Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Fluorophores Based on a Minimal Thienylthiazole Core: Towards Multifunctional Materials with Solid State Red Emissions, Solvatochromism and AIE Behaviour

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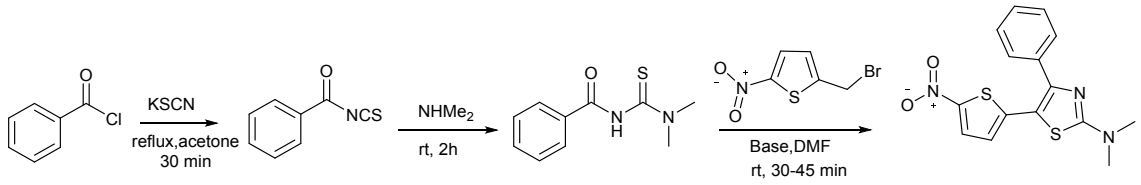
General Information

All the reagents and solvents were of AR/spectroscopic grade and were used without further purification. Varian Cary 100 Bio UV-Vis spectrophotometer was used for UV-Vis spectroscopy measurements. Fluorescence spectra were recorded using Horiba Jobin Yvon Fluoromax-4 spectrometer and molecules were excited at their absorption maximum. Absolute quantum yields of the samples were recorded on Horiba Fluoromax Quanta-ϕ with a calibrated integrating sphere system under laboratory conditions. Single crystal data were obtained using Bruker Kappa APEXII single crystal X-ray diffractometer. Melting points were determined using DSC (DSC Q20, TA Instruments). TLC was performed using silica gel 60 F254 (Merck) plates and visualization of fluorescence was done using UV lamp of wavelength 365nm. Column chromatography was performed using 60-120 mesh silica gel. Thin films were prepared by spin coating technique with a sample concentration 2mg in 5mL (chloroform) on glass plates.

Experimental

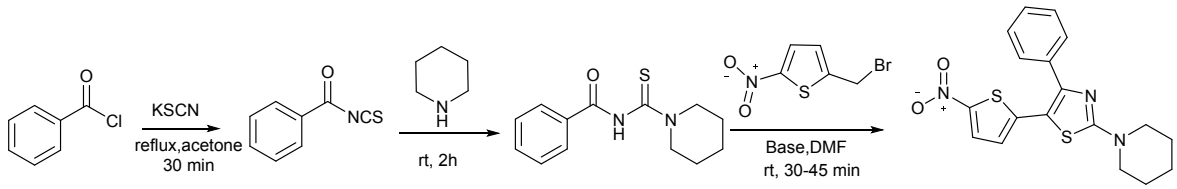
Synthesis of 5-TPTZ-1



Scheme 1. Synthesis of **5-TPTZ-1**

Benzoyl chloride (116.1 µL,1mmol) in acetone (5mL) was added slowly to a solution of KSCN (97.18 mg,1mmol) in acetone (3mL), refluxed for 30 min and then cooled to room temperature. To the cooled mixture, a 40% solution of N,N-dimethylamine (126.6 µL,1mmol) in acetone (1 mL) was added slowly and the mixture was stirred for 2 h. On addition to crushed ice, a white precipitate of thiourea was obtained which was filtered, dried and recrystallized from ethanol. To a solution of thiourea in DMF (2mL), 2-bromomethyl-5-nitrothiophene (222 mg, 1mmol) was added followed by triethylamine (91 µL,1.2 mmol) and stirred for 30-45 min. The reaction mixture was slowly added to crushed ice with vigorous stirring and the precipitate was filtered and dried. The compound was obtained as a red solid (yield=61%) on purification by silica gel column chromatography using petroleum ether -ethyl acetate (100:1) as eluent.

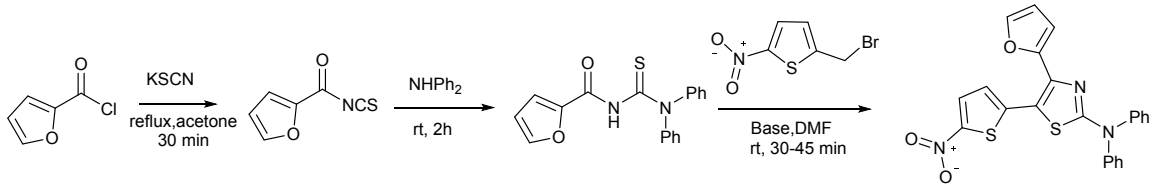
Synthesis of 5-TPTZ-2



Scheme 2. Synthesis of **5-TPTZ-2**

Benzoyl chloride (116.1 µL,1mmol) in acetone (5 mL) was added slowly to a solution of KSCN (97.18 mg,1 mmol) in acetone (3 mL), refluxed for 30 min and then cooled to room temperature.To the cooled mixture, piperidine (98.8 µL, 1mmol) in acetone was added slowly and the mixture was stirred for 2 h. On addition to crushed ice, a white precipitate of thiourea was obtained which was filtered, dried and recrystallized from ethanol. To a solution of thiourea in DMF (2mL), 2-bromomethyl-5-nitrothiophene (222 mg, 1mmol) was added followed by triethylamine (91 µL, 1.2 mmol) and stirred for 30-45 min after which the reaction mixture was worked up. The filtered and dried precipitate afforded **5-TPTZ-2** as a red solid (yield=65%) on purification by silica gel column chromatography using petroleum ether -ethyl acetate (100:1) as eluent.

Synthesis of 5-TPTZ-3



Scheme 3. Synthesis of **5-TPTZ-3**

Furan-2-oyl chloride (98.6 µL, 1mmol) in acetone (5 mL) was added slowly to a solution of KSCN (97.18 mg, 1 mmol) in acetone (3 mL), refluxed for 30 min and then cooled to room temperature. To the cooled mixture, diphenylamine (169.2 mg, 1mmol) in acetone (1mL) was added slowly and the mixture was stirred for 2 h. On addition to crushed ice, a white precipitate of thiourea was obtained which was filtered, dried and recrystallized from ethanol. To a solution of thiourea in DMF (2mL), 2-bromomethyl-5-nitrothiophene (222 mg, 1mmol) was added followed by triethylamine (91 µL, 1.2 mmol) and stirred for 30-45 min. The precipitate obtained after reaction mixture work up was filtered and dried to obtain **5-TPTZ-3** as a red solid (Yield=51%) after purification by silica gel column chromatography using petroleum ether -ethyl acetate (100:1) as eluent.

Photophysical studies

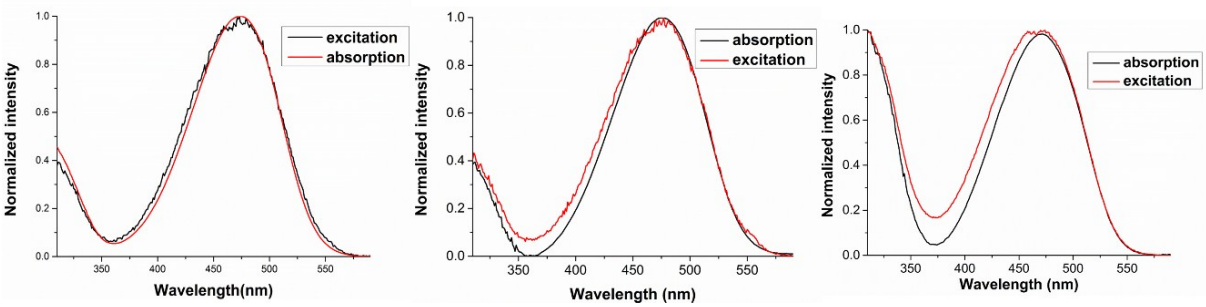


Fig.S1 Absorption and excitation spectra (recorded at their emission maxima) of **5-TPTZ-1, 5-TPTZ-2** and **5-TPTZ-3** in THF respectively.

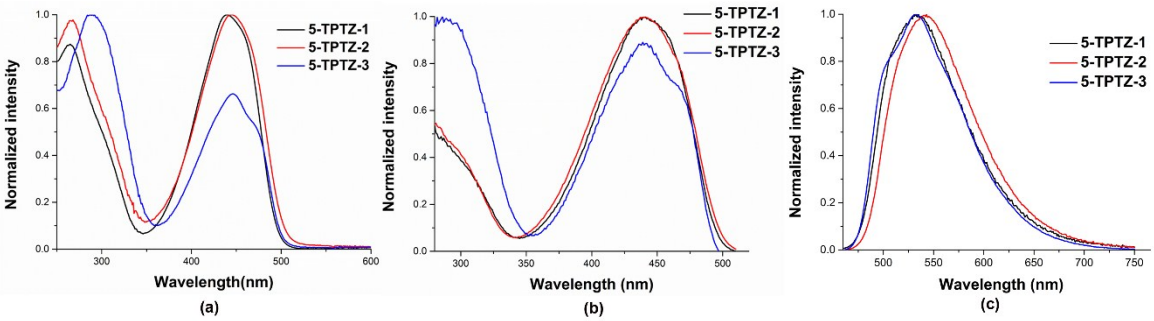


Fig.S2 (a) Absorption, (b) excitation (recorded at their emission maxima) and (c) emission spectra of **5-TPTZ-1, 5-TPTZ-2** and **5-TPTZ-3** in n-hexane.

Solvatochromism

Table S1 : Spectroscopic properties of **5-TPTZ-1**

Solvent	$E_T(30)$	Δf	λ_{ab}		λ_{em}		Stokes shift (cm^{-1})
			(nm)	(cm^{-1})	(nm)	(cm^{-1})	
n-Hexane	31	0.002	440	22727	533	18762	3965
Toluene	33.9	0.016	468	21367	579	17271	4096
Ethyl acetate	38.1	0.2	469	21322	604	16557	4765
THF	37.4	0.21	473	21142	614	16287	4855
DCM	40.7	0.218	483	20704	641	15601	5103
Acetonitrile	45.6	0.306	479	20876	646	15479	5397

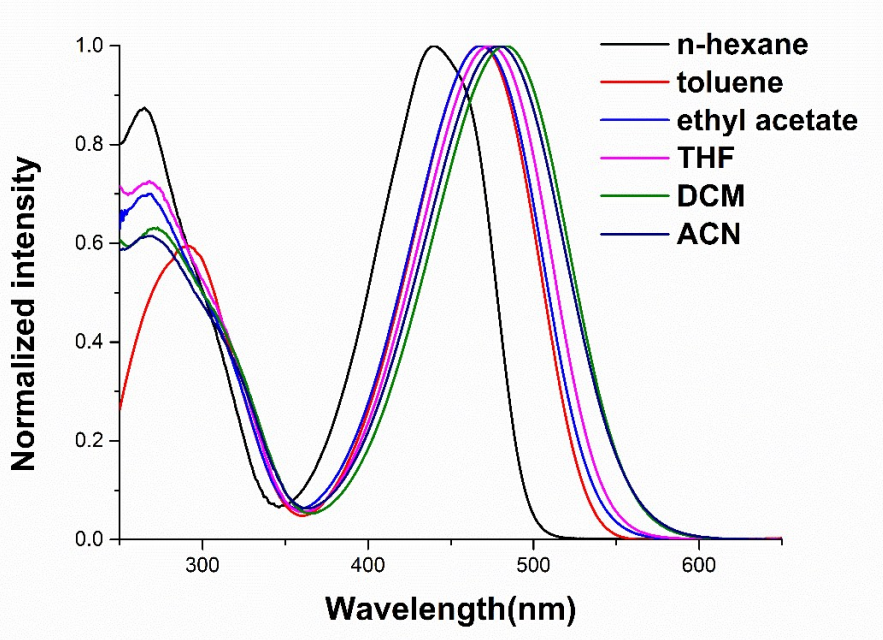


Fig.S3 Absorption spectra of **5-TPTZ-1** in various solvents

The solvent-dependent fluorescence was evaluated using the Lippert−Mataga equation[1]

$$\Delta\vartheta = \vartheta_{ab} - \vartheta_{em} = \frac{2\Delta f}{hca^3}(\mu_e - \mu_g)^2 + constant$$

Fig.S4 Lippert−Mataga equation plot of **5-TPTZ-1** (left) and emission spectra (right) in various solvents

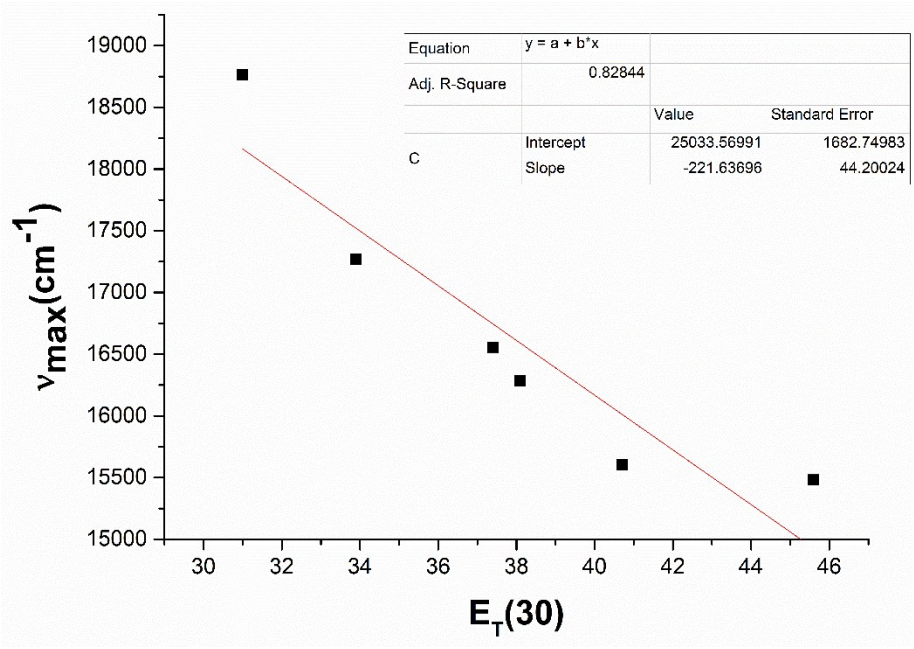


Fig.S5 Emission maxima as a function of solvent polarity index E_T(30) of **5-TPTZ-1**

X-ray crystallographic analysis

Diffraction data were collected on Bruker Kappa APEX-II single crystal X-ray diffractometer using graphite-monochromated Mo- Kα radiation (λ = 0.71073 Å) at 296 K. Crystal cell constants were calculated by least-squares global refinement. The structures were solved by direct methods using SHELXL-2014.[2] Graphics were generated using MERCURY 3.6 X-ray crystal analysis software. Crystals were obtained by slow evaporation from ethanol. Summary of structural data for the molecules is provided in Table.

Table S2 : Crystal data

	5-TPTZ- 1	**5-TPTZ -2**	**5-TPTZ-3**
Empirical formula	C_{15} H_{13} N_3 O_2 S_2	C_{18} H_{17} N_3 O_2 S_2	$C_{23}H_{15}$ N_3O_3 S_2
Formula weight	331.40	371.46	445.50
Temperature(K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic

Space group	P 2_1/n	Pbca	P-1
a/Å	a = 5.9198(12)	a = 12.6077(7)	a = 5.5393(3)
b/Å	b = 15.753(3)	b = 7.6101(4)	b = 10.8879(5)
c/Å	c = 16.190(3)	c = 36.685(2)	c = 17.6155(10)
α/°	90	90	76.715(4)
β/°	91.91(3)	90	87.017(3)
γ/°	90	90	86.648(3)
V/Å^3	1509.0(5)	3519.8(3)	1031.40(10)
Z, D_{calc} Mg/m^3	4, 1.459	8, 1.402	2, 1.434
Reflections collected	6413	16515	26644
Independent reflections	6413	3837	4054
Max. and min. transmission	0.9675 and 0.9466	0.9843 and 0.9249	0.967 and 0.923
Goodness-of-fit on F^2	1.016	1.058	1.040
R_1 (all data)	0.0844	0.0866	0.0698
wR_2 [I>2 σ(I)]	0.0982	0.1015	0.0822

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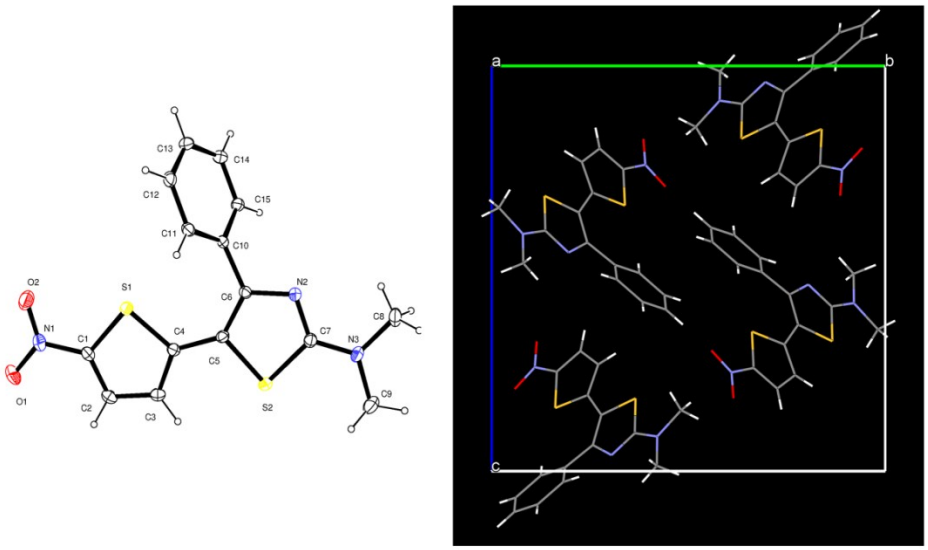

Fig. S6 Ortep diagram (left) and unit cell of **5-TPTZ- 1** along a axis (right)

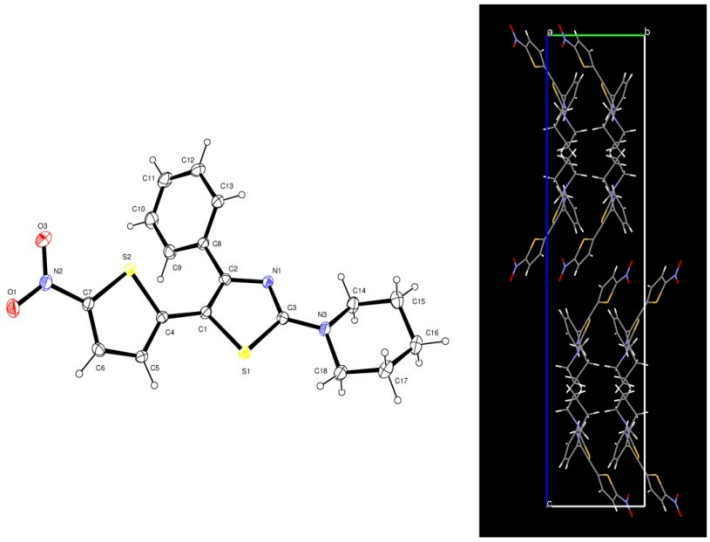

Fig. S7 Ortep diagram (left) and unit cell of **5-TPTZ- 2** along a axis (right)

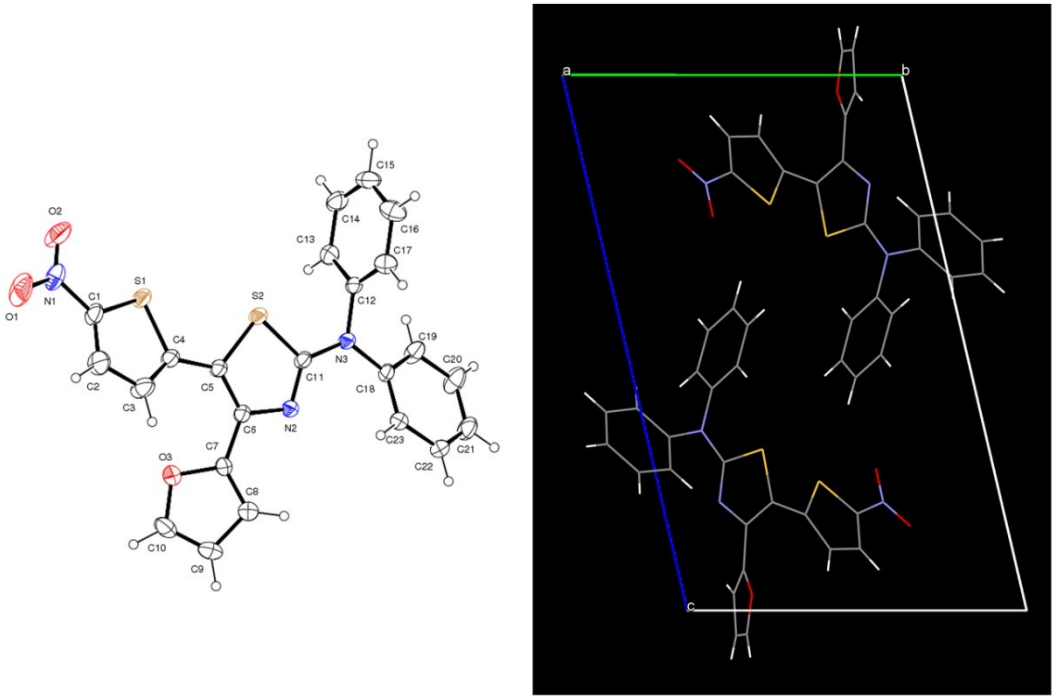

Fig. S8 Ortep diagram (left) and unit cell of **5-TPTZ-3** along a axis (right)

Computational methods

DFT calculations

We used Gaussian 09 package[3] for DFT calculations. Initial geometry was taken from the single crystal XRD data. Molecules were optimized using PBE0/6-31G(d,p) level and absence of any imaginary frequency confirmed that the molecules are minimum in potential energy surfaces. Absorption spectra were calculated using TD DFT calculations. Effect of solvents was modelled using polarizable continuum model. The intramolecular charge transfer nature was confirmed by the frontier molecular orbital analysis.

Table S3 : Results of PBE0/6-31G(d,p) calculations

Compound	**Energy (eV)**	**λ cal (nm)**	**Osc. Strength**	**Main transitions**
5-TPTZ-1	2.60	475.2	0.5001	HOMO->LUMO (99%)
	3.87	320.0	0.0223	H-6->LUMO (42%), HOMO->L+1 (25%)
5-TPTZ-2	2.59	478.6	0.5459	HOMO->LUMO (99%)
	3.86	320.7	0.0284	H-6->LUMO (32%), HOMO->L+1 (47%)
5-TPTZ-3	2.45	504.8	0.4989	HOMO->LUMO (99%)
	3.30	375.6	0.1181	H-1->LUMO (97%)

Coordinates of **5-TPTZ- 1**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.229834	-1.233634	-0.080927
2	6	0	-2.701708	-2.365219	0.490856
3	1	0	-3.304446	-3.218379	0.774563
4	6	0	-1.315996	-2.250035	0.666188
5	1	0	-0.701205	-3.024277	1.110476
6	6	0	-0.796215	-1.032163	0.235354
7	6	0	0.594490	-0.669207	0.209079
8	6	0	1.243652	0.550296	0.100598

9	6	0	3.043798	-0.731813	-0.016465
10	6	0	5.333069	-0.051738	-0.374646
11	1	0	5.573296	-0.031207	-1.444850
12	1	0	6.245201	-0.263700	0.188600
13	1	0	4.941019	0.920911	-0.081566
14	6	0	4.736844	-2.458502	-0.177878
15	1	0	4.185795	-3.065673	0.547916
16	1	0	5.798988	-2.540837	0.056942
17	1	0	4.566072	-2.865180	-1.183156
18	6	0	0.609504	1.882713	0.155500
19	6	0	-0.287824	2.215319	1.176983
20	1	0	-0.532503	1.478117	1.936082
21	6	0	-0.847491	3.487222	1.233594
22	1	0	-1.538035	3.736345	2.033744
23	6	0	-0.515276	4.440708	0.273716
24	1	0	-0.954210	5.433097	0.317938
25	6	0	0.389707	4.121719	-0.737213
26	1	0	0.657266	4.864409	-1.483037
27	6	0	0.955806	2.852977	-0.792465
28	1	0	1.669866	2.600665	-1.570315
29	7	0	-4.588914	-0.990305	-0.364879
30	7	0	2.596898	0.505620	-0.048721
31	7	0	4.343519	-1.070453	-0.076851
32	8	0	-5.401506	-1.877855	-0.117215
33	8	0	-4.880702	0.102859	-0.853427
34	16	0	-2.050526	-0.014975	-0.415098

35	16	0	1.795206	-1.953165	0.153930

E(RPBE1PBE) =-1689.1176192a.u

Coordinates of **5-TPTZ- 2**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.112539	-0.510465	0.293521
2	6	0	-0.382654	0.779361	0.190720
3	6	0	-2.338202	-0.263420	0.179827
4	6	0	1.444698	-1.046066	0.255097
5	6	0	1.816106	-2.337705	0.621897
6	1	0	1.119191	-3.047555	1.052429
7	6	0	3.169794	-2.620678	0.398383
8	1	0	3.664508	-3.555676	0.628027
9	6	0	3.823839	-1.542109	-0.145422
10	6	0	0.418393	2.020459	0.179347
11	6	0	1.367246	2.274535	1.176433
12	1	0	1.528981	1.541287	1.961258
13	6	0	2.084884	3.465899	1.176156
14	1	0	2.814083	3.655471	1.958143
15	6	0	1.861895	4.415839	0.181896
16	1	0	2.424241	5.344928	0.181172
17	6	0	0.908336	4.176040	-0.805994
18	1	0	0.726122	4.917209	-1.578589

19	6	0	0.183992	2.989107	-0.803709
20	1	0	-0.568142	2.801031	-1.563771
21	6	0	-4.542173	0.745146	0.220577
22	1	0	-3.950427	1.621906	-0.041542
23	1	0	-4.862136	0.854974	1.268389
24	6	0	-5.758982	0.593254	-0.682076
25	1	0	-5.434034	0.621099	-1.729546
26	1	0	-6.419996	1.451826	-0.523675
27	6	0	-6.487806	-0.716974	-0.403017
28	1	0	-6.895639	-0.699591	0.617134
29	1	0	-7.337679	-0.836856	-1.082679
30	6	0	-5.526086	-1.891718	-0.547017
31	1	0	-6.015607	-2.836130	-0.287734
32	1	0	-5.192973	-1.971504	-1.589048
33	6	0	-4.304429	-1.716854	0.348260
34	1	0	-4.595323	-1.795251	1.407269
35	1	0	-3.581079	-2.511534	0.145641
36	7	0	-1.736208	0.906138	0.118215
37	7	0	5.194033	-1.462023	-0.463205
38	7	0	-3.671810	-0.425773	0.119959
39	8	0	5.892853	-2.455100	-0.274667
40	8	0	5.611034	-0.395489	-0.919432
41	16	0	-1.244491	-1.629217	0.347059
42	16	0	2.802889	-0.168360	-0.391067

E(RPBE1PBE) = -1805.7309316a.u

Coordinates of **5-TPTZ- 3**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.829459	-0.859596	0.234056
2	6	0	4.827309	0.375836	0.835069
3	1	0	5.718673	0.826320	1.252768
4	6	0	3.543856	0.941316	0.855278
5	1	0	3.313115	1.897278	1.303266
6	6	0	2.578814	0.140342	0.259441
7	6	0	1.160172	0.360846	0.132005
8	6	0	0.401278	1.506458	-0.068175
9	6	0	0.827622	2.870837	-0.288304
10	6	0	0.078220	4.003271	-0.474520
11	1	0	-1.000280	4.048382	-0.468401
12	6	0	1.000928	5.065341	-0.679727
13	1	0	0.776126	6.106742	-0.858952
14	6	0	2.239779	4.506603	-0.608170
15	1	0	3.240565	4.900071	-0.699453
16	6	0	-1.276936	0.063930	-0.005566
17	6	0	-2.780633	-1.825782	-0.073146
18	6	0	-2.412315	-2.535595	-1.217223
19	1	0	-1.959543	-2.010378	-2.052735
20	6	0	-2.636428	-3.908121	-1.275444

21	1	0	-2.349295	-4.460870	-2.164575
22	6	0	-3.240307	-4.565050	-0.206029
23	1	0	-3.419264	-5.634649	-0.257197
24	6	0	-3.618530	-3.848665	0.928243
25	1	0	-4.088940	-4.358203	1.763545
26	6	0	-3.386414	-2.479491	1.000702
27	1	0	-3.671345	-1.910653	1.880410
28	6	0	-3.682195	0.450181	0.112658
29	6	0	-4.813138	0.179735	-0.660936
30	1	0	-4.804389	-0.658221	-1.350727
31	6	0	-5.942542	0.982753	-0.543192
32	1	0	-6.816593	0.764761	-1.149589
33	6	0	-5.950593	2.061881	0.336662
34	1	0	-6.831656	2.690074	0.424481
35	6	0	-4.819466	2.327894	1.105696
36	1	0	-4.817591	3.161820	1.801406
37	6	0	-3.688259	1.525797	1.004312
38	1	0	-2.811848	1.734059	1.606379
39	7	0	5.939938	-1.714600	0.066086
40	7	0	-0.955075	1.319565	-0.135592
41	7	0	-2.554440	-0.415264	0.002467
42	8	0	7.031122	-1.332126	0.478309
43	8	0	5.744749	-2.796938	-0.488241
44	8	0	2.148730	3.176749	-0.371843
45	16	0	3.274522	-1.344322	-0.332691
46	16	0	0.080129	-1.021318	0.224611

E(RPBE1PBE) =-2069.9508531a.u

MD calculations

We have selected orthorhombic box with a buffer size of 7 Å. The initial structure was taken from the crystal packing and consisted of 32 molecules. The force field used was OPLS_2005 and TIP3P solvent model was used for modelling water molecules. Coulombic interactions were incorporated using smooth particle mesh Ewald with a cut off 9 Å. Nose-Hoover thermostat method and Martyna-Tobias-Klein barostat method was applied. The system was relaxed (a series of minimizations and short molecular dynamics simulations were performed to relax the model system) before performing the actual simulation and all other parameters were kept as default. MD stimulation was performed for 10ns with a time step of 2 fs using NPT ensemble.

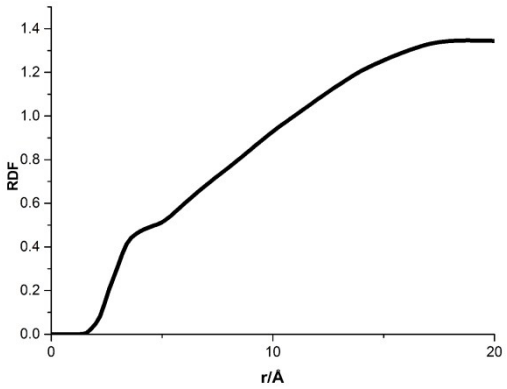

Fig. S9 RDF between **5-TPTZ-1** and water

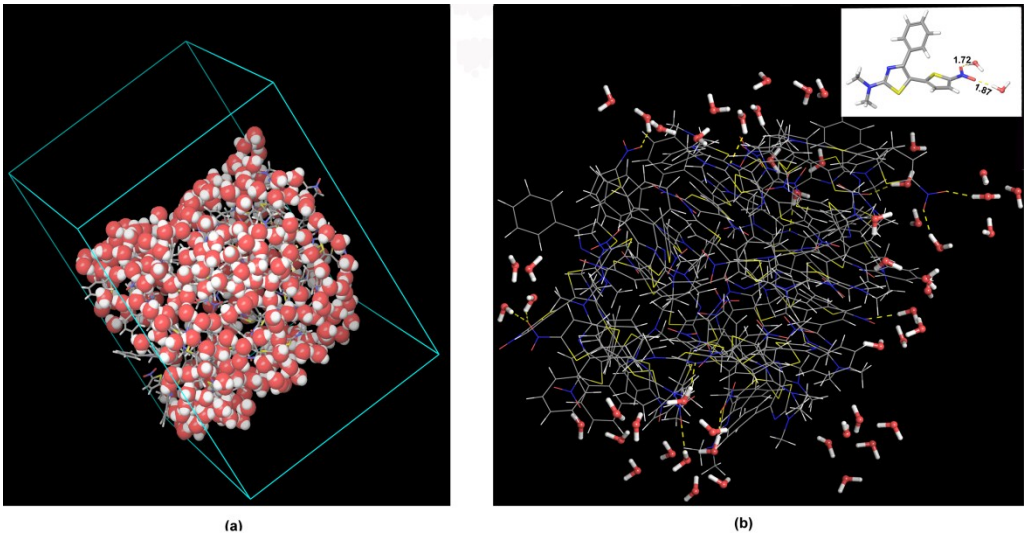

Fig. S10 (a) **5-TPTZ-1** aggregate surrounded by water molecules. (b) Intermolecular H-bonding between aggregate and water (specific H-bonding interaction between nitro group and a water molecule shown in inset)

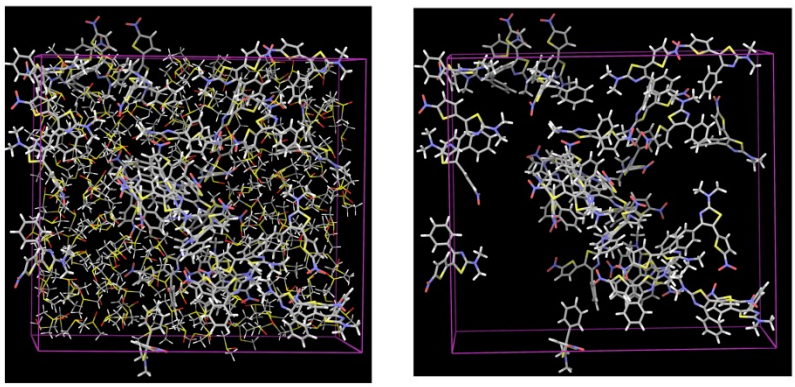

Fig. S11 5-TPTZ-1 molecules and DMSO after 10ns MD simulation (right -without DMSO for clarity)

References

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