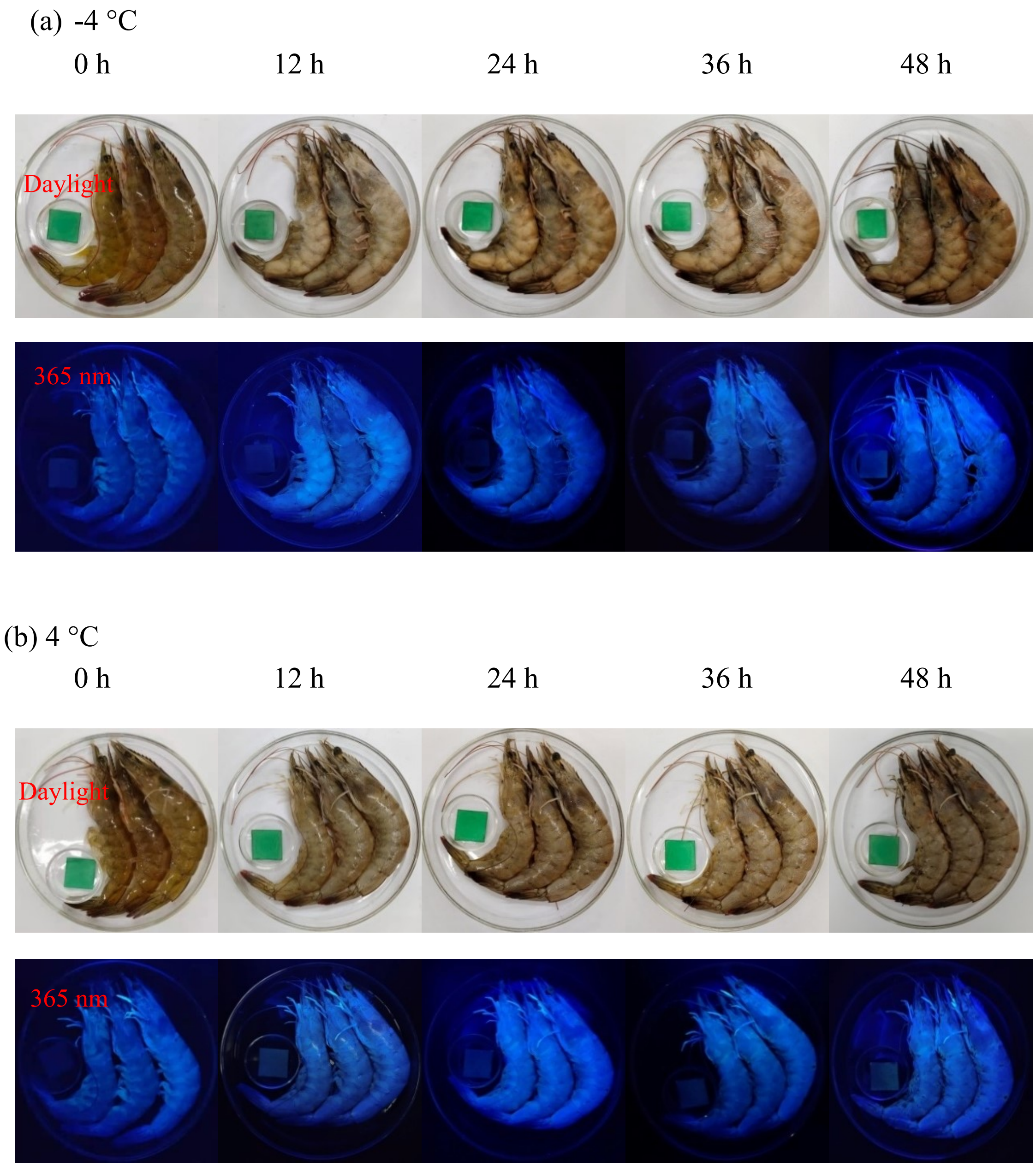


Figure S26. Photos of monitoring shrimp spoilage at (a) -4 °C and (b) 4 °C by **PPCy-1**-loaded filter paper under daylight and 365 nm irradiation.

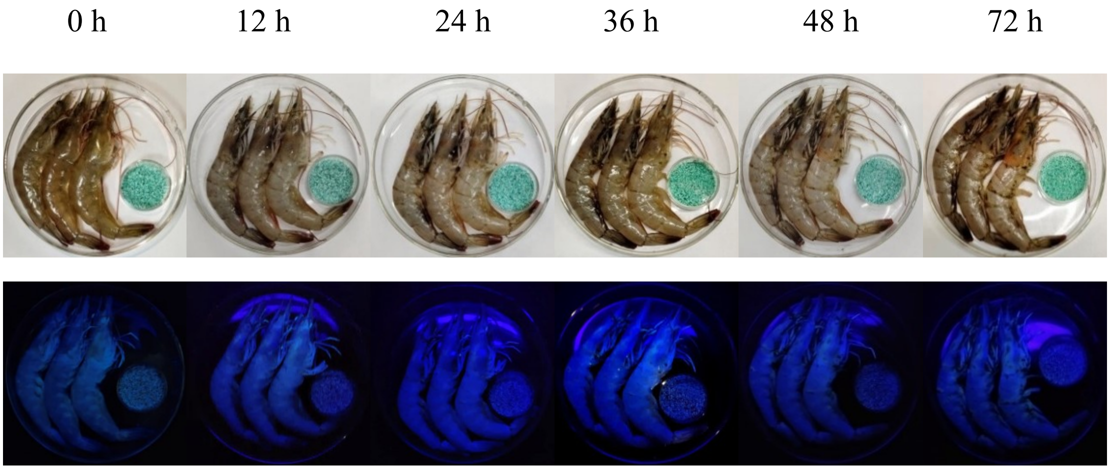


Figure S27. Photos of monitoring shrimp spoilage at 4 °C by **PPCy-1**-loaded CAD-40 resin under daylight and 365 nm irradiation.