Electronic Supplementary Information (ESI)

CF_3 H-bonding Locked Aromatic Stacking of Picric Acid with Mechanofluorochromic fluorophores: Highly Selective Reusable Sensor and Rewritable Fluorescence Platform

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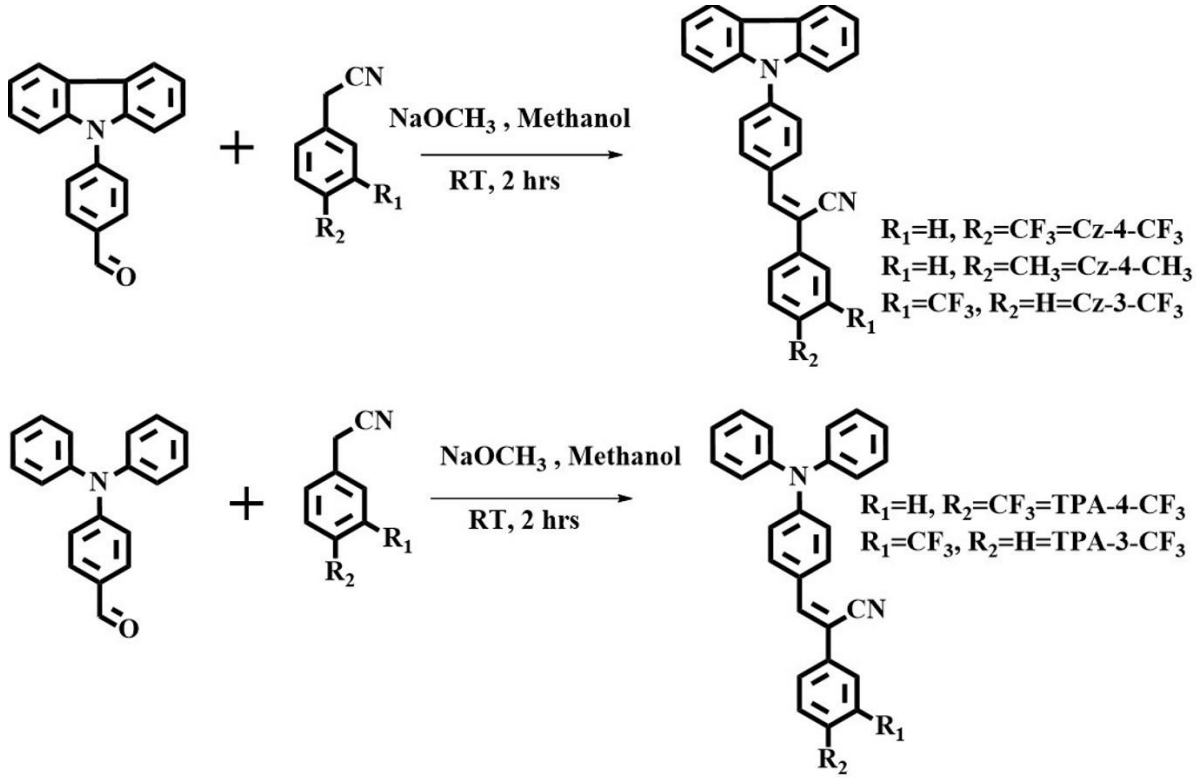
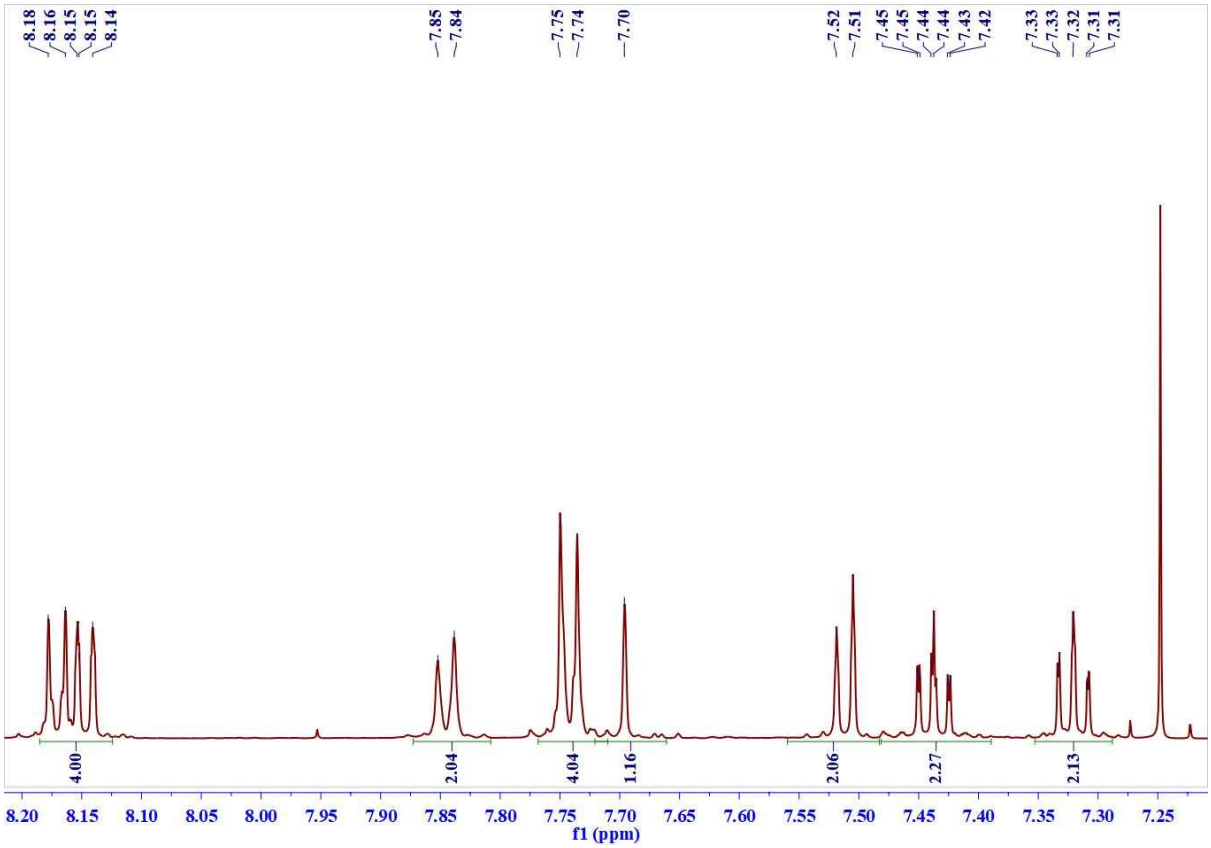
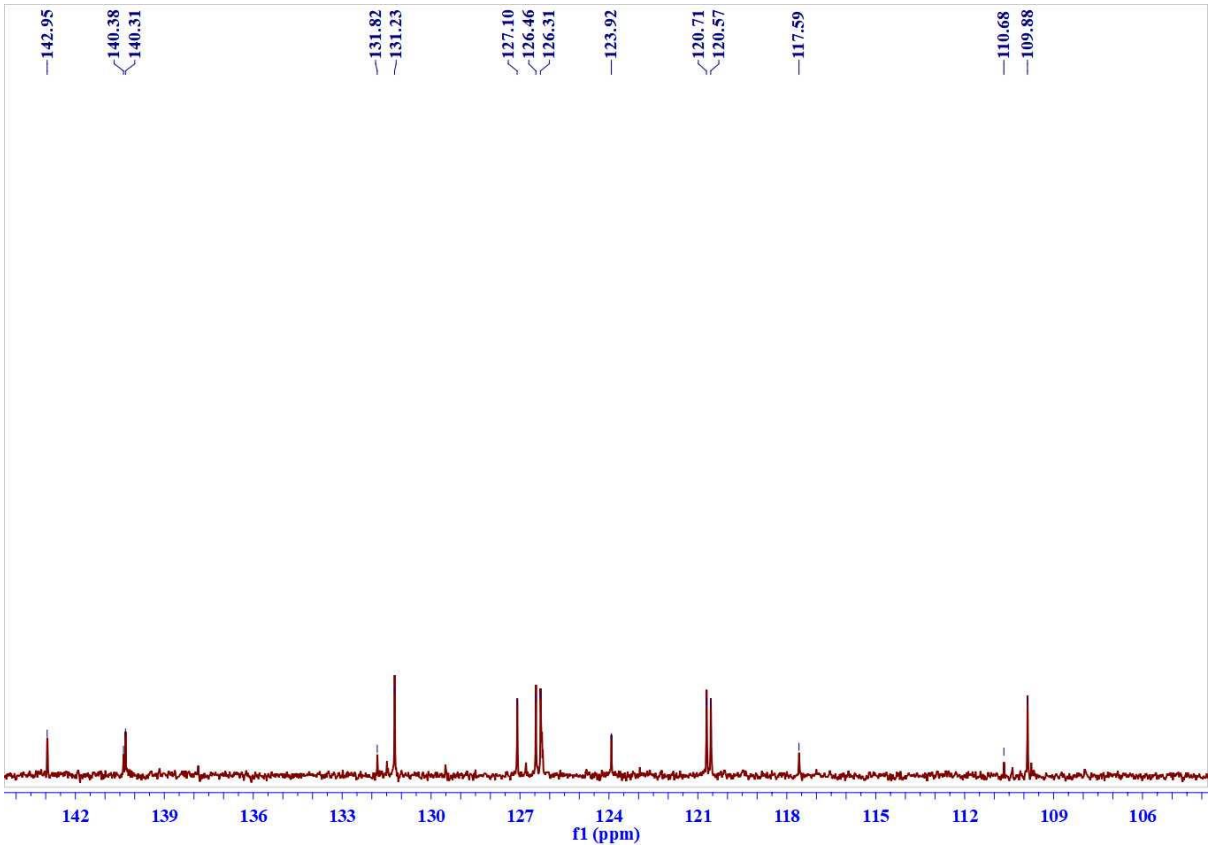
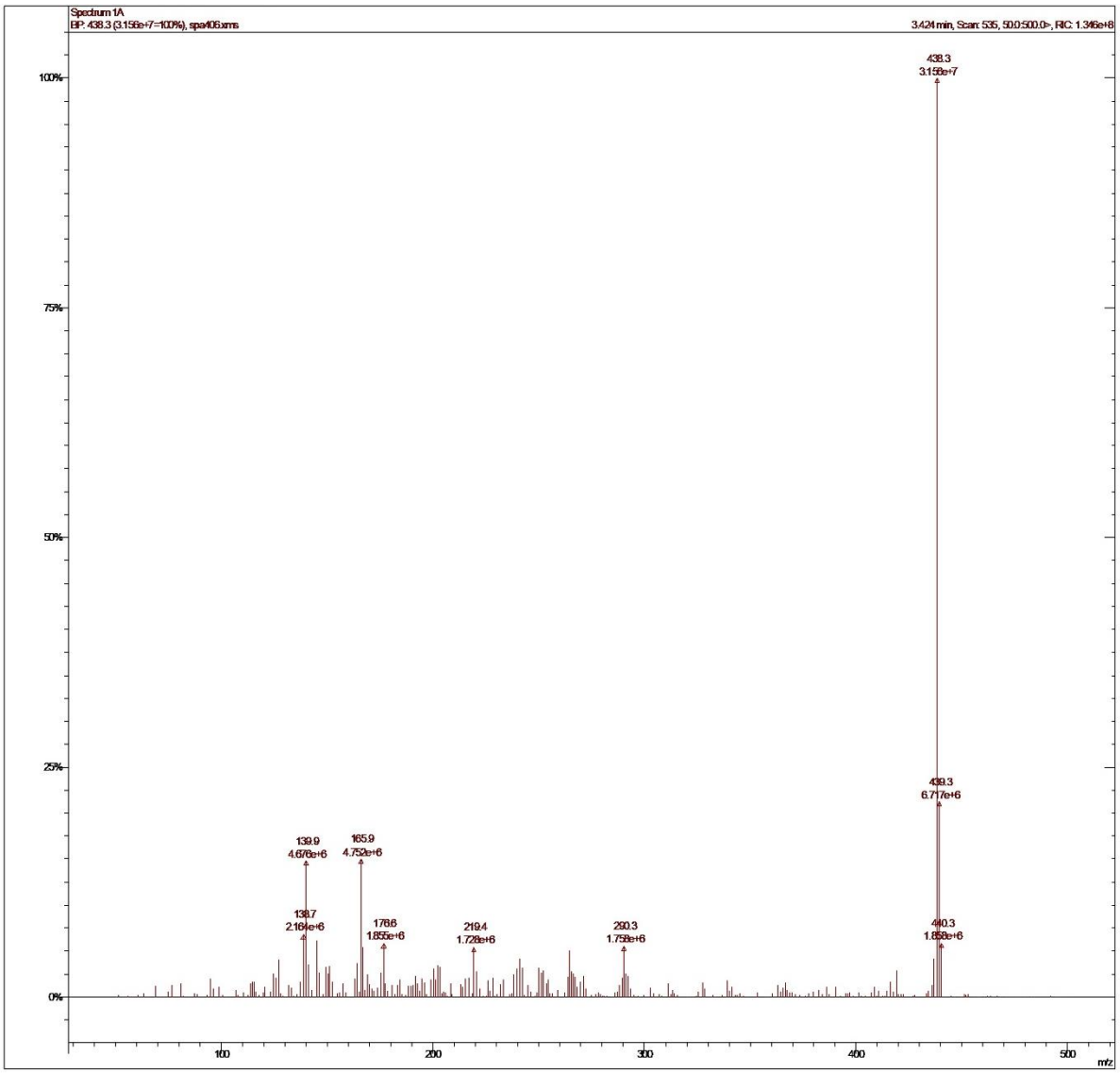


Scheme S1. Synthesis of Cz-4-CF_3, Cz-4-CH_3,Cz-3-CF_3, TPA-4-CF_3 and TPA-3-CF_3.

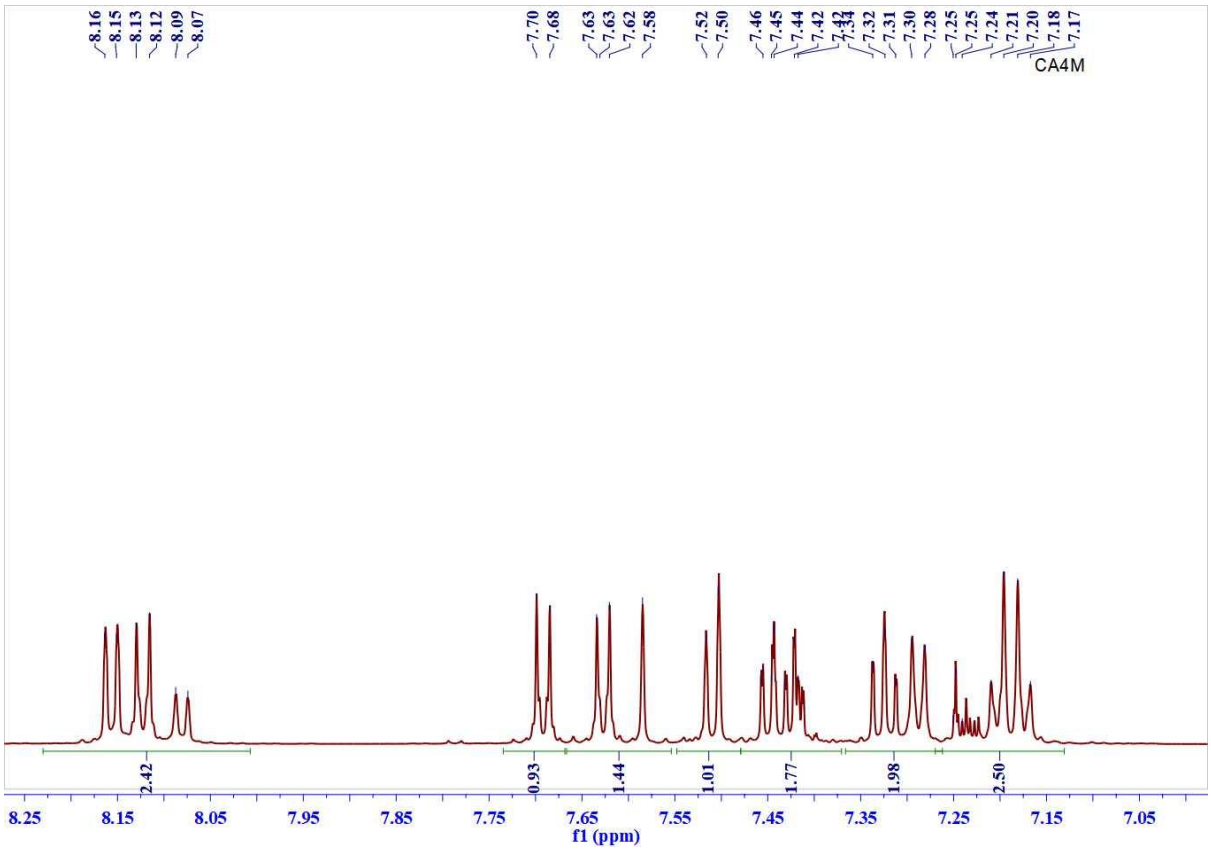


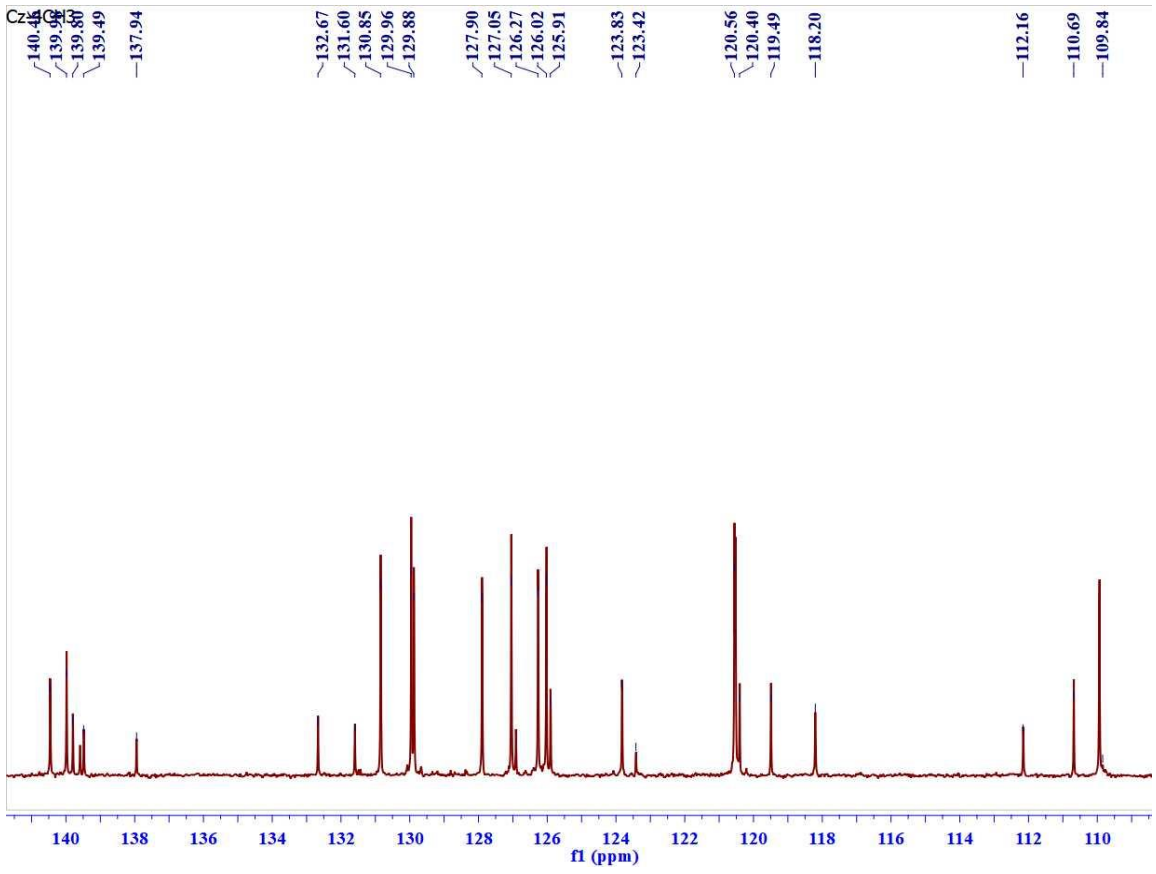


^{1}H and ^{13}C NMR of **Cz-4-CF$_3$** (solvent = $CDCl_3$).

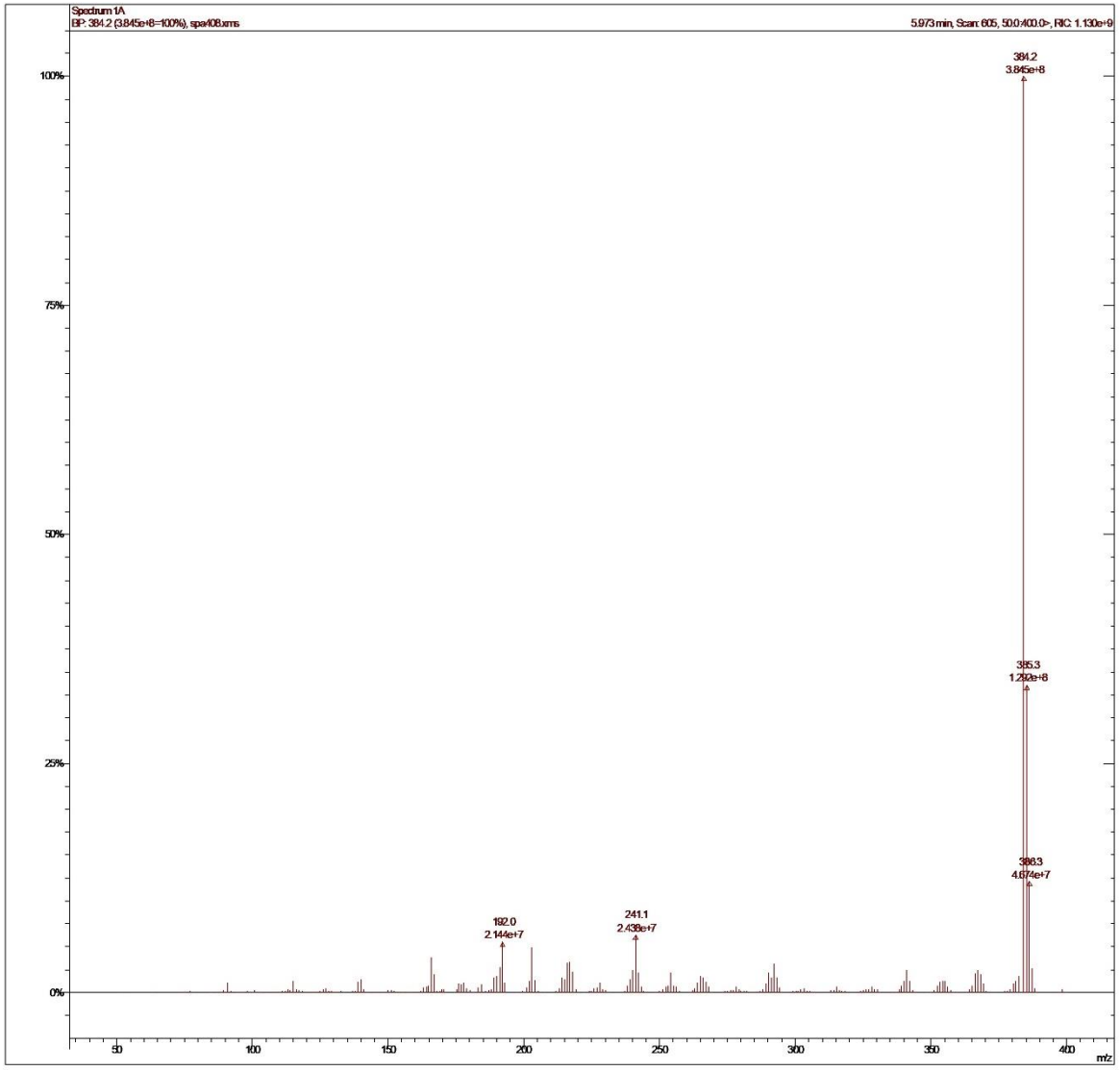


***Cz*-4-CF_3:** m/z calcd for $C_{28}H_{17}F_3N_2$ (M + H): 438.13, found: 438.3.

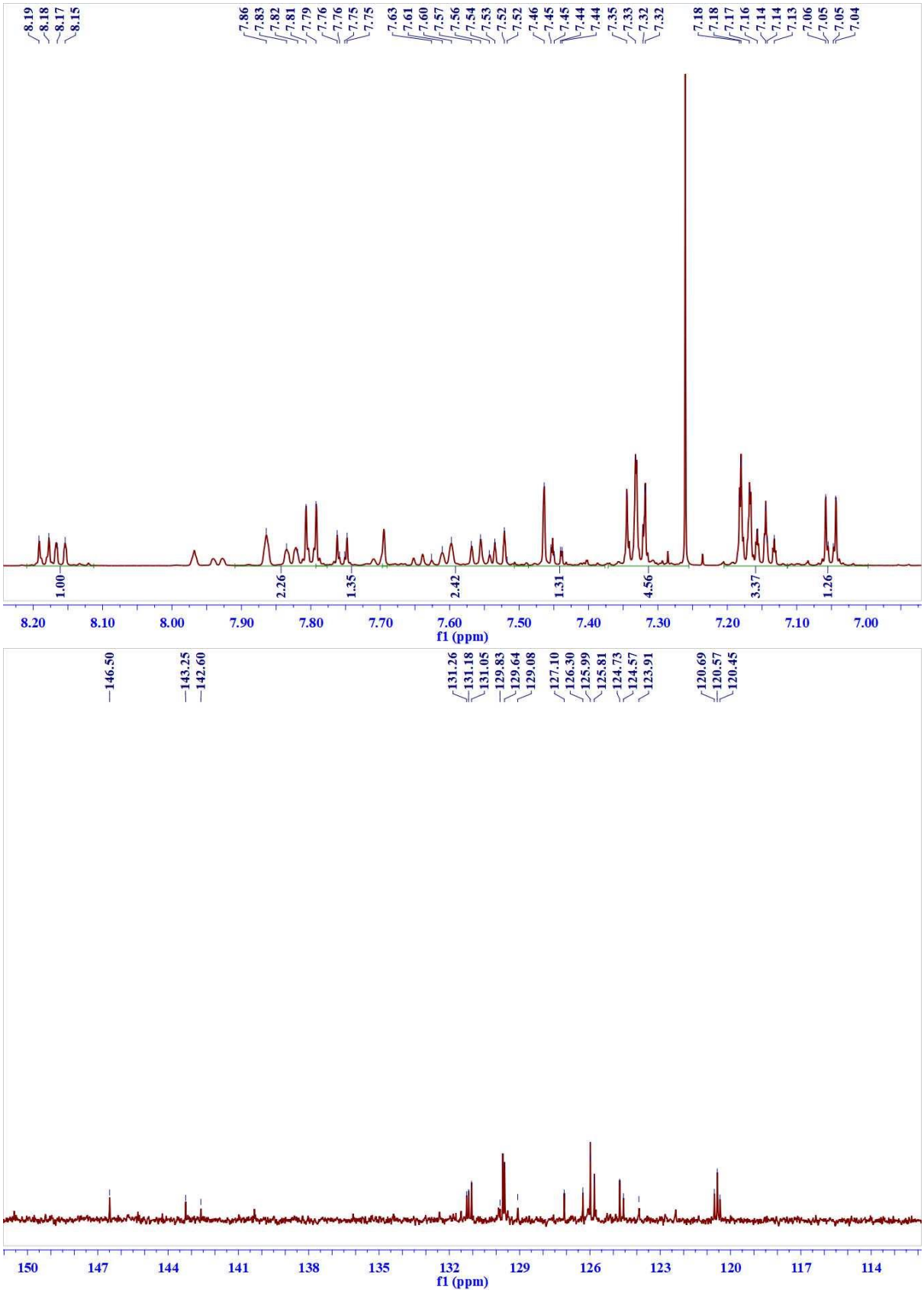




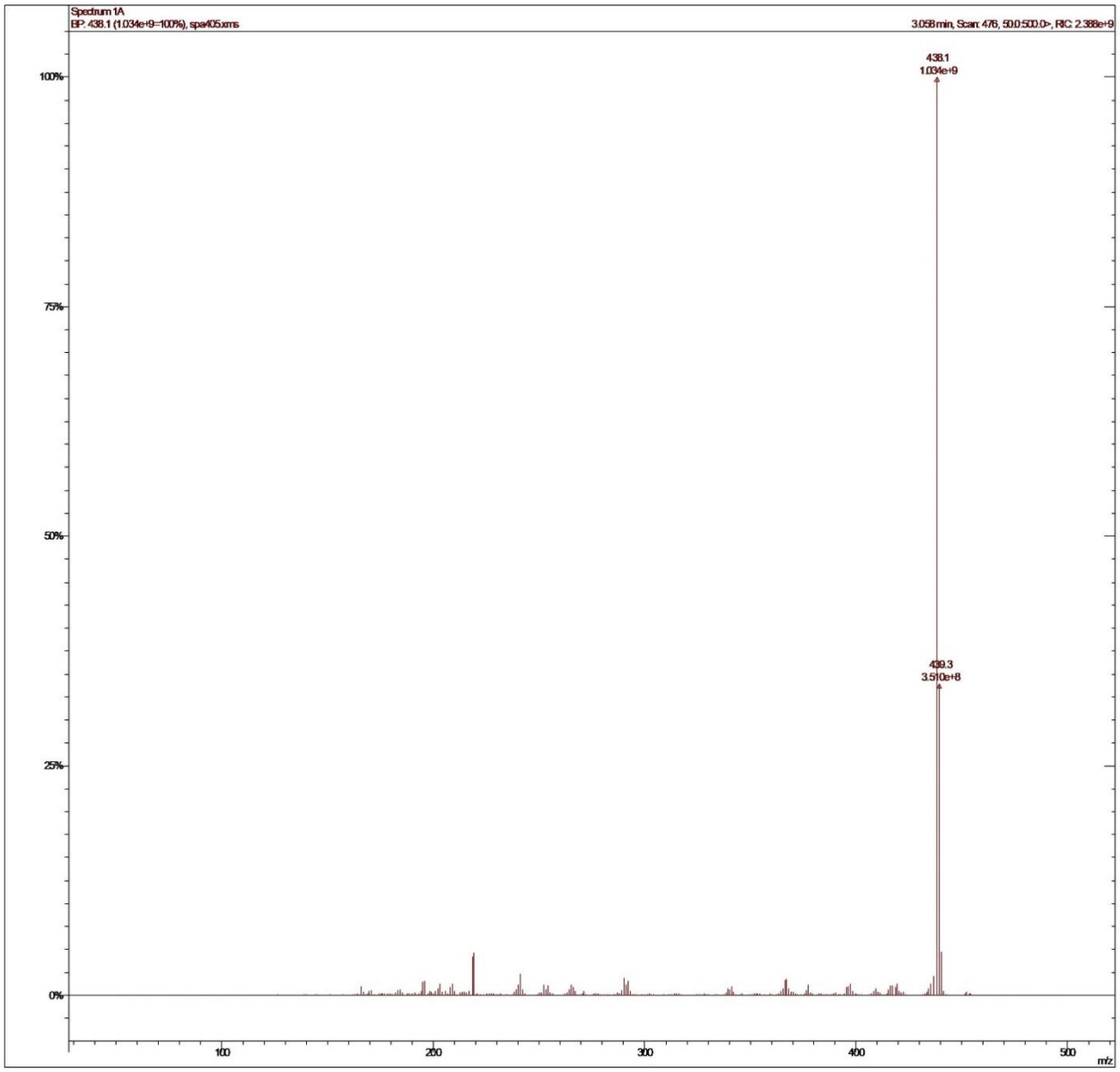
^{1}H and ^{13}C NMR of **Cz-4-CH$_3$** (solvent = $CDCl_3$).



***Cz*-4-CH_3:** m/z calcd for $C_{28}H_{20}N_2$ (M + H): 384.16, found: 384.2.



^{1}H and ^{13}C NMR of **Cz-3-CF_3** (solvent = $CDCl_3$).



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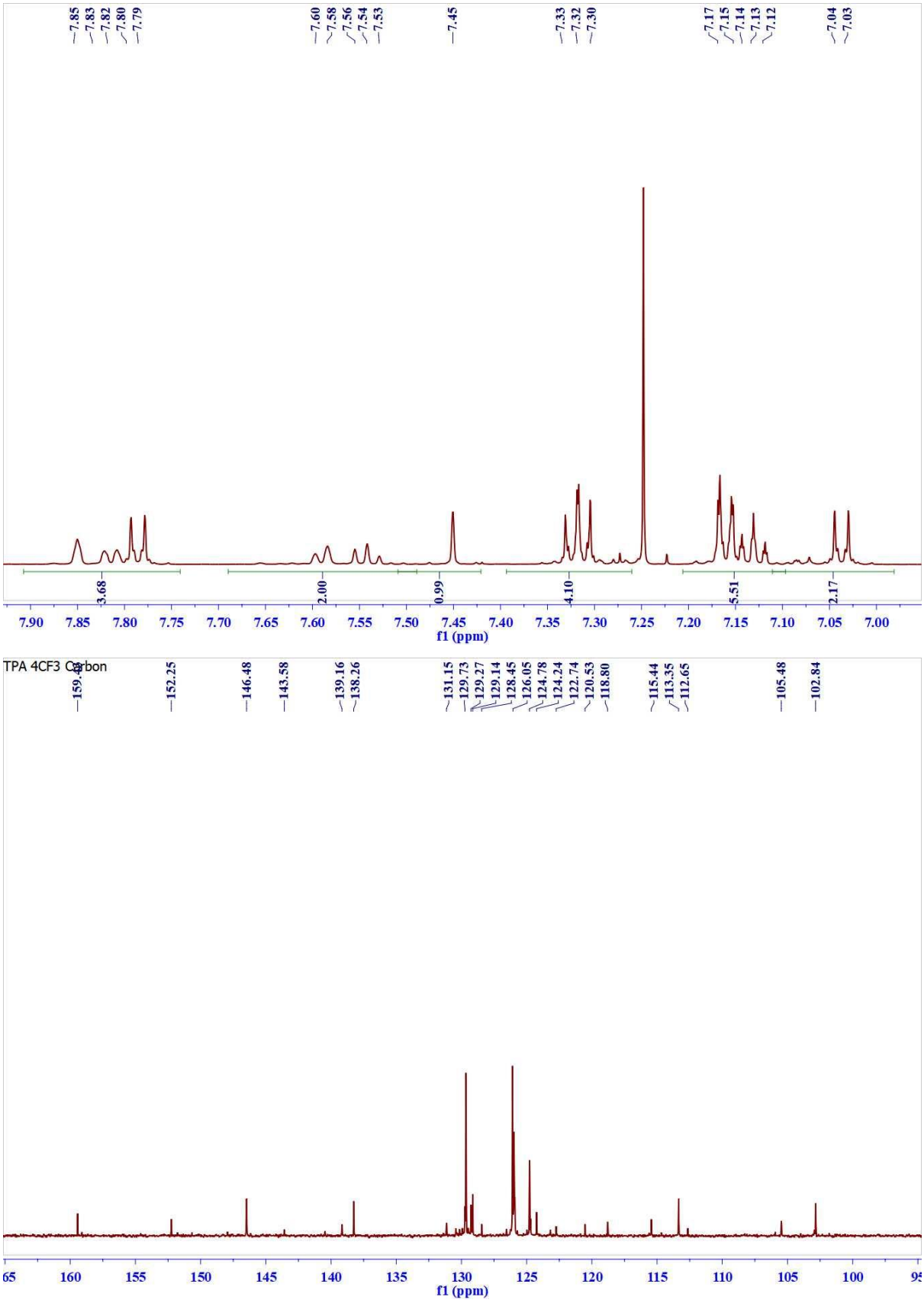
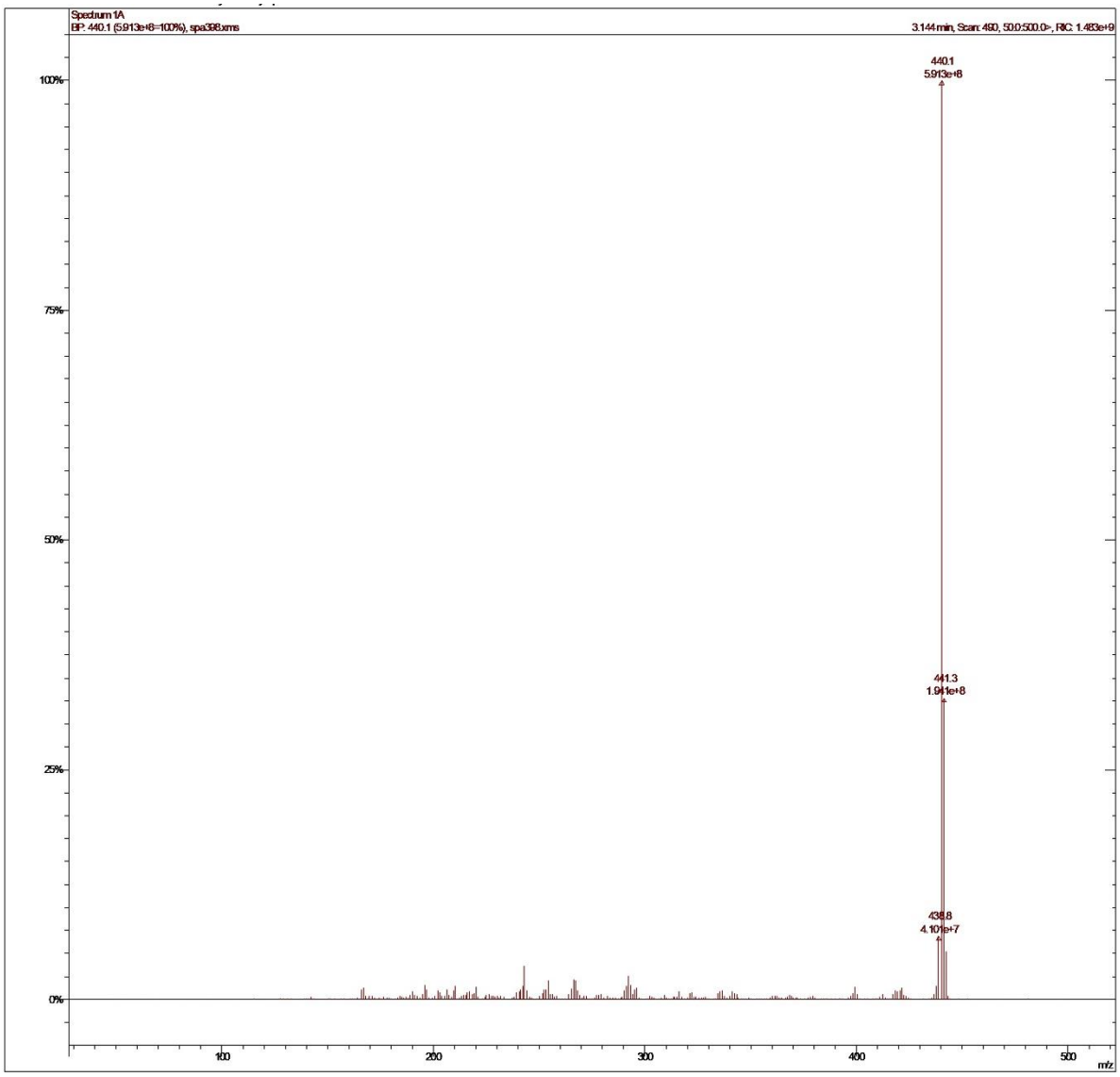
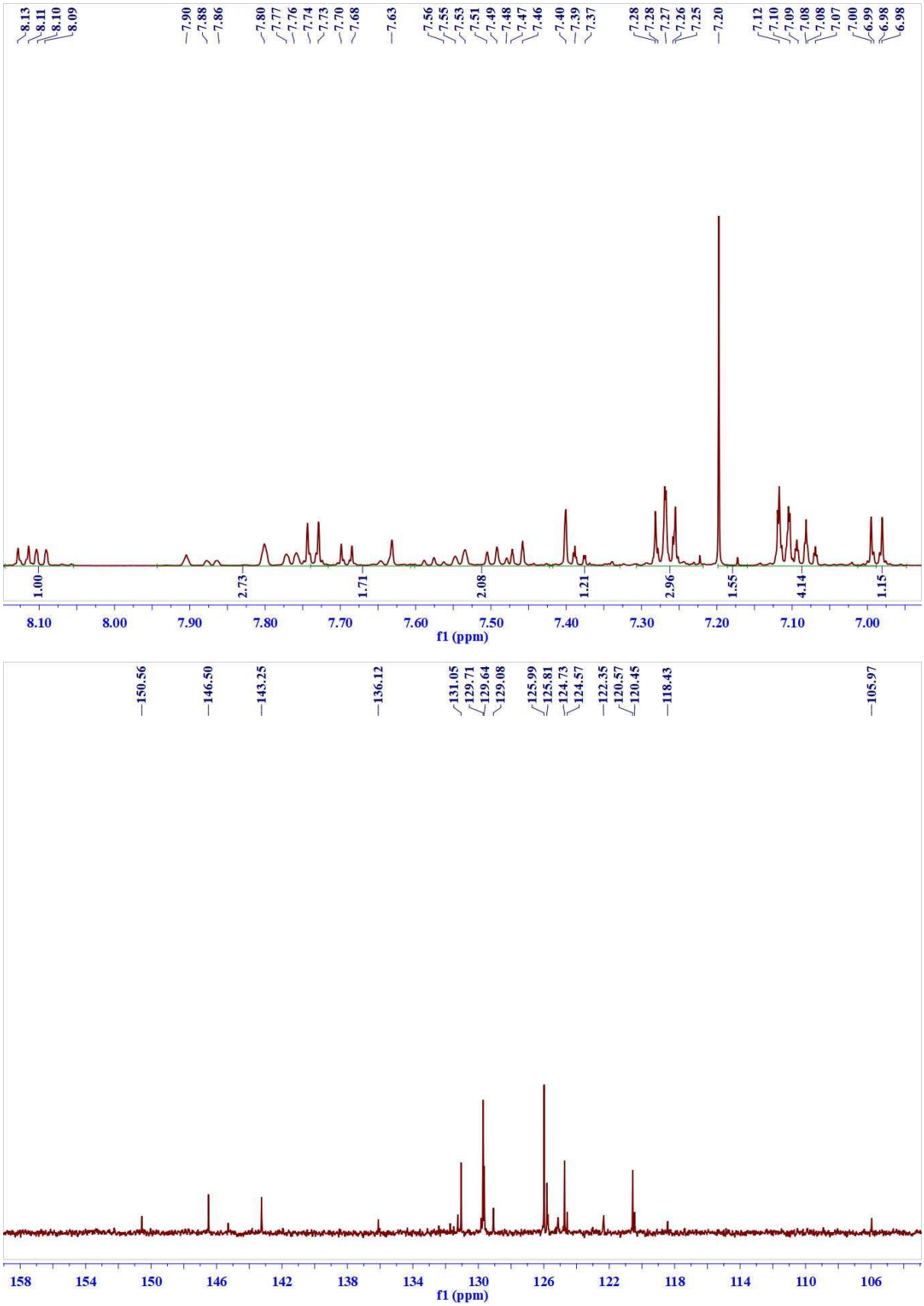


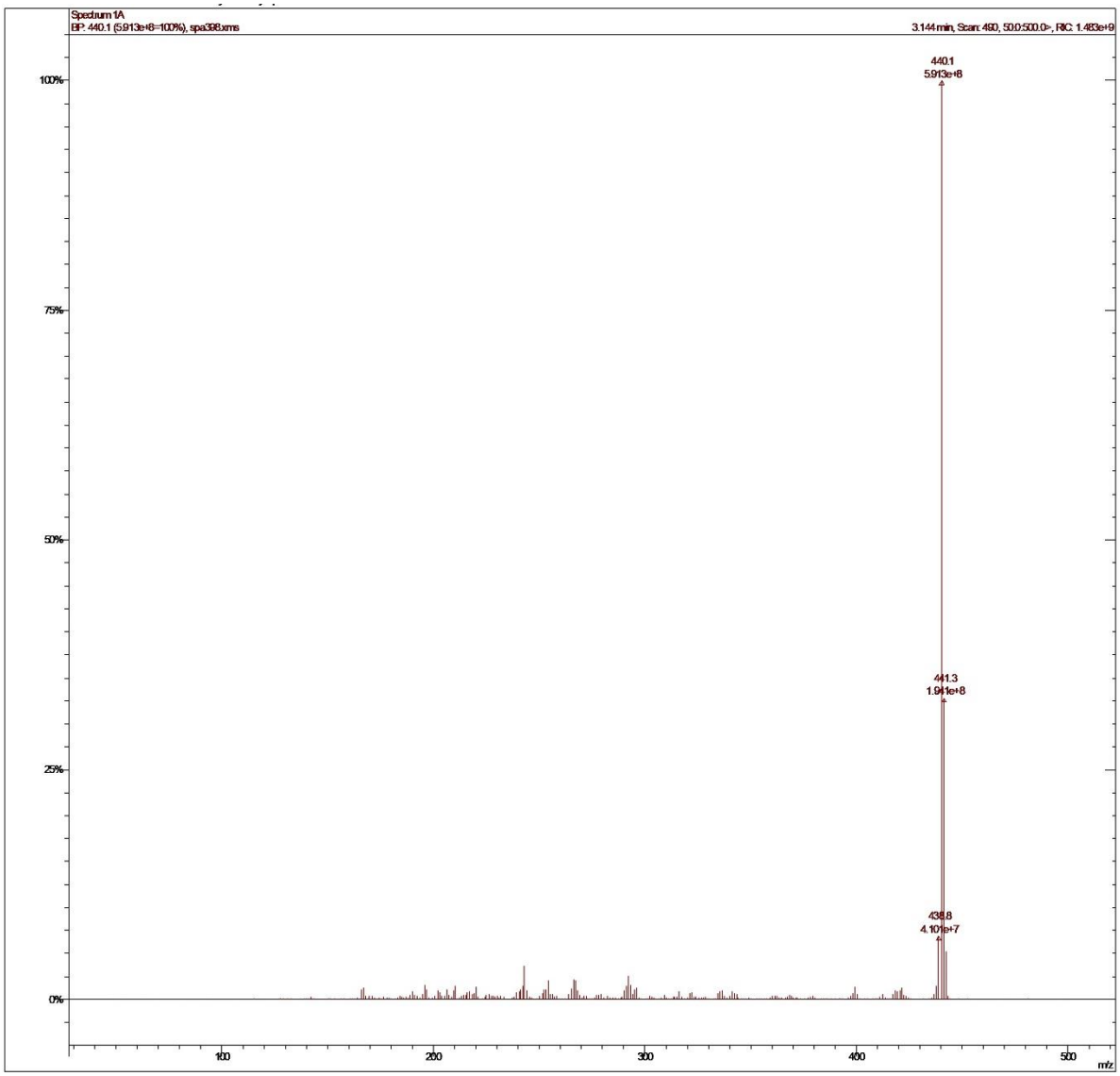
^{1}H and ^{13}C NMR of **TPA-4-CF$_3$** (solvent = $CDCl_3$).



TPA-4-CF$_3$: m/z calcd for $C_{28}H_{19}F_3N_2$ (M + H): 440.15, found: 440.1.



^{1}H and ^{13}C NMR of **TPA-3-CF_3** (solvent = $CDCl_3$).



TPA-3-CF$_3$: m/z calcd for $C_{28}H_{19}F_3N_2$ (M + H): 440.15, found: 440.1.

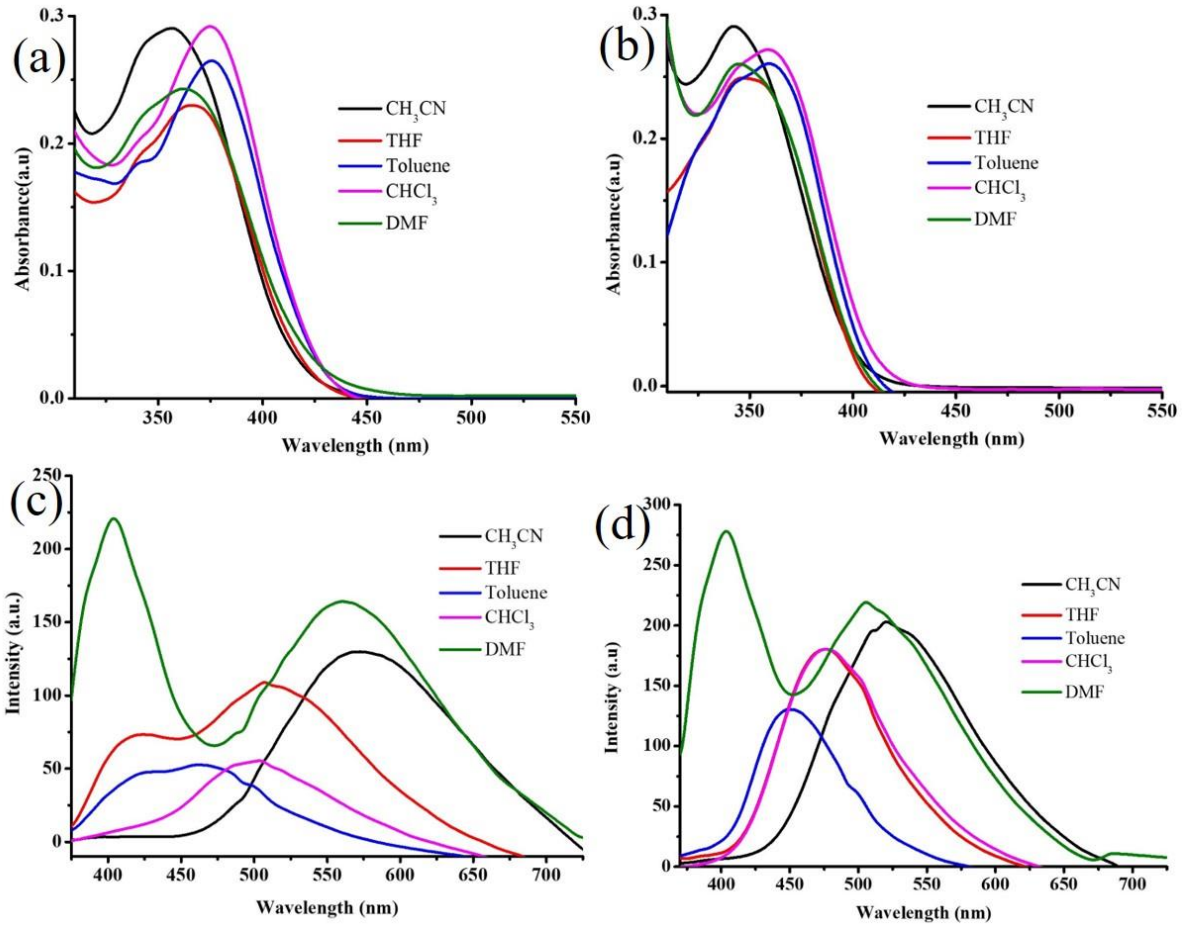


Fig. S1. Absorption (a,b) and fluorescence (c, d) spectra of (a, c) Cz-4-CF_3 and (b, d) Cz-4-CH_3 in different solvents.

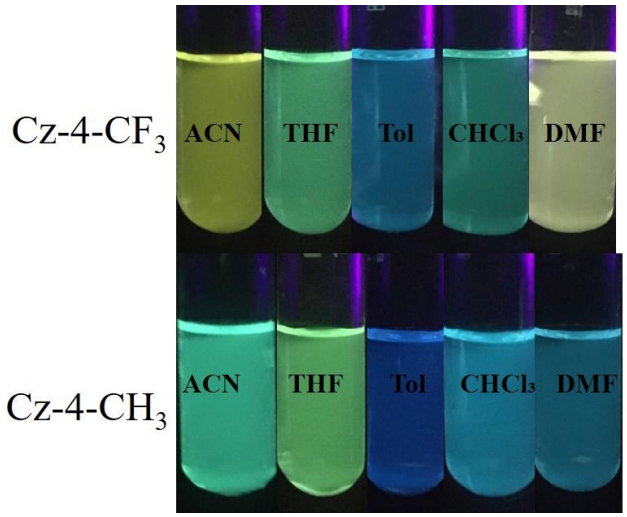


Fig. S2. Digital fluorescence images of Cz-4-CF_3 and Cz-4-CH_3 in different solvents.

Table S1. Quantum yield of Cz-4-CF_3 and Cz-4-CH_3 in solvents with respect to quinine sulphate.

Solvent	Quantum yield (Φ_F)	
	Cz-4-CF_3	Cz-4-CH_3
CH_3CN	0.023	0.040
$CHCl_3$	0.010	0.045
DMF	0.040	0.064
THF	0.018	0.039
Toluene	0.012	0.029

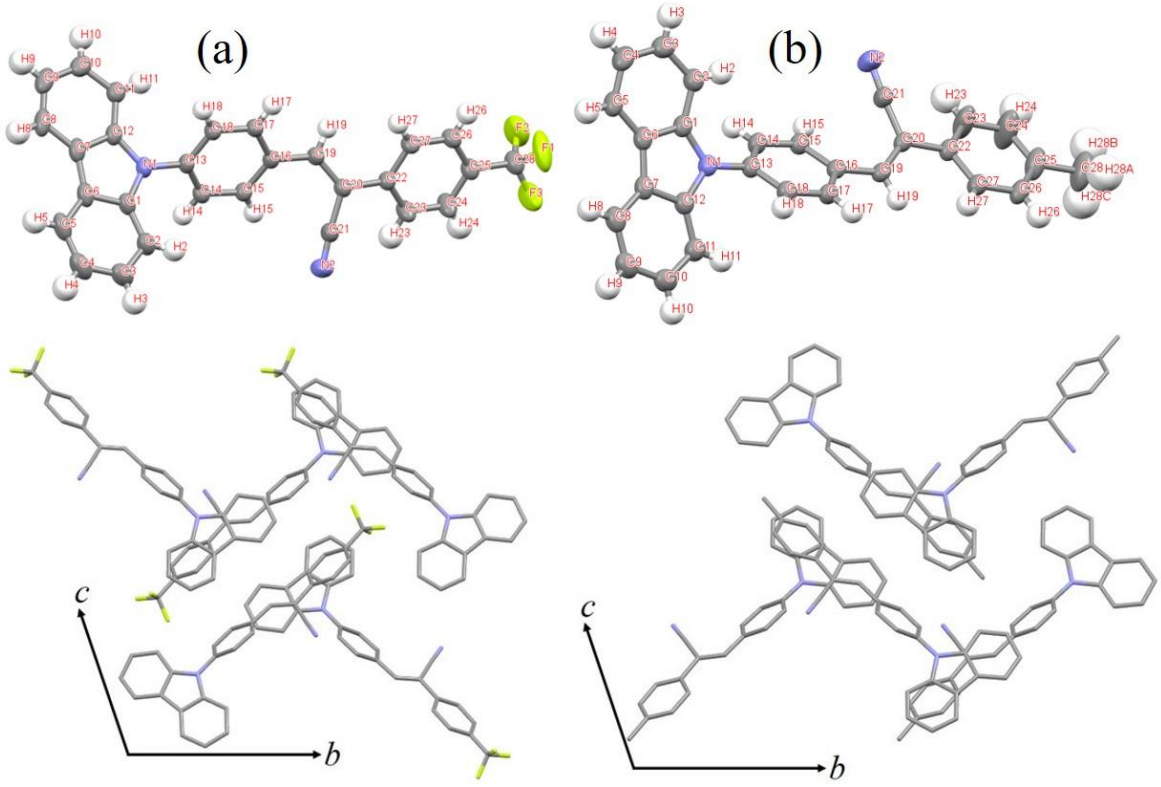


Fig. S3. Thermal ellipsoid and molecular packing in the crystal lattice of (a) **Cz-4-CF_3** and (b) **Cz-4-CH_3.** Hydrogen atoms are omitted for clarity. C (grey), N (blue) and F (yellow).

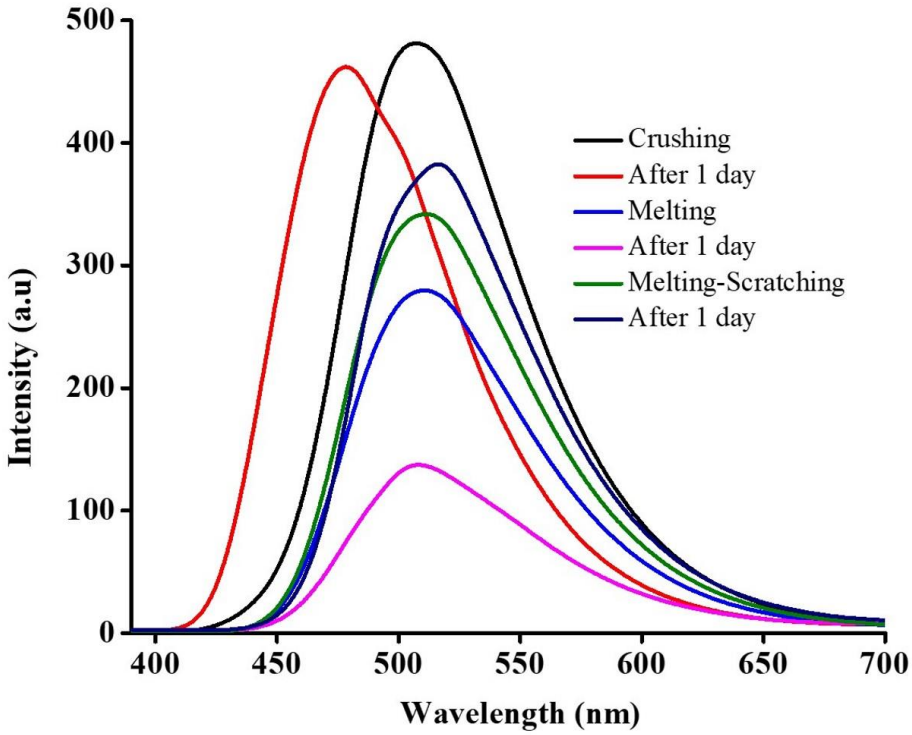


Fig. S4. Self-reversible fluorescence spectra of Cz-4-CF_3 after different external treatment.

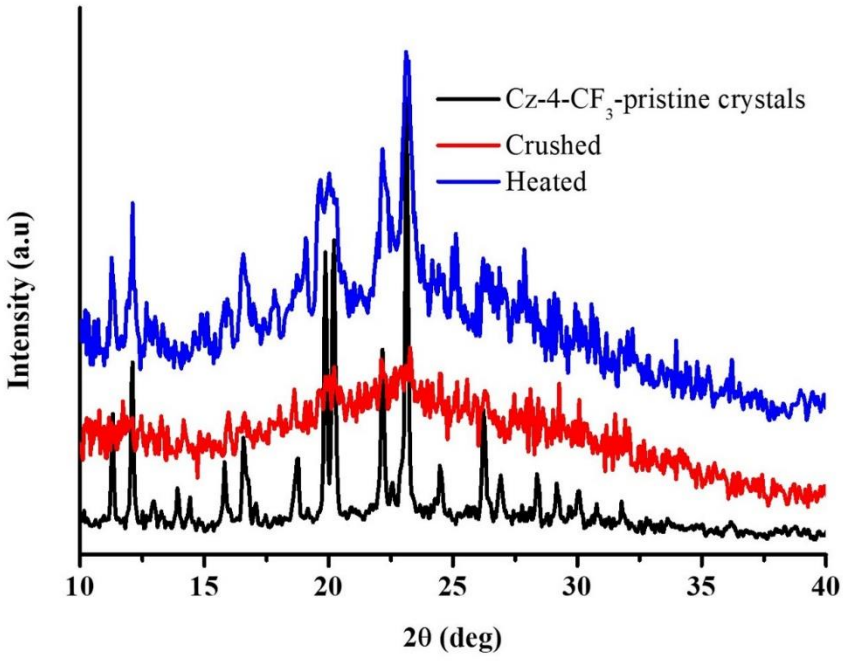


Fig. S5. PXRD pattern of Cz-4-CF_3. Crushing sample measurement was performed immediately after crushing since it would self-reverse to initial state with time.

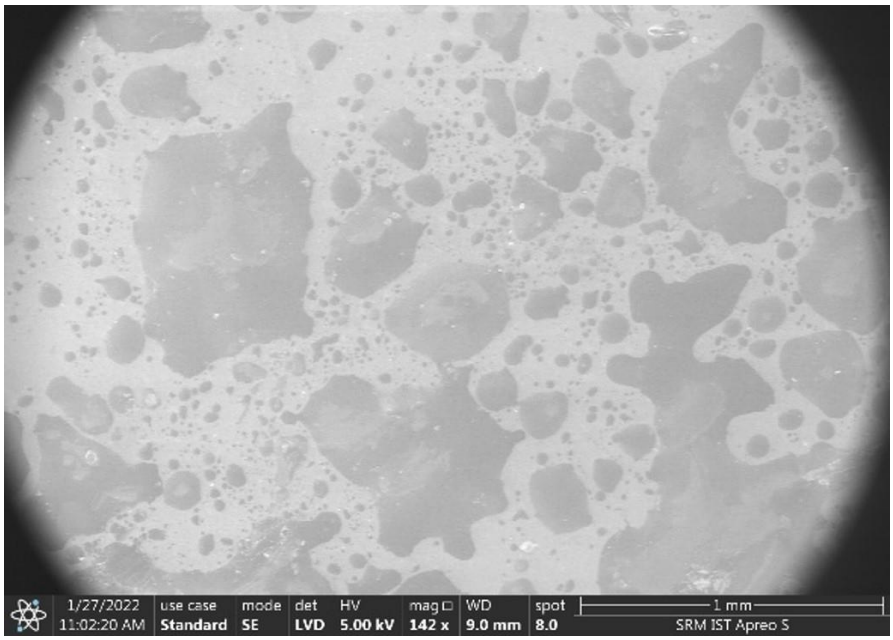


Fig. S6. SEM image of Cz-4-CF_3 at melt state.

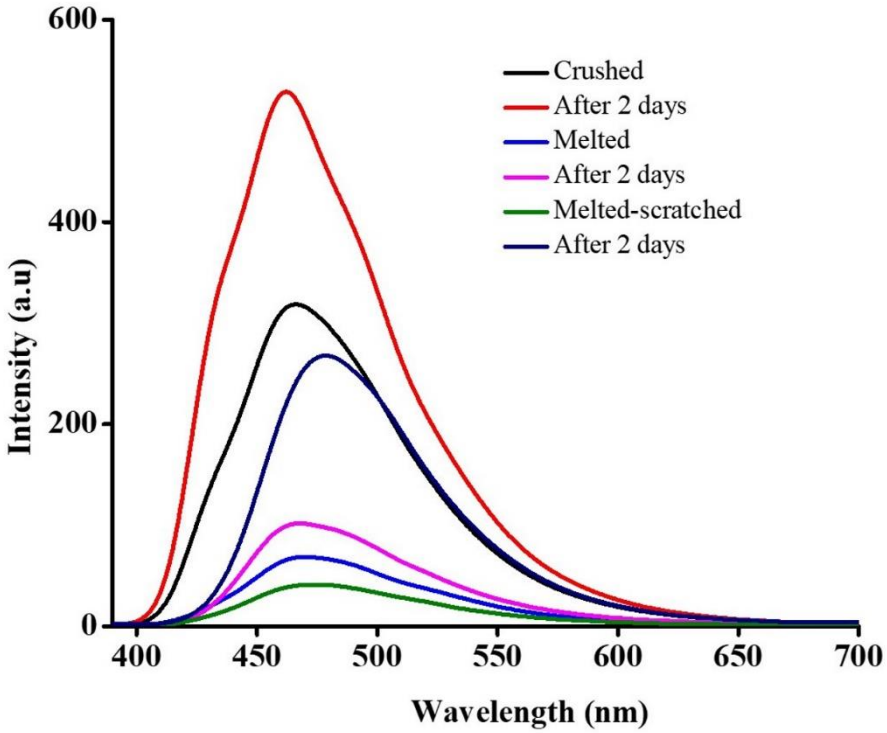


Fig. S7. Self-reversible fluorescence spectra of Cz-4-CH_3 after different external treatment.

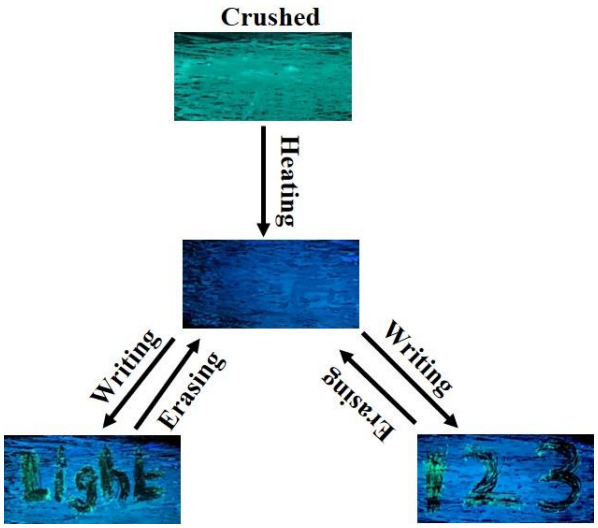


Fig. S8. Demonstrating rewritable fluorescent platforms using **Cz-4-CF$_3$** by crushing and heating. λ_{exc} = 365 nm.

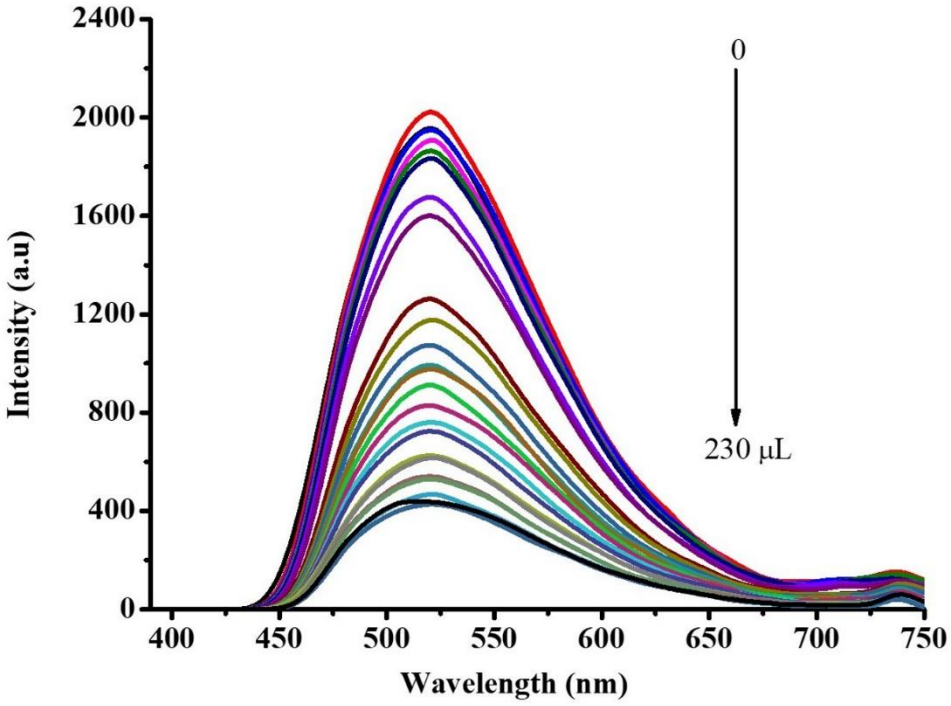


Fig. S9. PA (10^{-4} M) concentration dependent fluorescence change of Cz-4-CF$_3$ (10^{-4} M).

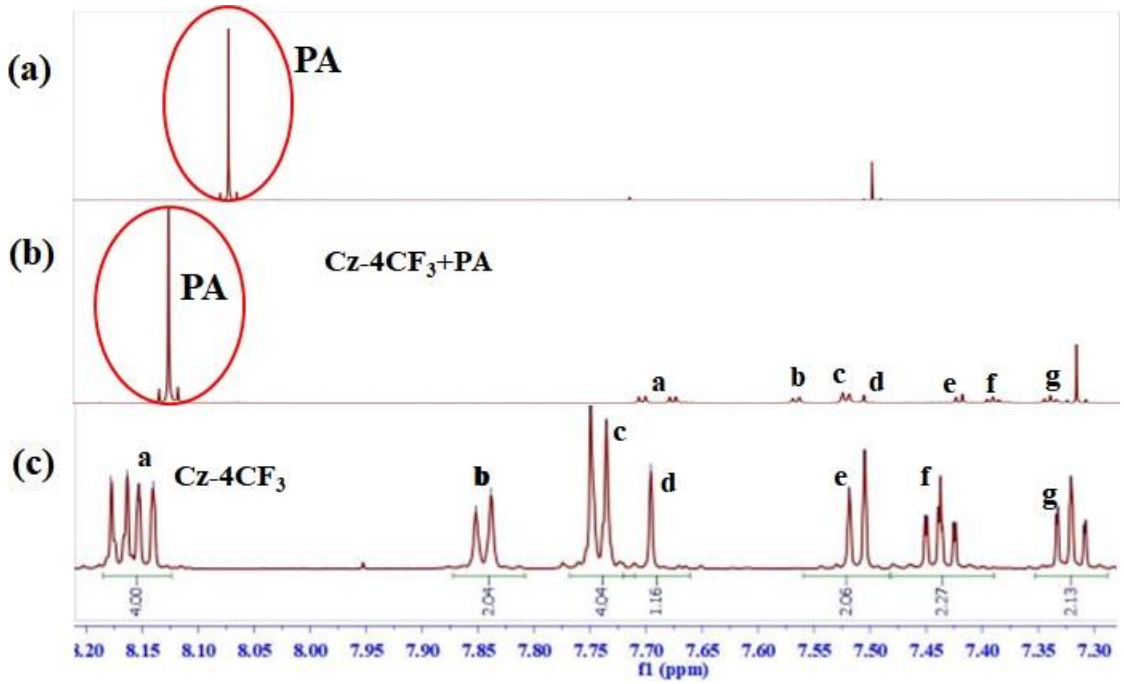


Fig. S10. (a) ^{1}H NMR spectra of **PA** (ii) upon the addition of 1 equiv of **PA** into **Cz-4-CF$_3$**(1:1 ratio); (iii) ^{1}H NMR spectra of **Cz-4-CF$_3$** in $CDCl_3$.

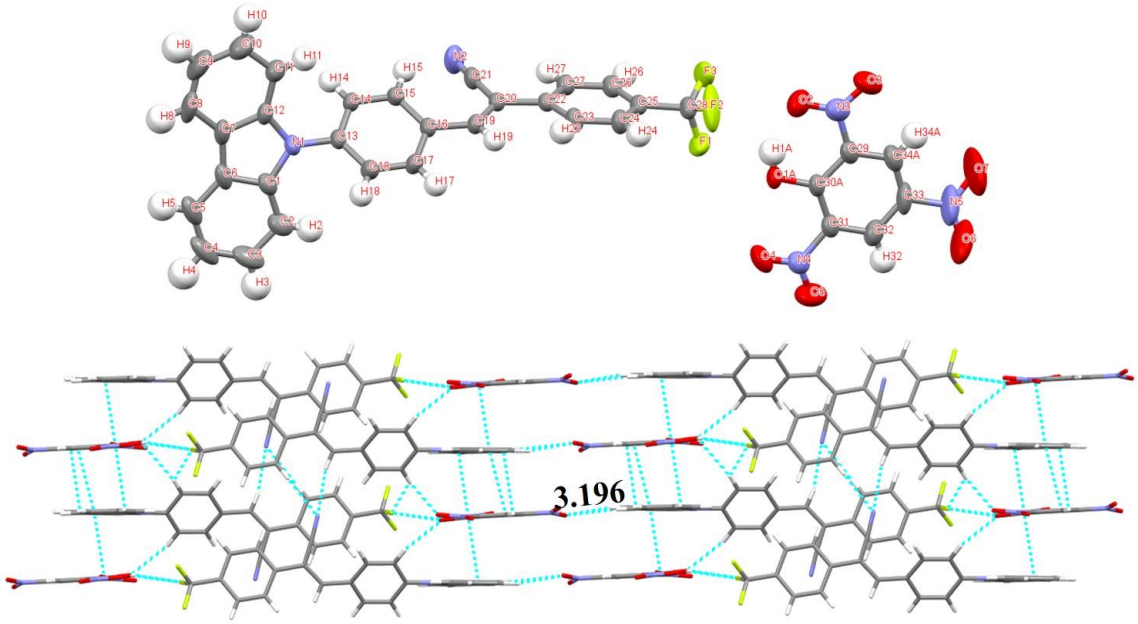


Fig. S11. Thermal ellipsoid and aromatic π-stacking between carbazole and PA aromatic unit and intermolecular interactions in the crystal lattice of **Cz-4-CF$_3$-PA**. C (grey), H (white), N (blue), O (red) and F (yellow). Dotted lines indicate the hydrogen bonding and π…π interactions in Å and distances along with e.s.d values are 3.196 (6).

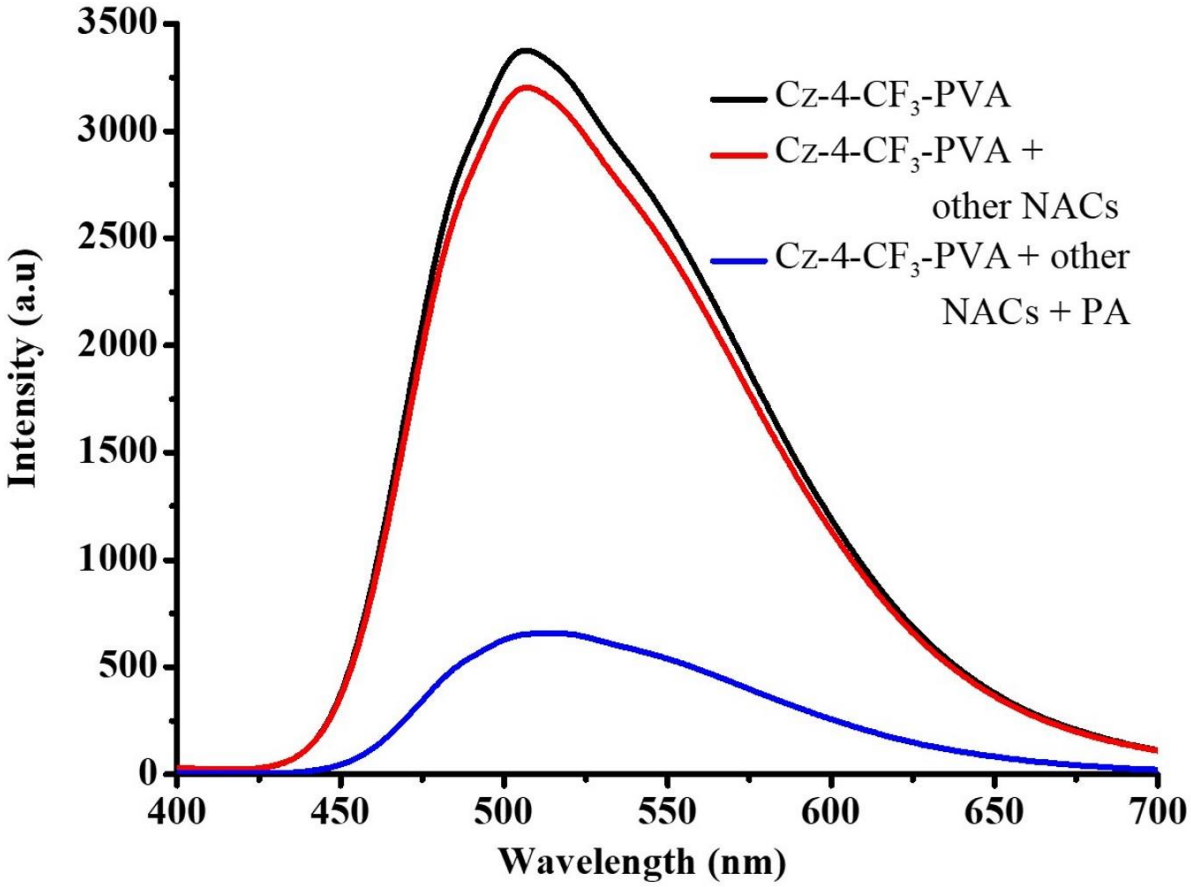


Fig. S12. Fluorescence sensing of Cz-4-CF_3-PVA thin film towards PA (10^{-4} M) in presence of other nitroaromatices (NACs, 10^{-4} M).

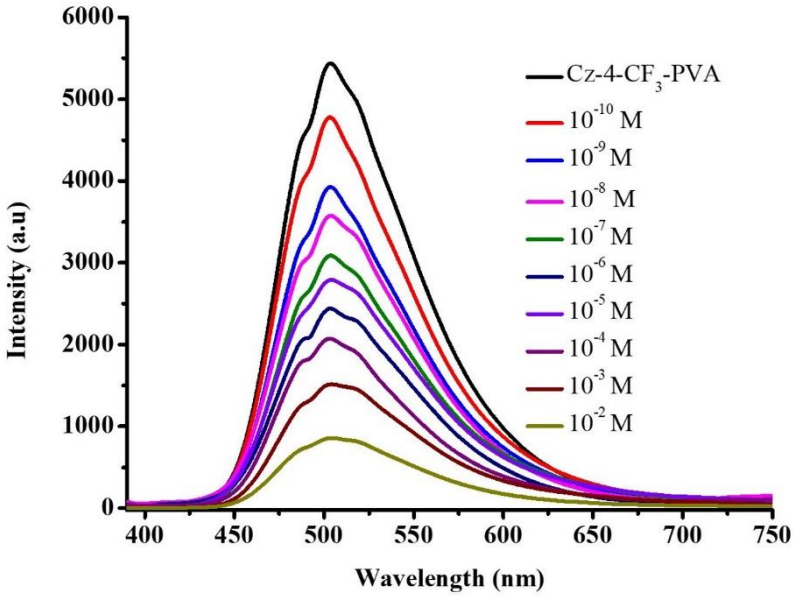


Fig. S13. Fluorescence sensing of Cz-4-CF_3-PVA thin film towards PA in different concentration. The film was dipped for 30s and recovered back upon dipping in pure water for 1-2 min.

Table S2. Cz-4-CF_3-PVA thin film sensing of PA in real water samples with known concentration.

Sample	Spiked (M)	Detected (M)	Recovery (%)
Sea water	10^{-3}	$1.05x10^{-3}$	105%
	10^{-6}	$1.04x10^{-6}$	104%
River water	10^{-3}	$0.98x10^{-3}$	98%
	10^{-6}	$1.01x10^{-6}$	101%
Pond water	10^{-4}	$0.99x10^{-4}$	99%
	10^{-7}	$1.02x10^{-7}$	102%
Lake water	10^{-4}	$0.96x10^{-4}$	96%
	10^{-7}	$1.03x10^{-7}$	103%

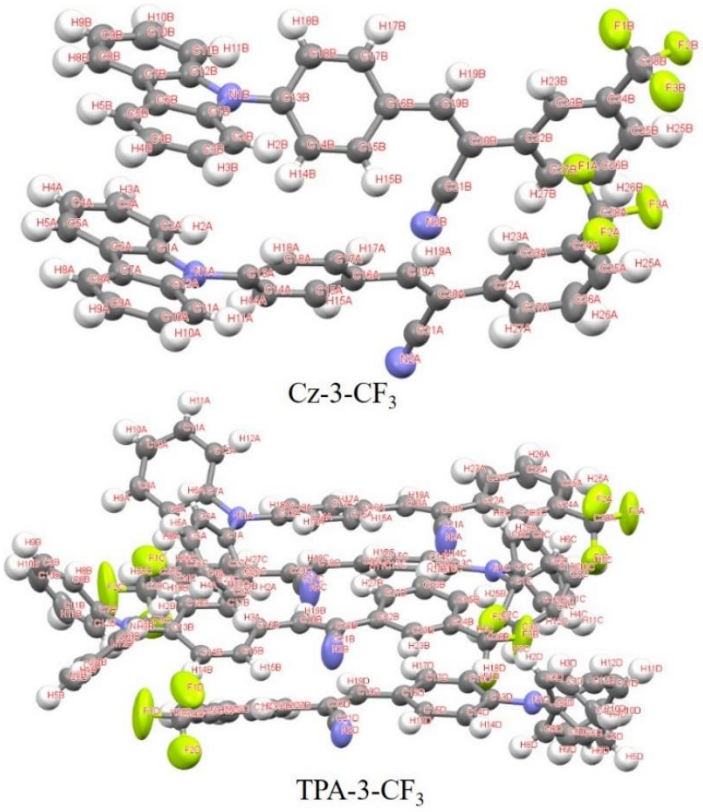


Fig. S14. Thermal ellipsoids of Cz-3-CF_3 and TPA-3-CF_3.

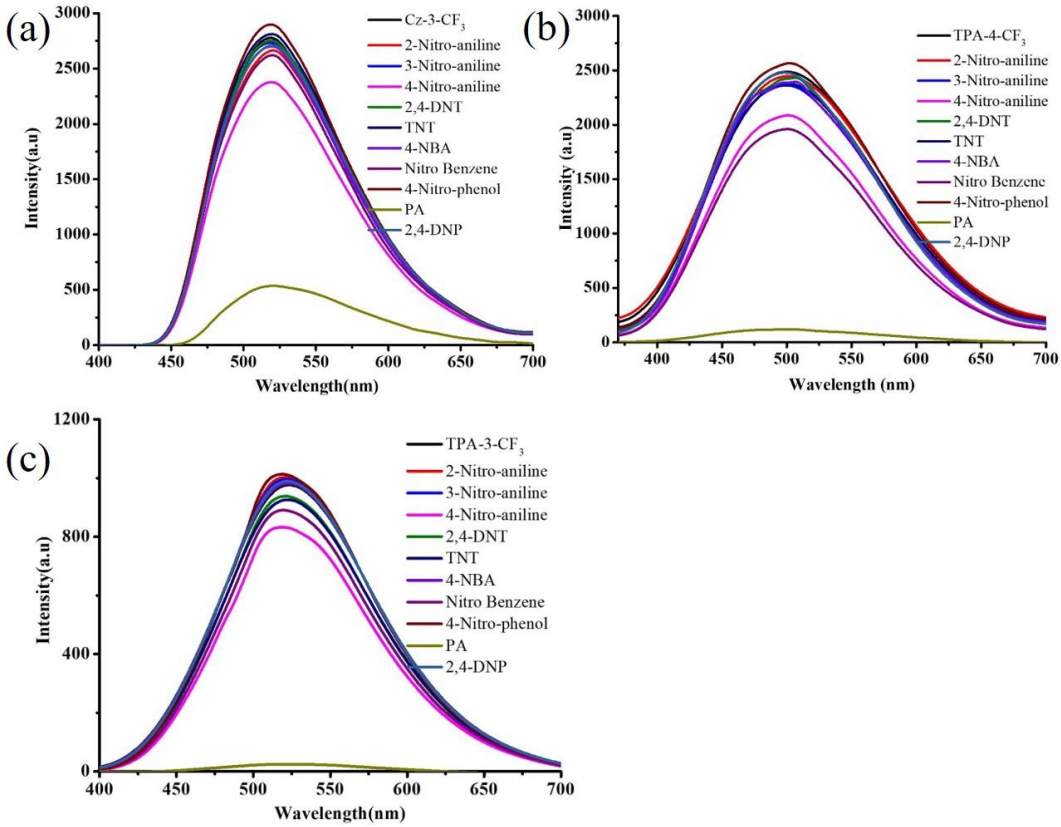


Fig. S15. Fluorescence sensing of (a) Cz-3-CF_3, (b) TPA-4-CF_3 and (c) TPA-3-CF_3 towards PA (10^{-4} M).

Table S3. Comparative study with various types of PA probes reported recently.

Chemosensors	**Other NACs interferences**	**LOD**	**Mode of detection**	**Reusability**	**Reference**
Cz-4CF$_3$	**Nil**	**51.4nm**	**Solution, Solid and polymer film**	**Reusable in filter paper, thin film by washing with water**	**Present work**
Organogelator	4-NP, 2,4-DNP	700ppt	Gel/solution state	------	[1]
Conjugated polymer nanoparticles	Nil	Not reported	Solution, solid and vapor phase	------	[2]
Curcumin-BF_2 complexes	Nil	4.21nM 11.61 nM	Test Strips, solution	------	[3]
Conjugated polyelectrolyte (PMI)	4-NP, 2,4-DNP	56.11×10^{-11}M	Test Strips, solution	------	[4]
N,N,N-trimethyl-2-(pyren-1-yloxy)ethanaminium bromide (PyOEA)	Nil	23.2 nM	Test Strips, solution	------	[5]
Triphenylamine based fluorophore	DNP	~5ppb	Solid and solution state	------	[6]
Cyanostilbene derivatives	Not reported	$2.85x10^{-7}$ $1.96x10^{-6}$ M	Solid and solution state	------	[7]
Trifluoromethyle decorated MOFs	DNP, ONP, PNP	3×10^{-5}M 9×10^{-6}M	Solid and solution state	Reusable in solution by centrifuged and washed with methanol	[8]
Conjugated polymer (PFAM)	2,4-DNP, 4-NP	57.8nm	Solid, strips, solution	Reusable in filter paper, by washing with water	[9]
Pyrene-derived pH-responsive polymeric probe	4-NP, 2,4-DNP	56 μM	Solution and polymer film	Reusable in film, by washing with water	[10]
1,8-naphthalimide-conjugated sulfonamide probe	2,4-DNP 4-NP (at high conc)	25.6 pM	Strips and solution state	------	[11]
Naphthalene based Schiff base	DNP, NP, DNT, DNBA, DNB	0.11 μM	Strips and solution state	------	[12]
Ln(III) based probes	Nil	0.5 μM	Strips, sol-gel and solution state	------	[13]
π-Conjugated polymers	DNT, DNP, NB, NT	47.39×10^{-8} M	Filter paper, solution	Reusable in filter paper by washing with water	[14]
Arylene-vinylene Terpyridine Conjugates	NB, NT, DNT, NBA, HNB, DNT	$1.31\text{-}2.94\times10^{-7}$M	Test Strips, solution	Reusable in filter paper by washing with water	[15]
Dansyl tagged copolymer	DNT, TNT	3.7μM	Solution state, thin film and filter paper	------	[16]
Quinoxaline-based luminogen	DNB, TNT	28.7nM	Test Strips, solution	------	[17]
Pyrene appended imidazolium probe	4-NP, 2,4-DNP	10nM	solution	------	[18]
Quinoline-benzimidazole conjugate	2,4-DNP, NA	4.86ppb	Test Strips, solution	------	[19]
Fluorene based chemosensor	2,4-DNP	22ppt, 0.23ppt	Solution	------	[20]
Cyanine based chemosensor	Nil	8.24nm, 8.44nm	Test Strips, solution	------	[21]

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