C_3-symmetric twisted organic salt as efficient mechano-/thermo-responsive molecule: a reusable, and sensitive, fluorescent thermometer

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Contents:

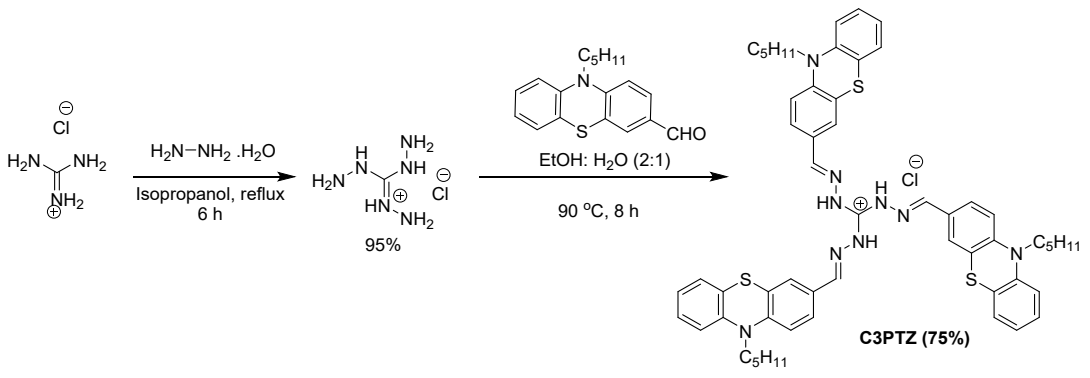
Experimental section

***Materials*:** Phenothiazine, hydrazine hydrate and guanidinium chloride were purchased from Alfa aesar. All other reagents were purchased from common suppliers and used without further purification. Column chromatography was performed using Silica gel 100-200 mesh. Reactions were monitored by thin-layer chromatography on precoated silica gel 60 F254 plates (Merck & Co.) and were visualized by UV (mainly 365 nm). The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution using Bruker Advance DRX (400 MHz). The signals were referenced to TMS, and the solvent used was deuterated chloroform (7.26 ppm in ^{1}H NMR, 77.16 ppm in ^{13}C NMR). Chemical shifts are reported in ppm, and multiplicities are indicated by s (singlet), d (doublet), t (triplet), and dd (doublet of a doublet). All data were plotted using Origin Pro 8.5 software.

***Synthesis*: C3PTZ** was synthesized in a two-step manner. Initially, triamino guanidinium chloride (TAG) was obtained from guanidinium chloride (GC) in the following reported method.[1]

Guanidinium chloride (1 mmol) was taken in 30 mL of isopropanol in a 100 mL round bottom flask. Hydrazine hydrate (50-60%) (4.5 mmol) was added to the above solution and was refluxed for 6 h. After the reaction, the precipitate was filtered and was washed with 50 mL of isopropanol to obtain TAG (yield: 95%).

TAG (1.10 g, 7.81 mmol) was dissolved in a hot mixture of ethanol (300 mL) and water (150 mL). After adjusting the pH of the mixture to 3 with HCl (aqueous), the solution of *N*-hexylphenothiazine aldehyde (8.36 g, 25.16 mmol) in ethanol (100 mL) was added slowly. The resulting solution was refluxed at 90 °C for 8 h. The residue was washed with water several times, which produced a yellow powder.



Scheme S1: Synthetic scheme for **C3PTZ**.

C3PTZ: Yield 6.76 g (75%), m.p. 250-252 °C, IR (ν cm^{-1}, in KBr): 3568, 3054, 2953, 2929, 2868, 1773, 1718, 1631, 1603, 1574, 1551, 1495, 1465, 1442, 1395, 1364, 1333, 1286, 1249, 1218, 1162, 1101, 1040. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 3H), 8.47 (s, 3H), 7.87 (d, *J* = 6.5 Hz, 3H), 7.34 (s, 3H), 7.17 (dd, *J* = 8.0, 6.2 Hz, 3H), 7.09 (dd, *J* = 7.4, 0.5 Hz, 3H), 6.93 (t, *J* = 7.6 Hz, 3H), 6.83 (d, *J* = 8.0 Hz, 3H), 6.74 (d, *J* = 8.5 Hz, 3H), 3.70 (br, 6H), 1.91 (br, 6H), 1.32 (br, 12H), 0.88 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 147.2, 147.1, 144.1, 128.3, 127.4, 127.3, 127.1, 126.9, 123.8, 122.8, 115.5, 115.2, 47.8, 29.1, 26.4, 22.4, 14.1. HR-MS for $C_{55}H_{60}N_6S_3^+$, calc. 942.4128, found 942.4266.

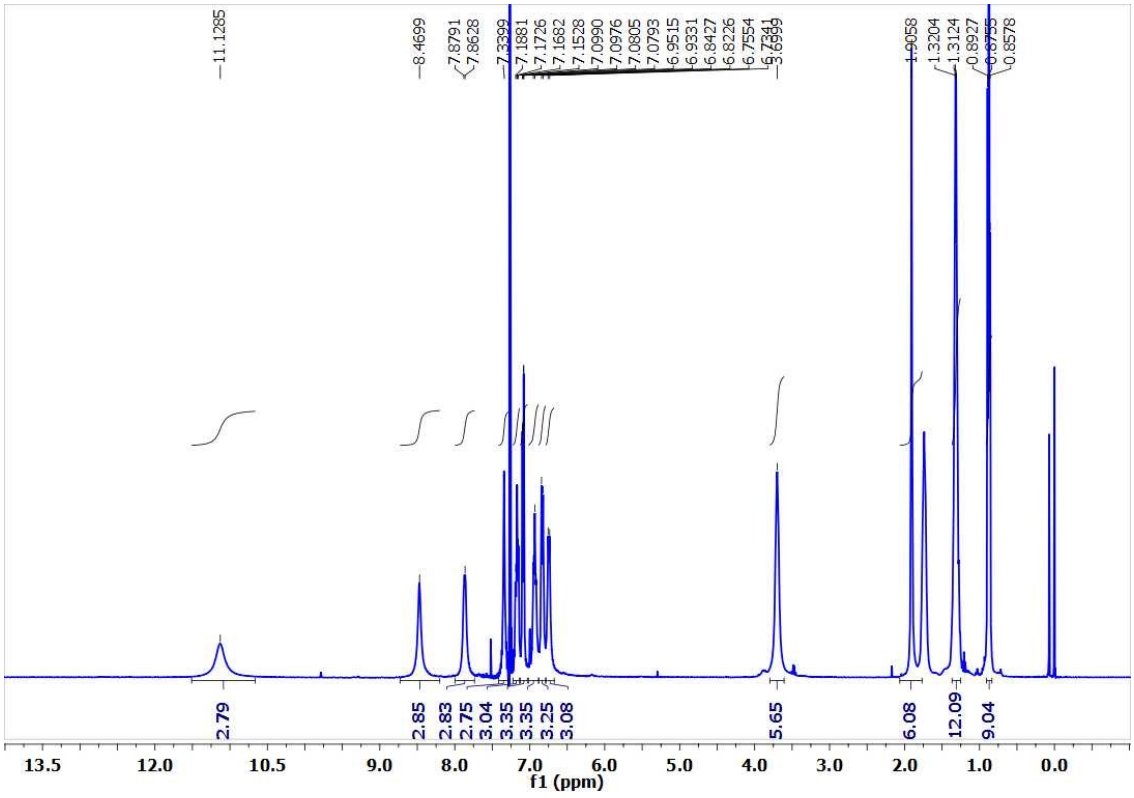


Figure S1: ^{1}H NMR spectrum of **C3PTZ** in $CDCl_3$.

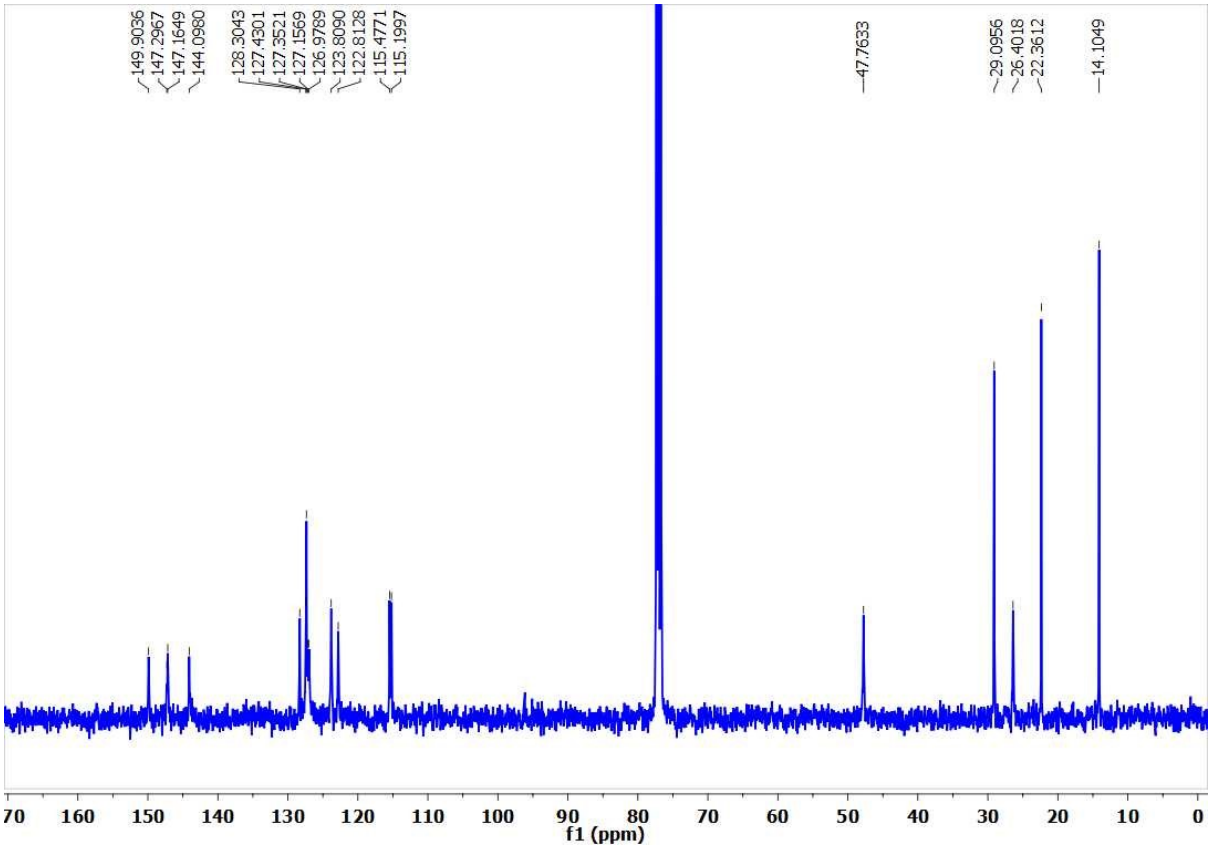


Figure S2: ^{1}C NMR spectrum of **C3PTZ** in $CDCl_3$.

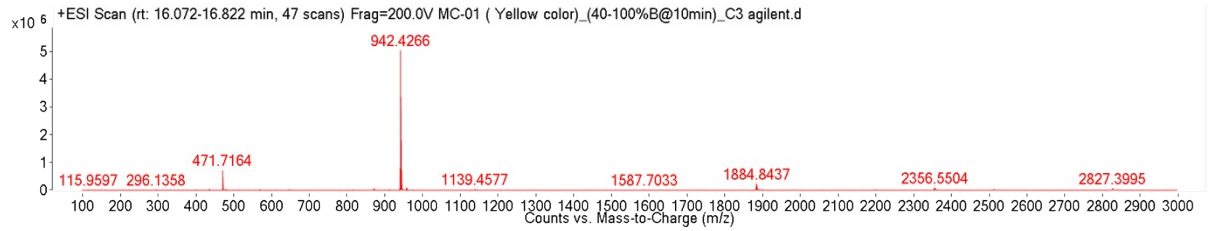


Figure S3: HR-MS spectrum for **C3PTZ.**

Methods and Measurements:

Steady-state absorption and fluorescence measurements: The electronic absorption spectra were recorded with a UV 3600 Plus (Shimadzu). The fluorescence spectra were recorded on a Hitachi spectrofluorometer (F7000, Japan) using a 1 cm pathlength quartz cuvette for solution-state spectra and Fluorolog, Horriba for solidstate emission spectra. A stock solution of 10^{-3} M was prepared in 1,4-dioxane. The final concentration of the probe was adjusted to 10 μM. The solid-state absorbance and emission spectra were recorded in the pristine, ground, thermal heating, solvent fumed solid samples.

Powder X-ray diffraction and IR spectra measurement: The powder X-ray diffraction (PXRD) pattern was recorded using a Rigaku Ultima IV X-ray diffractometer. The parameters were kept constant for the samples before and after the applications of stimuli: a step width of 0.2 with a scan rate of 2°/min from 5-45° (Cu, Ka, λ = 1.54Å). The IR spectra were recorded using an FTIR spectrometer (FT/IR-4200, Jasco). KBr was used as a matrix for recording the IR spectra.

Absolute quantum yield and lifetime decay measurement: The solid-state absolute quantum yield was measured using a calibrated integrating sphere method with an absolute error of 2%. Time-resolved fluorescence measurements were performed using a time-correlated single-photon counting (TCSPC) unit (Horiba Deltaflex). The laser used for all samples was 403 nm. Aluminum foil was used as the IRF for all of the solid samples. All measurements were performed at room temperature. The decay fitting was completed, keeping the χ^2 value close to unity.

Thermal analysis study: Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60 simultaneous DTATG apparatus with increasing temperature rate at 5 °C/min in N_2 atmosphere, and differential scanning calorimetry was recorded using a Themys One$^+$ with a temperature range of 30-650 °C at 5 °C/min under N_2 atmosphere.

Computational Details:

Geometry optimizations of all the compounds are carried out with the aid of Density-Functional Theory (DFT) using B3LYP exchange-correlation functional and 6-31G(d) basis set, as implemented in the Gaussian 16 suite of programs.[1] Excited-states calculation were performed using time-dependent DFT (TD-DFT) methods with different DFT functionals (viz., B3LYP, PBE0, ωB97XD, M06-2X and LC-ω*PBE. ω value was tuned in LC-ω*PBE functional and found to be 0.154 Bohr[2,3] From the TD-DFT calculation (Table S3), we found that LC-ω*PBE functional is the best choice for the optical properties of this molecule. The D3 version of Grimme's dispersion was included for dimer calculations.[4] All of the DFT and TD-DFT calculations were done in acetonitrile (ε = 37.5) using the polarizable continuum model (PCM).[5] Long alkyl group attached with the N-atom (viz., -C_5H_{11}) of pentylphenothiazine

(PTZ), was substituted by methyl group to reduce the computational cost. Non-covalent interaction (NCI) plot calculations are carried out using Multiwfn 3.6 package.[6,7]

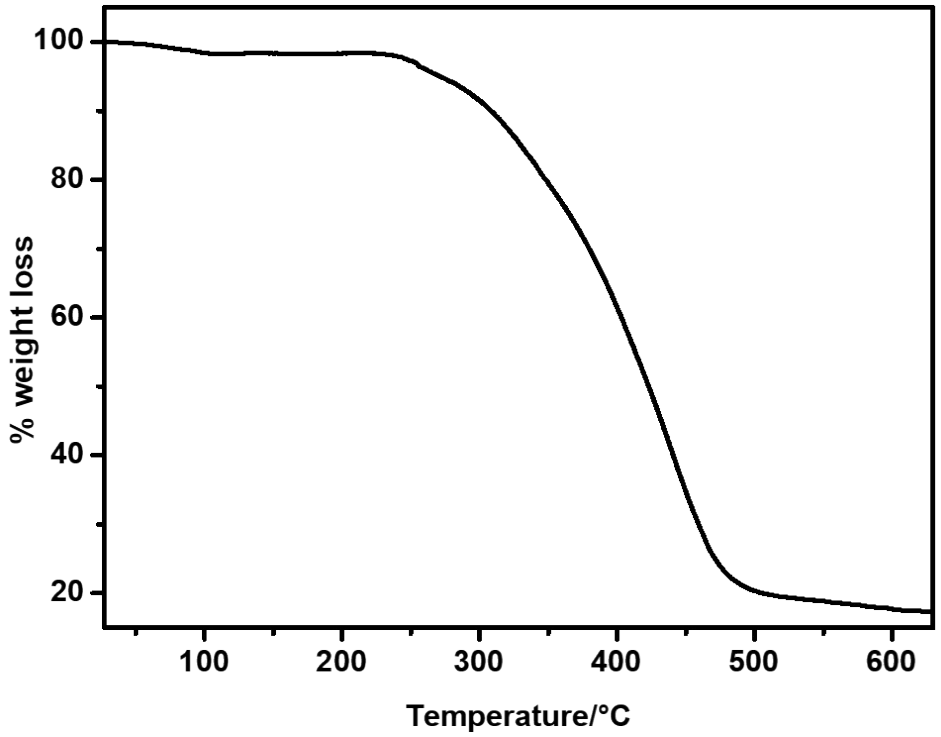


Figure S4: TGA plot for **C3PTZ**.

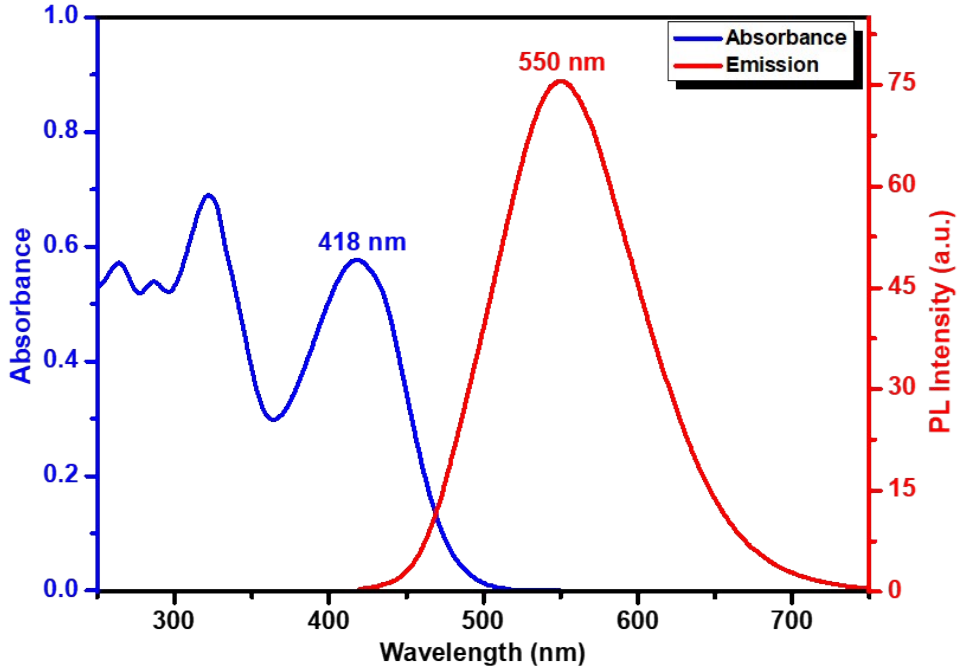


Figure S5: Absorption and FL spectra for **C3PTZ**, λ_{ex}= 405 nm.

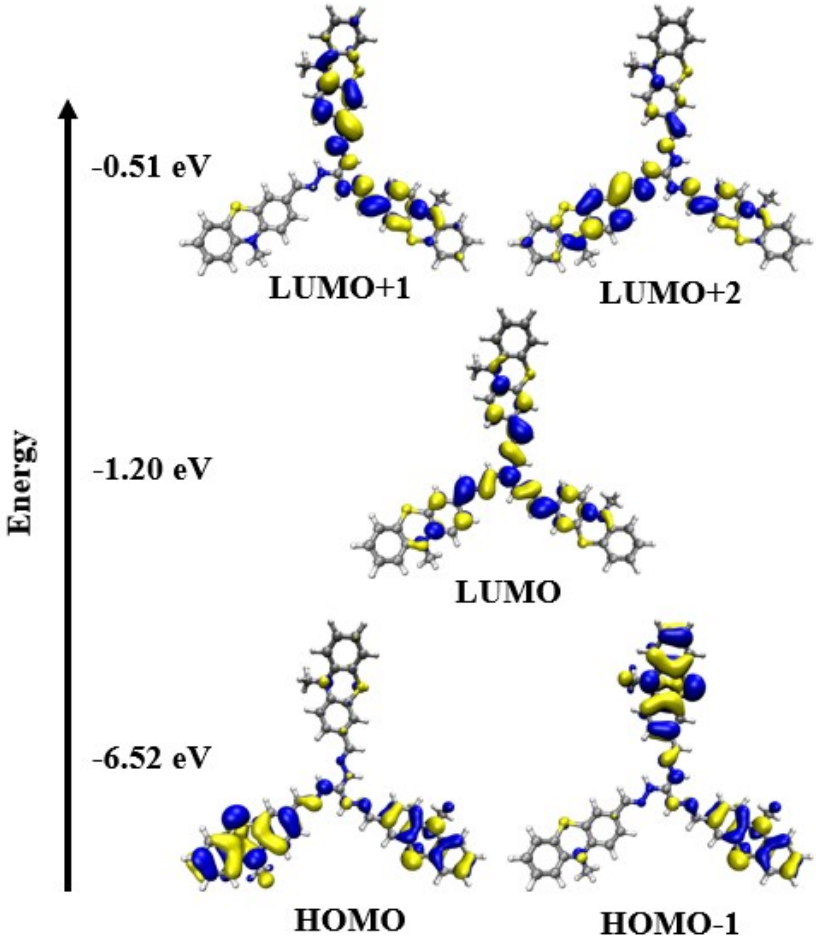


Figure S6: Frontier Molecular Orbitals (FMO)

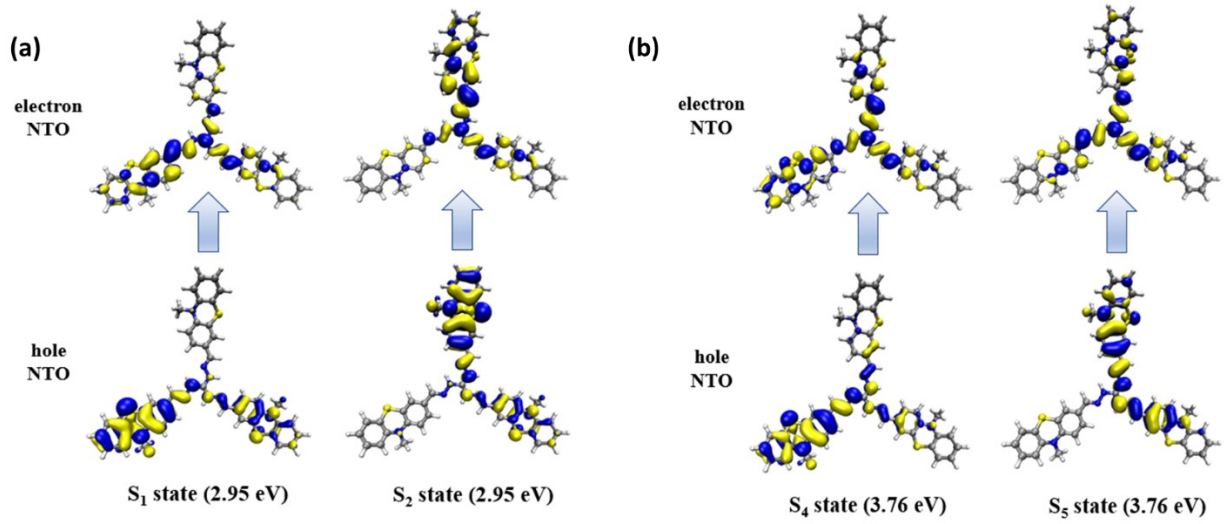


Figure S7: Natural transition orbitals (NTOs) for (a) S_1 and S_2 (b) S_4 and S_5 states.

Table S1: Calculated Lowest Energy (i.e., S_1 state) Optical Absorption using TDDFT (using Acetonitrile solvent)

DFT	B3LYP	PBE0	ωB97XD	M062X	**LC-ω*PB E**	Experiment
Energy (nm)	466	439	357	370	**420**	418
Oscillator strength	f=0.61	f=0.71	f=1.08	f=0.97	***f*=0.91**	-

Table S2: Absorption Wavelength Excited States using LC-ω*PBE.

State	Calculated wavelength (nm)	Osc. Strength (f)	Configurations (H=HOMO, L=LUMO)	Expt. Absorption (nm)
S_1	420	0.91	H→L (60%); [H-2]→[L+2] (14%)	418
S_2	420	0.91	[H-1]→L (60%); [H-2]→[L+1] (14%)	418
S_3	394	0.00	[H-2]→L (46%); [H-1]→[L+1] (21%); H→[L+2] (21%)	-
S_4	330	0.66	[H-6]→L (9%); [H-3]→L (17%); [H-2]→[L+2] (10%)	326
S_5	330	0.66	[H-7]→L (9%); [H-4]→L (17%); H→[L+1] (10%)	326

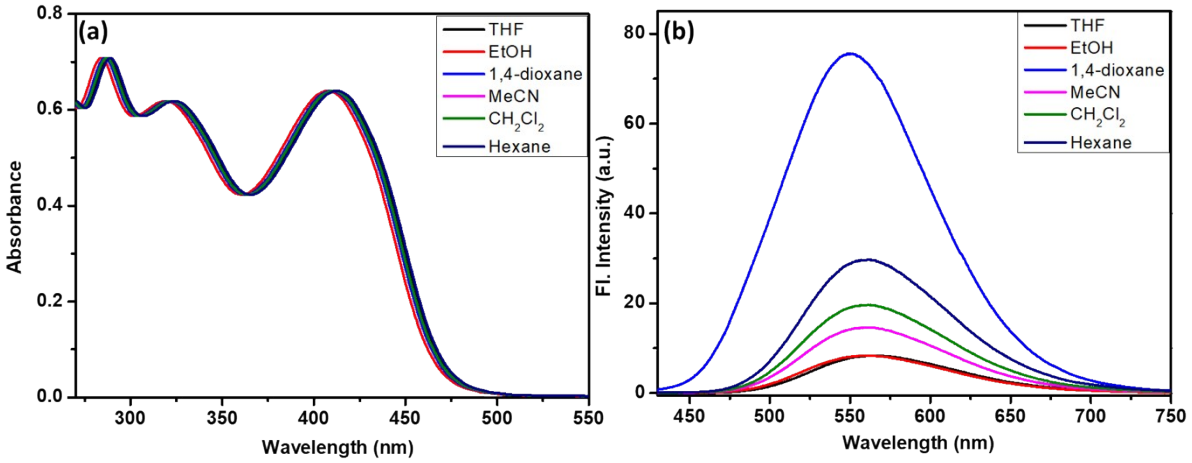


Figure S8: Absorption and FL spectra for **C3PTZ** in different solvents, λ_{ex}= 405 nm

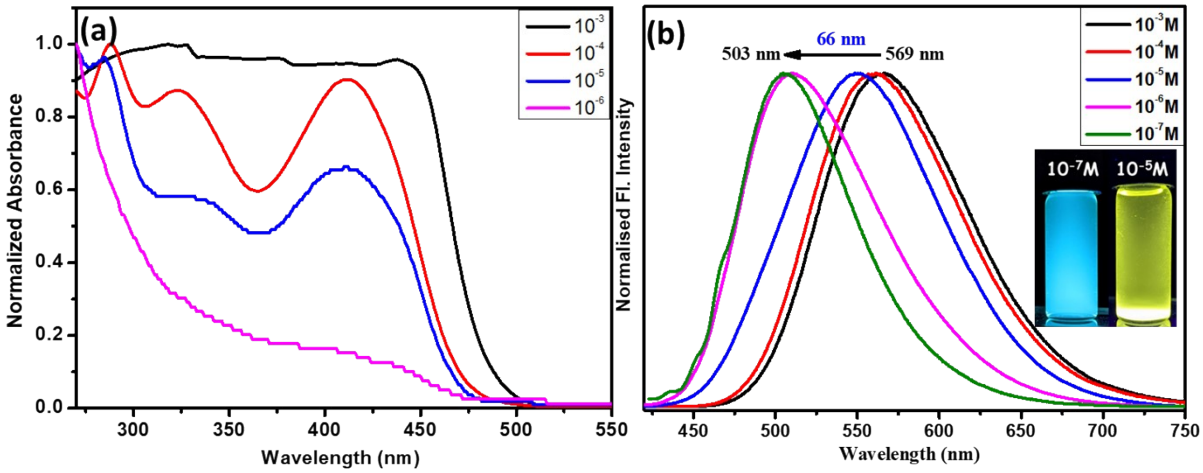


Figure S9: (a) Absorbance and (b) FL spectra for **C3PTZ** in 1,4-dioxane at different concentrations, λ_{ex}= 405 nm.

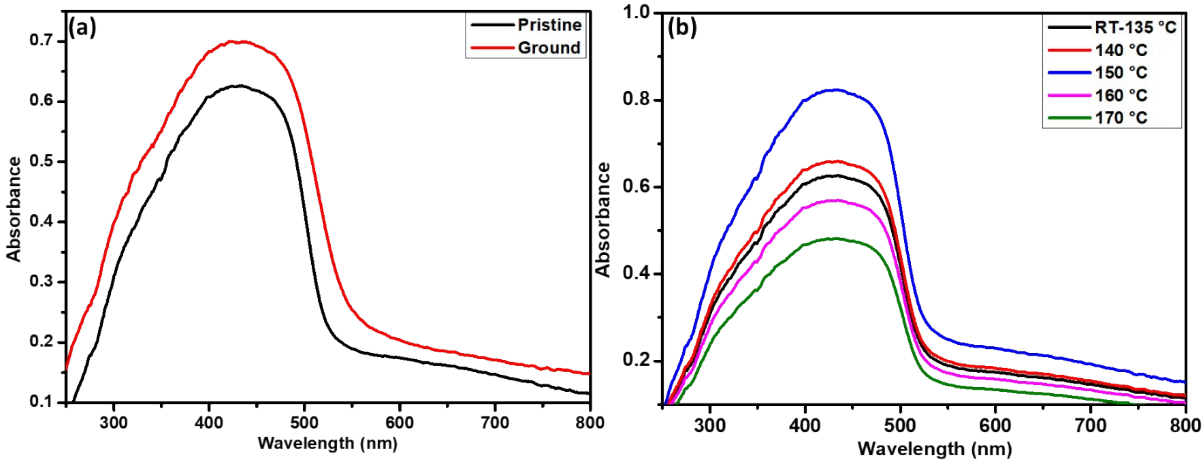


Figure S10: Absorption spectra for **C3PTZ** (a) before and after grinding and (b) at different temperatures.

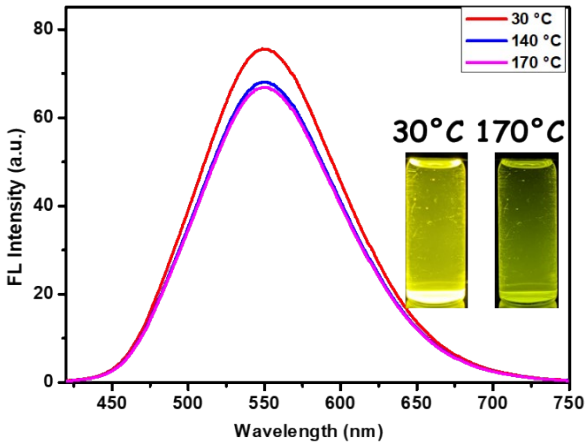


Figure S11: Temperature dependant FL spectra for **C3PTZ** in dimethyl acetamide.

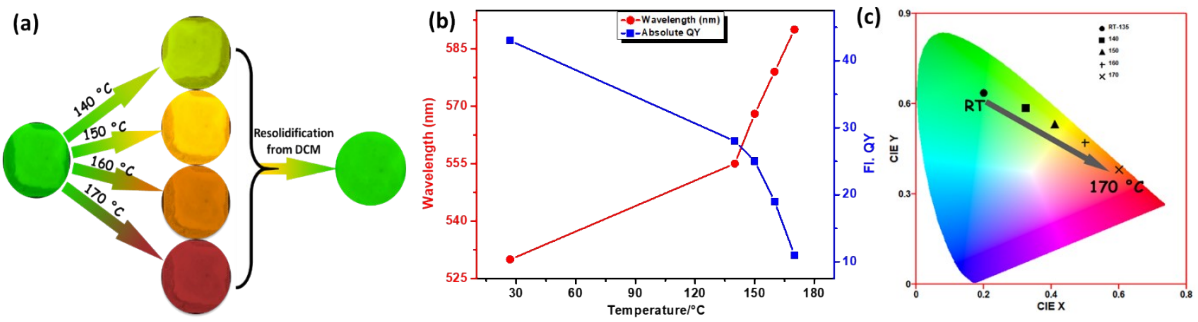


Figure S12: (a) Reversible thermochromic of **C3PTZ** upon resolidification from DCM. (under 365 nm UV lamp) (b) The plot of wavelength and absolute Φ_f *vs.* Temp (c) CIE chromaticity diagram with temp dependence.

Table S2: Photophysical parameters for **C3PTZ**

States	λ_{abs}(nm)	λ_{emi}(nm)	Φ_f(%)	CIE coordinate	<τ>(ns)	K_r (x10^6 s^{-1})	K_{nr} (x10^6 s^{-1})	K_r/K_{nr}
Pristine	435	530	43	(0.210,0.630)	**1.65**	260.06	346.00	0.75
Ground	440	575	36		**1.52**	236.84	421.05	0.56
140 °C		555	28	(0.320,0.580)	**1.37**	204.38	525.55	0.38
150 °C		568	25	(0.412,0.530)	**1.03**	242.72	728.15	0.33
160 °C		579	19	(0.503,0.472)	**0.87**	218.39	931.03	0.23
170 °C		590	11	(0.604,0.380)	**0.73**	150.68	1219.18	0.12

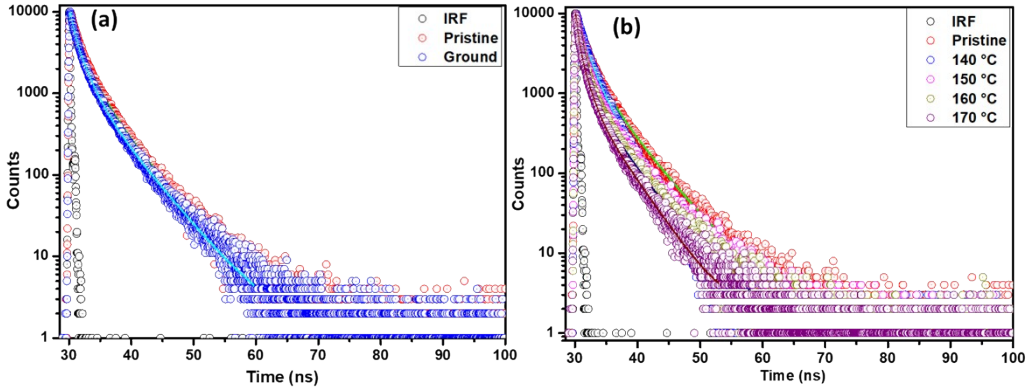


Figure S13: Lifetime decay plot for **C3PTZ** for pristine and after stimuli.

Table S3: Lifetime decay table for **C3PTZ**

States	τ_1(ns)	τ_2(ns)	τ_3(ns)	α_1(%)	α_2(%)	α_3(%)	χ^2	<τ>(ns)
Pristine	1.78	0.43	4.63	0.43	0.42	0.15	1.10	1.65
Ground	1.46	0.38	3.32	0.47	0.32	0.21	1.09	1.52
140 °C	1.71	4.76	0.42	0.38	0.11	0.51	1.16	1.37
150 °C	1.36	0.30	4.35	0.35	0.56	0.09	1.10	1.03
160 °C	1.21	0.27	4.03	0.31	0.60	0.08	1.17	0.87
170 °C	1.14	3.78	0.26	0.28	0.06	0.66	1.23	0.73

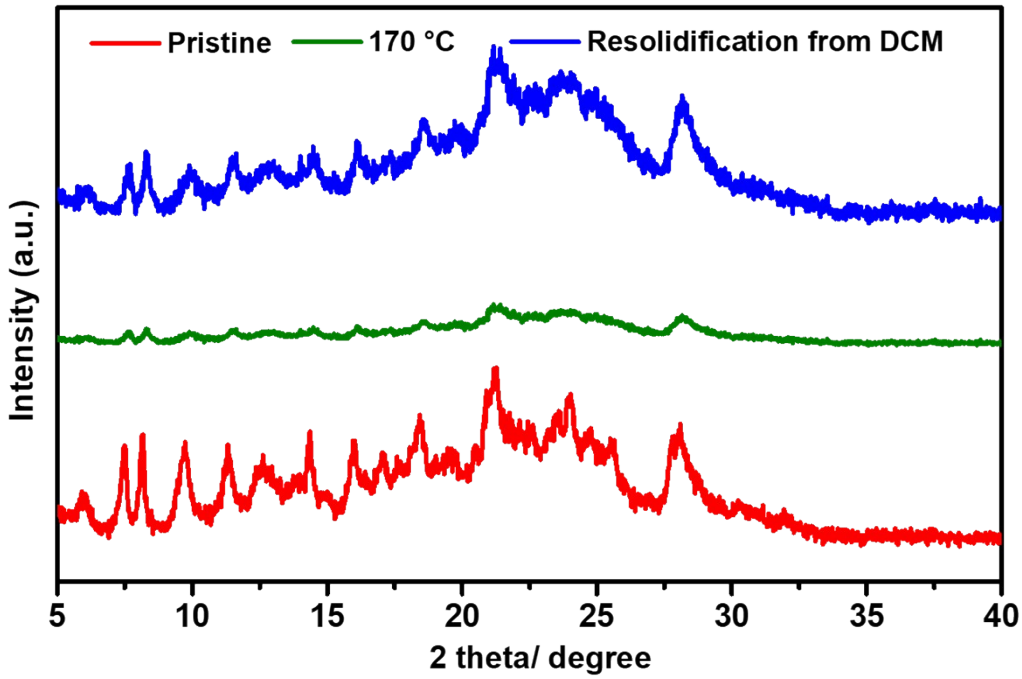


Figure S14: PXRD pattern for **C3PTZ** for pristine, 170 °C and resolidification from DCM.

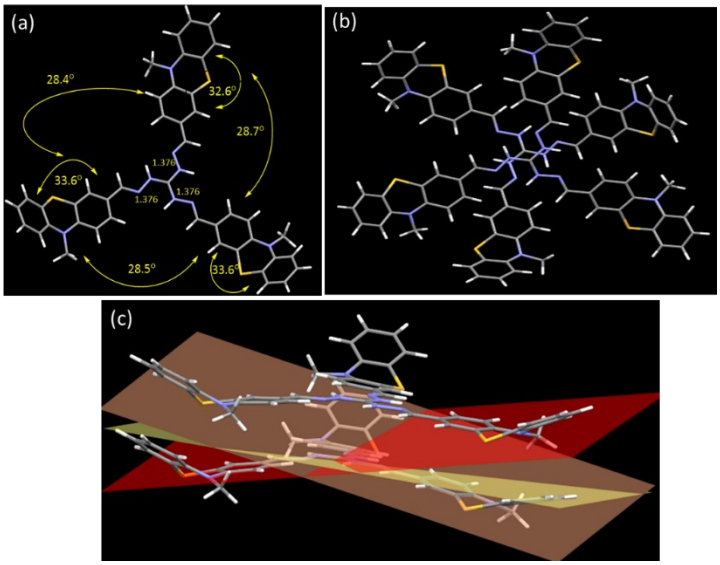


Figure S15: (a) Optimized molecular structure of **C3PTZ** with selected bond angles and distances. (b) staggered form (c) propeller-shape (shown in a molecule present in the dimer) with interplanar angles 12°,15°, 23°.

Non-covalent Interaction (NCI) Calculation

The non-covalent interaction (NCI) method is used to study weak interaction. (Johnson *et al.*, J. Am. Chem. Soc. **2010**, *132,* 6498). In the Figure, the green colour iso surface between two molecules indicates week π…π interaction.

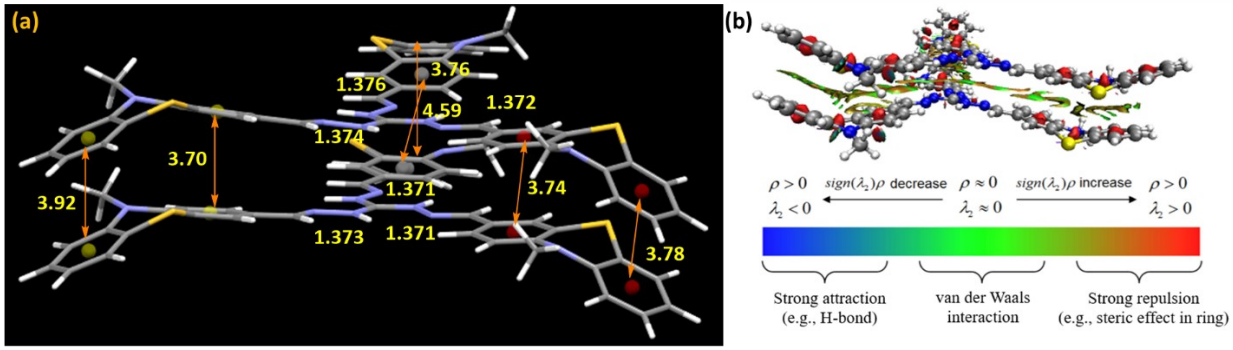


Figure S16: (a) Optimized **C3PTZ** dimer (eclipsed) with selected (N-N) bond lengths (Å) and possible centroid···centroid distances (Å). (b) Non-covalent interaction (NCI) plot with isovalue of 0.5 a.u. and λ_2 is the second largest eigenvalue of the Hessian matrix of electron density.

van der Waals interaction regions always have a very small value of electron density (ρ). On the other hand, the regions corresponding to strong steric effect or evident attractive weak interaction (e.g. H-bond, Halogen bond) have relatively large ρ value. However, the real-space

function sign (λ_2)ρ is negative for attraction interaction and is positive for steric repulsion. λ_2 is the second largest eigenvalue of the Hessian matrix of electron density.

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