Supplementary Information

Dual state emissive triphenylamine-coumarin fluorescent polymorphs: halochromic reversible fluorescence switching and π-π stacking facilitated picric acid sensing

Time-resolved fluorescence measurement

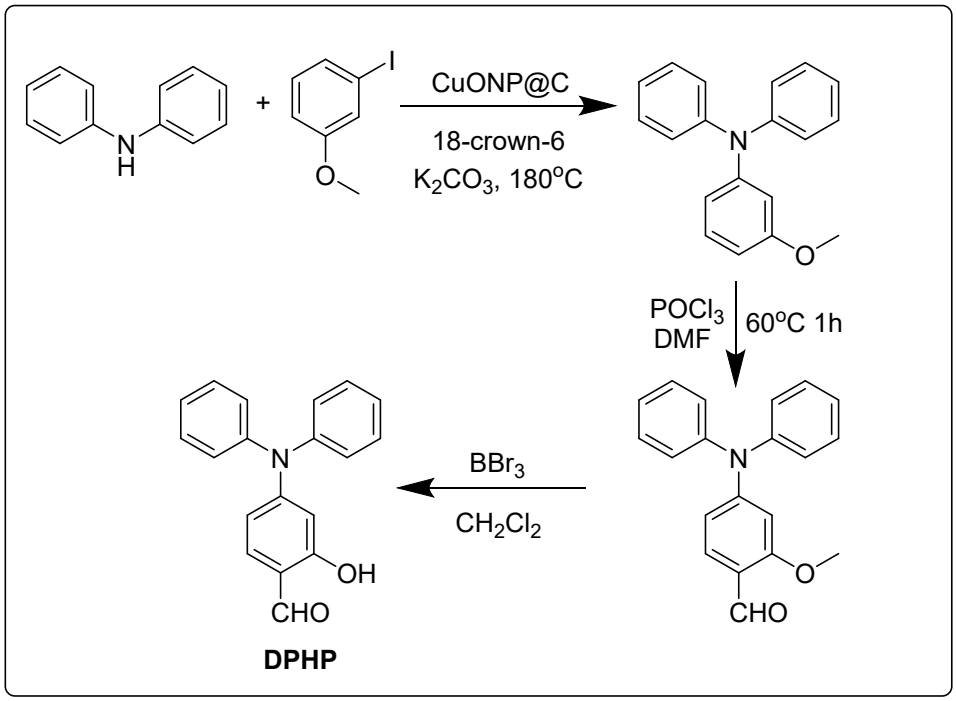
Fluorescence lifetimes were measured from time-resolved intensity decay by the method of time-correlated single-photon counting (TCSPC) technique by FluoroCube-01-NL spectrometer (Horiba Jobin Yovon IBH Ltd.) using a nano LED light source at 340 nm, and the signals were collected at the magic angle (54.7◦) polarization. The IRF of the detector is (fwhm) =750 ps. DAS6 software was used to deconvolute the fluorescence decays. The relative contribution of each component was obtained from the bi-exponential fitting and finally expressed by the following equation.

$a_n = B_n / \sum B_i$

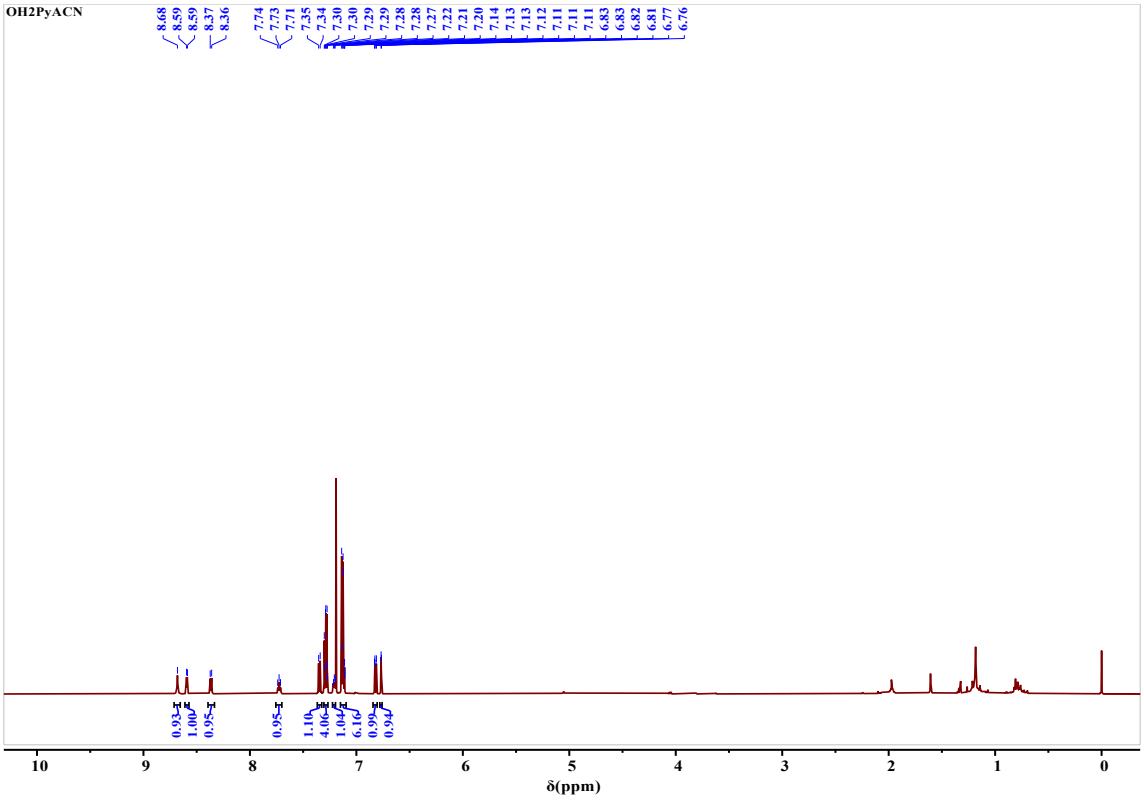
B_i is the pre-exponential factor. The mean fluorescence lifetimes for the decay curves were calculated from the decay times and the relative contribution of the components using the following equation.

$\langle \tau \rangle = \sum a_i \tau_i^2 / \sum a_i \tau_i$

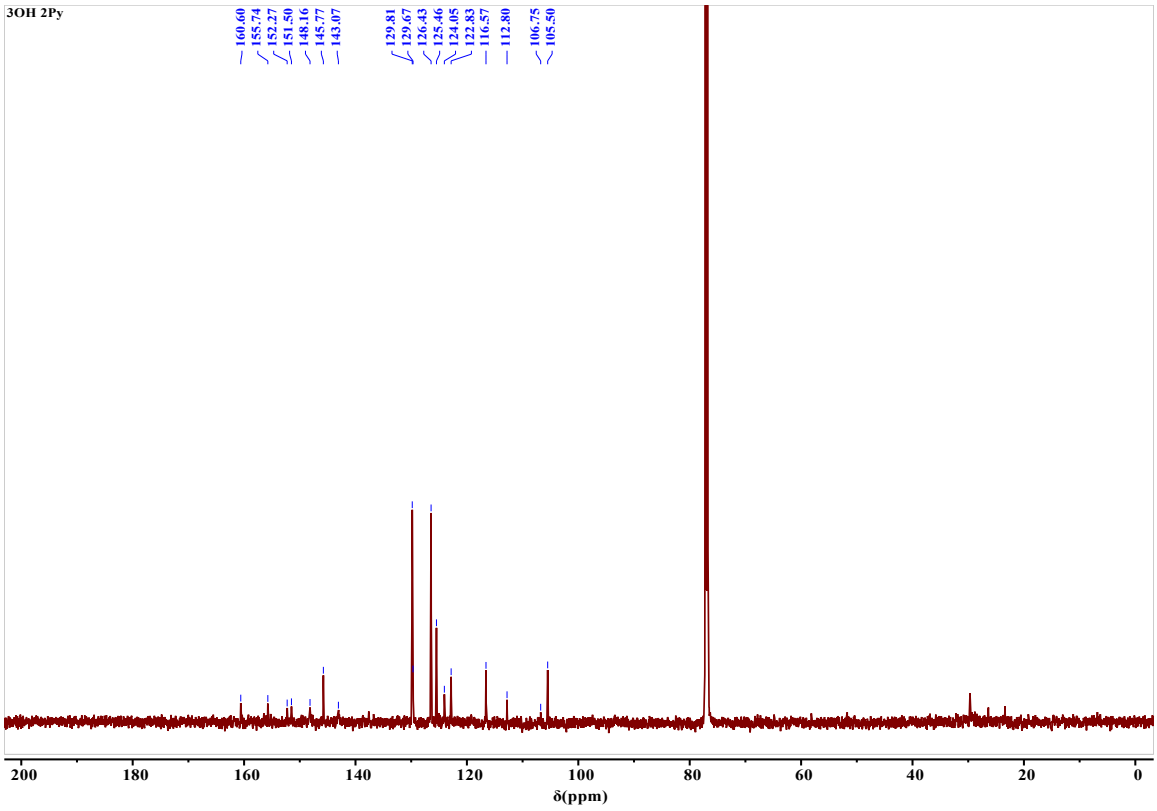
τ_i and a_i are the fluorescence lifetime and its coefficient of the i^{th} component, respectively.



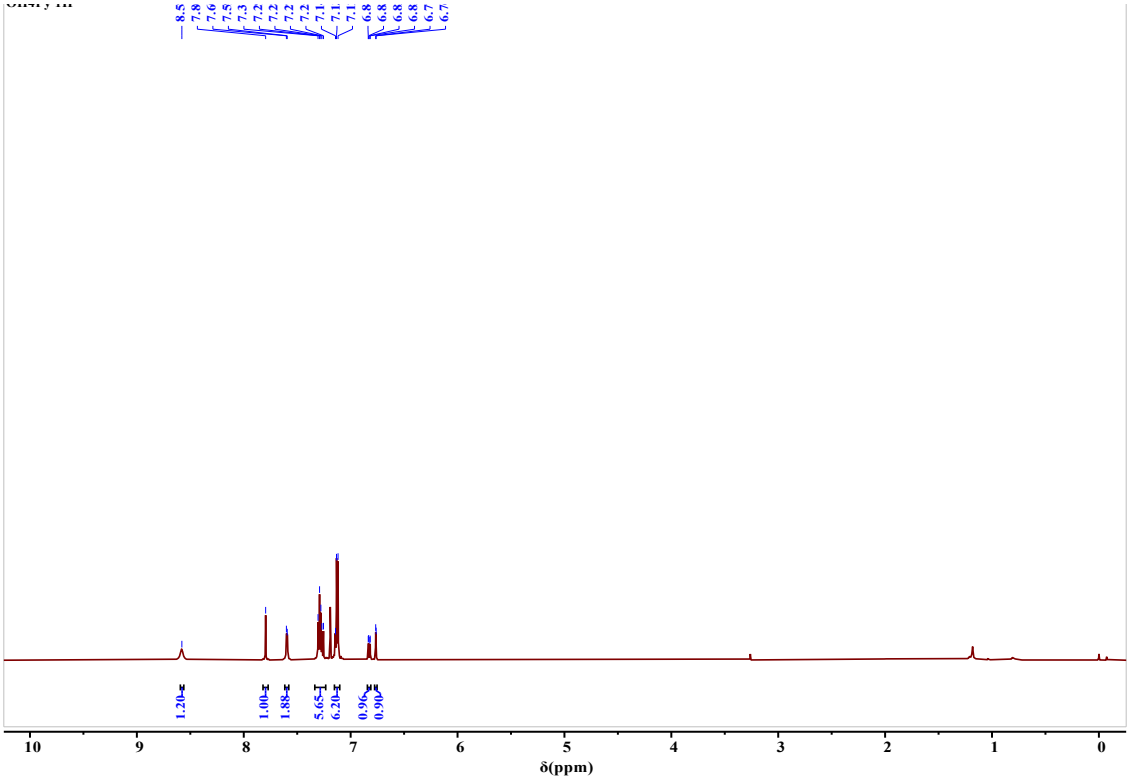
Scheme S1. Synthesis of **4-(diphenylamino)-2-hydroxybenzaldehyde.**



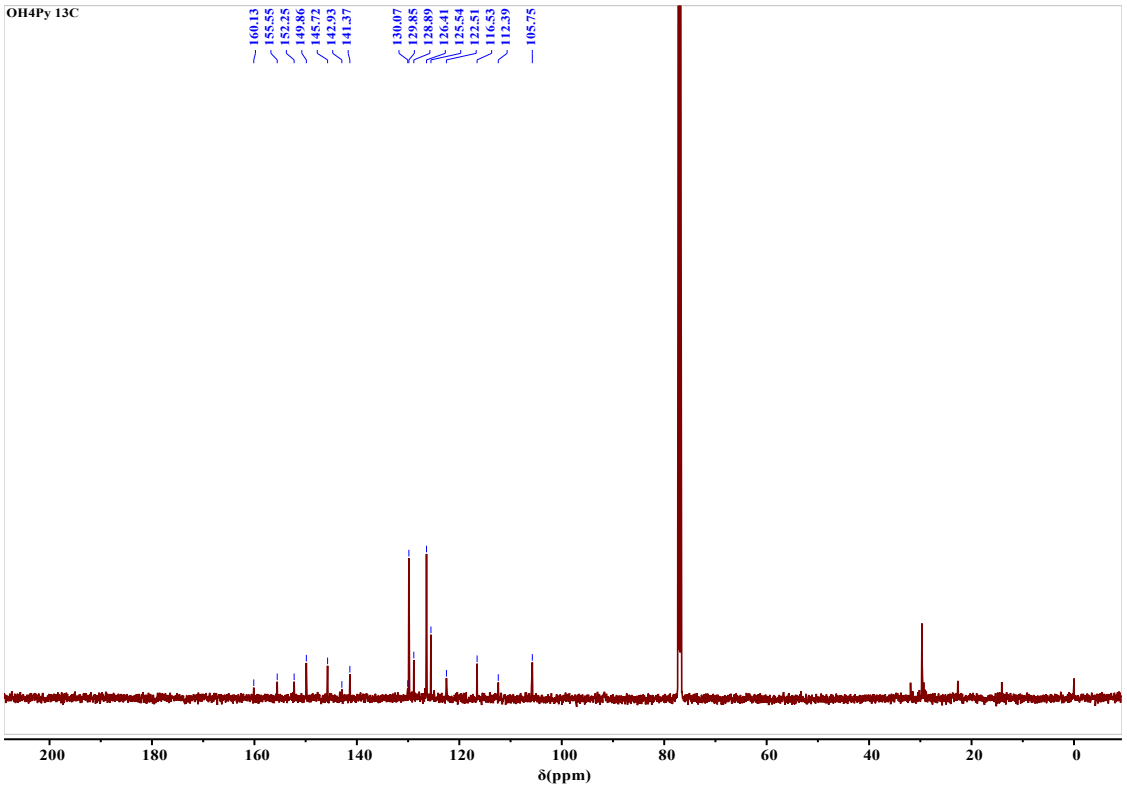
^{1}H NMR spectra of DP2C.



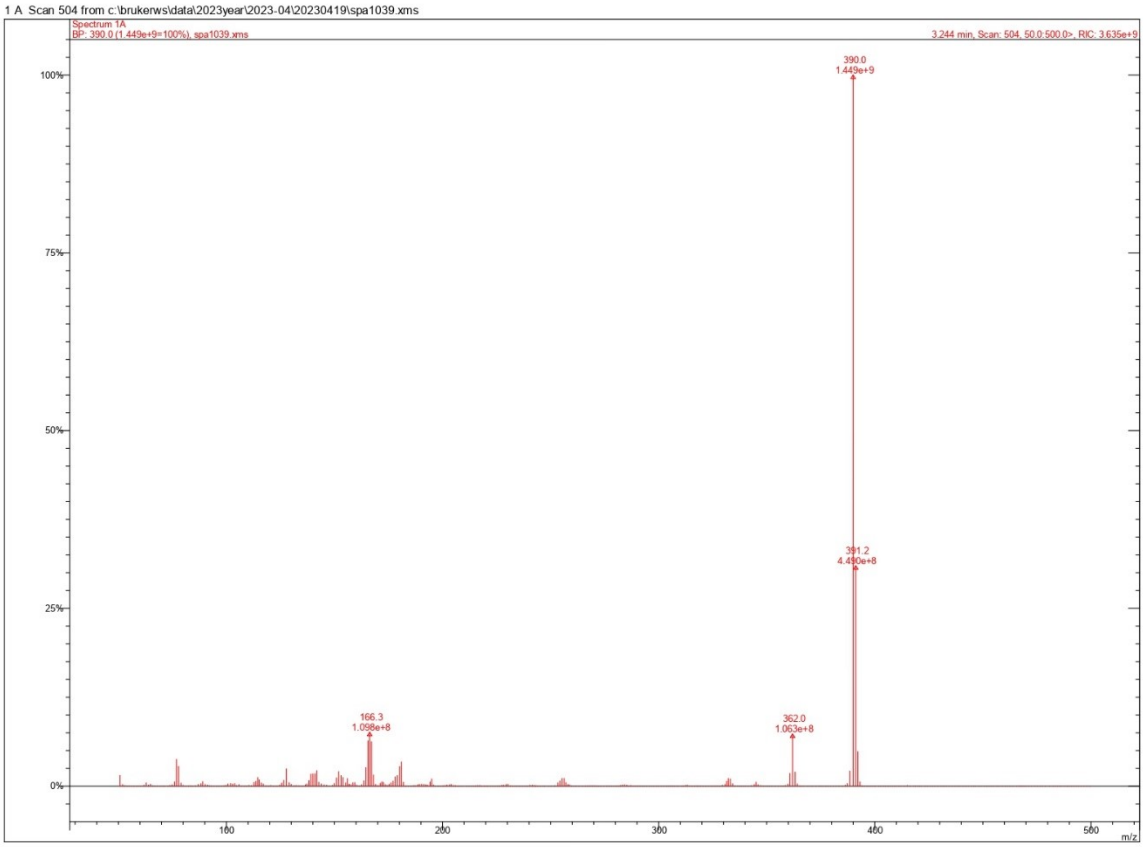
^{13}C NMR spectra of DP2C.



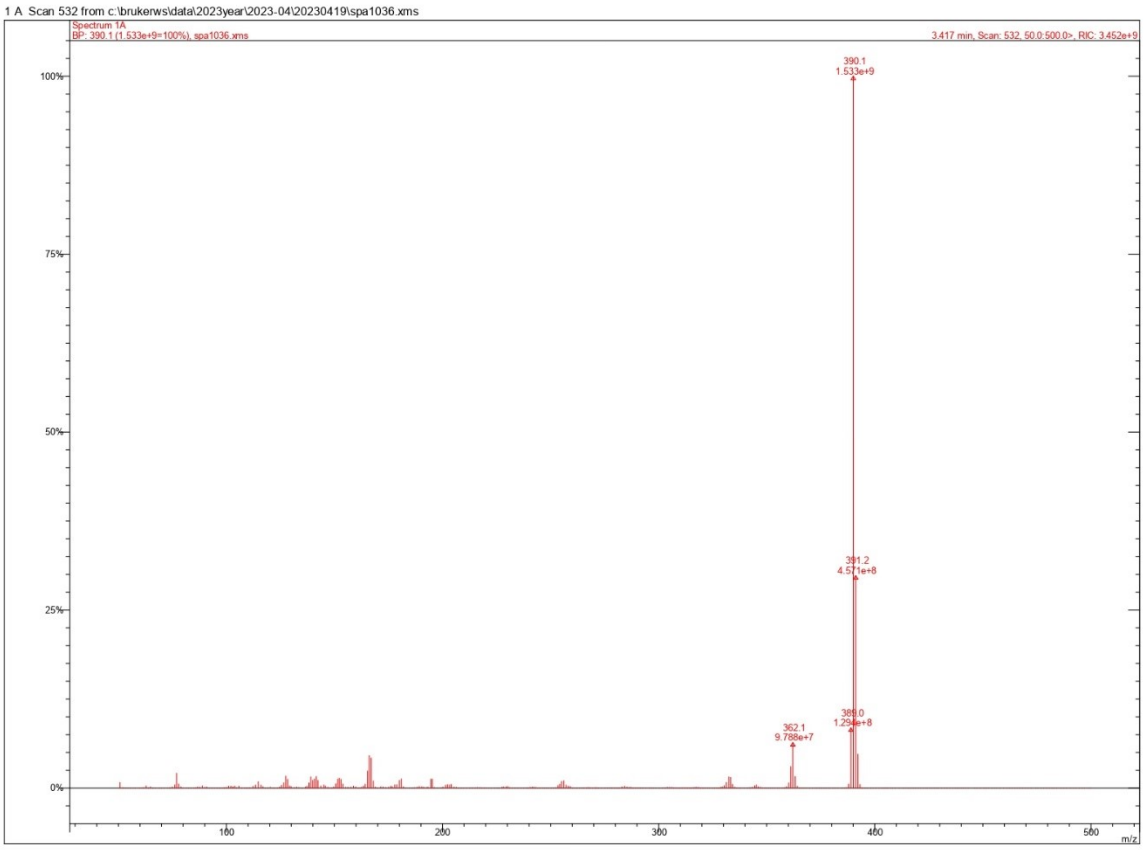
^{1}H NMR spectra of DP4C.



^{13}C NMR spectra of DP4C.



***HRMS spectra of DP2C*.** Calculated: 390.1368; found: 389.9920.



***HRMS spectra of DP4C*.** Calculated: 390.1368; found: 390.0590.

Table S1. Crystallographic data of **DP2C-Y** (CCDC No. 2415627).

Empirical formula	C26 H18 N2 O2	
Formula weight	390.42	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.719(2) Å	α = 90°
	b = 15.663(3) Å	β = 94.40(3)°
	c = 11.782(2) Å	γ = 90°
Volume	1972.3(7) $Å^3$	
Z	4	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.065 mm^{-1}	
F(000)	816	
Crystal size	0.079 x 0.059 x 0.038 mm^3	
Theta range for data collection	1.689 to 24.999°.	
Index ranges	-14<=h<=14, -21<=k<=21, -15<=l<=15	
Reflections collected	18293	
Independent reflections	4977 [R(int) = 0.0716]	
Completeness to theta = 22.210°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.969	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4977 / 0 / 272	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1298	
R indices (all data)	R1 = 0.0697, wR2 = 0.1413	
Extinction coefficient	0.089(7)	
Largest diff. peak and hole	0.231 and -0.233 $e \cdot Å^{-3}$	

Table S2. Crystallographic data of **DP2C-O** (CCDC No. 2415628).

Empirical formula	C26 H18 N2 O2	
Formula weight	390.42	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.687(3) Å	α = 90°
	b = 18.485(4) Å	β = 109.68(3)°
	c = 15.322(3) Å	γ = 90°
Volume	3916.8(15) $Å^3$	
Z	8	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.066 mm^{-1}	
F(000)	1632	
Crystal size	0.069 x 0.059 x 0.048 mm^3	
Theta range for data collection	1.473 to 25.000°.	
Index ranges	-19<=h<=19, -24<=k<=24, -20<=l<=20	
Reflections collected	36637	
Independent reflections	9905 [R(int) = 0.0836]	
Completeness to theta = 22.210°	100.0 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.907	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9905 / 30 / 588	
Goodness-of-fit on F^2	0.992	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.1165	
R indices (all data)	R1 = 0.0964, wR2 = 0.1378	
Extinction coefficient	0.0326(13)	
Largest diff. peak and hole	0.175 and -0.182 $e \cdot Å^{-3}$	

Table S3. Crystallographic data of **DP4C** (CCDC No. 2415629).

Empirical formula	C26 H18 N2 O2	
Formula weight	390.42	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 41.681(8) Å	α = 90°
	b = 6.6370(13) Å	β = 102.94(3)°
	c = 14.028(3) Å	γ = 90°
Volume	3782.1(14) $Å^3$	
Z	8	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	0.068 mm^{-1}	
F(000)	1632	
Crystal size	0.101 x 0.021 x 0.020 mm^3	
Theta range for data collection	1.777 to 25.996°.	
Index ranges	-57<=h<=57, -9<=k<=9, -19<=l<=19	
Reflections collected	18981	
Independent reflections	5306 [R(int) = 0.0719]	
Completeness to theta = 22.210°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.923	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5306 / 0 / 272	
Goodness-of-fit on F^2	1.079	
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1381	
R indices (all data)	R1 = 0.0638, wR2 = 0.1469	
Extinction coefficient	0.0100(9)	
Largest diff. peak and hole	0.348 and -0.301 $e·Å^{-3}$	

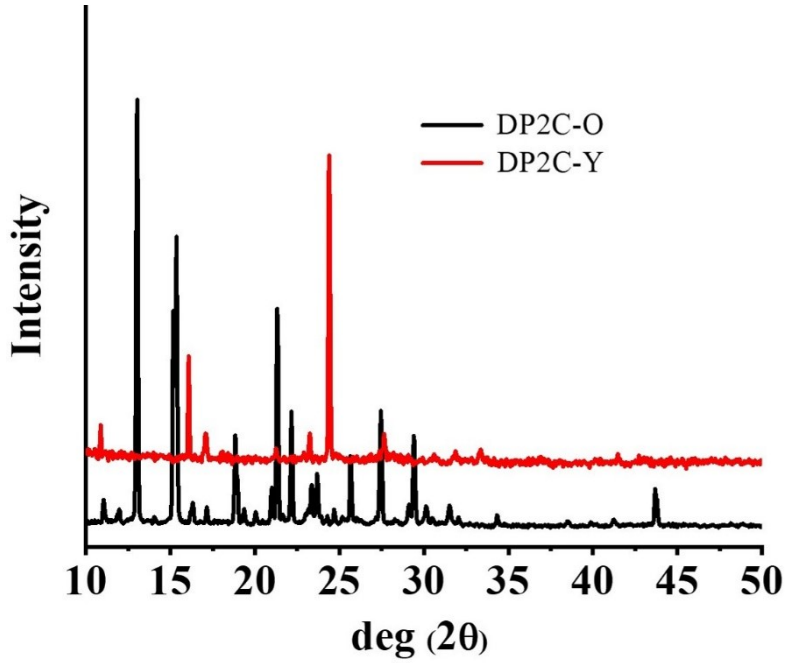


Figure S1. PXRD of **DP2C-Y** and **DP2C-O** polymorphs.

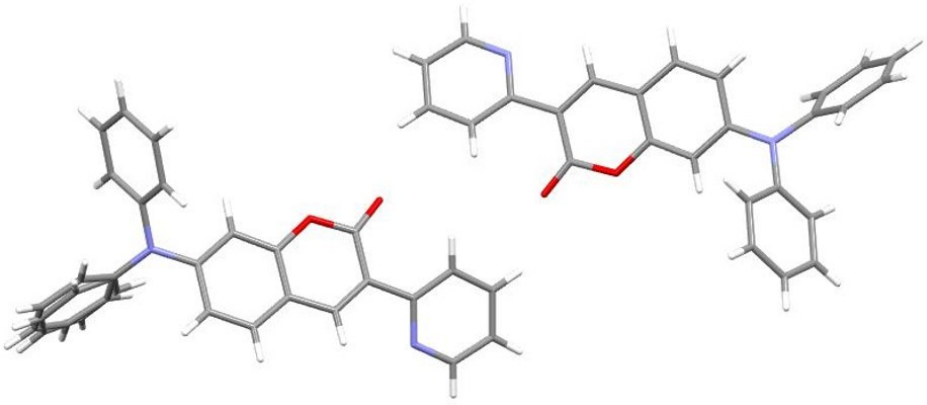


Figure S2. Molecular structure of **DP2C-O** in the crystal lattice.

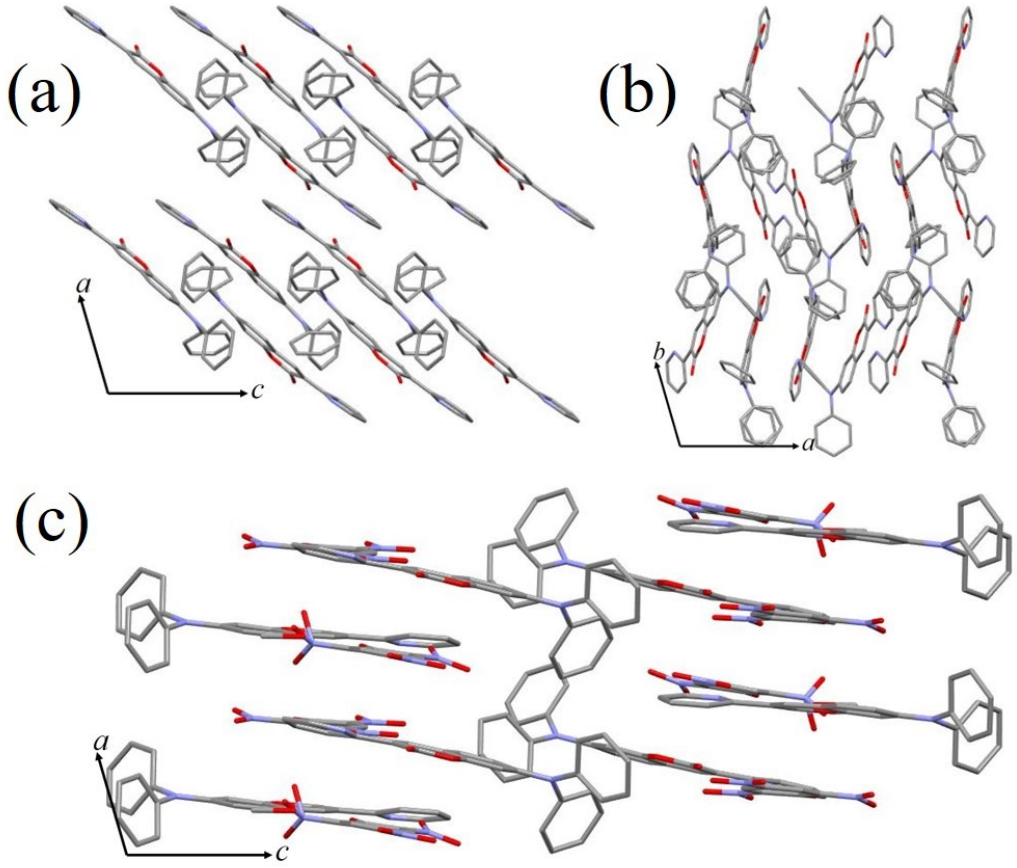


Figure S3. Molecular packing in the crystal lattice (a) **DP2C-Y**, (b) **DP2C-O** and (c) **DP4C.**

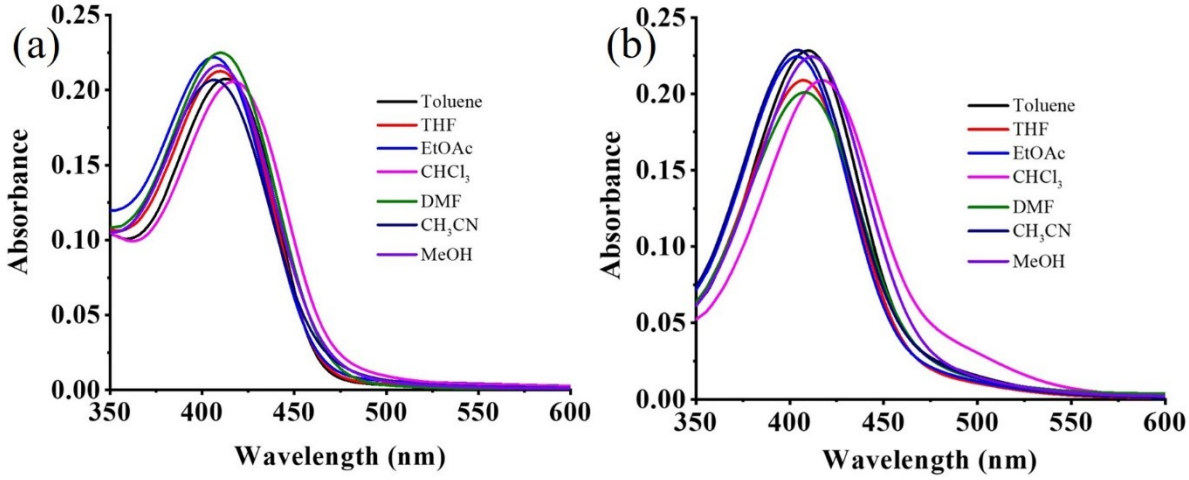


Figure S4. Absorption spectra of (a) **DP2C** and (b) **DP4C** in different organic solvents.

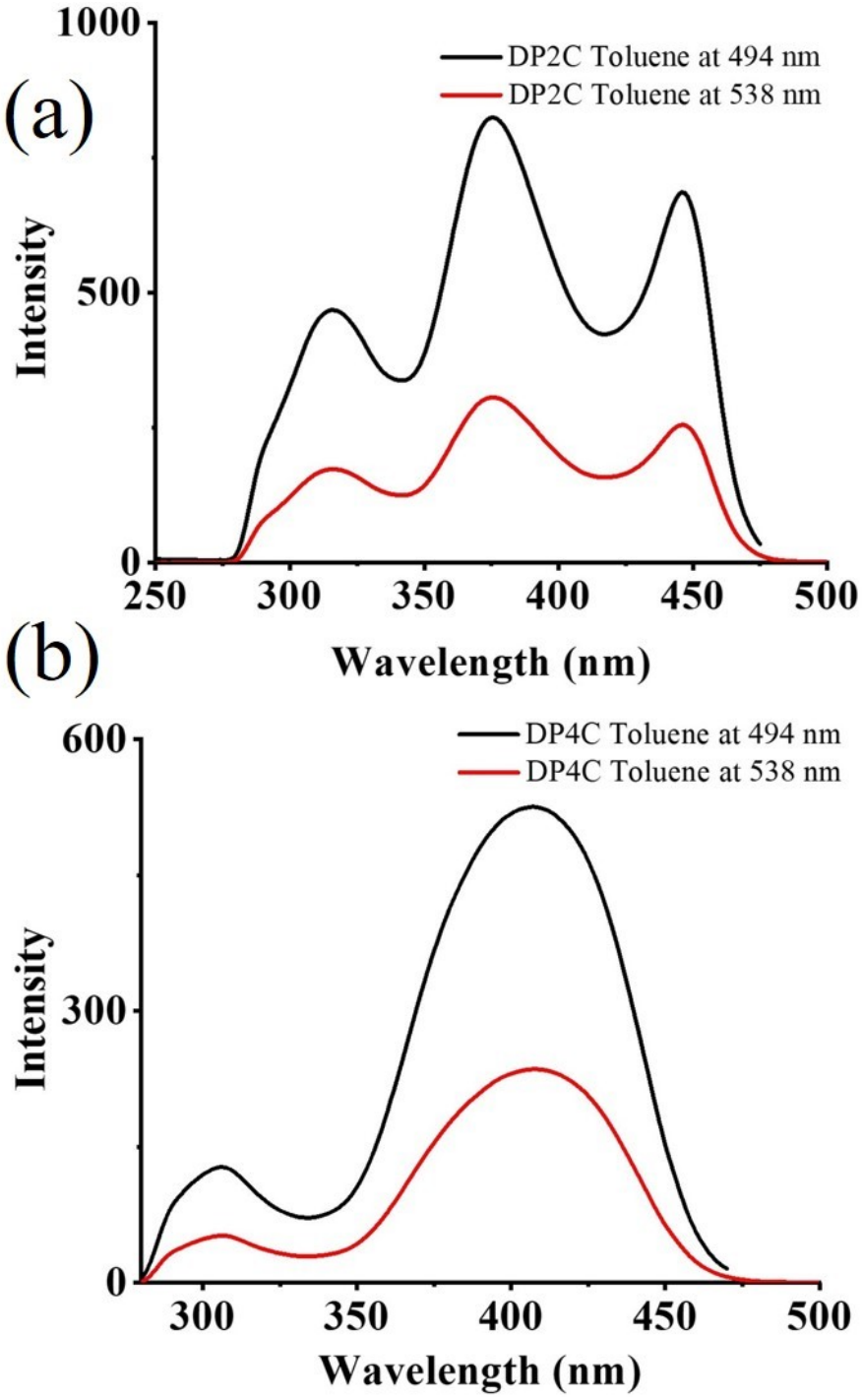


Figure S5. Excitation spectra of (a) **DP2C** and (b) **DP4C** in toluene.

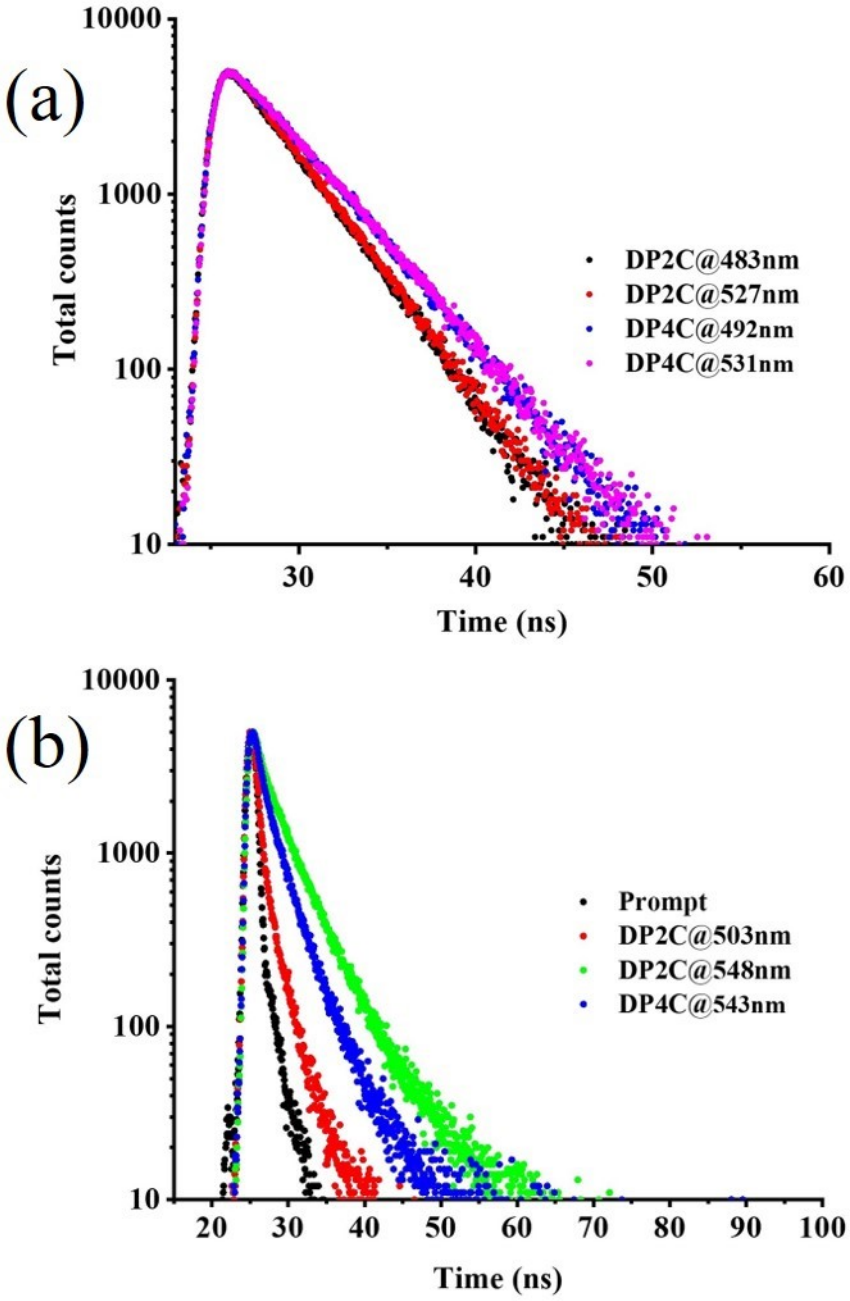


Figure S6. Excited state lifetime decay profiles of (a) solution and (b) solid-state of **DP2C** and **DP4C**.

Table S4. Fluorescence lifetime decay of **DP2C** and **DP4C** in solids and toluene. a_1, a_2 are relative individual component contributions to τ_1, τ_2 $\alpha\nu\delta$ $< \tau >$ (ns) is the average lifetime from multiple decay profiles.

	Compound (λ_{max})	τ_1 (ns)	τ_2 (ns)	Relative Intensity		$<\tau>$ (ns)	χ^2
				a1	a2		
Solids	DP2C (497nm)	0.18	2.32	66.04	33.96	0.27	1.24
	DP2C (537nm)	2.88	6.87	66.01	33.99	3.59	1.10
	DP4C (547nm)	2.12	5.84	76.43	23.57	2.49	1.25
Toluene	DP2C (483nm)	0.54	3.11	2.78	97.22	2.75	1.03
	DP2C (530nm)	1.64	3.20	1.06	98.94	3.17	1.03
	DP4C (491nm)	0.28	3.73	2.16	97.84	2.96	1.00
	DP4C (532nm)	1.97	3.75	0.56	99.44	3.73	1.01

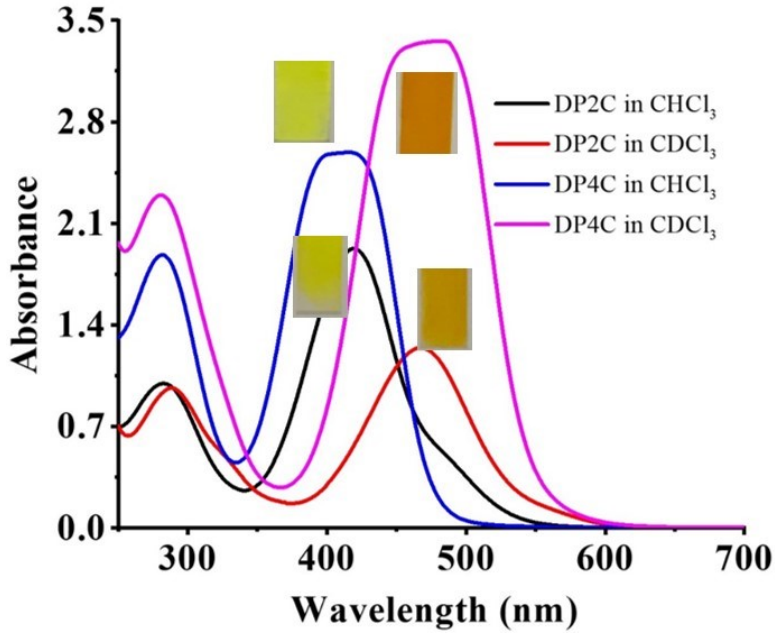


Figure S7. Absorption spectra of **DP2C** and **DP4C** in $CHCl_3$ and $CDCl_3$. Digital colorimetric and fluorescence images are shown in the inset.

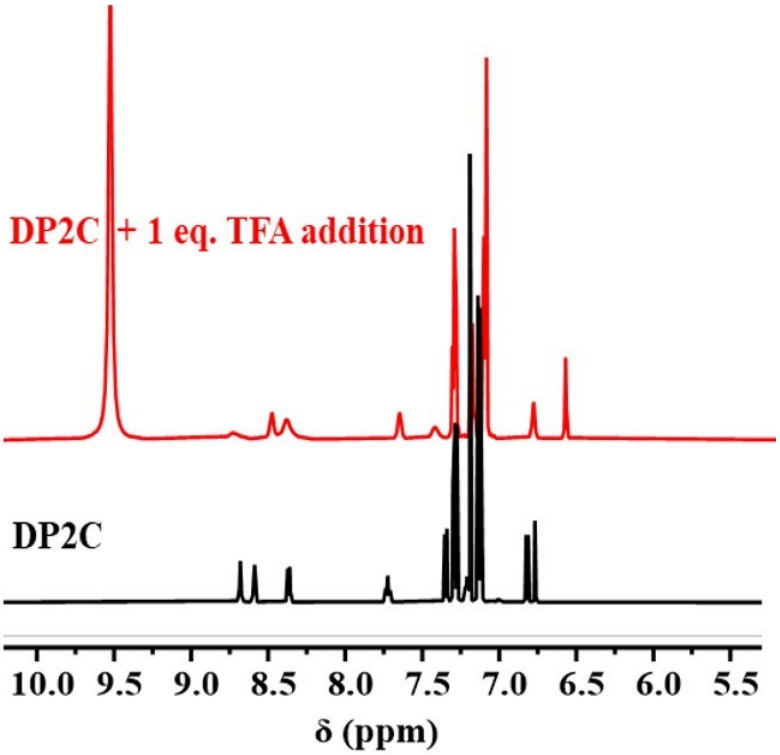


Figure S8. ^{1}H-NMR spectra of **DP2C** in $CDCl_3$ before and after adding TFA.

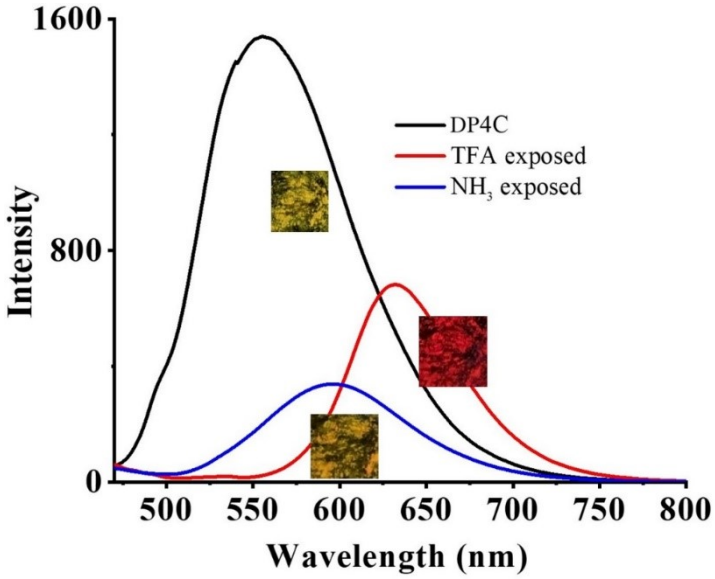


Figure S9. TFA and NH_3 exposure dependent fluorescence switching of **DP4C** solids. Digital fluorescence images are shown in the inset.

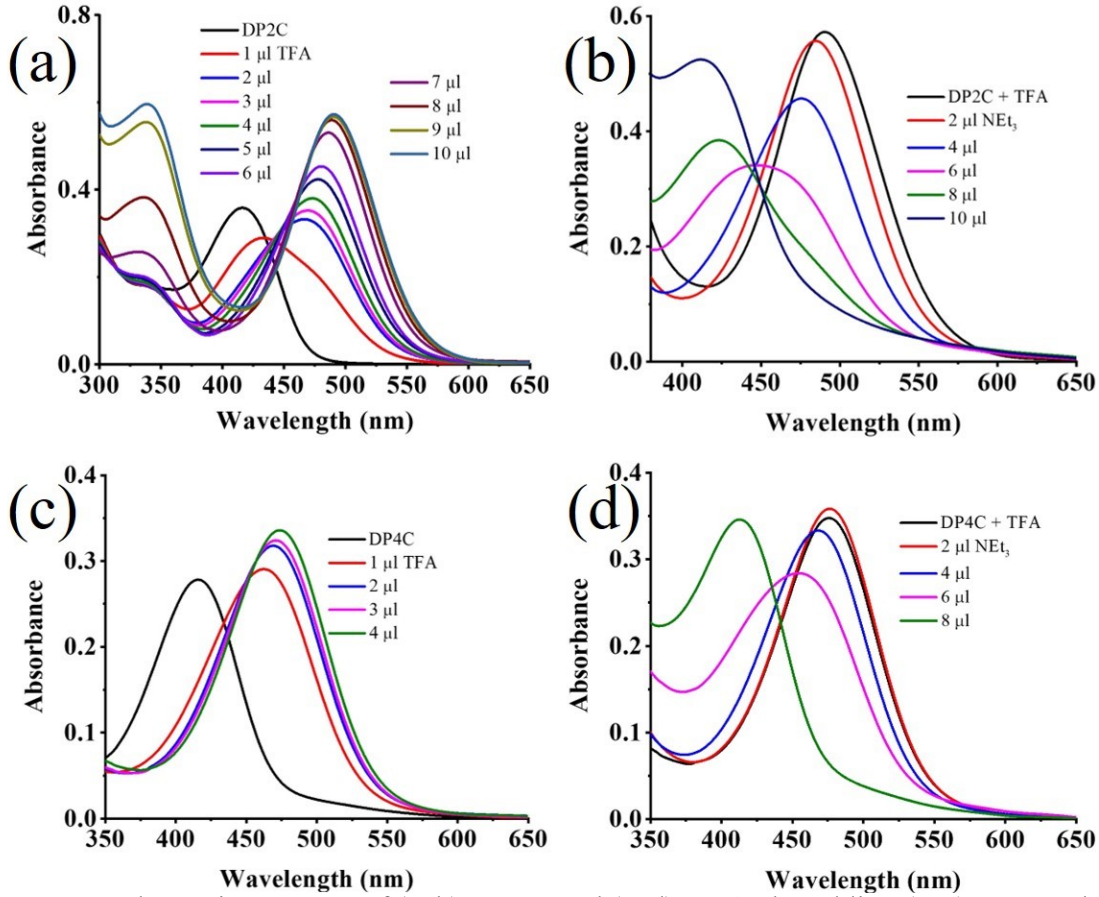


Figure S10. Absorption spectra of (a, b) **DP2C** and (c, d) **DP4C** by adding (a, c) TFA and (b, d) NEt_3.

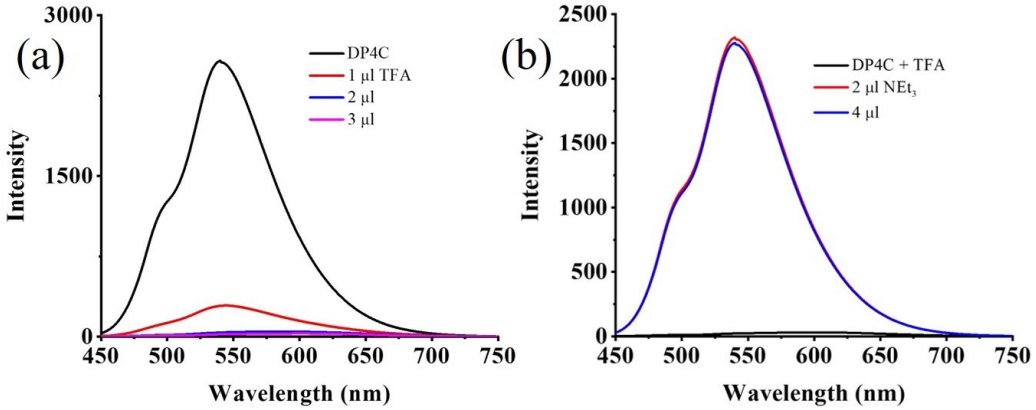


Figure S11. Fluorescence switching of **DP4C** by adding (a) TFA and (b) NEt_3 in $CHCl_3$.

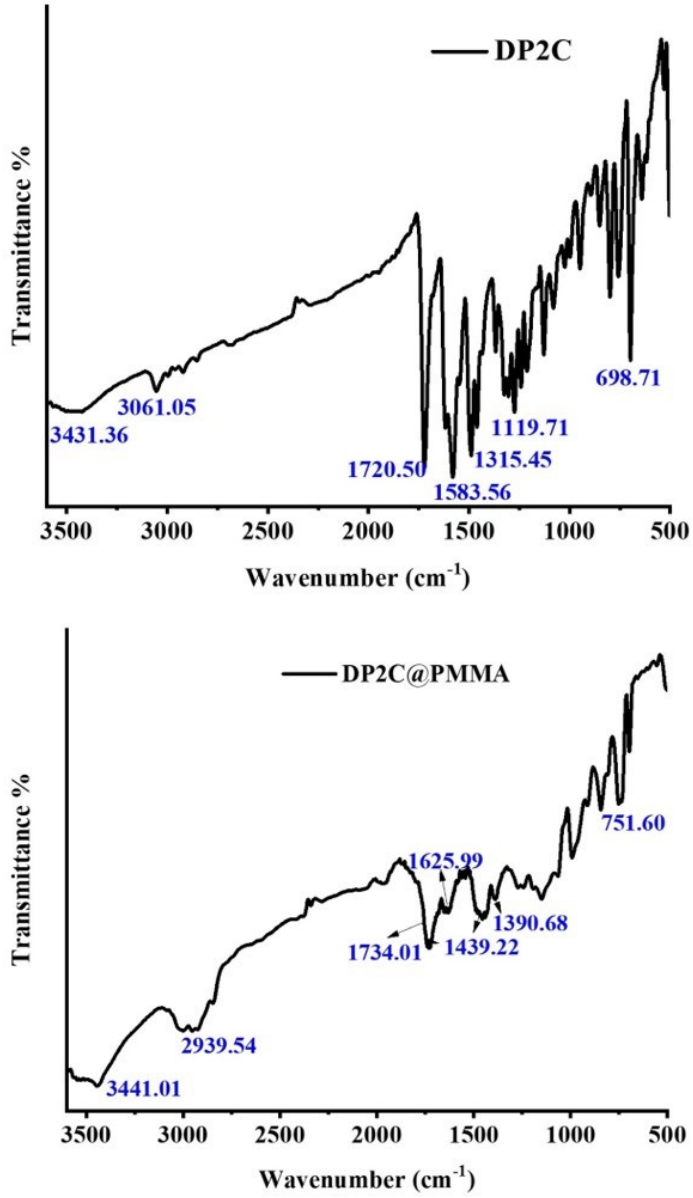


Figure S12. FTIR spectra of **DP2C** and **DP2C**-PMMA.

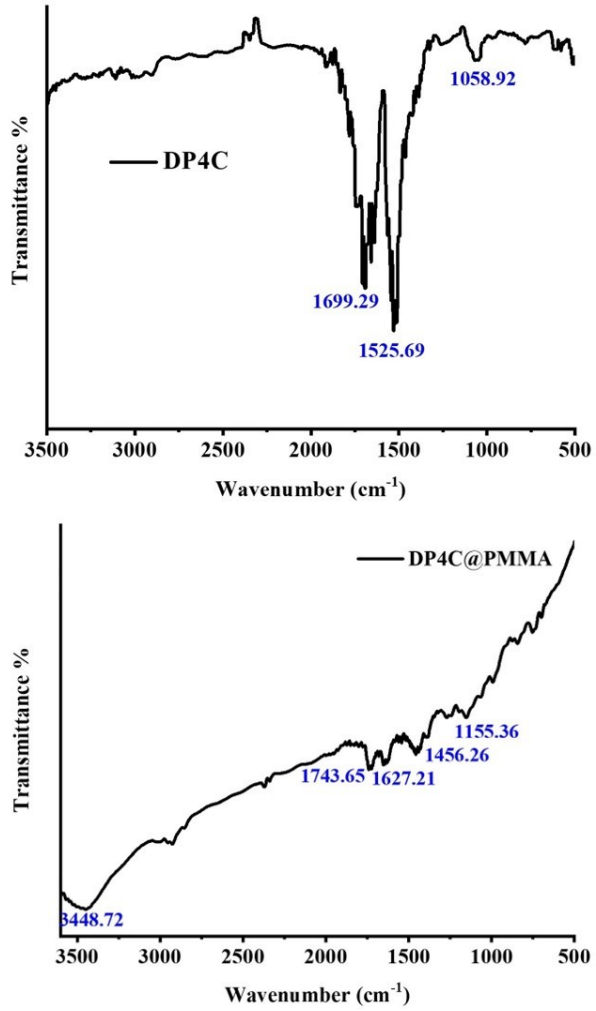


Figure S13. FTIR spectra of **DP4C** and **DP2C**-PMMA.

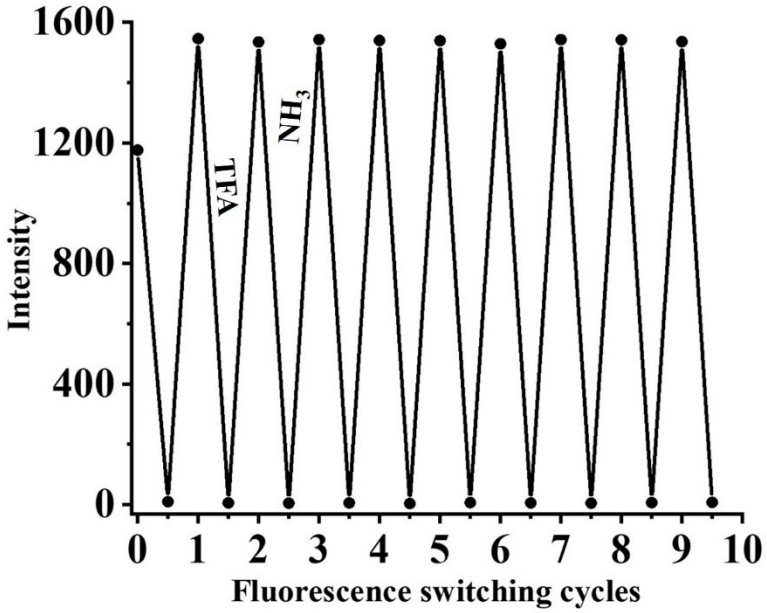


Figure S14. Reversible fluorescence switching cycles of **DP2C**-PMMA by TFA and NH_3 exposure.

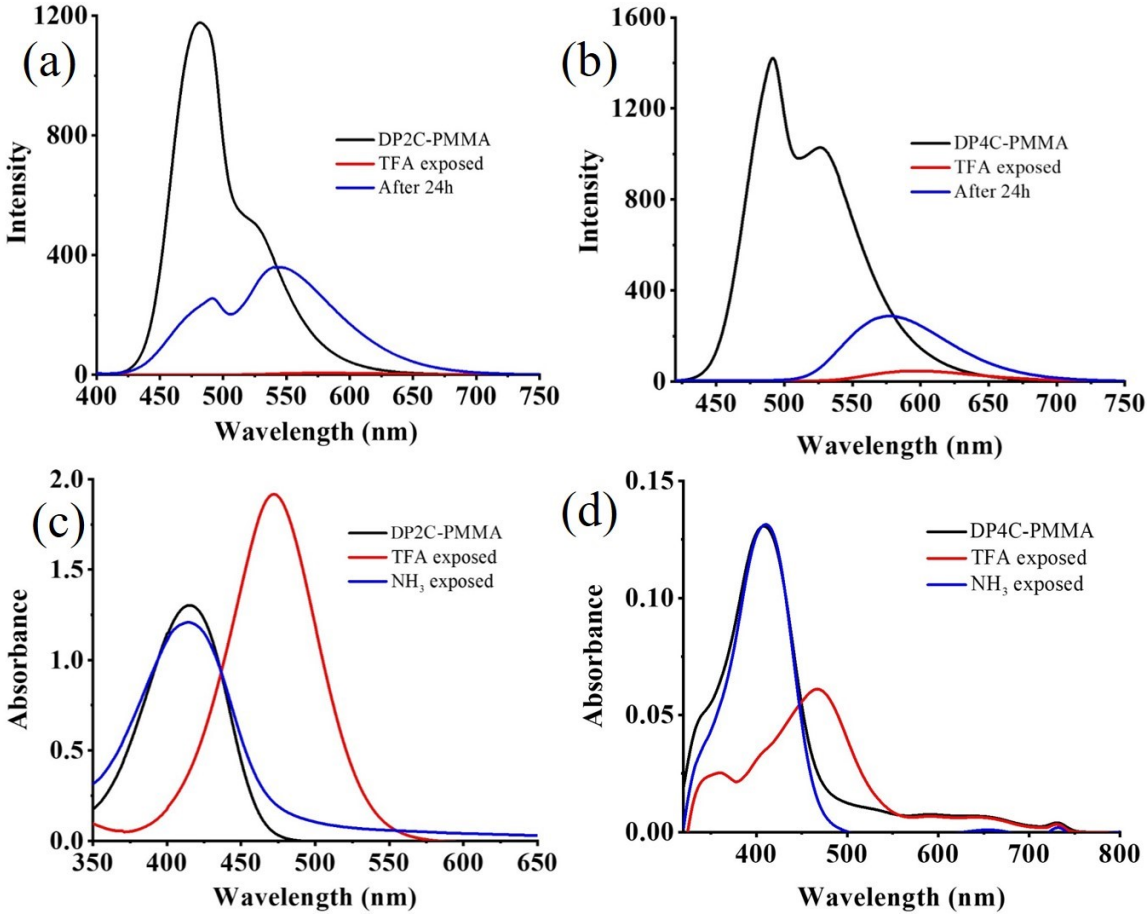


Figure S15. (a, b) Self-recovering of fluorescence after TFA exposure and reversible absorption change by TFA/NH3 exposure of (a, c) **DP2C**-PMMA and (b, d) **DP4C**-PMMA.

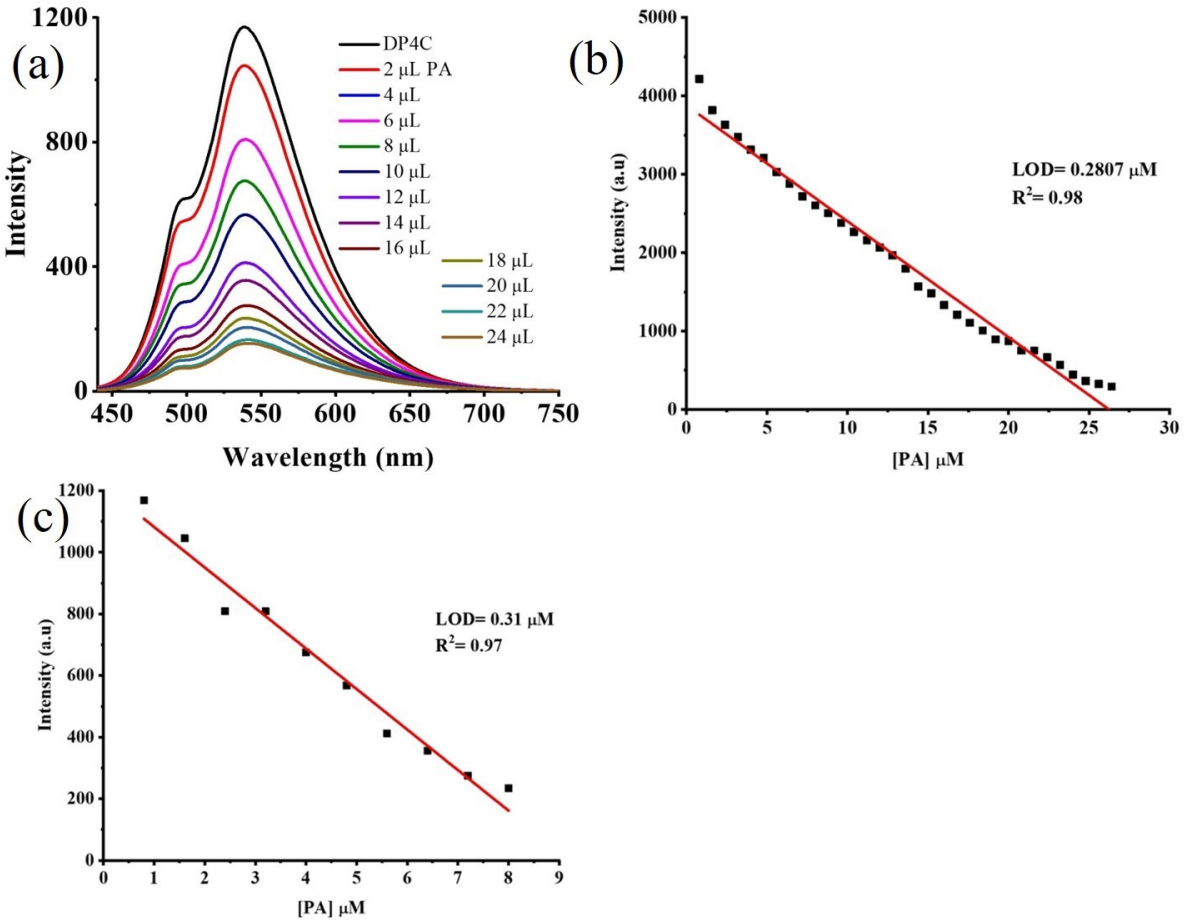


Figure S16. (a) PA concentration dependent fluorescence quenching of **DP4C** in $CHCl_3$ and limit detection of (b) **DP2C** and (c) **DP4C**.

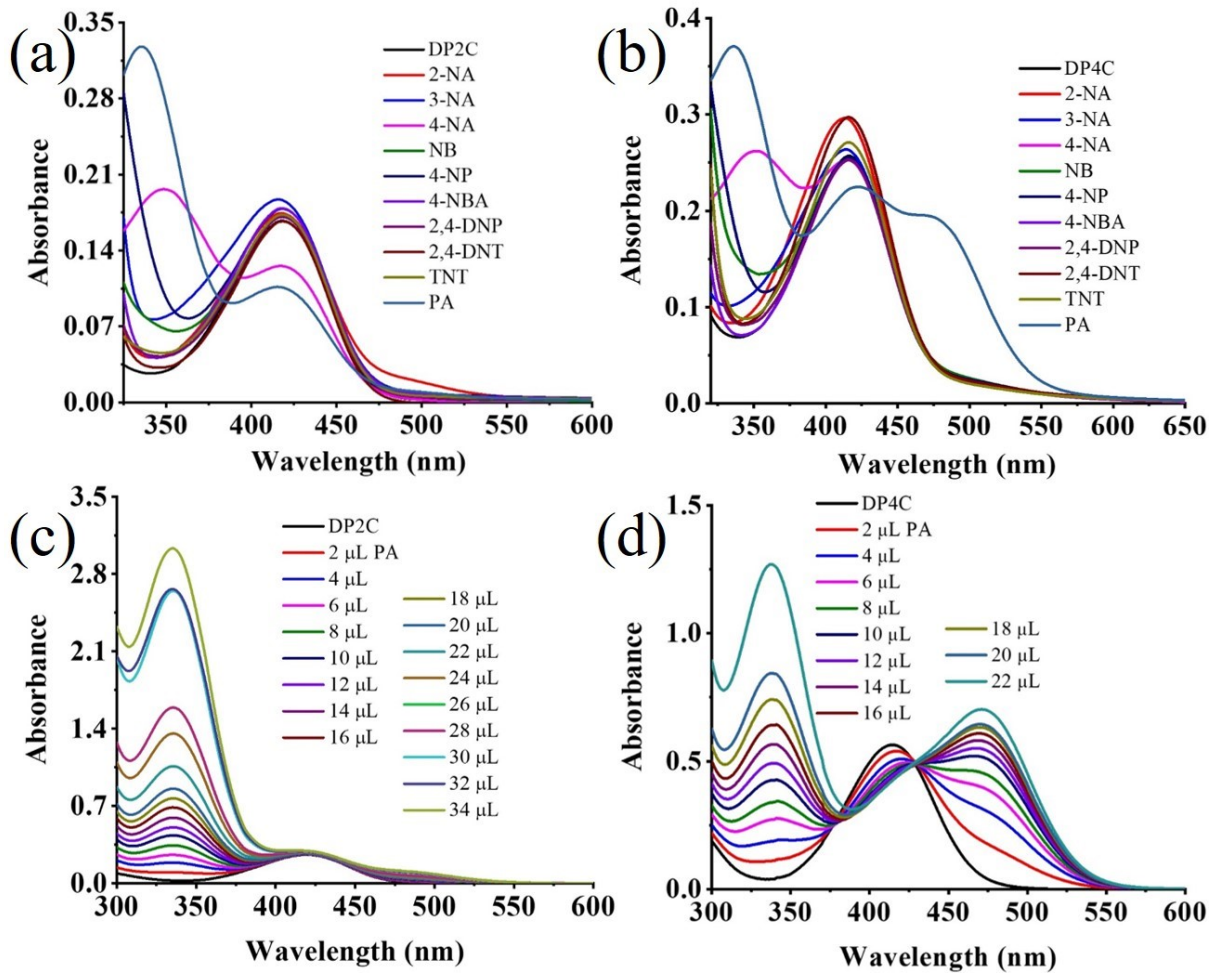


Figure S17. Absorption of (a) **DP2C** and (b) **DP4C** in $CHCl_3$ with NACs. PA concentration dependent absorption changes of (c) **DP2C** and (d) **DP4C** in $CHCl_3$.

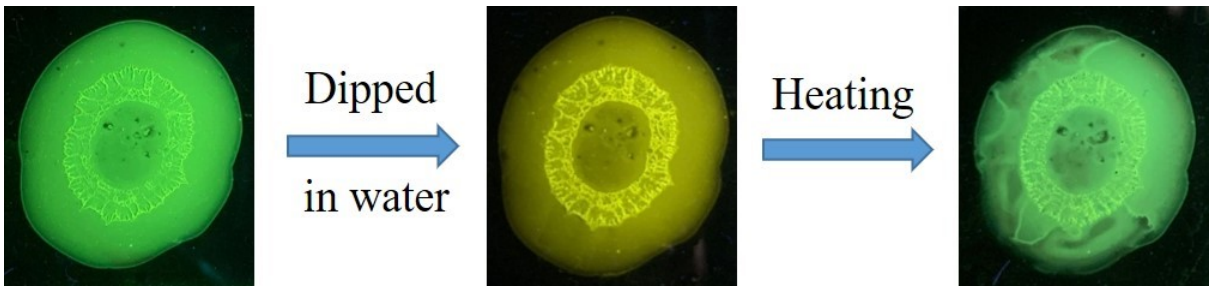


Figure S18. Digital fluorescence color changes of **DP2C**-PVA upon dipping into water and drying.

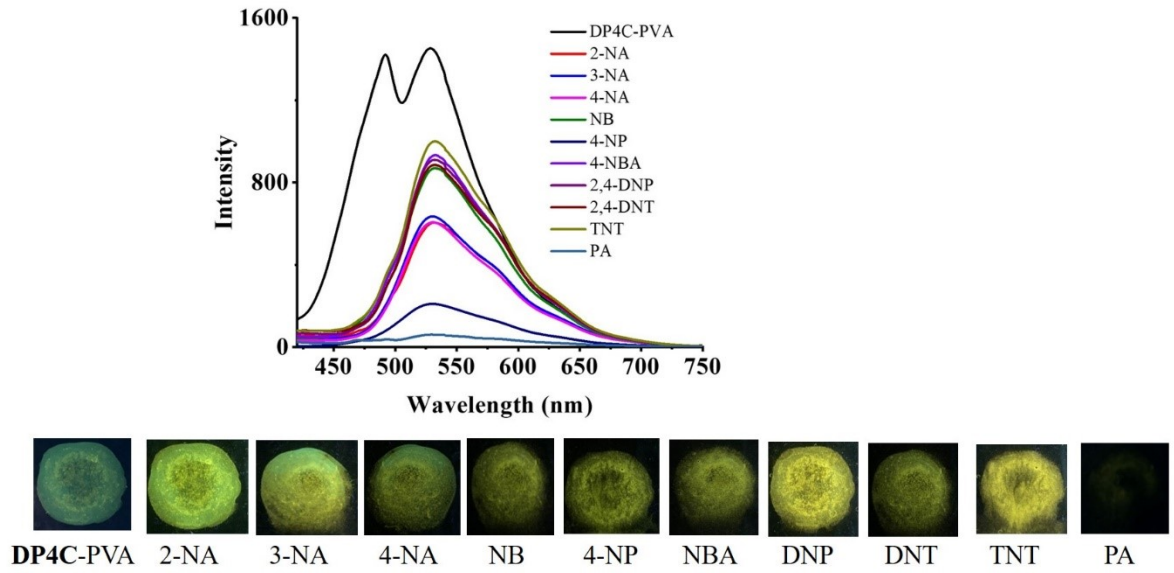


Figure S19. Florescence sensing of PA by **DP4C**-PVA thin film upon dipping into NACs in water and corresponding digital fluorescence images.

Table S5. Crystallographic data of **DP2C-PA** (CCDC No. 2415630)

Empirical formula	C65 H46 N10 O19	
Formula weight	1271.12	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.4780(13) Å	α = 90°
	b = 15.020(3) Å	β = 93.10(3)°
	c = 28.896(6) Å	γ = 90°
Volume	2807.4(10) $Å^3$	
Z	2	
Density (calculated)	1.504 Mg/m^3	
Absorption coefficient	0.087 mm^{-1}	
F(000)	1316	
Crystal size	0.059 x 0.048 x 0.039 mm^3	
Theta range for data collection	1.355 to 25.000°.	
Index ranges	-8<=h<=8, -20<=k<=19, -2<=l<=38	
Reflections collected	13336	

Independent reflections	13336 [R(int) = ?]
Completeness to theta = 22.210°	97.9 %
Absorption correction	Empirical
Max. and min. transmission	1.000 and 0.936
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13336 / 221 / 861
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.1024, wR2 = 0.2620
R indices (all data)	R1 = 0.1385, wR2 = 0.2918
Absolute structure parameter	-0.6(8)
Extinction coefficient	0.176(17)
Largest diff. peak and hole	0.807 and -0.560 e·Å^{-3}