Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Acceptor-donor-acceptor-linked triphenylamine and phenothiazine motifs as cousin molecules: Methyl-effect on stimuli-responsiveness, crystallochromism and dual-state emission

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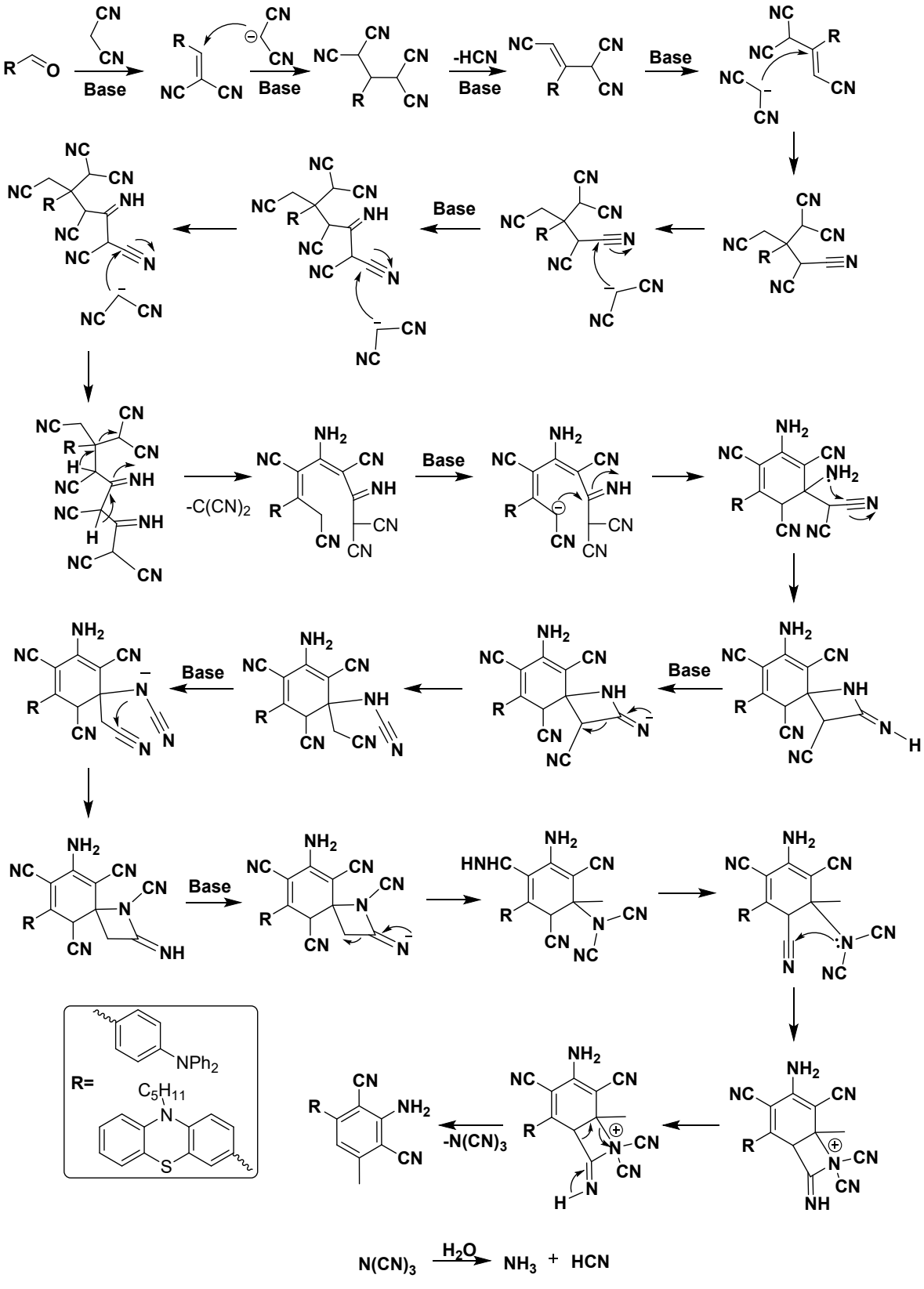
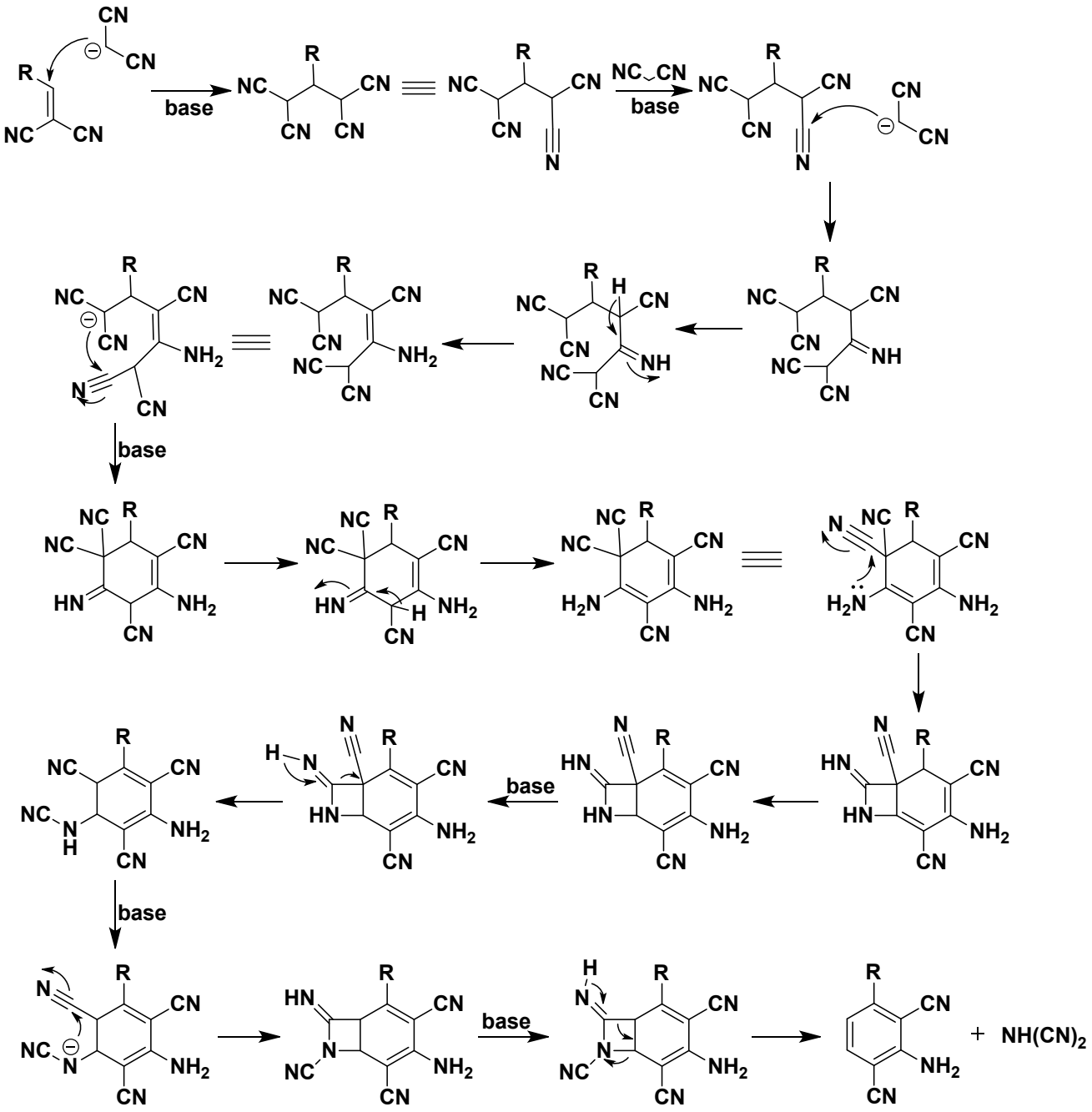
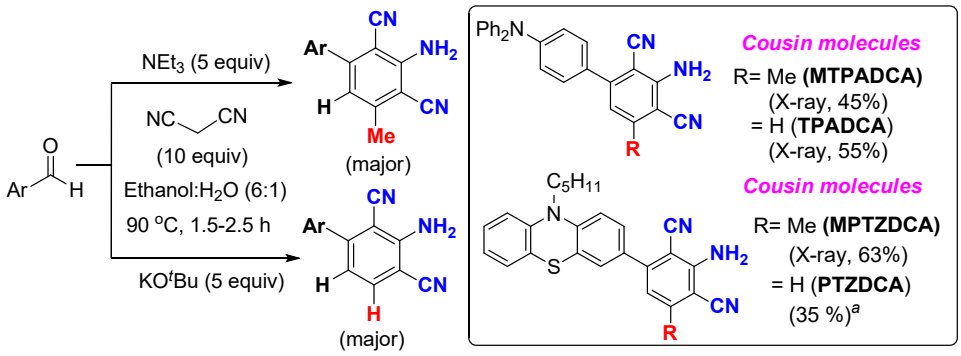


Scheme S1 Plaussible mechanistic path for **MTPADCA** and **MPTZDCA**[1]



Scheme S2 Plaussible mechanistic path for **TPADCA** and **PTZDCA** (newly proposed)

Table S1 Reaction Optimization



Entry	R	Solvent	Base	Time(h)	Methylated Pdt. (%)	Non-methylated Pdt. (%)
1	TPA	EtOH:H_2O (6:1)	Et_3N	1.5	45	12
2	TPA	EtOH:H_2O (6:1)	NaOH	1.5	42	52
3	TPA	EtOH:H_2O (6:1)	KO^{t}Bu	1.5	18	55
4	TPA	EtOH:H_2O (6:1)	K_2CO_3	1.5	12	17
5	TPA	EtOH:H_2O (6:1)	NH_4OAc	1.5	Trace	15
6	TPA	EtOH:H_2O (6:1)	Pipyridine	1.5	22	Trace
7	TPA	Toluene	Et_3N	2.5	0	0
8	TPA	Toluene	NaOH	2.5	0	0
9	TPA	Toluene	Pipyridine	2.5	0	0
10	TPA	Toluene	Pyrrolidine	2.5	Trace	20
11	TPA	Acetonitrile	Pyrrolidine	2.5	Trace	Trace

12	PTZ	EtOH:H_2O (6:1)	Et_3N	1	63	Trace
13	PTZ	EtOH:H_2O (6:1)	NaOH	1.5	15	62
14	PTZ	EtOH:H_2O (6:1)	^tBuOK	1.5	Trace	35
15	PTZ	EtOH:H_2O (6:1)	Et_3N	1.5	63	20
16	PTZ	Acetonitrile	Pipyridine	2.5	25	Trace

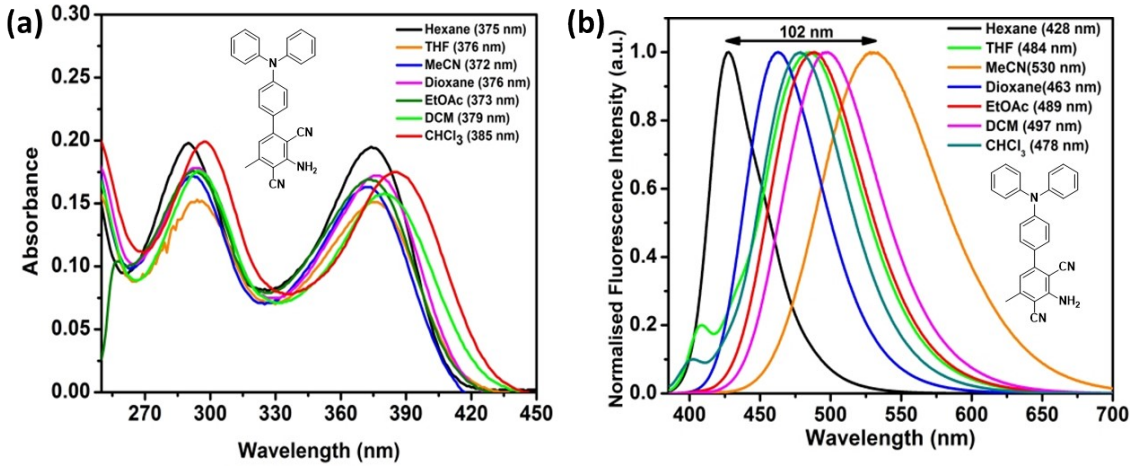


Fig. S1 Solution state (a) absorption & (b) normalized emission spectra for **MTPADCA** (10^{-5} M)

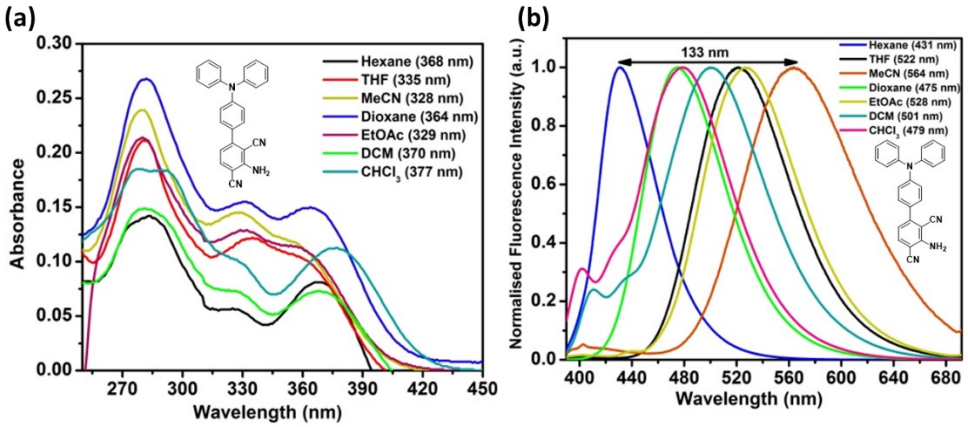


Fig. S2 Solution state (a) absorption & (b) normalized emission spectra for **TPADCA** (10^{-5} M)

Table S2 Comparison Table of emission in solution state for **MTPADCA** & **TPADCA**

Solvent [$E_T(30)$]	λ_{abs} (nm) **TPADCA**	λ_{abs} (nm) **MTPADCA**	$\lambda_{em.}$ (nm) **TPADCA**	$\lambda_{em.}$ (nm) **MTPADCA**	Relative Φ_f * (%) **TPADCA**	Relative Φ_f * (%) **MTPADCA**
Hexane (31)	368	374	431	428	35	37
1,4-Dioxane (36)	364	376	475	463	28	27
THF (37.4)	335	376	522	484	26	23
EtOAc (38.1)	329	373	528	489	26	25
$CHCl_3$ (39.1)	377	385	479	478	24	20
DCM (39.6)	370	379	501	497	25	24
MeCN (45.6)	328	372	564	530	31	29

*Relative Φ_f (Relative quantum yield) is calculated using coumarin-53B as a reference.

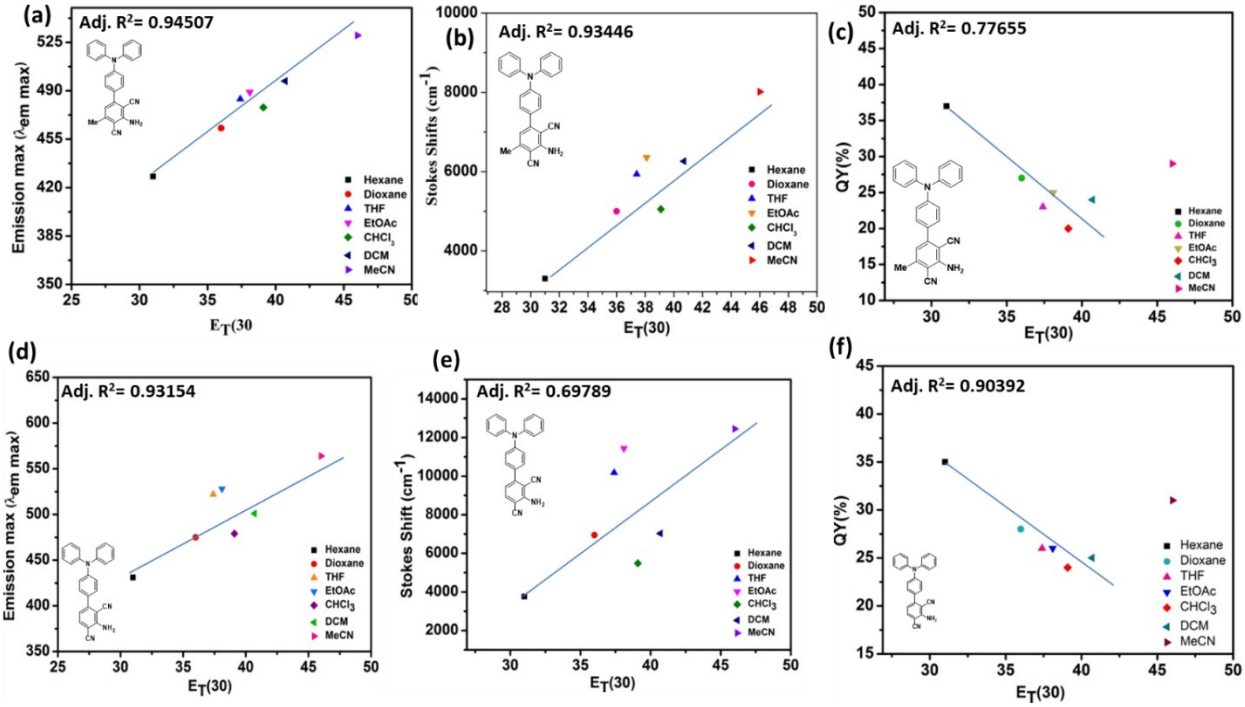


Fig. S3 Solvatofluorochromic behavior for **MTPADCA**: (a)-(c) and **TPADCA**: (d)-(f)

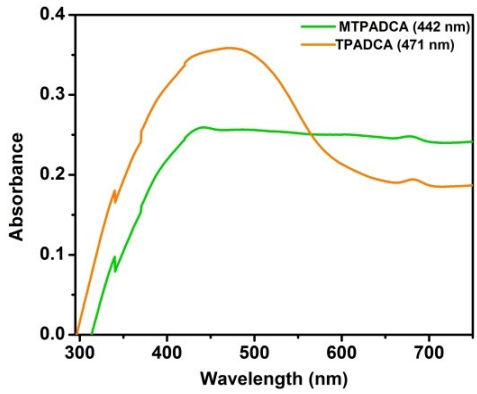


Fig. S4 Solid state absorption spectra for **TPA** cousin molecules

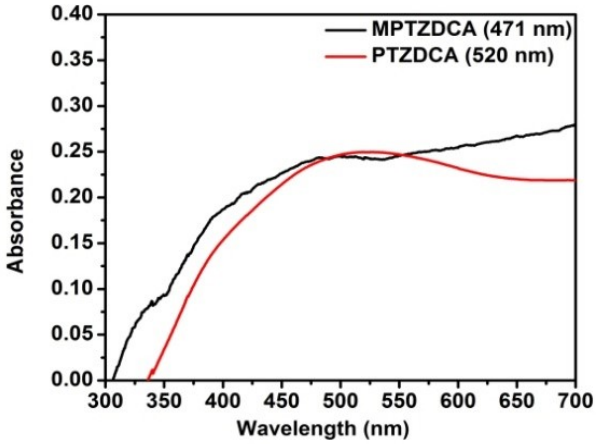


Fig. S5 Solid state absorption spectra for **PTZ** cousin molecules

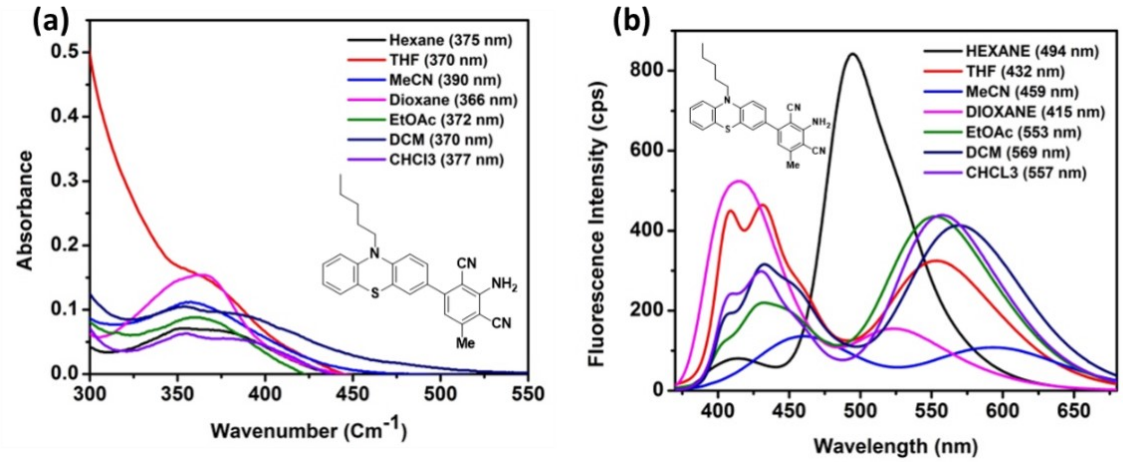


Fig. S6 Solution state (a) absorbance & (b) emission of **MPTZDCA** (10^{-5} M)

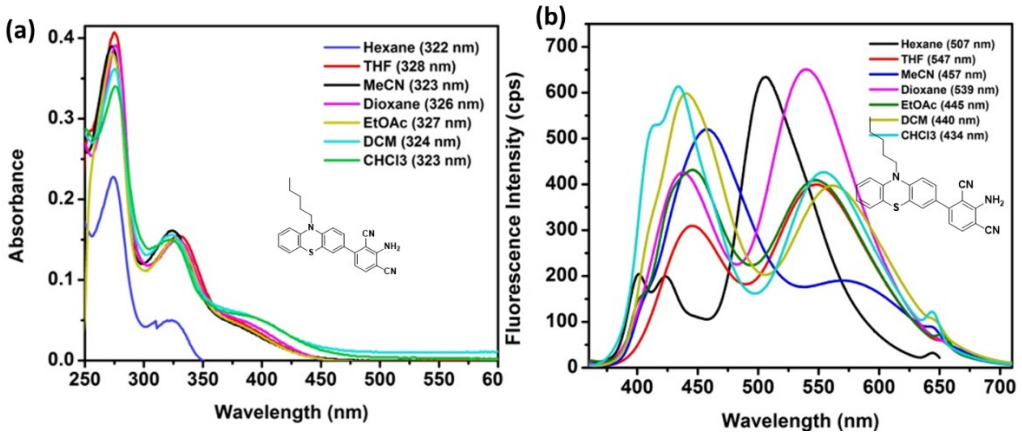


Fig. S7 Solution state (a) absorbance & (b) emission of **PTZDCA** (10^{-5} M)

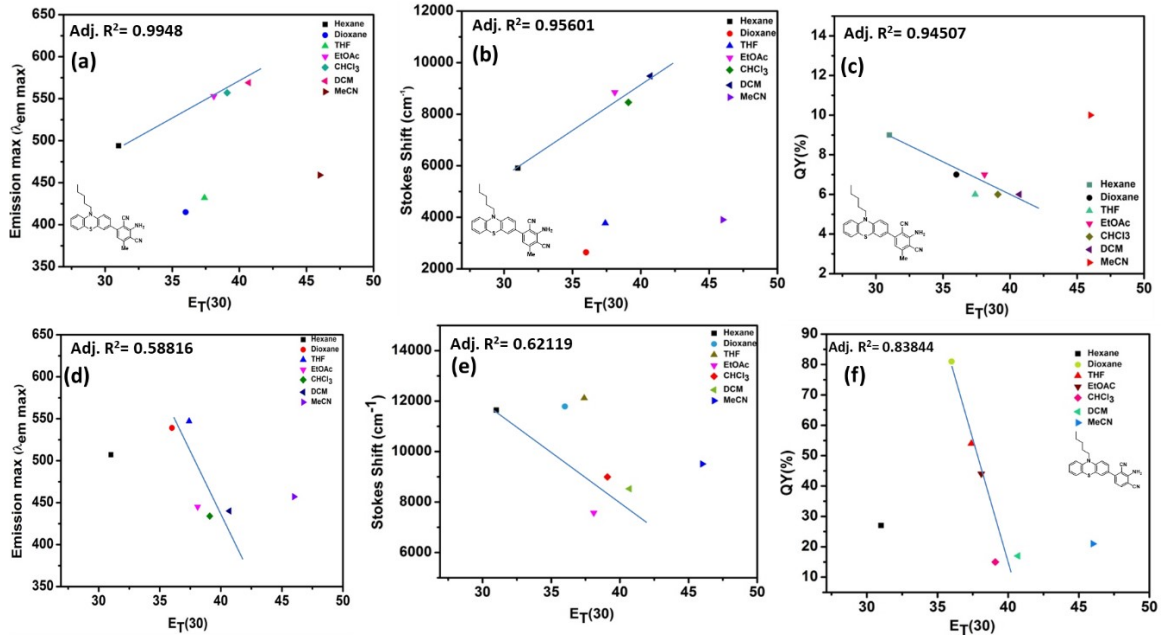


Fig. S8 Solvatofluorochromic behavior for **MPTZDCA**: (a)-(c) and **PTZDCA**: (d)-(f)

Table S3 Comparison Table of emission in solution state for **MPTZDCA** & **PTZDCA;** the relative quantum yields (Φ_f) are reported here with a standard of coumarin-53B as a reference

Solvent (E_T30)	$\lambda_{abs.}$ (nm) **PTZDCA**	$\lambda_{abs.}$ (nm) **MPTZDCA**	$\lambda_{em.}$ (nm) **PTZDCA**	$\lambda_{em.}$ (nm) **MPTZADCA**	Relative Φ_f (%) **PTZDCA**	Relative Φ_f (%) **MPTZDCA**
Hexane (31)	322	375	507	494	27	9
1,4-Dioxane (36)	326	366	539	415	81	7
THF (37.4)	328	370	547	432	54	6
EtOAc (38.1)	327	372	445	553	44	7
$CHCl_3$ (39.1)	323	377	434	557	15	6

DCM (39.6)	324	370	440	569	17	6
MeCN (45.6)	323	390	457	459	21	10

Table S4 HOMO and LUMO for **MTPADCA** and **TPADCA** obtained from DFT studies with CAMB3LYP 6-31g (d,p) basis set

Molecules	Dipole moment (D)	HOMO (eV)	LUMO (eV)	Gap (eV)	λ_{abs}	λ_{emi}
MTPADCA	4.482	-6.774001926	-1.045733486	5.73	442	501
TPADCA	4.5698	-6.814819002	-1.138252192	5.68	471	578

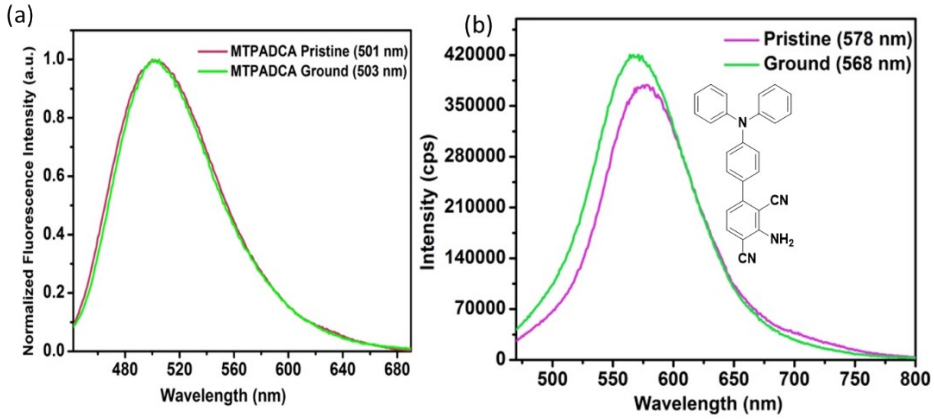


Fig. S9 Fluorescence spectra of (a) **MTPADCA** under stimuli λ_{ex} = 442 nm (b) MIEE- effect of **TPADCA;** λ_{ex} =471 nm

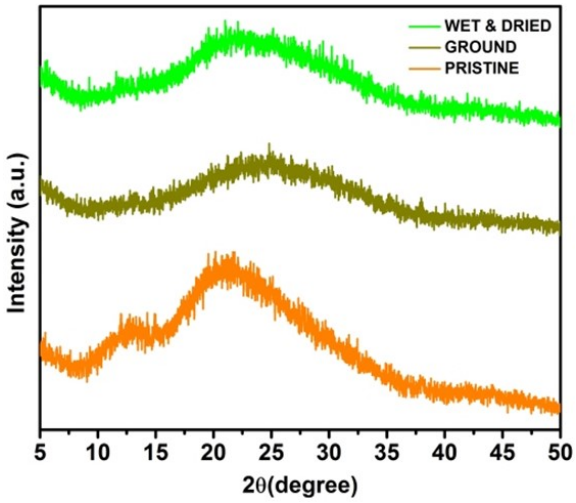


Fig. S10 PXRD pattern of **TPADCA** at pristine and ground state

Table S5 Intermolecular interactions in **MTPADCA**, **TPADCA** & **MPTZDCA** crystals

Molecules	N…N (Å)	C-H…π (Å)	CN…HC (Å)	NC…C (Å)	C≡N…H_2N (Å)	H…H (Å)	S…H (Å)
MTPADCA	3.082	2.803	2.690, 2.687	3.362	2.331	2.189	
TPADCA	-	2.808	2.400	-	-	-	
MPTZDCA (19 interactions)	3.013	2.828, 2.882, 2.760 2.883 2.886, 2.876,2.883, 2.803	2.580, 2.706	3.369, 3.381, 3.323	2.422, 2.456	2.371 2.344	2.880

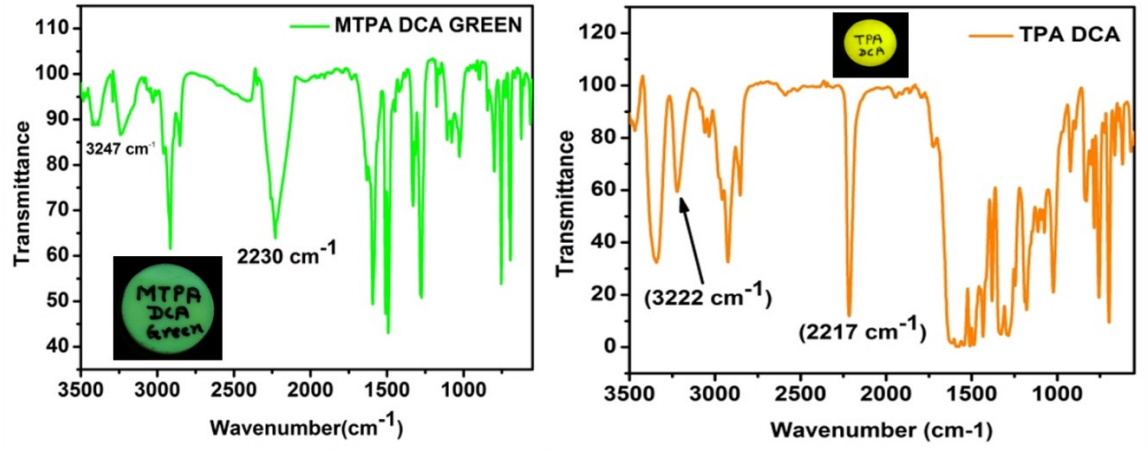


Fig. S11 IR comparison of **MTPADCA & TPADCA**

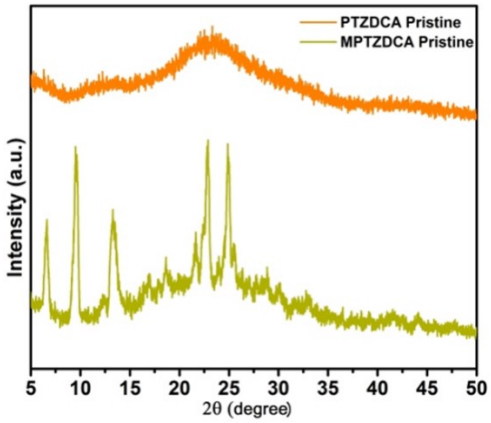


Fig. S12 PXRD pattern of **MPTZDCA & PTZDCA**

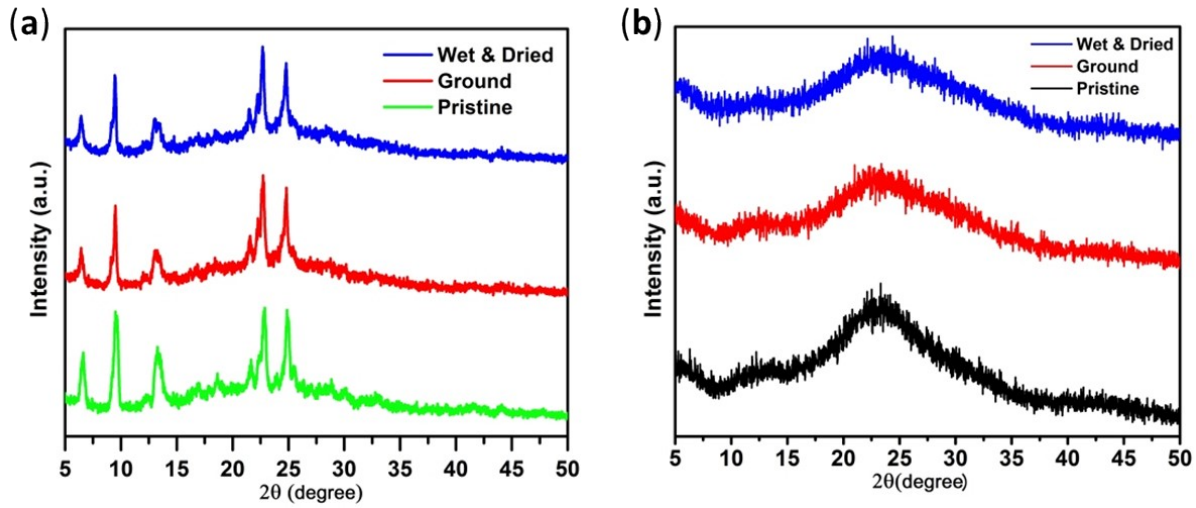


Fig. S13 PXRD pattern of (a) **MPTZDCA & (b) PTZDCA** after grinding the sample.

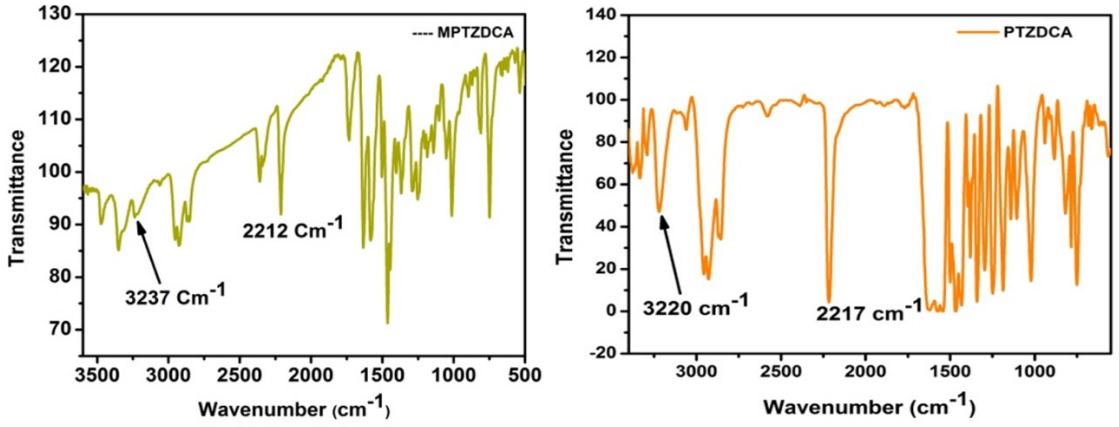


Fig. S14 IR comparison of **MPTZDCA & PTZDCA**

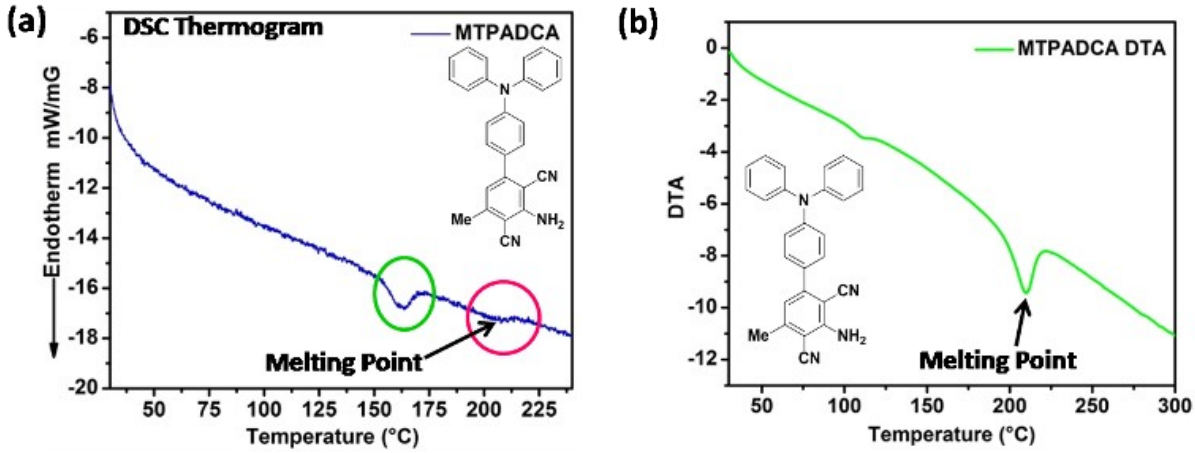


Fig. S15 (a) DSC and (b) DTA thermogram for **MTPADCA**

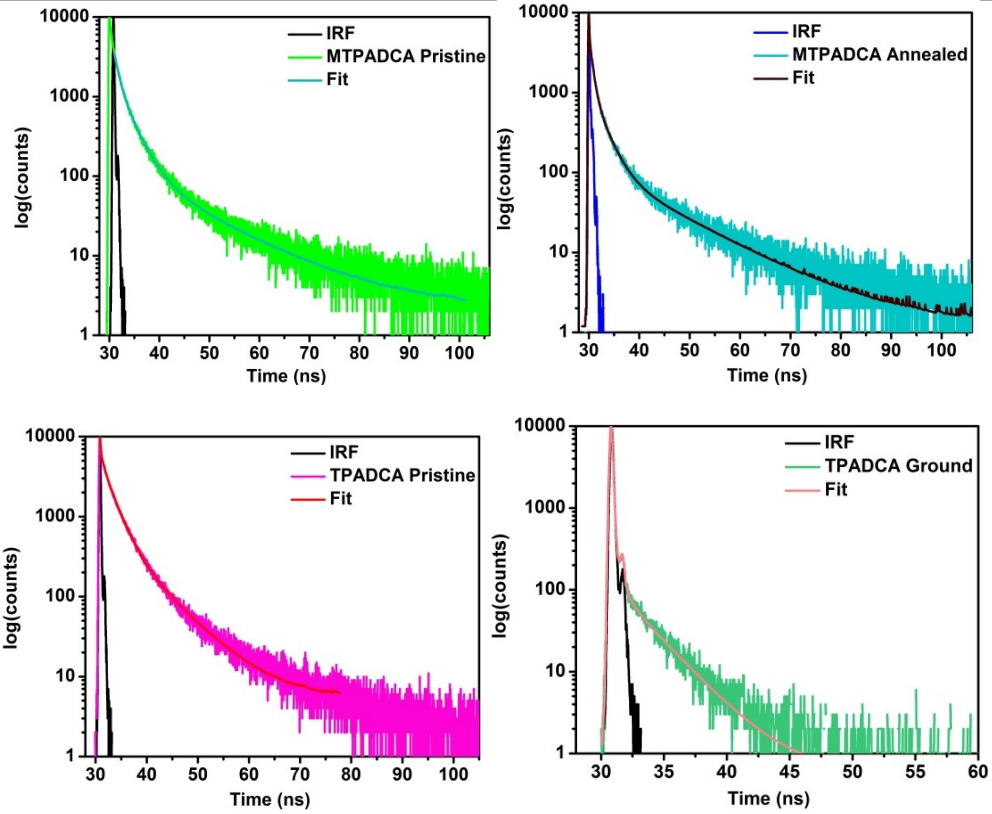
Explanation: As we found a quick emission color change starting at 155 °C, we closely observed the DSC feature around the temperature range (Fig. S15a). A clear endothermic peak at ~160 °C is recognized in the DSC thermogram, which indicates a phase transition and is possibly associated with the TFC behavior. The DSC thermogram does not show a sharp melting transition, implying that the compound loses crystallinity after the initial phase transition. Although a small signature appears at ~207 °C in the DSC profile, a sharp melting point at 207 °C is detected in the DTA (Differential Thermal Analysis) thermogram (Fig. S15b).

Table S6 Crystal Data Table:

Compounds	**MTPADCA**	**TPADCA**	**MPTZDCA**
Emp. Formula	$C_{27}H_{20}N_4$	$C_{26}H_{18}N_4$	$C_{26}H_{24}N_4S$
Formula weight	400.47	386.44	424.55
Crystal system	monoclinic	monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P -1
a /Å	10.1248(2)	17.0172(3)	8.9131(4)
b /Å	9.8792(2)	14.7978(3)	11.8184(4)
c /Å	21.3435(3)	8.29705(16)	21.8914(9)
/degree	90	90	91.003(3)
/degree	97.401(2)	98.9384(18)	95.825(4)
/degree	90	90	106.344(4)
V /Å^3	2117.10(7)	2063.96(7)	2198.84(16)
Z	4	4	4
D_{calc} /g cm^{-3}]	1.216	1.244	1.282
/mm^{-1}	.626	.589	1.458
F (000)	819.0	808.0	896.0
Data/ restraints/ parameters	4491/0/282	4377/0/272	10060/0/562
S	1.083	1.059	1.061
+R1 [I>2(I)]	0.0532(3974)	0.0670(3233)	0.0671(8733)
wR2 [all data]	0.1564(4491)	0.2056(4377)	0.1933(10060)
Max./min. residual electron dens. [eÅ^{-3}]	0.320/ -0.420	0.737/ -0.192	0.785/ -0.984
CCDC No.	2062771	2062770	2041739

Table S7 Lifetime data (ns) and the related parameters. $K_r = \Phi_f/\tau$; $K_{nr} = (1- \Phi_f)/\tau_f$

Compounds	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	α_1	α_2	α_3	α_4	χ^2	τ (ns)	Φ_f (%)	$k_r(s^{-1}) \times 10^6$	$k_{nr}(s^{-1}) \times 10^6$	k_r/k_{nr}
MTPADCA Pristine	2.838	12.993	0.848	-	0.336	0.027	0.637	-	1.173	1.844	25.11	136.171	406.128	0.335
MTPADCA Annealed	0.581	2.338	12.704	0.056	0.087	0.024	0.002	0.887	1.151	0.182	3.6	198.000	5300.000	0.037
TPADCA Pristine	2.118	0.223	6.821	-	0.239	0.729	0.031	-	1.197	0.883	2.79	31.597	1100.906	0.029
TPADCA Ground	0.649	0.039	2.669	-	0.001	.998	0.001	-	1.085	0.0417	5.67	1359.712	22621.103	0.060
MPTZDCA Pristine	1.742	4.078	0.081	-	0.059	0.066	0.874	-	1.035	0.445	2.06	46.292	2200.899	0.021
MPTZDCA Ground	0.93	3.638	0.049	-	0.011	0.007	0.983	-	1.103	0.083	5.81	700	11348.193	0.062
PTZDCA Pristine	0.049	3.222	-	-	0.995	0.005	-	-	1.065	0.067	1.45	216.417	14708.956	0.015
PTZDCA Ground	2.842	0.044	-	-	0.001	0.999	-	-	1.014	0.047	3.39	721.277	20555.319	0.035



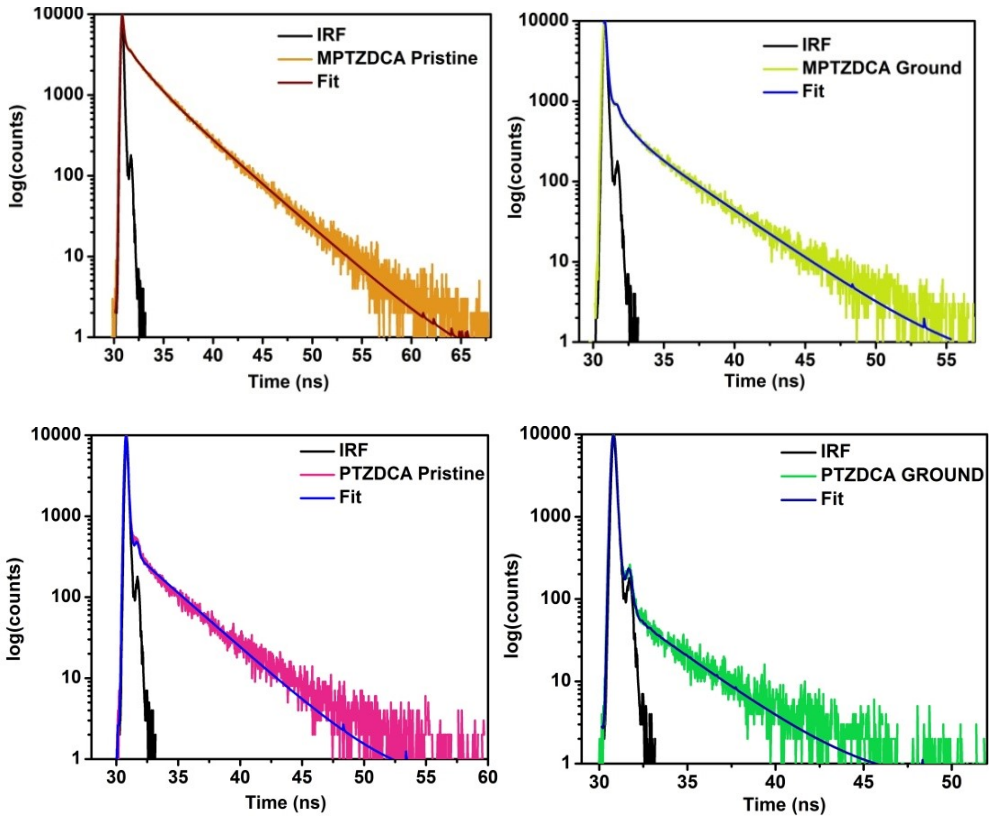


Fig. S16 Life-time decay profiles for all the compounds as stated in the box.

NMR Spectra:

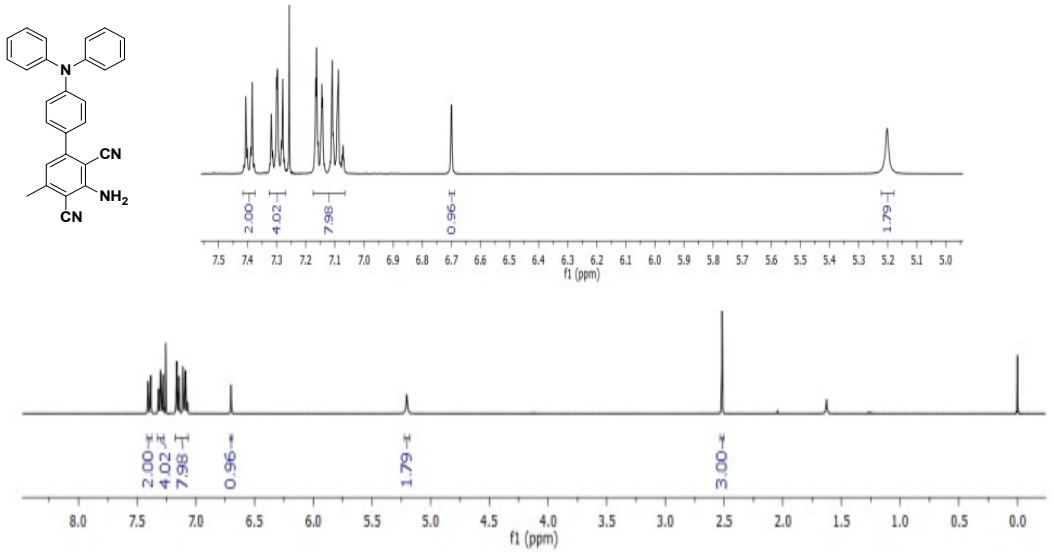


Fig. S17 ^{1}H NMR spectra of **MTPADCA**

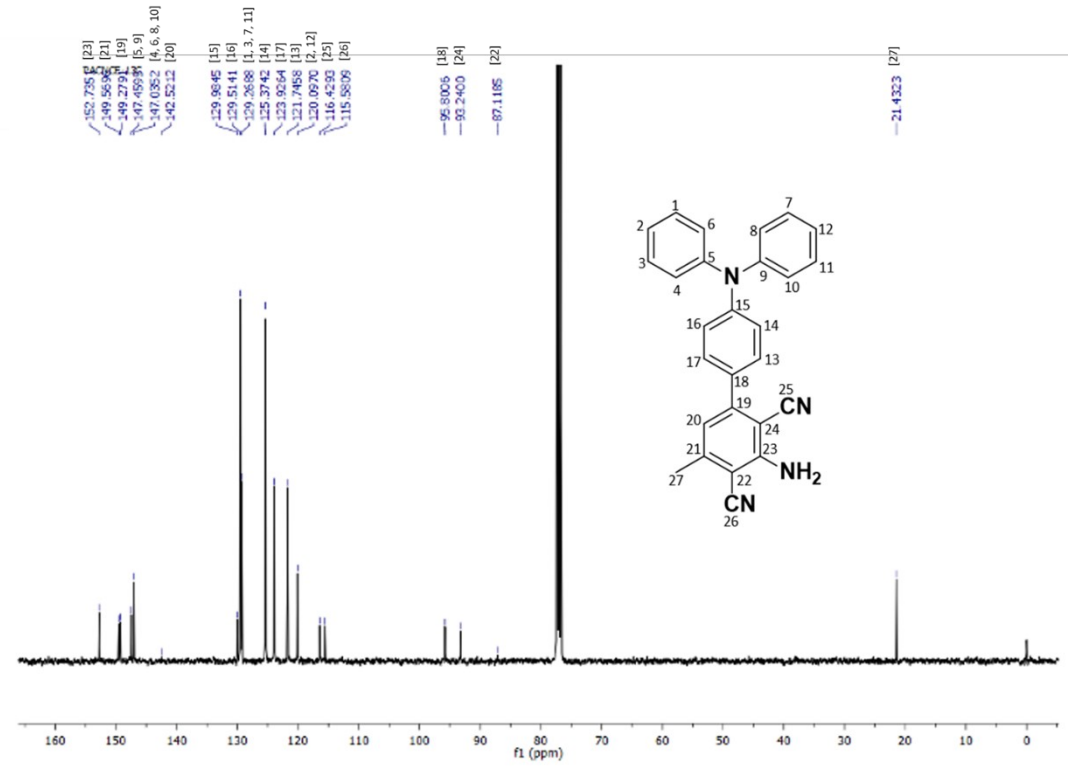


Fig. S18 ^{13}C NMR spectra of **MTPADCA.** The signals are assigned with the corresponding ^{13}C nuclei, and the numberings (in bracket) are given in the structure.

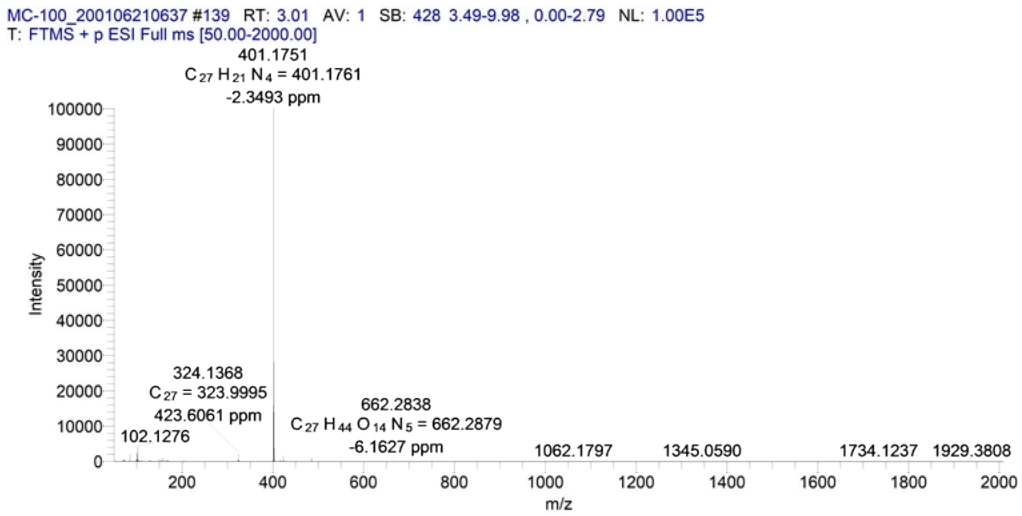


Fig. S19 HR-MS spectra of **MTPADCA**

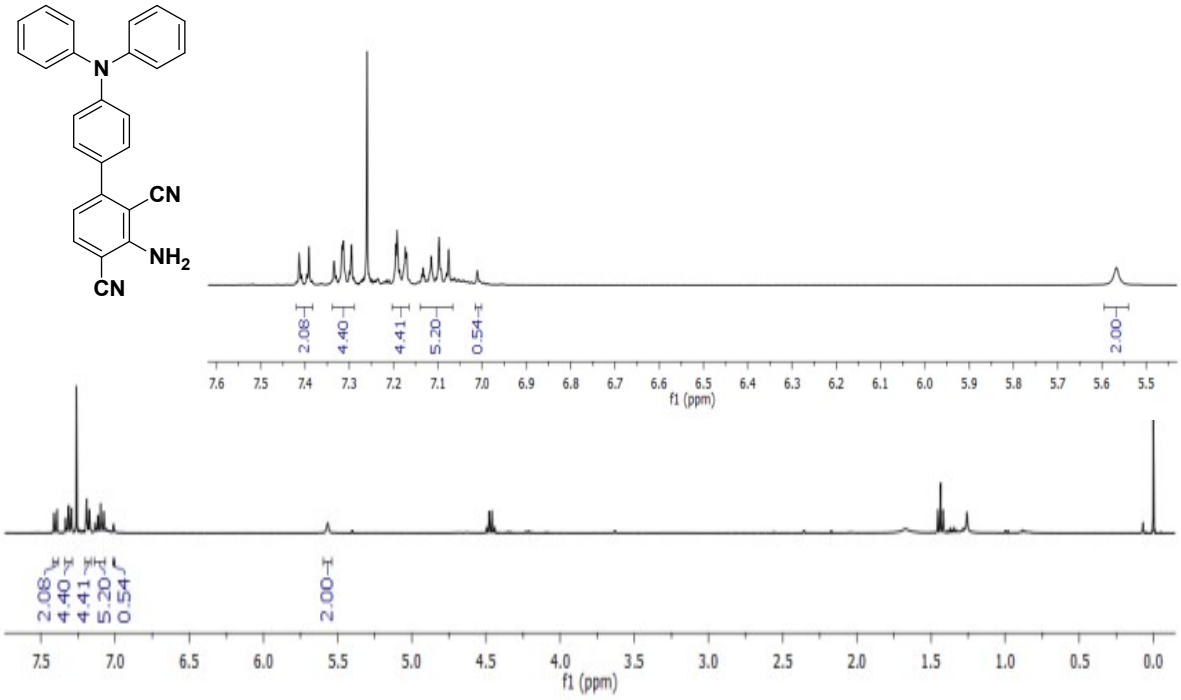


Fig. S20 ^{1}H NMR spectra of **TPADCA** (little adventitious solvent $CH_3CH_2OC(O)CH_3$ is present)

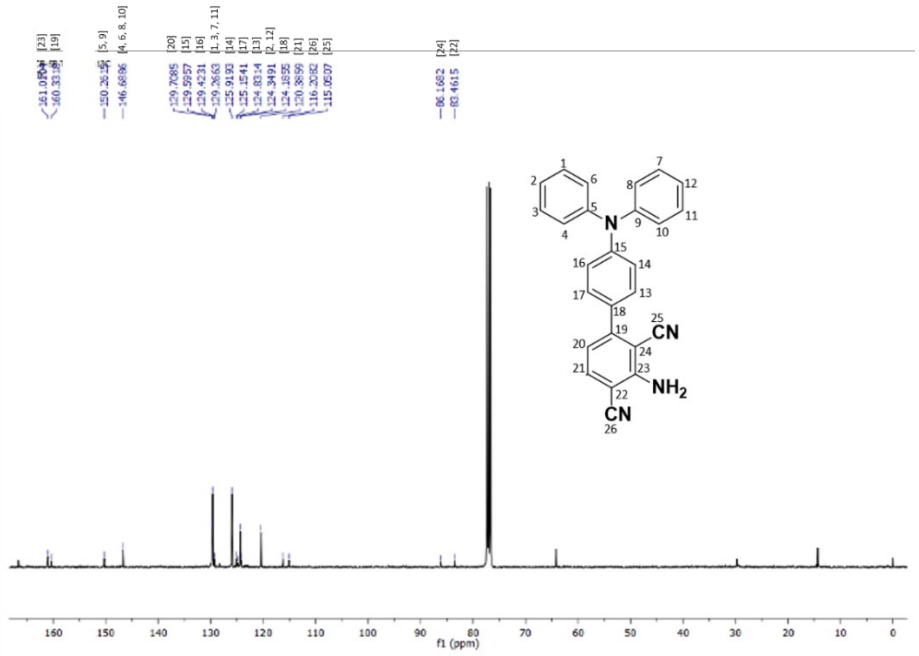
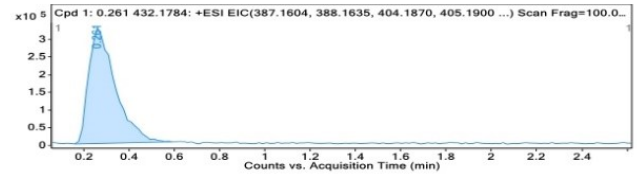


Fig. S21 ^{13}C NMR spectra of **TPADCA.** (Signals from adventitious solvent $CH_3CH_2OC(O)CH_3$ are assigned at δ 166.6 [*C*(O)CH_3], 64.1 (O*C*H_2), 22.1 [C(O)*C*H_3], 14.5 (*C*H_3CH_2O-). The signals are assigned with the corresponding ^{13}C nuclei, and the numberings (in bracket) are given in the structure.

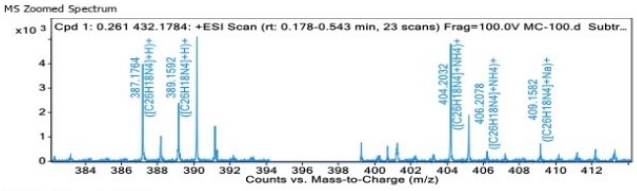
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 0.261 432.1784	0.261	386.1651	4860	C26 H18 N4	386.1531	31.04

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: 0.261 432.1784	404.2032	0.261	Find By Formula	386.1651



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	*Calc m/z*	Diff (ppm)	z	Abund	Formula	Ion
387.1764	387.1604	-41.36	1	4009.25	C26H18N4	(M+H)+
388.1758	388.1635	-31.59	1	1040.95	C26H18N4	(M+H)+
389.1592	389.1665	18.86	1	2392.72	C26H18N4	(M+H)+
404.2032	404.187	-40.07	1	4859.57	C26H18N4	(M+NH4)+
405.204	405.19	-34.7	1	1881.44	C26H18N4	(M+NH4)+
406.2078	406.193	-36.6	1	414.73	C26H18N4	(M+NH4)+
409.1582	409.1424	-38.79	1	722.17	C26H18N4	(M+Na)+
410.1635	410.1454	-43.96	1	241.77	C26H18N4	(M+Na)+

Fig. S22 HR-MS spectra of **TPADCA**

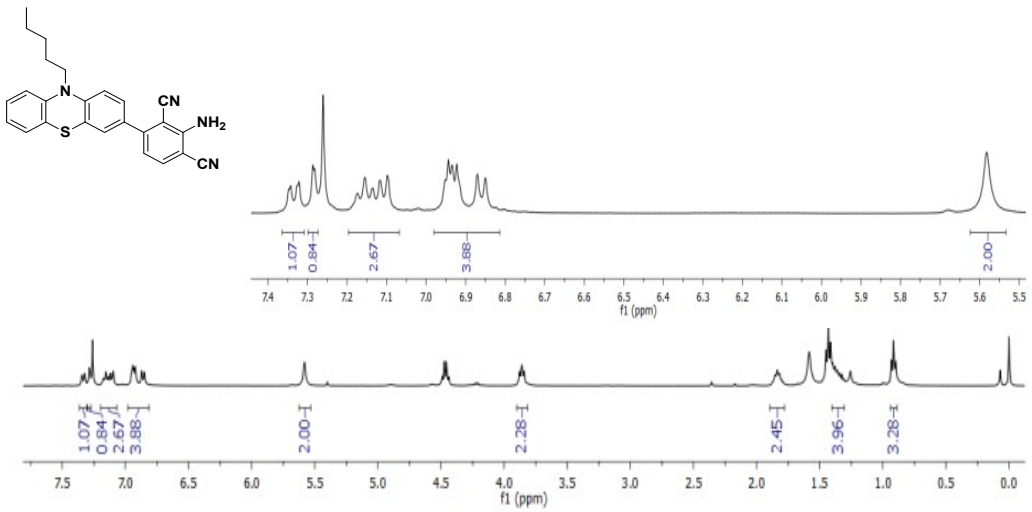


Fig. S23 ^{1}H NMR spectra of **PTZDCA** (adventitious solvent $CH_3CH_2OC(O)CH_3$ is present)

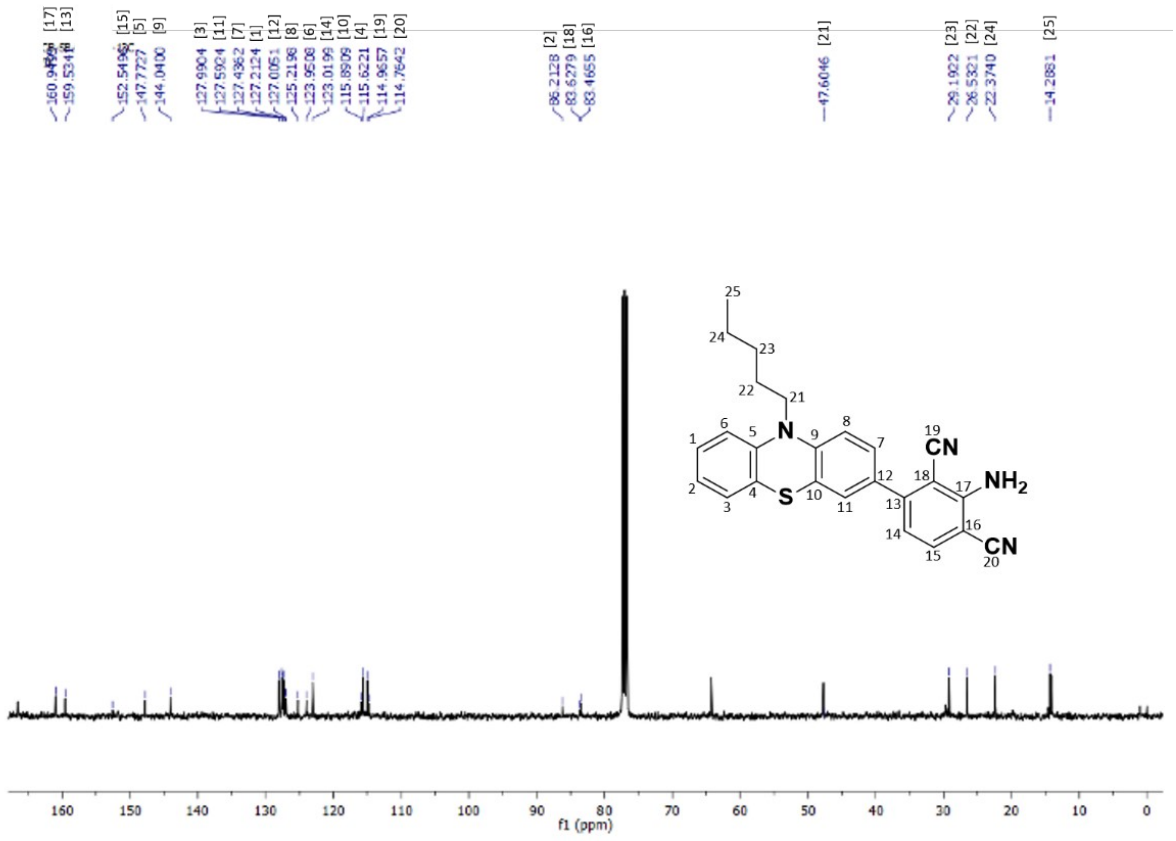
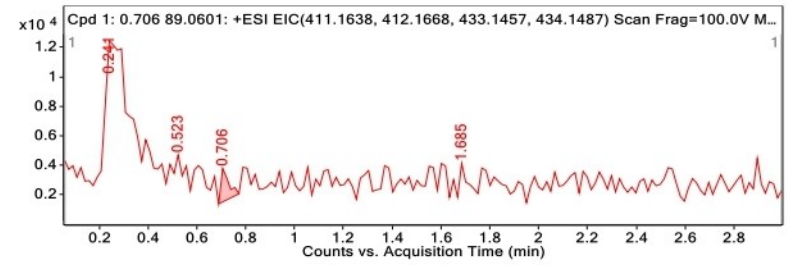


Fig. S24 ^{13}C-NMR spectra of **PTZDCA.** The signals are assigned with the corresponding ^{13}C nuclei, and the numberings (in bracket) are given in the structure. Signals due to adventitious solvent $CH_3CH_2OC(O)CH_3$ are assigned at δ 166.6 [*C*(O)CH_3], 64.1 (O*C*H_2), 22.1 [C(O)*C*H_3], 14.5 (*C*H_3CH$_2$O-).

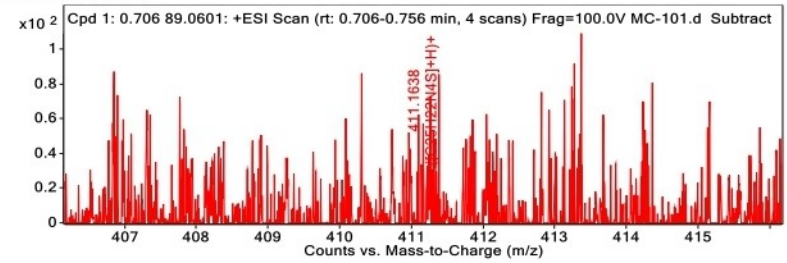
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 0.706 89.0601	0.706	410.1565	58	C25 H22 N4 S	410.1565	0.02

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: 0.706 89.0601	411.1638	0.706	Find By Formula	410.1565



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	*Calc m/z*	Diff(ppm)	z	Abund	Formula	Ion
411.1638	411.1638	-0.02	1	57.97	C25H22N4S	(M+H)+

Fig. S25 HR-MS spectra of **PTZDCA**

References

1 B. Mohammadi, H. Kazemi, M. Shafieey, *Monatsh Chem.*, 2014, **145**, 1649–1652.

END