Concentration-tuned Response to Selective Biogenic Amines using a Reusable Fluorophore: Monitoring Protein-rich Food Spoilage

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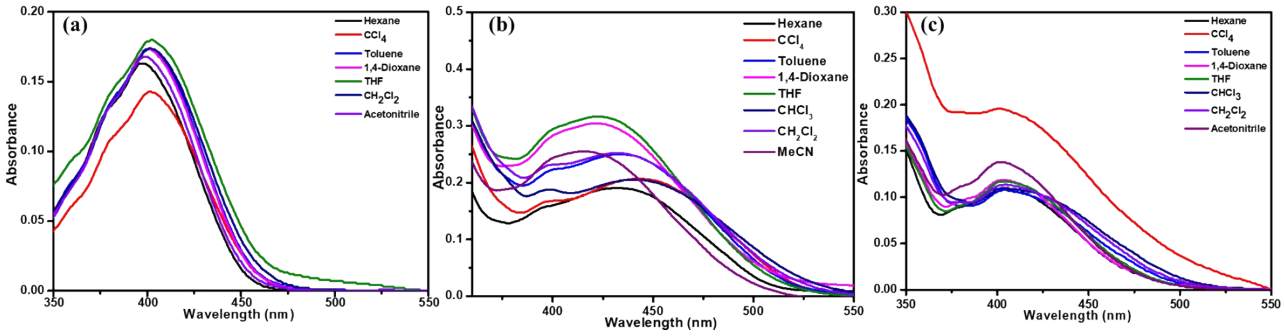


Figure S1. UV-Vis spectra of (a) **TAA**, (b) **TCN,** and (c) **TCNA** in a different polar solvent. λ_{abs} = 402 nm.

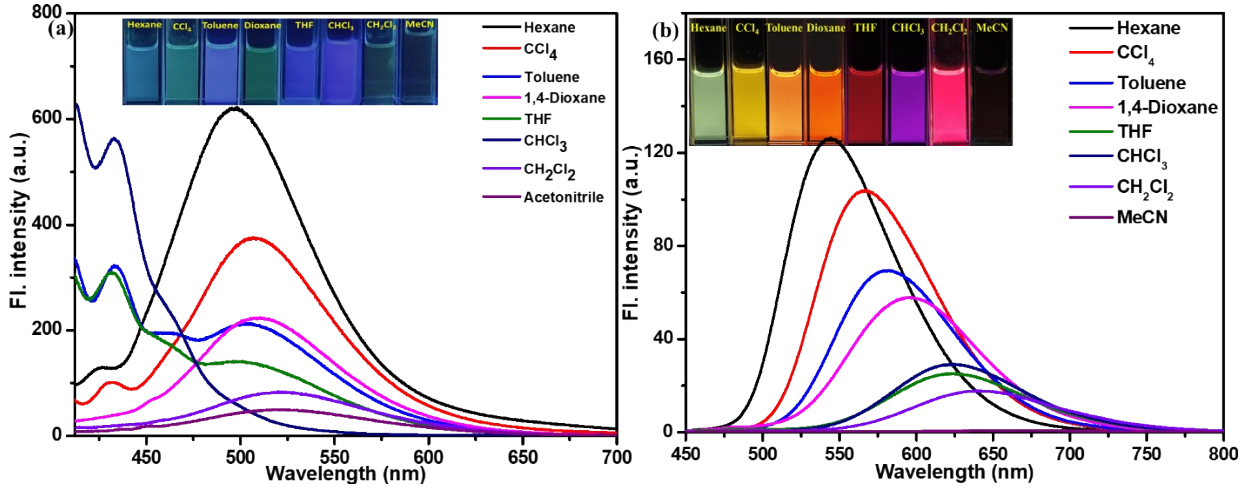


Figure S2. Emission spectra of (a) **TAA** and (b) **TCN** in different polar solvent. λ_{ex} = 402 nm.

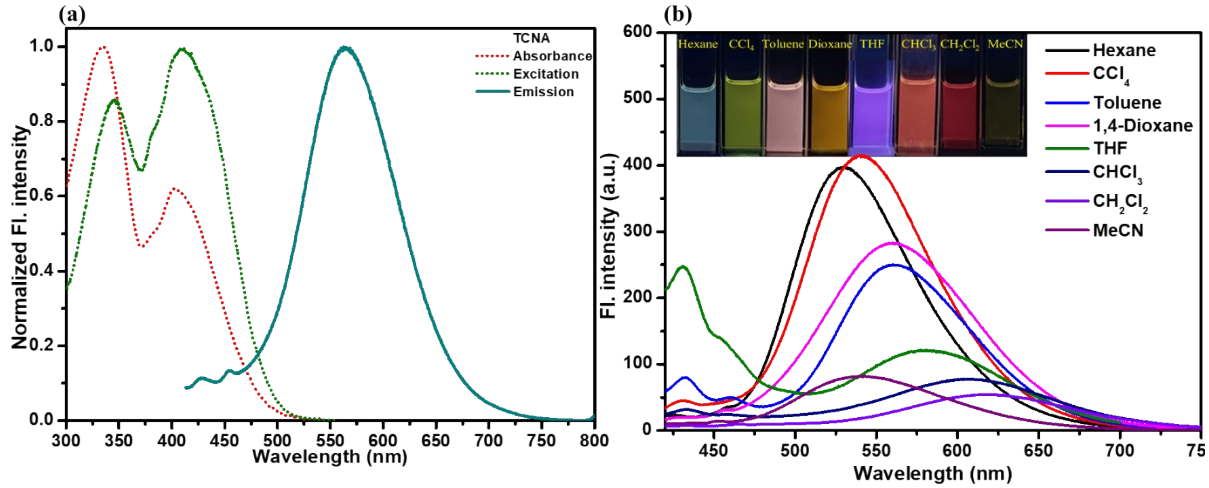


Figure S3. (a) Excitation, absorption, and emission profiles of **TCNA** in 1,4-dioxane (10 μM). (b) Emission spectra of TCNA in diverse polar solvents. (λ_{ex} ~402 nm). The color variations in solvents are shown in the inset (taken under 365 nm UV- lamp).

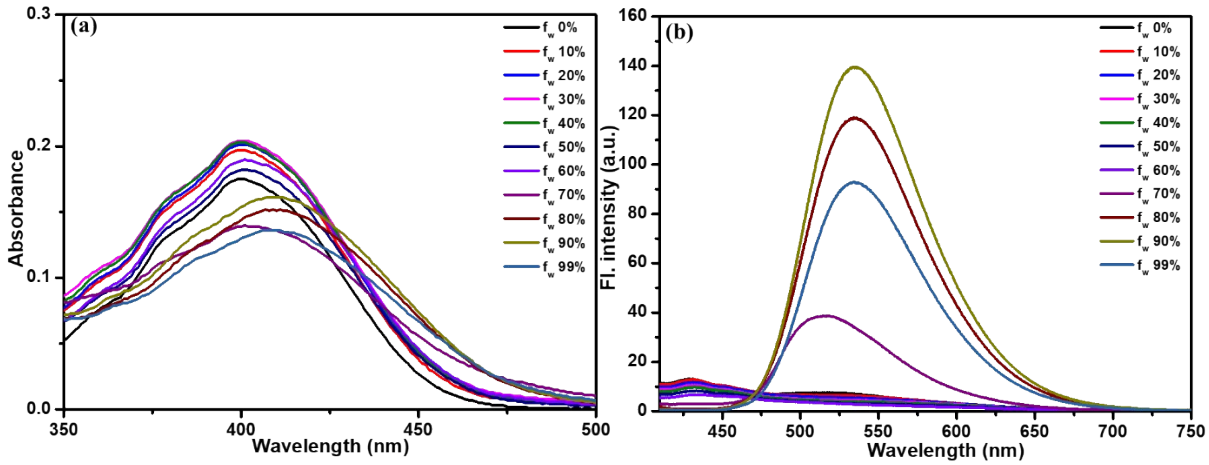


Figure S4. Absorbance and Emission spectra of **TAA** at different f_w in acetonitrile. λ_{ex} = 402 nm.

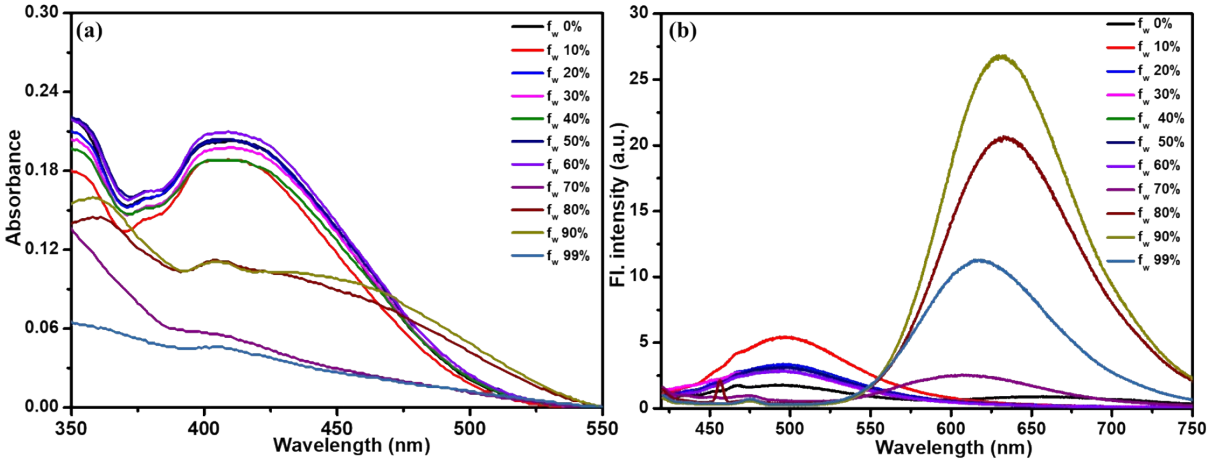


Figure S5. Absorbance and Emission spectra of **TCN** at different f_w in acetonitrile. λ_{ex} = 410 nm.

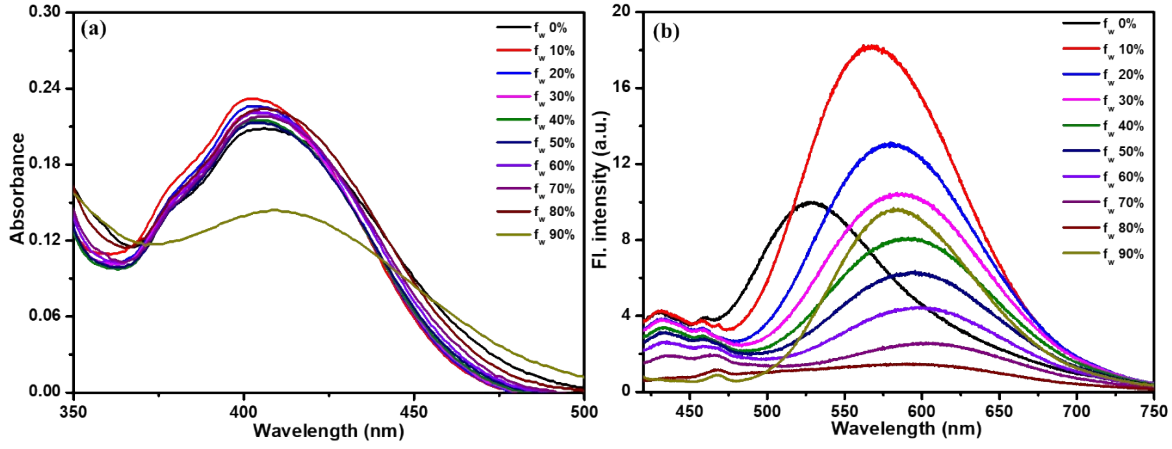


Figure S6. Absorbance and Emission spectra of **TCNA** at different f_w in acetonitrile. λ_{ex} = 404 nm.

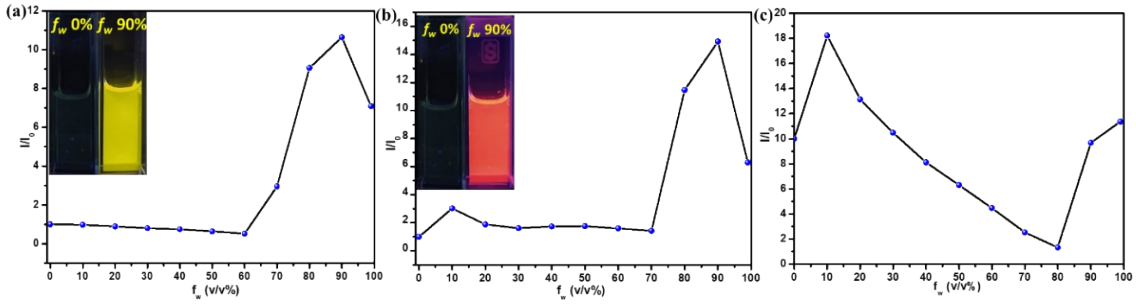


Figure S7. The I/I_0 plot (I_0: FL intensity before addition of water and I: FL intensity after addition of water) [concentration of the probe: 10 μM] of (a) **TAA**, (b) **TCN** and (c) **TCNA.** The image is taken at f_w = 0% and f_w = 90% for **TAA** and **TCN** under 365 nm UV lamp.

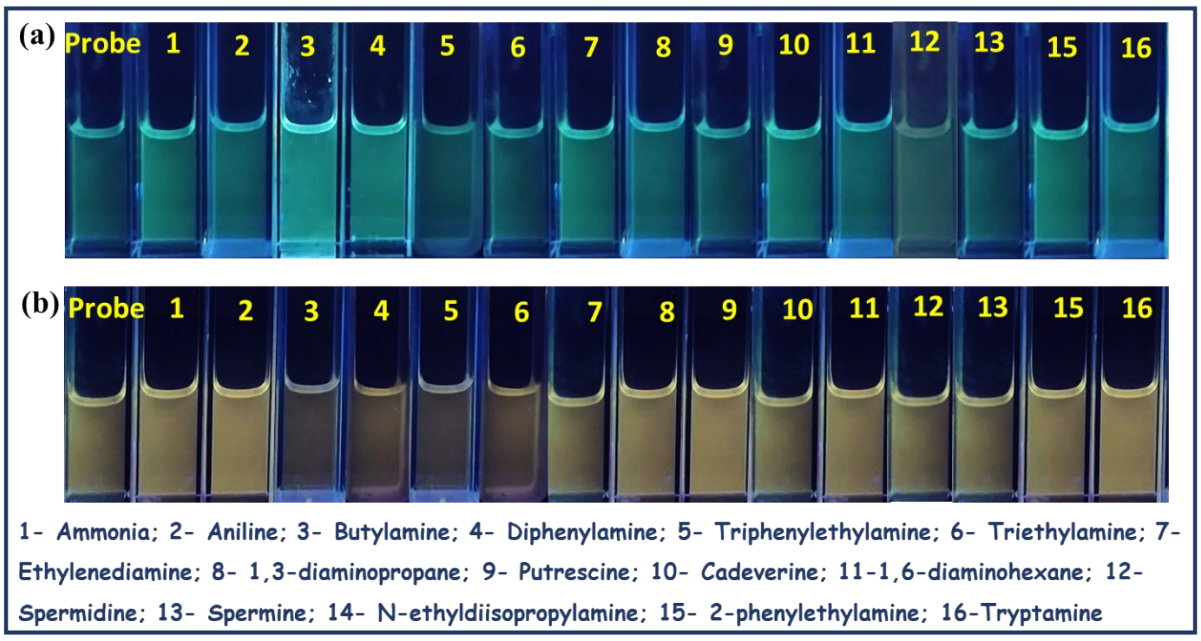
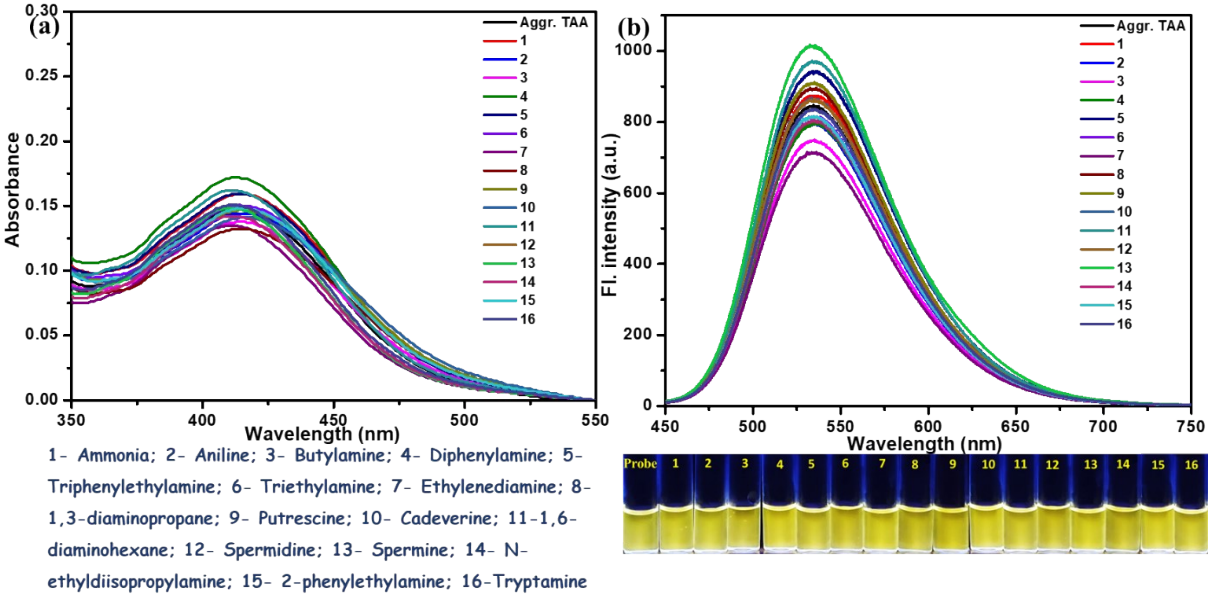


Figure S8. Images of (a) **TAA** and (b) **TCN** with different amines in 10μM 1,4-dioxane solution. All the images were taken under a 365 nm UV lamp.



Structure of biogenic amines (BAs) used in this study.

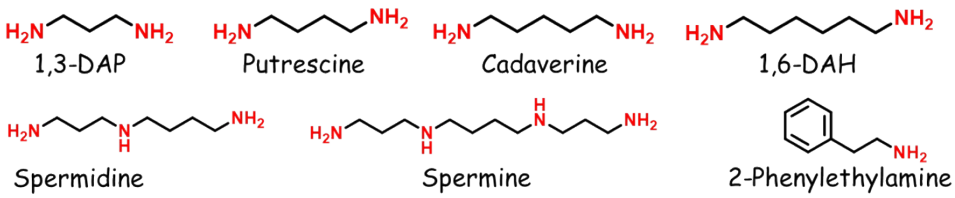


Figure S9. Absorbance and Emission spectra of aggregated **TAA** [10 μM in MeCN + f_w (*v/v*) = 90%] with different amine solutions (10 μM in DMAc). λ_{ex} = 413 nm.

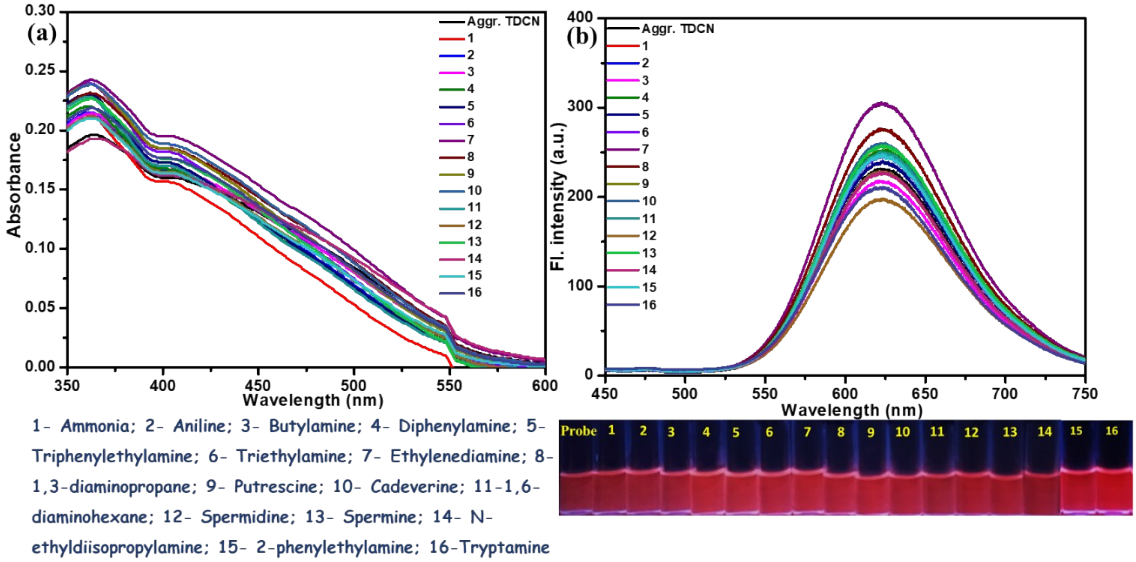
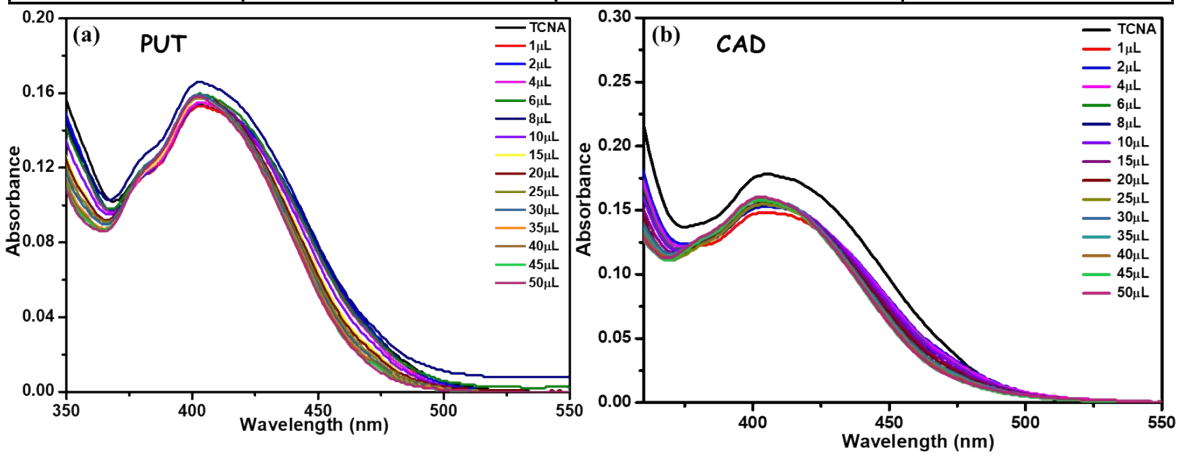


Figure S10. Absorbance and Emission spectra of aggregated **TCN** [10 μM in MeCN + f_w(*v/v*) = 90%] with different amine solutions (10 μM in DMAc). λ_{ex} = 413 nm.

Table S1: Variation in emission maxima after the gradual addition of different volumes of amine in the solution state

Volume of amine added in μL	$\lambda_{max.}$ (nm) for Putrescine	$\lambda_{max.}$ (nm) for Cadaverine	$\lambda_{max.}$ (nm) for Spermidine
TCNA	564	564	564
1	561	563	556
2	559	562	556
4	557 (7 nm blue Shift)	561 (3 nm blue Shift)	553
6	554	561	554
8	550	560	552
10	546 (18 nm blue Shift)	558 (6 nm blue Shift)	552
15	544 (20 nm blueshift)	557 (7 nm blue Shift)	548
20	542 (22 nm blueShift)	553 (11 nm blue Shift)	548
25	541 (23 nm blueShift)	550 (14 nm blueShift)	547
30	539 (25 nm blueShift)	549	546
35	536 (28 nm blue Shift)	545	545
40	535 (29 nm blue Shift)	542	545
45	533 (31 nm blue Shift)	542	542
50	532 (32 nm blue Shift)	542	541 (23 nm blue Shift)



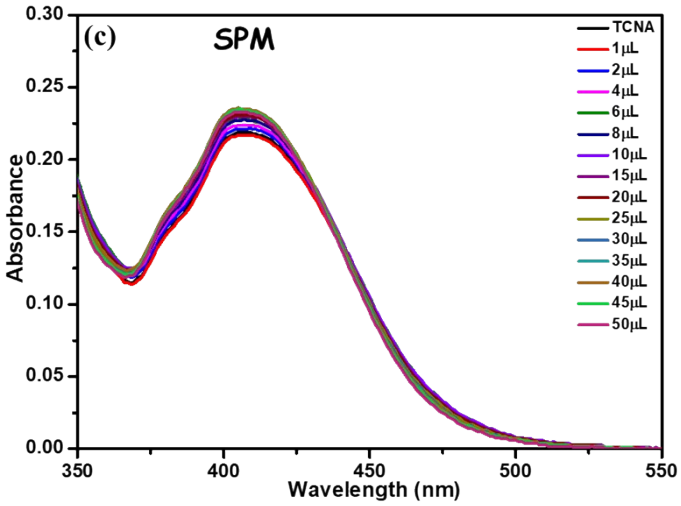


Figure S11. Absorbance spectra of **TCNA** upon gradual addition of different volumes of (a) Putrescine, (b) Cadaverine, and (c) Spermidine.

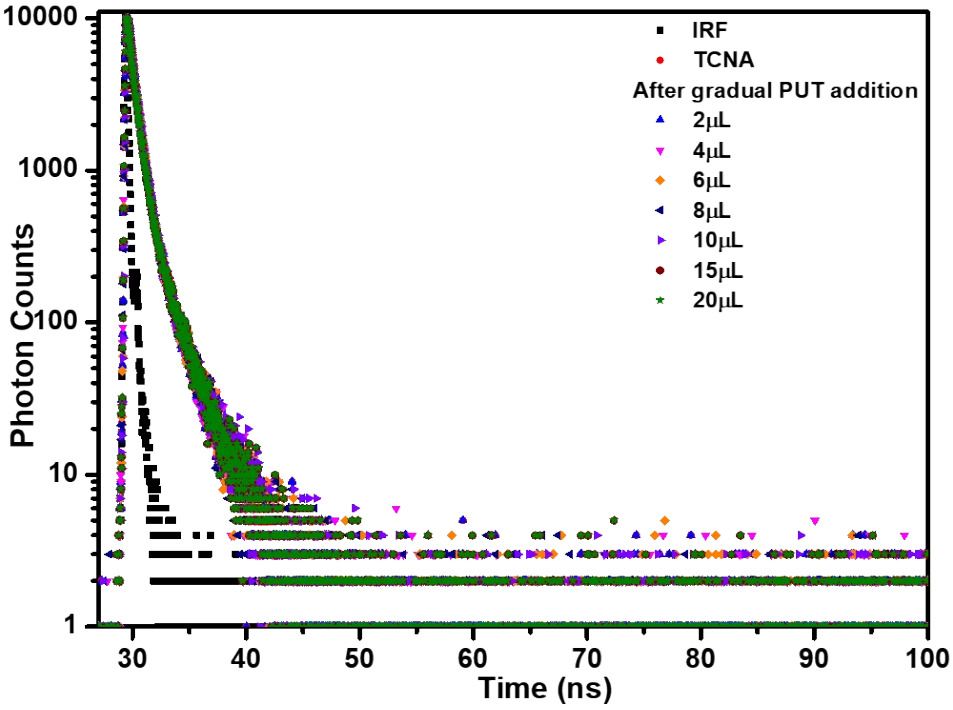


Figure S12. Lifetime decay plot of **TCNA** [10 μM in 1,4-dioxane] and after addition of Putrescine solution (10^{-6} M).

Table S2: Lifetime components; All lifetimes (τ) are in ns, and λ_{ex} = 405 nm

Samples	α_1	α_2	α_3	τ_1	τ_2	τ_3	<τ>	χ^2
TCNA	0.36	0.60	0.03	0.17	0.67	2.37	0.54	0.99

TCNA +2 µL PUT	0.36	0.60	0.03	0.16	0.67	2.36	0.54	1.0
TCNA +4 µL PUT	0.44	0.52	0.03	0.17	0.69	2.34	0.51	0.99
TCNA +6 µL PUT	0.44	0.52	0.028	0.17	0.69	2.34	0.50	1.01
TCNA +8 µL PUT	0.44	0.52	0.03	0.17	0.67	2.28	0.50	0.99
TCNA +10 µL PUT	0.46	0.49	0.03	0.16	0.67	2.31	0.48	1.01
TCNA +15 µL PUT	0.49	0.46	0.04	0.16	0.64	2.18	0.46	1.05
TCNA +20 µL PUT	0.50	0.45	0.04	0.17	0.58	1.99	0.43	1.01

Table S3: Excitation, Emission maxima, and absolute quantum yield of thin films after exposure to different amine vapors

Sl. No.	Amine	Volume of amine added in 200mL sealed glass bottle	λ_{ex} (nm)	λ_{emi} (nm)	$\Delta\lambda$ (nm)	Φ_f (%)	Concentration of Amine in mg/L
1	-	Only Probe	524	604	0	2	0
2	Ammonia	30µL	524	604	0	2	109.5
3	Butylamine	30µL	437	561	43	6.57	111
4	Ethylenediamine	30µL	437	561	43	4	134.85
5	1,3-DAP	30µL	437	561	43	5	132
6	PUT (Putrescine)	30µL	437	513	91	10.40	131.55
7	CAD (Cadaverine)	30µL	437	555	49	7.40	130.5

8	1,6-DAH	30µL	437	560	44	4.63	126
9	2-Phenylethylamine	30µL	437	562	42	1.95	144.3
10	DIPEA	30µL	437	560	44	6	113.5
11	Spermidine	30µL	437	550	54	14.40	138.75
12	Spermine	30µL	524	604	0	2	140.5

Table S4: Variation in λ_{ex} (nm) and Φ_f(%) after the addition of different putrescine volume

Volume of PUT (in µL)	λ_{ex} (nm)	λ_{em} (nm)	Φ_f(%)	Conc. of PUT added (mg/L or ppm)
TCNA	524	604	2	0
1	437	576	2.50	4.43
5	437	560	2.93	21.93
8	437	556	3.73	35.08
10	437	552	3.47	43.85
15	437	531	3.47	65.78
20	437	513	10.21	87.7
25	437	514	10.20	109.63
30	437	513	10.40	131.55

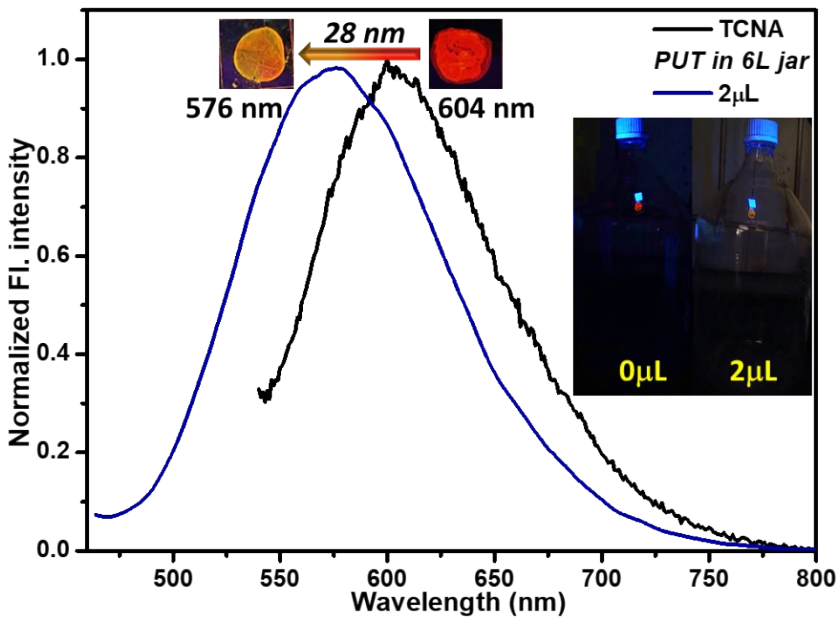


Figure S13A. Normalized FL spectra of the probe before and after exposing to Putrescine in a 6L jar.

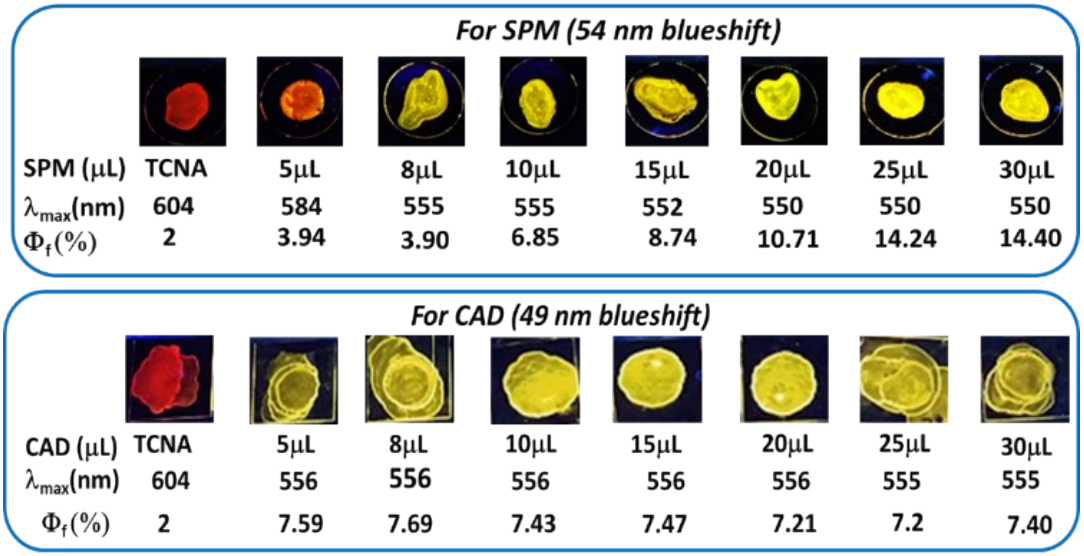


Figure S13B. Difference in emission for **SPM** and **CAD** (See Fig S14 and Table S5 - S6) for the emission spectra and other related parameters)

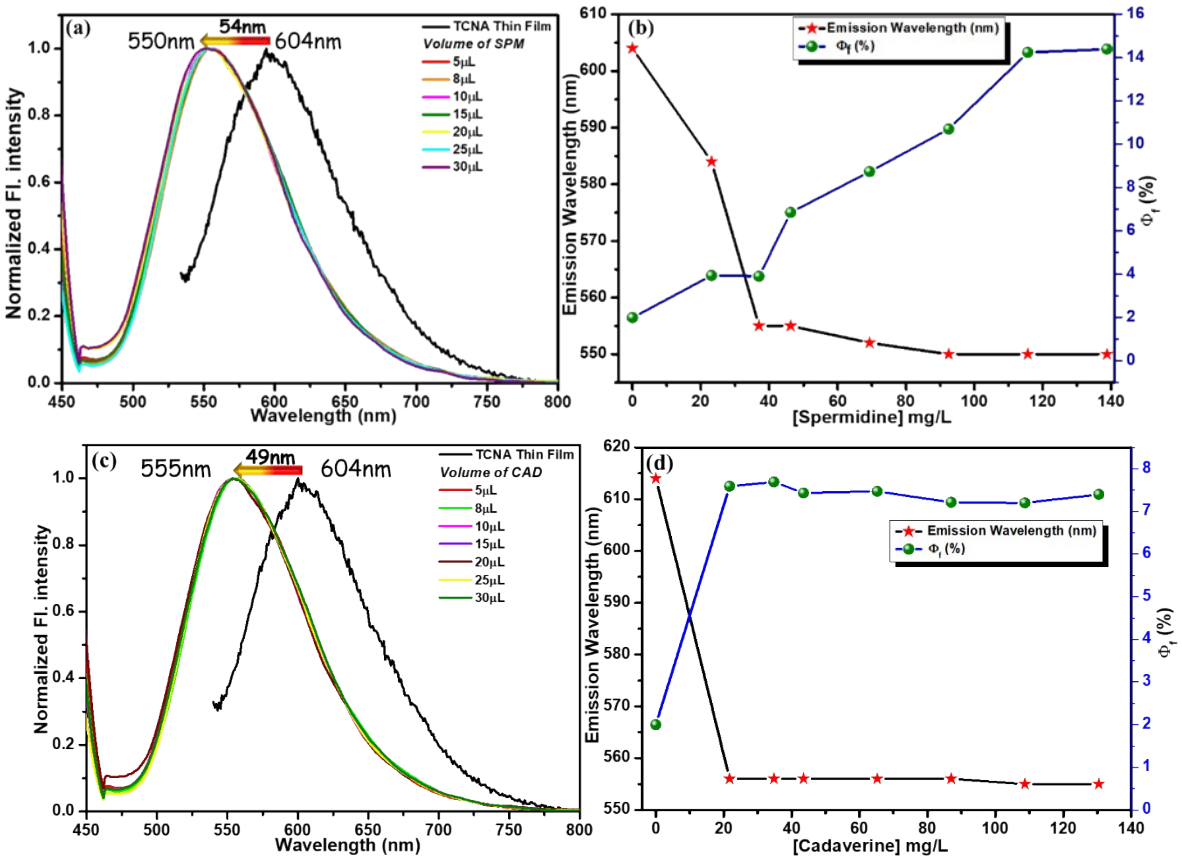


Figure S14. Normalized FL spectra of the probe before and after exposing to (a) Spermidine, (c) Cadaverine vapor; Change of emission wavelength and QY with different concentrations of (b) Spermidine and (d) Cadaverine vapor.

Table S5: Variation in λ_{ex} (nm) and Φ_f(%) after the addition of different Spermidine volume

Volume of SPM (in µL)	λ_{ex} (nm)	λ_{em} (nm)	Φ_f(%)	Conc. of SPM added (mg/L or ppm)
TCNA	524	604	0.75	0
5	437	584	3.94	23.13
8	437	555	3.90	37
10	437	555	6.85	46.25
15	437	552	8.74	69.37
20	437	550	10.71	92.5
25	437	550	14.24	115.62
30	437	550	14.40	138.75

Table S6: Variation in λ_{ex} (nm) and Φ_f(%) after the addition of different Cadaverine volume

Volume of CAD (in µL)	λ_{ex} (nm)	λ_{em} (nm)	Φ_f(%)	Conc. of CAD added (mg/L or ppm)
TCNA	524	604	0.65	0
5	437	556	7.59	21.75
8	437	556	7.69	34.8
10	437	556	7.43	43.5
15	437	556	7.47	65.25
20	437	556	7.21	87
25	437	555	7.2	108.75
30	437	555	7.40	130.5

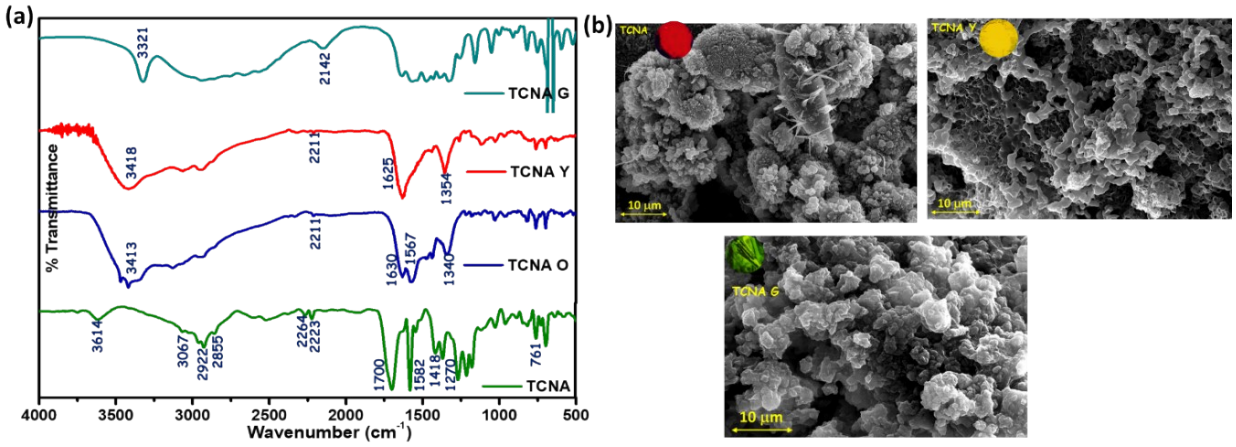


Figure S15. (a) FT-IR spectra of all the forms of **TCNA** as KBr pellet at different stages after exposure to PUT vapor (b) SEM images of mainly three distinctly visualized states.

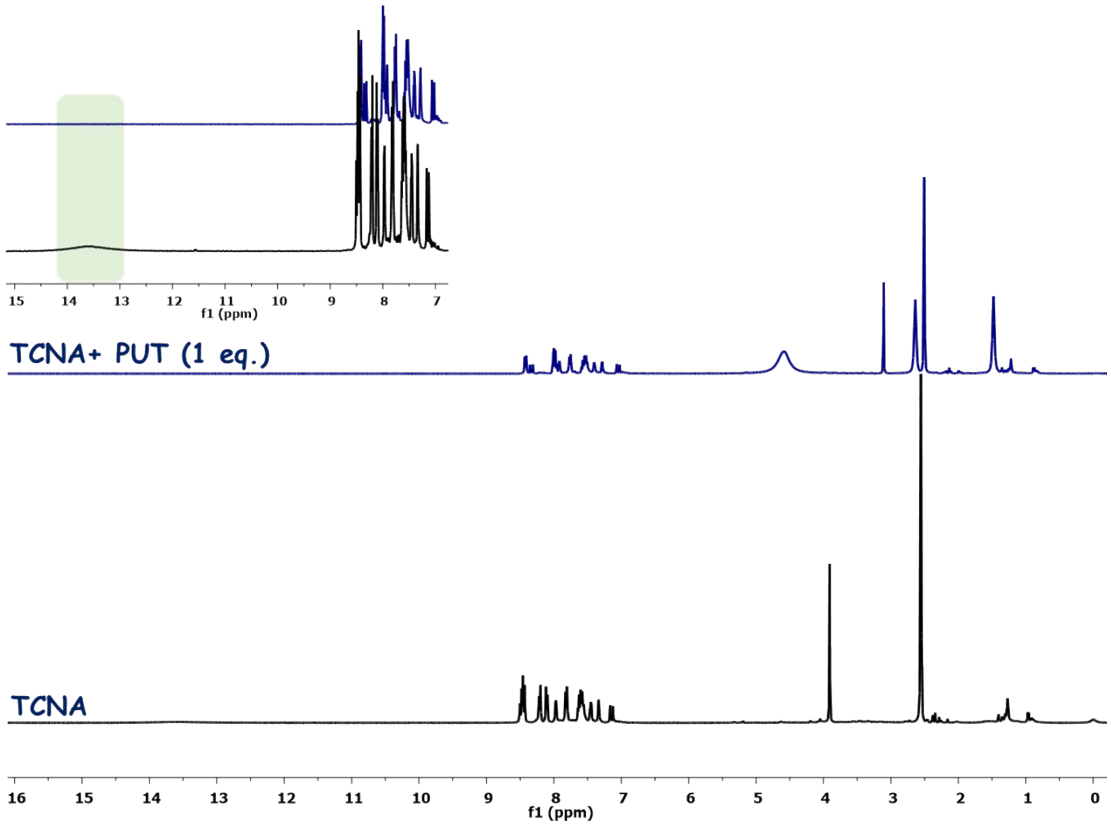


Figure S16. A complete ^{1}H NMR spectra of **TCNA** and **TCNA +PUT** (1 equiv) in DMSO-d_6 .

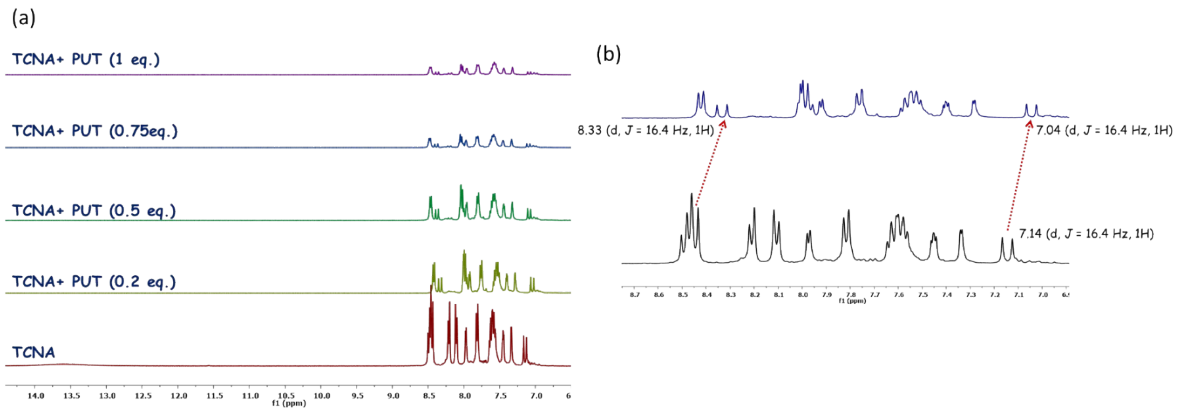


Figure S16A. (a) The partial NMR spectra (titration with PUT) (only aromatic part) (b) Expanded ^{1}H-NMR spectra (shown in Figure S16) of **TCNA** in DMSO-d_6 before and after the addition of 1eq. of PUT.

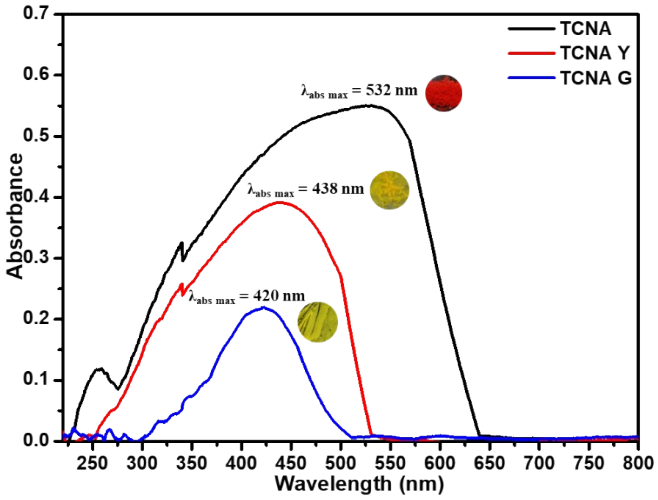


Figure S17. Solid state absorbance spectra of **TCNA**, **TCNA Y** and **TCNA G**.

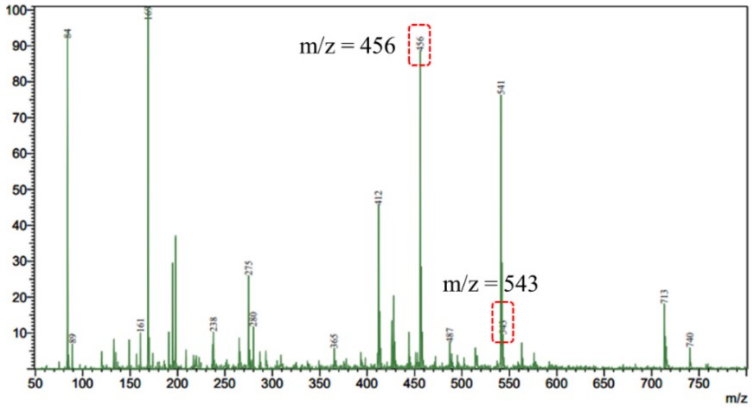


Figure S18. LC-MS spectra of **TCNA** after exposure to putrescine

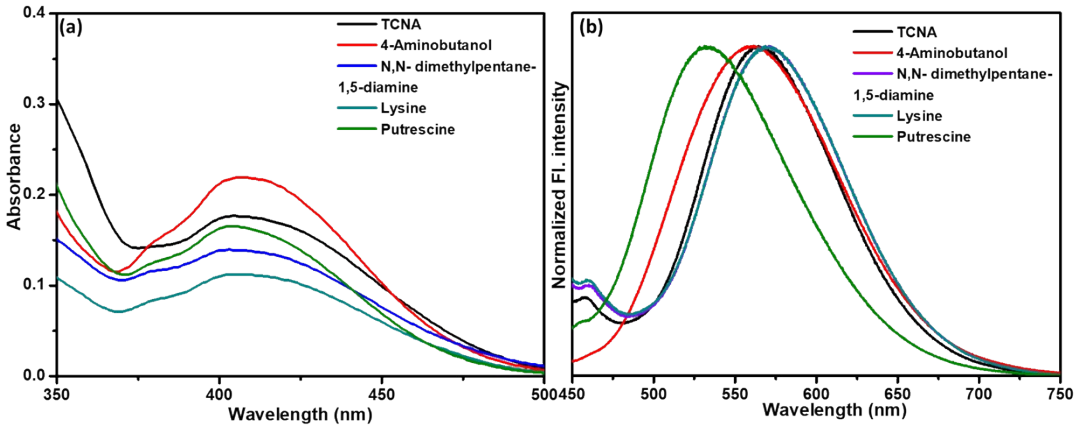
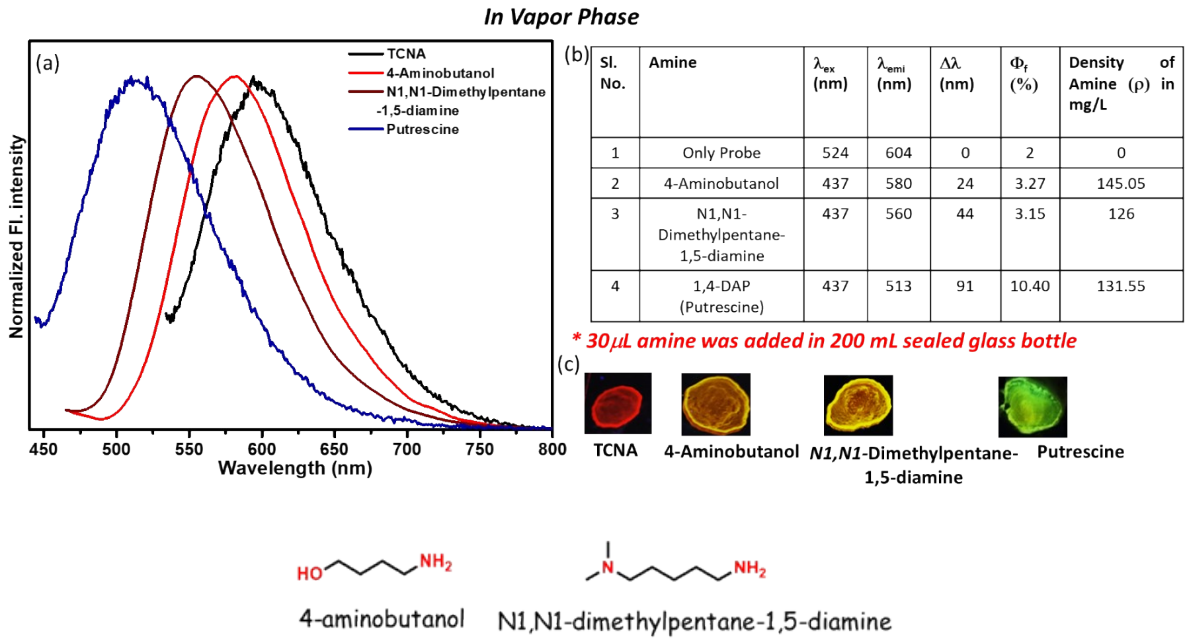
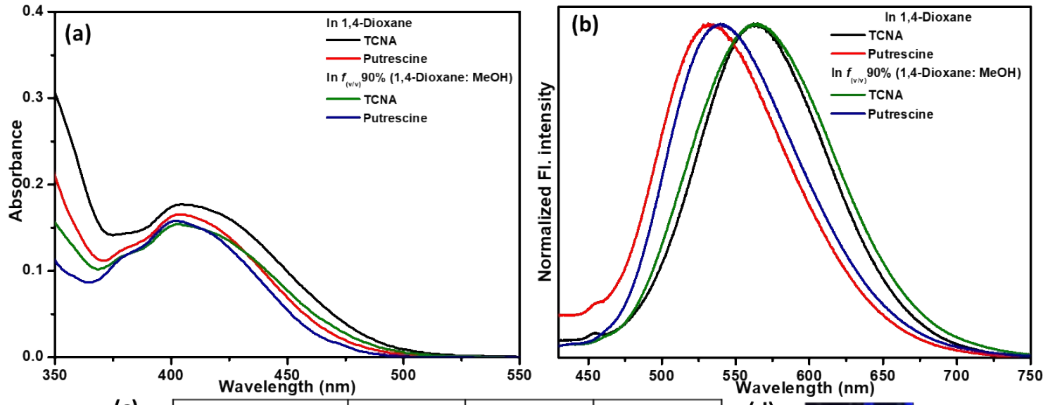


Figure S19: The (a) absorption and (b) emission spectra of the probe **TCNA** (10 μM in 1,4-dioxane) after addition of different amine (10 μM in dimethylacetamide DMAc) . λ_{ex}= 404 nm



Sl. No.	Amine	λ_{ex} (nm)	λ_{emi} (nm)	$\Delta\lambda$ (nm)	Φ_f (%)	Density of Amine (ρ) in mg/L
1	Only Probe	524	604	0	2	0
2	4-Aminobutanol	437	580	24	3.27	145.05
3	N1,N1-Dimethylpentane-1,5-diamine	437	560	44	3.15	126
4	1,4-DAP (Putrescine)	437	513	91	10.40	131.55

Figure S20: (a) Normalized FL spectra of **TCNA** thin film before and after exposure to different amine vapor (λ_{ex}: 524 nm for probe; 437 nm after exposure to amine vapor). (b) All the photophysical parameters (c) Images of the emissive films under 365 nm UV lamp.



(c)

Solvent Systems	$\lambda_{max.}$ (nm) for TCNA (10μM)	$\lambda_{max.}$ (nm) for Putrescine (10μM in DMAc)	$\Delta\lambda$ (nm)
System-I : 1,4-Dioxane	564	532	32
System-II: 1,4-Dioxane: MeOH (9:1)	564	541	23

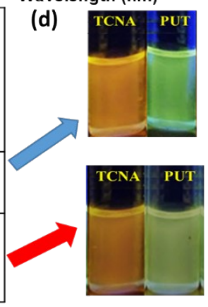


Figure S21 The (a) absorption spectra and (b) emission spectra of the probe **TCNA** (10 μM) after addition of putrescine. λ_{ex}= 404 nm. (c) The emission parameters along with the images under 365 nm UV-lamp.

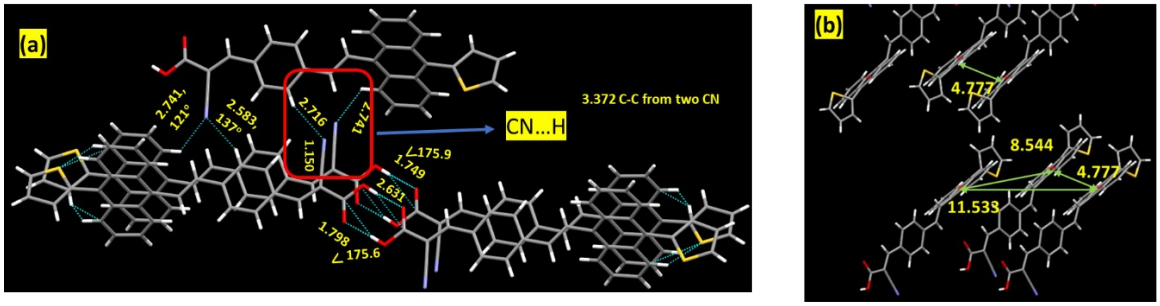


Figure S22. (a) **TCNA** crystal packing with supramolecular interactions of TCNA with few significant noncovalent interaction distances (Å), and angles (°) (CN…H interactions are shown in the square) (b) Crystal structure with centroid distances (Å) for **TCNA** obtained using Mercury software

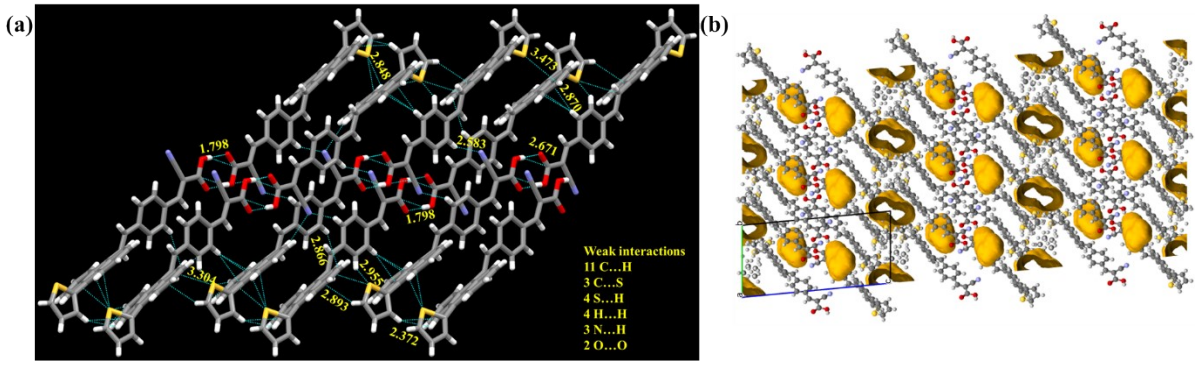


Figure S23. (a) Molecular packing (a-axis view) of **TCNA** with few significant non-covalent interaction distances (Å), (b) Void space for TCNA calculated using Mercury software.

Table S7: Crystallographic parameters for **TAA** and **TCNA**

Compounds	**TCNA**
Emp. Formula	$C_{30}H_{19}NO_2S$
Formula Weight	457.52
Crystal System	Triclinic
Space Group	P-1
a /Å	9.3617(2)
b /Å	11.53320(10)
c /Å	24.0179(2)
α/degree	83.4880
β/degree	80.9190

γ/degree	82.6190
V /Å^3	2527.99(6)
Z	2
$\rho_{calc.}$ /g cm-3	1.202
μ /mm^{-1}	1.339
F (000)	952
Data/ restraints/ parameters	10679/0/627
S	1.064
R1 [I>2σ(I)]	0.0447
wR2 [all data]	0.1232
Max/min. residual electron dens. [eÅ^{-3}]	0.35/-0.37

Table S8: The list of various intermolecular interactions (Å) for **TCNA**

TCNA	**S…H**	**H…H**	**C…H**	**N…H**	**C…S**	**O…H**	**O…O**	**C…C**
30 interactions	2.846 2.955 2.848 2.995	2.386 2.356 2.372 2.393	2.898 2.766 2.870 2.841 2.893 2.833 2.866 2.671 2.631 2.753 2.880	2.741 2.583 2.716	3.304 3.438 3.473	1.749 1.798	2.636 2.588	3.372

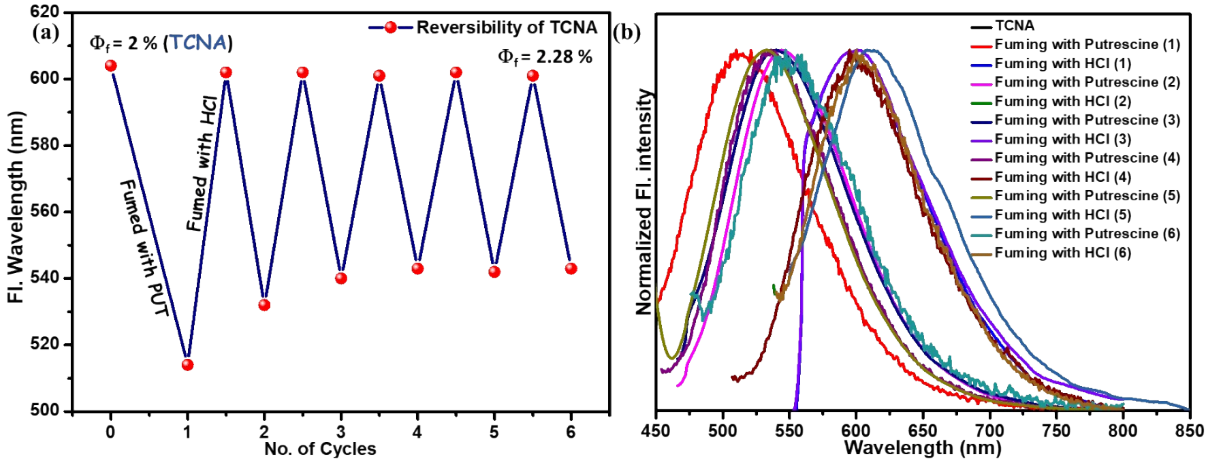


Figure S24. (a) Reversibility plot and (b) solid-state emission spectra of **TCNA** after exposure to putrescine vapor and subsequent HCl vapour

Table S9. Optical properties of **TCNA** and its salt molecule using CAM-B3LYP

Molecules	**TCNA**	**TCNA+PUT**	**TCNA+DAP**
Absorption	425.20 nm (*f*=0.9240)	399.32 nm (*f*=0.7846)	400.48 nm (*f*=0.8078)
Emission	564.20 nm (*f*=1.0961)	552.17 nm (*f*=0.9432)	554.37 nm (*f*=0.9793)
HOMO LUMO Energies (in eV)	HOMO=-6.76 LUMO=-2.09	HOMO=-6.41 LUMO=-1.19	HOMO=-6.44 LUMO=-1.25

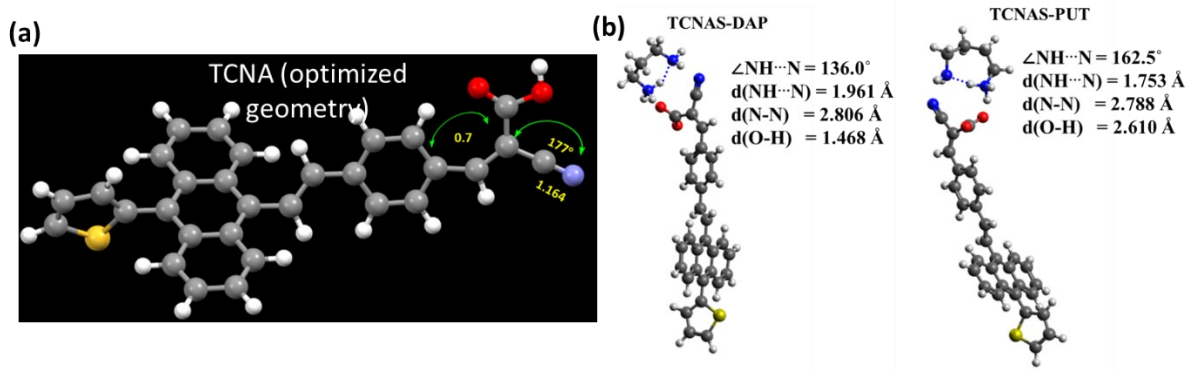


Figure S25. DFT-optimized structures with a few selected bond angles and distances.

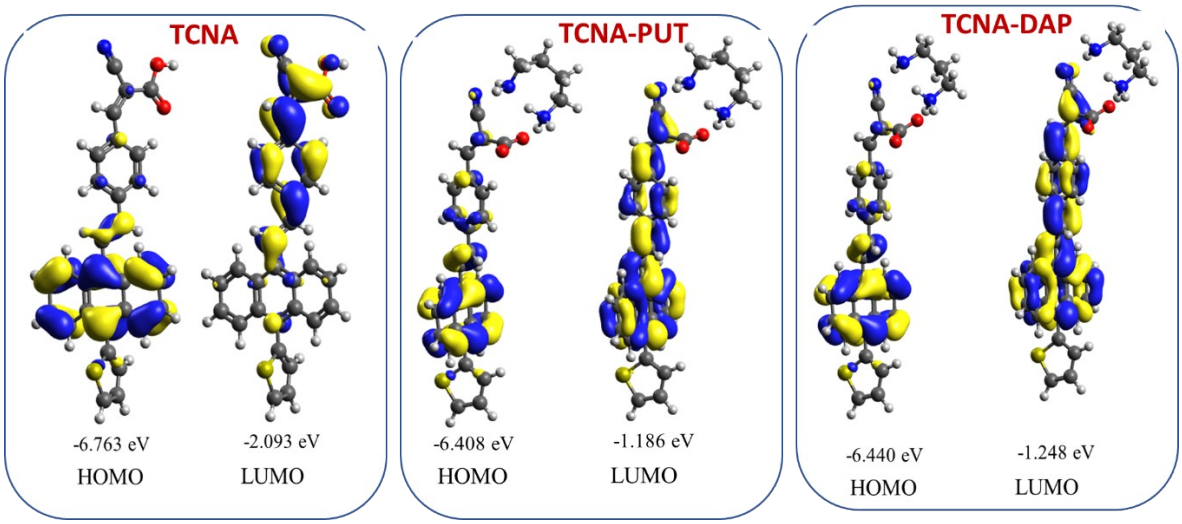


Figure S26. The HOMO-LUMO of **TCNA**, **TCNA-PUT** and **TCNA-DAP**

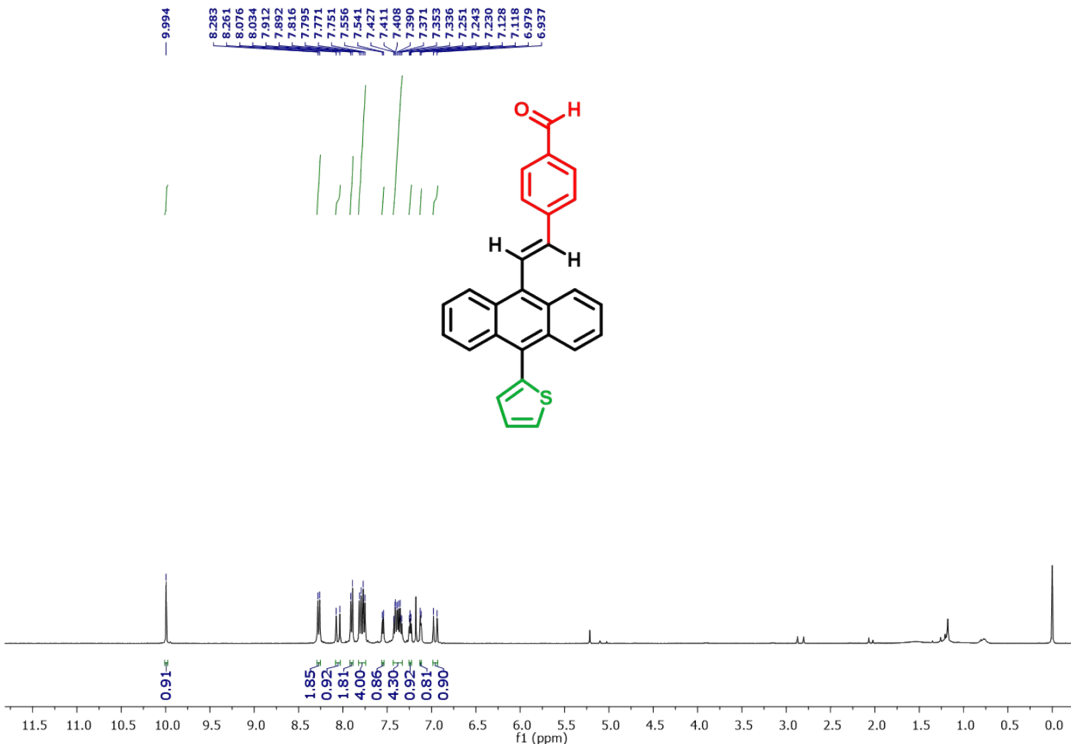


Figure S27. ^{1}H NMR spectrum for **TAA** in $CDCl_3$.

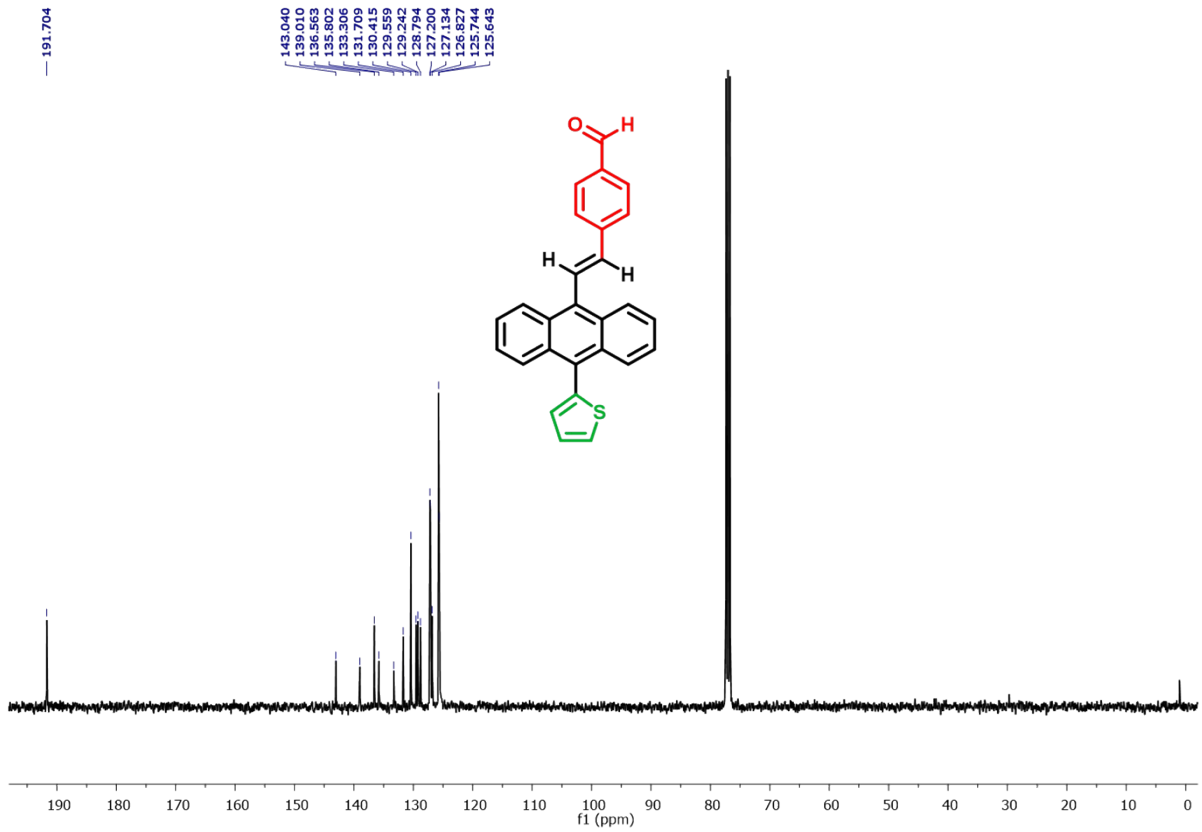


Figure S28. ^{13}C NMR spectrum for **TAA** in $CDCl_3$.

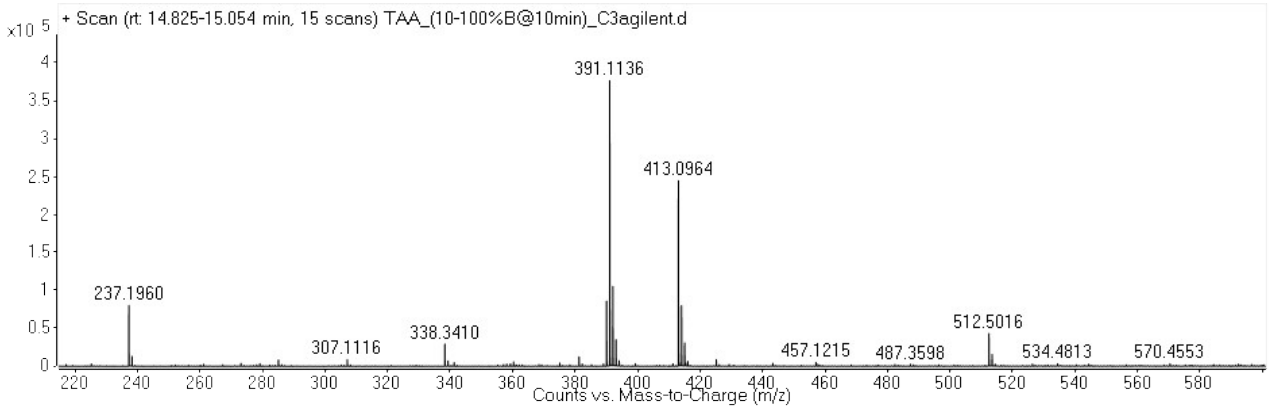


Figure S29. HRMS Spectra of **TAA**

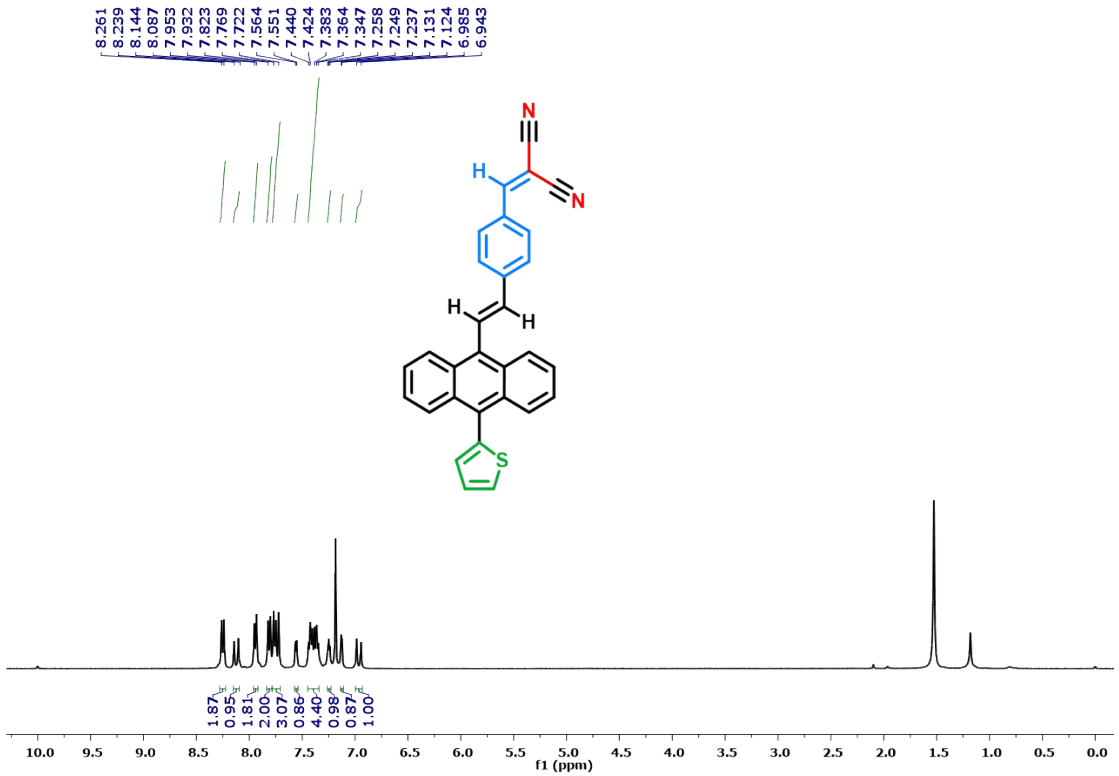


Figure S30. ^{1}H NMR spectrum for **TCN** in $CDCl_3$.

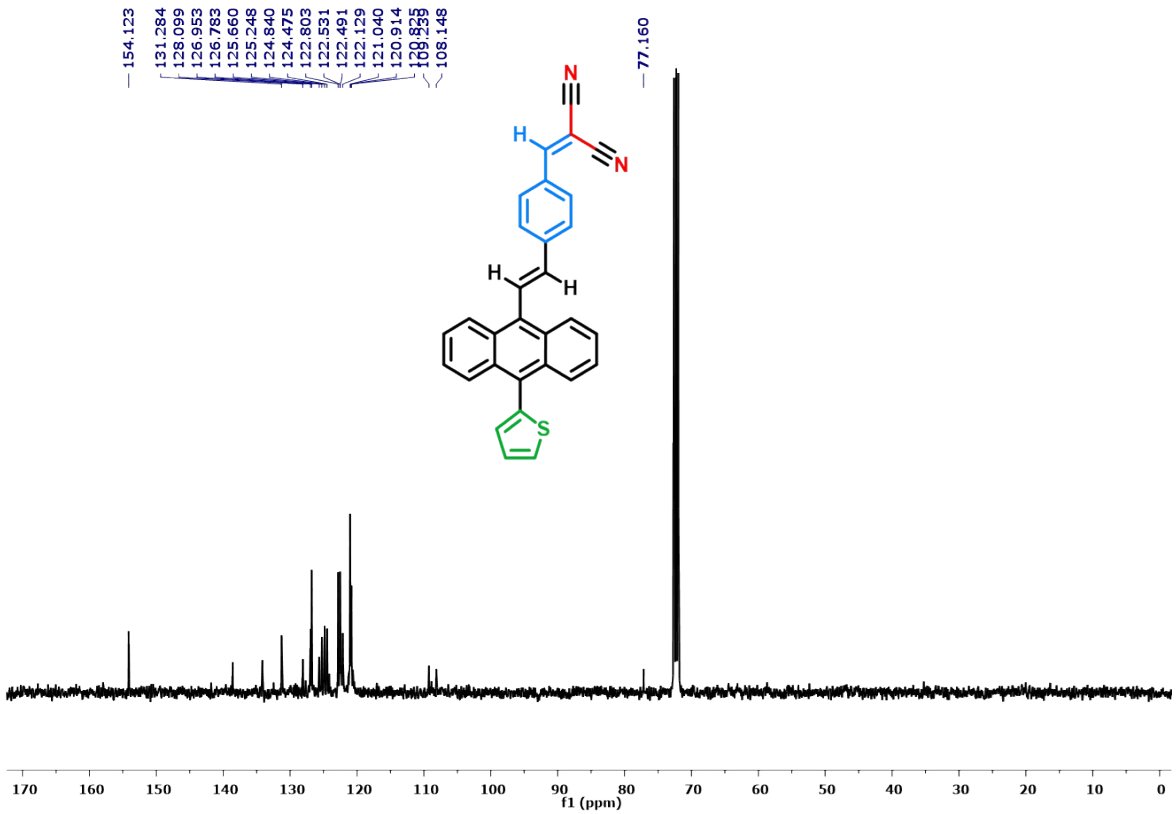


Figure S31. ^{13}C NMR spectrum for **TCN** in $CDCl_3$.

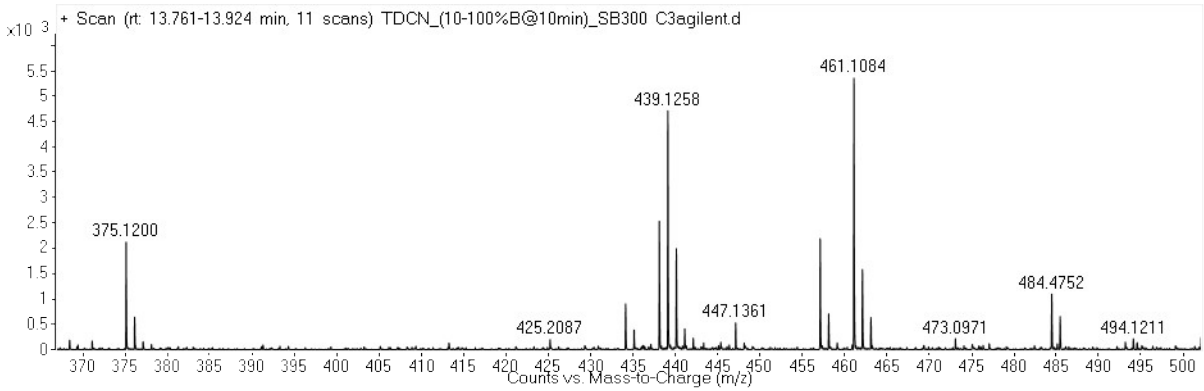


Figure S32. HRMS Spectra of **TCN**

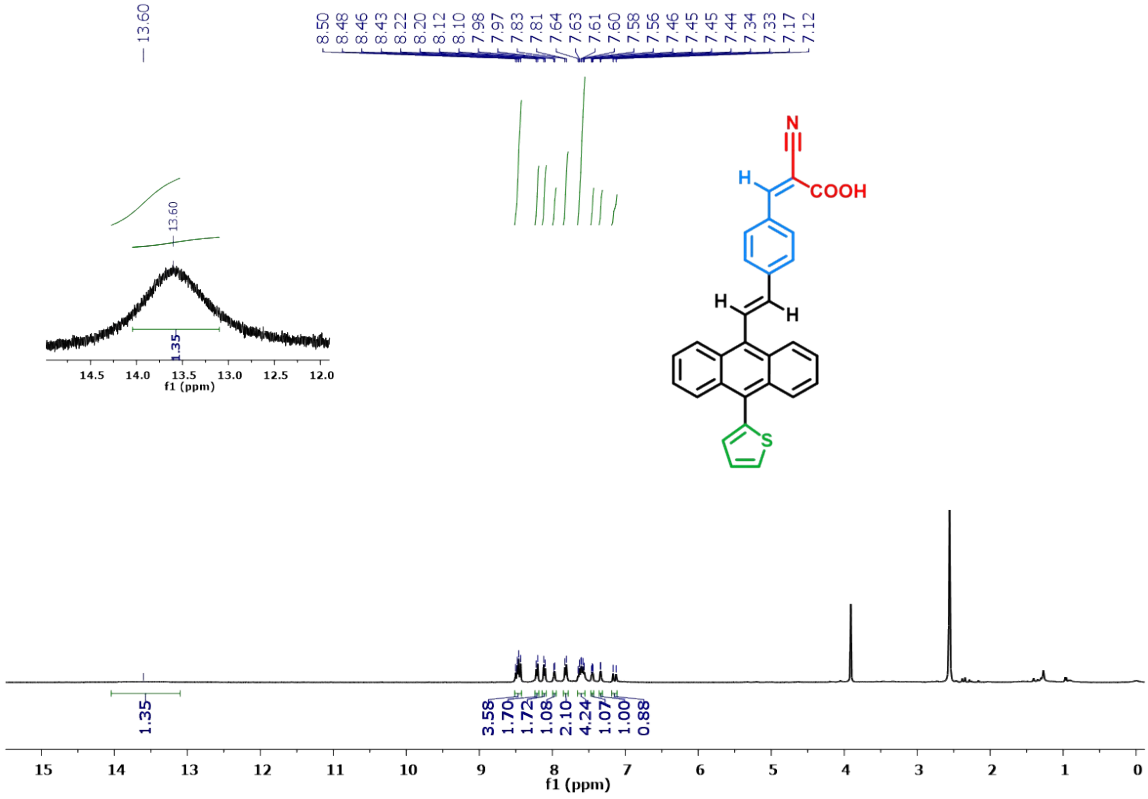


Figure S33. ^{1}H NMR spectrum for **TCNA** in DMSO-d_6.

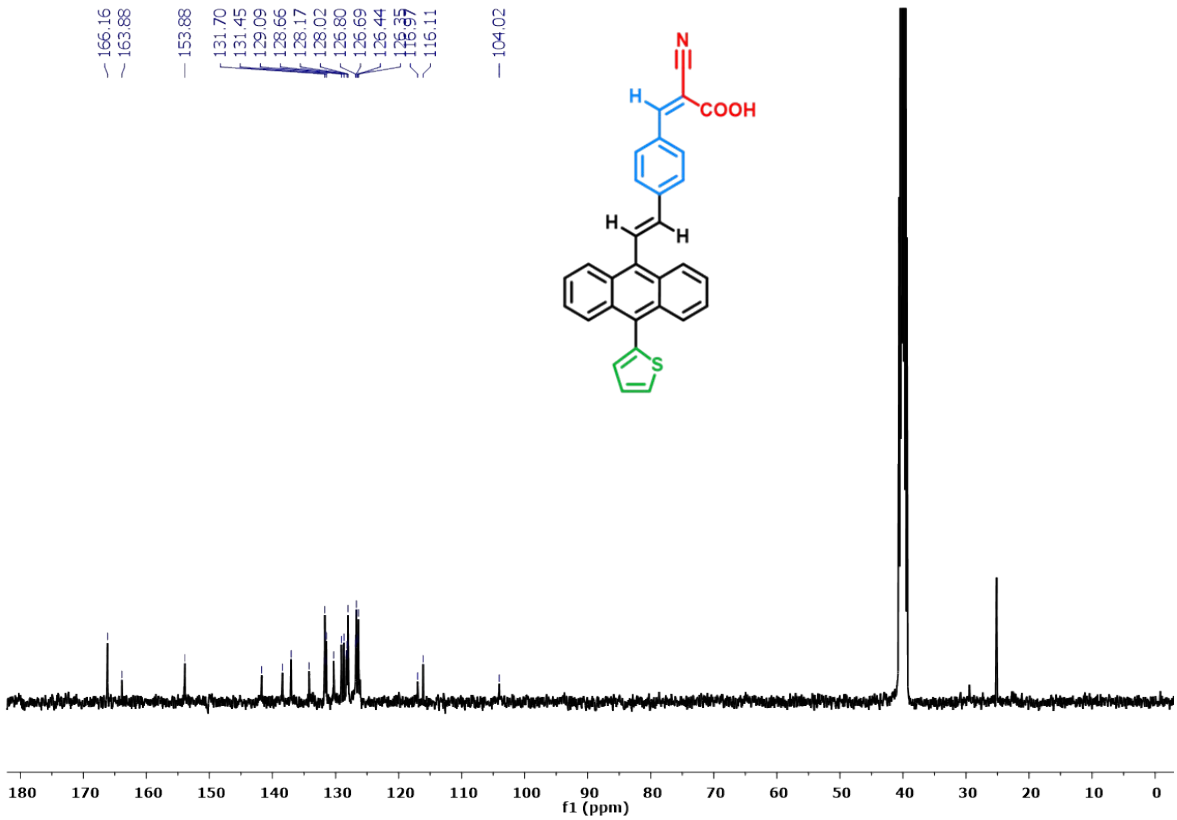


Figure S34. ^{13}C NMR spectrum for **TCNA** in DMSO-d_6.

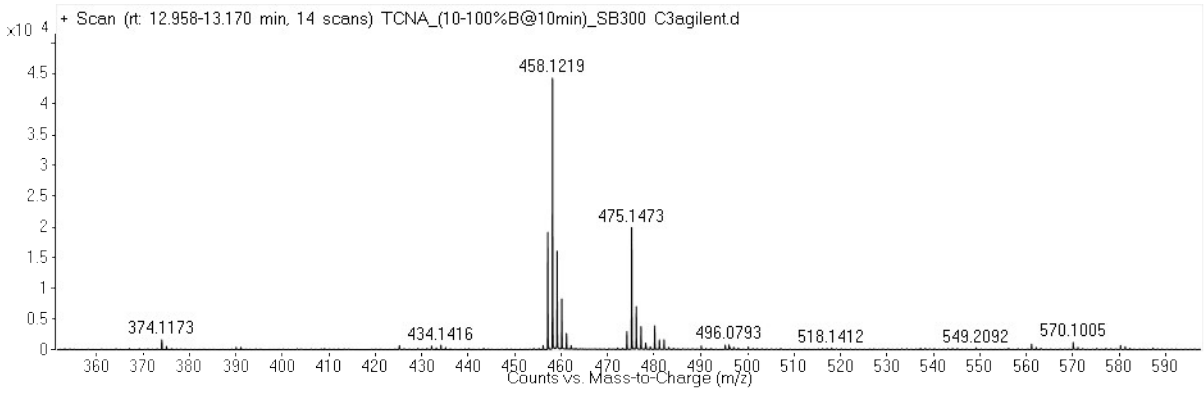


Figure S35. HRMS Spectra of **TCNA**

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