Supporting information

Single-Component TADF Gels: Study of Positional Isomer Effect on Gelation and Morphological Effect on Conductivity

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1. General information

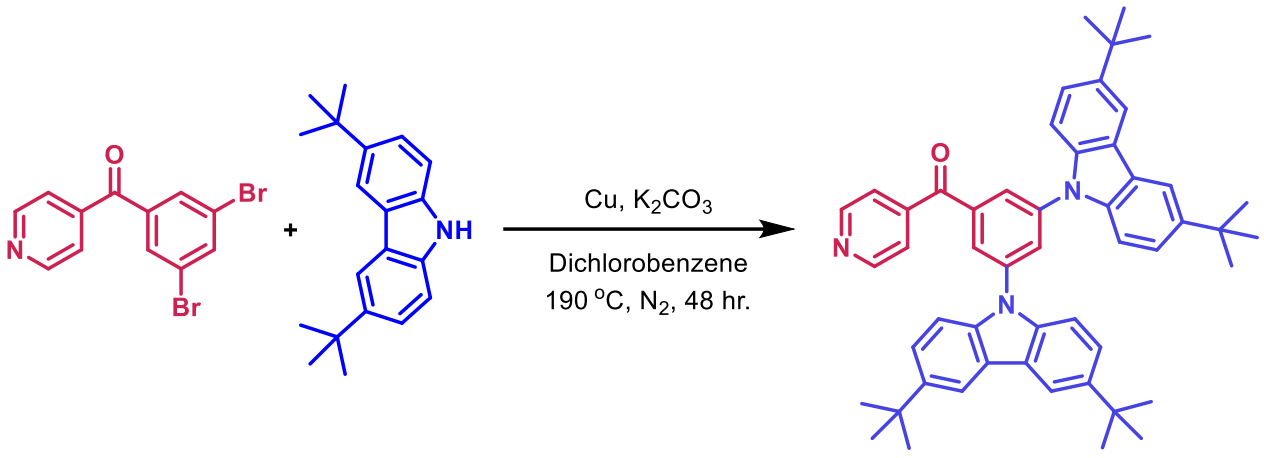
^{1}H and ^{13}C NMR were recorded in Bruker Advance 500 spectrometers, respectively. HRMS was measured using MAT-95XLHRMS. Single crystal XRDs were done in Bruker Smart Apex II Ultra X-ray diffractometer. UV-visible absorption spectra were recorded on a Jasco V-730 spectrophotometer. Fluorescence and phosphorescence spectra were recorded on a Hitachi F-7100 spectrophotometer. Photoluminescence quantum yield measurements were recorded on an integrated sphere setup connected with Hitachi F-7100 spectrophotometer. SEM images were taken from Carl Zess monochromator (MonoCL), CSLM images were taken from Leica SP8 Falcon (FLIM, FCS) confocal microscope. Transient photo luminance decay characteristics of the gel films were measured using an Edinburgh Instruments FLS980 spectrometer. The current-voltage measurement was done using a Keithley 2450 source meter. Powder XRD was measured in PANalytical X′Pert Pro X-ray diffractometer equipped with Cu Kα source (λ = 1.5406 Å).

2. Materials

The starting materials and reagents for the synthesis of emitters were commercially purchased and used without further purification. Deuterated solvent for nuclear magnetic resonance (NMR) was purchased from SYNMR CHEMICALS PVT.LTD.

3. Synthesis and NMR

Synthesis of 3,5-bis((3,6-di-*tert*-butyl-9*H*carbazol-9-yl)phenyl)(pyridin-4-yl)methanone (4BPy-*m*DTC)



Scheme S1. Synthesis of 4BPy-*m*DTC.

4BPy-*m*DTC (3,5-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)(pyridin-4-yl)methanone) was synthesized using reported procedures.[1] In an oven-dried seal tube containing magnetic stir bar initially fitted with a septa was charged with 4BPy-mDBr (3.0 g, 8.8 mmol), 3,6-di-*tert*-butyl carbazole (5.41 g, 19.3 mmol), Cu powder (1.23 g, 19.3 mmol), and K_2CO_3 (4.18 g, 38.7 mmol) was evacuated and purged with nitrogen gas three times. Under nitrogen atmosphere, anhydrous 1,2-dichlorobenzene (20 mL) was added to the reaction flask and sealed with a Teflon screw cap. The reaction mixture was stirred at 190 ºC for 48 hours. After completion of the reaction, the mixture was cooled to room temperature and filtered through a short Celite and Silica pad, and washed three times with ethyl acetate. The combined filtrate was concentrated under reduced pressure and the residue was purified by a silica gel column chromatography using ethyl acetate/*n*-hexane as the eluent to afford light green coloured (3,5-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)(pyridin-4-yl)methanone in 54% yield (3.5 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, J = 6.0 Hz, 2H), 8.12 (d, J = 1.8 Hz, 4H), 8.08 (s, 1H), 8.03 (d, J = 2.0 Hz, 2H), 7.69 (d, J = 6.1 Hz, 2H), 7.50 – 7.41 (m, 8H), 1.44 (s, 36H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.50, 150.82, 144.00, 143.58, 140.54, 139.21, 138.61, 128.65, 125.65, 124.13, 123.98, 122.85, 116.71, 108.95, 34.88, 32.04. HRMS (ES+-TOF): m/z calcd for $C_{52}H_{56}N_3O$ $[M + H]^+$, 738.4423 found, 738.4421.

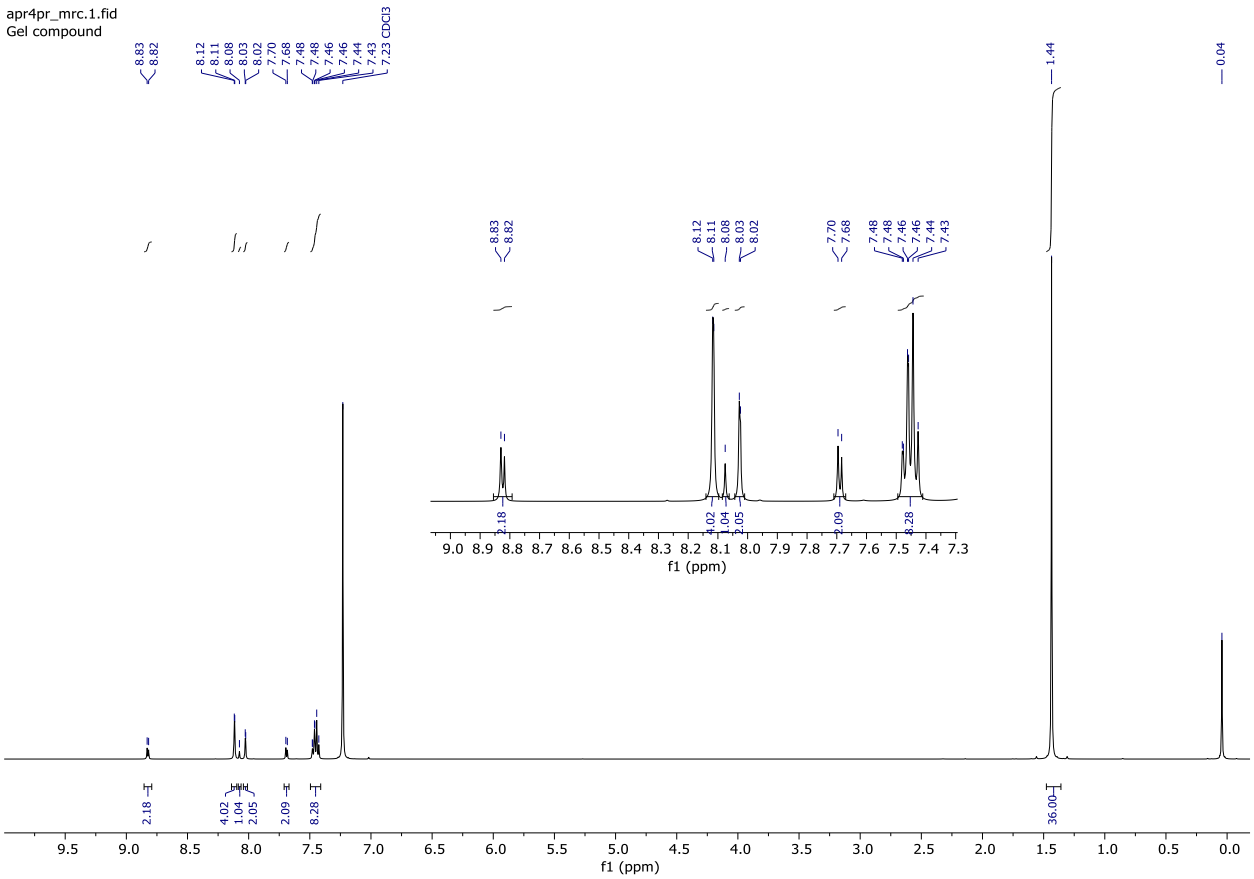


Fig. S1 ^{1}H NMR of 4BPy-*m*DTC in $CDCl_3$

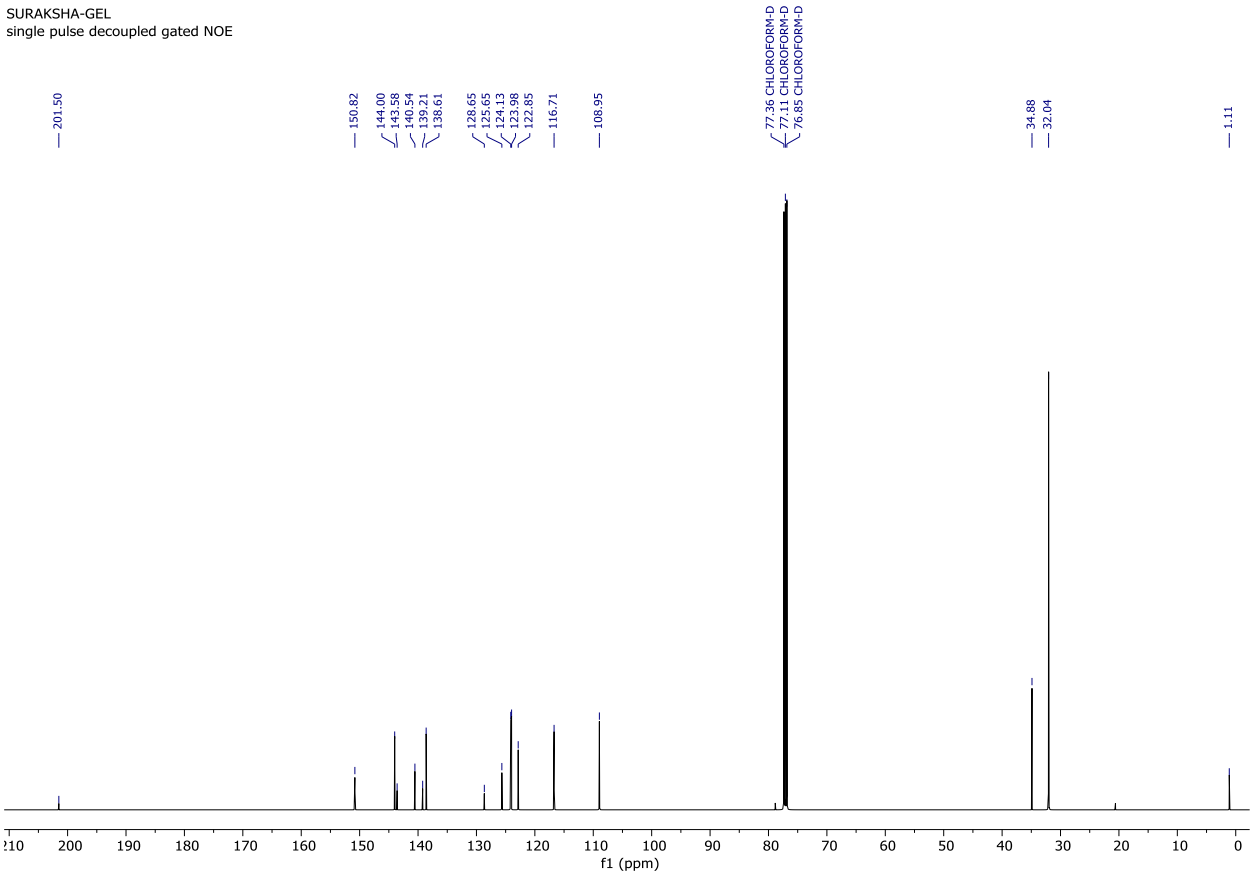


Fig. S2 ^{13}C NMR of 4BPy-*m*DTC in $CDCl_3$

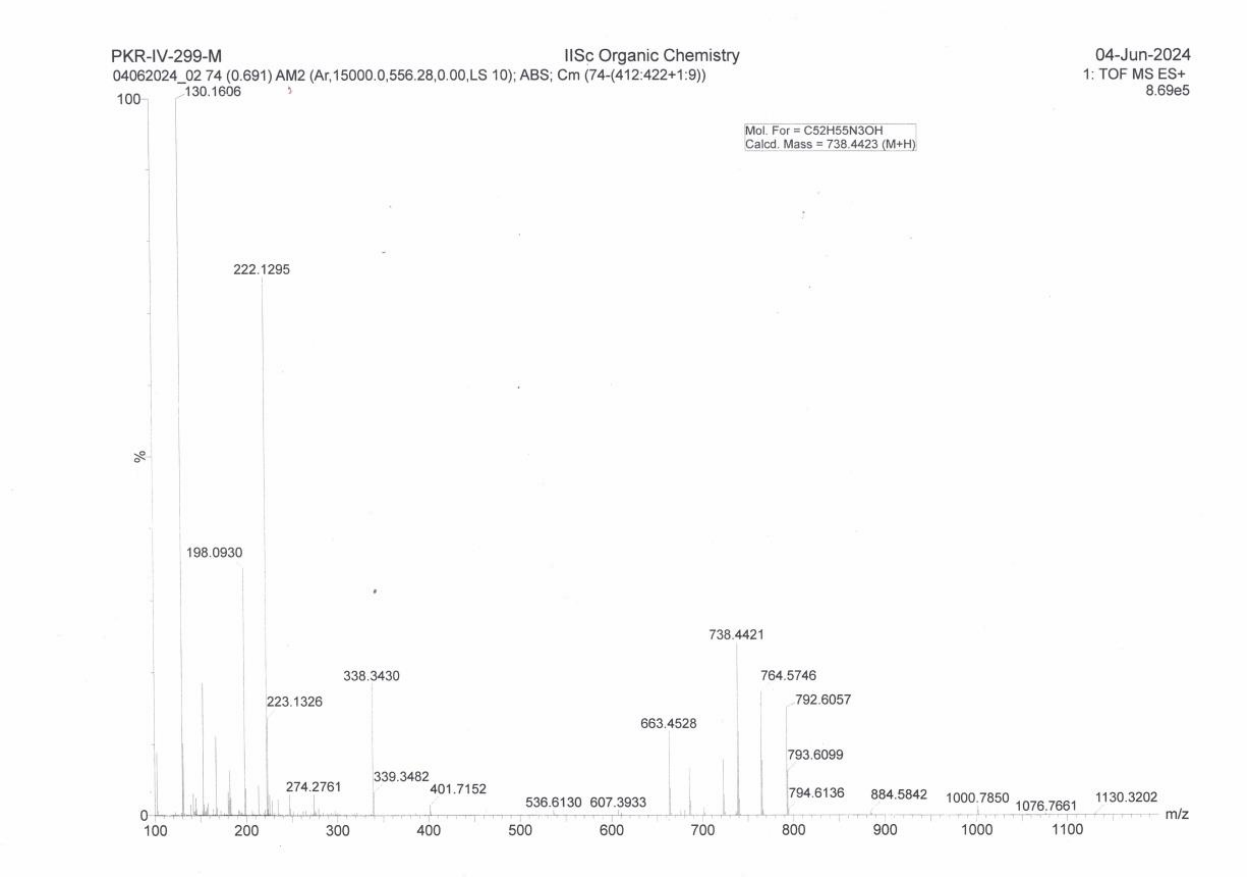
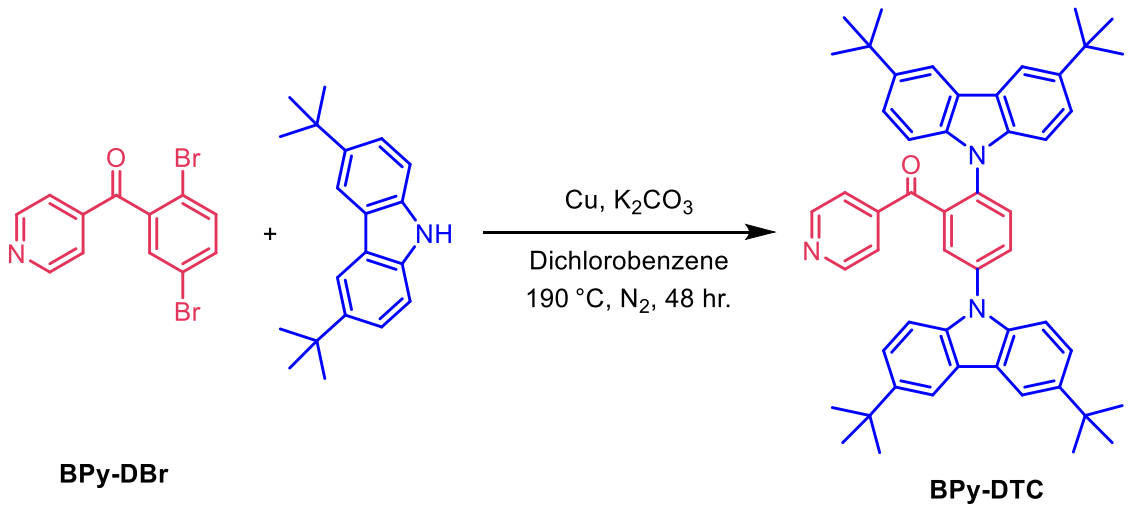


Fig. S3 HRMS of 4BPy-*m*DTC.

Synthesis of (2,5-bis(3,6-di-tert-butyl-9H-carbazol-9-yl)phenyl)(pyridin-4-yl)methanone (BPy-DTC)



Scheme S2. Synthesis of BPy-DTC.

BPy-DTC ((2,5-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)(pyridin-4-yl)methanone) was synthesized using the reported literature.[2] A procedure similar to the synthesis of 4BPy-*m*DTC was used for the synthesis of BPy-DTC using BPy-DBr (2.5 g, 7.33 mmol), 3,6-di-*tert*-butyl-9*H*-carbazole (5.1 g, 18.3 mmol), Cu (0.93 g, 14.7 mmol), K_2CO_3 (5.06 g, 36.7 mmol) and 1,2-dichlorobenzene (20 mL) to afford (2,5-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)(pyridin-4-yl)methanone) as a light greenish solid (3.4 g, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, J = 2.1 Hz, 3H), 8.04 (dd, J = 8.3, 2.6 Hz, 1H), 7.87 – 7.83 (m, 3H), 7.79 (d, J = 2.1 Hz, 2H), 7.58 – 7.50 (m, 4H), 7.45 (dd, J = 8.6, 2.0 Hz, 2H), 6.62 (d, J = 6.1 Hz, 2H), 1.47 (s, 18H), 1.42 (s, 18H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.10, 148.75, 143.95, 143.90, 142.12, 139.32, 138.77, 138.34, 136.67, 135.12, 131.08, 130.25, 129.09, 124.10, 124.00, 123.88, 123.40, 120.03, 116.65, 116.42, 109.19, 34.92, 34.85, 32.12, 32.04. HRMS (ES+-TOF): m/z calcd for $C_{52}H_{56}N_3O$ [M + H]$^+$, 738.4423 found, 738.4427.

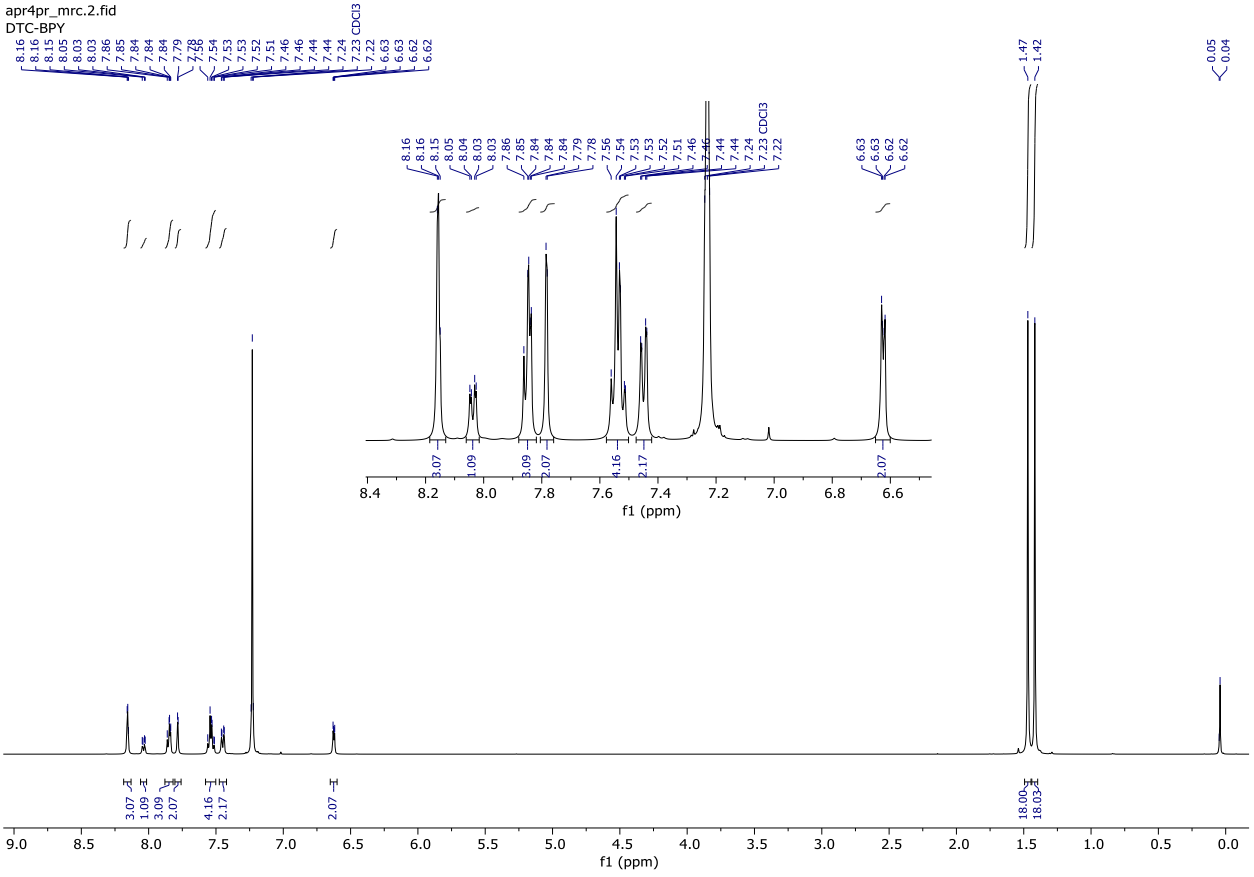


Fig. S4 ^{1}H NMR of BPy-DTC in $CDCl_3$

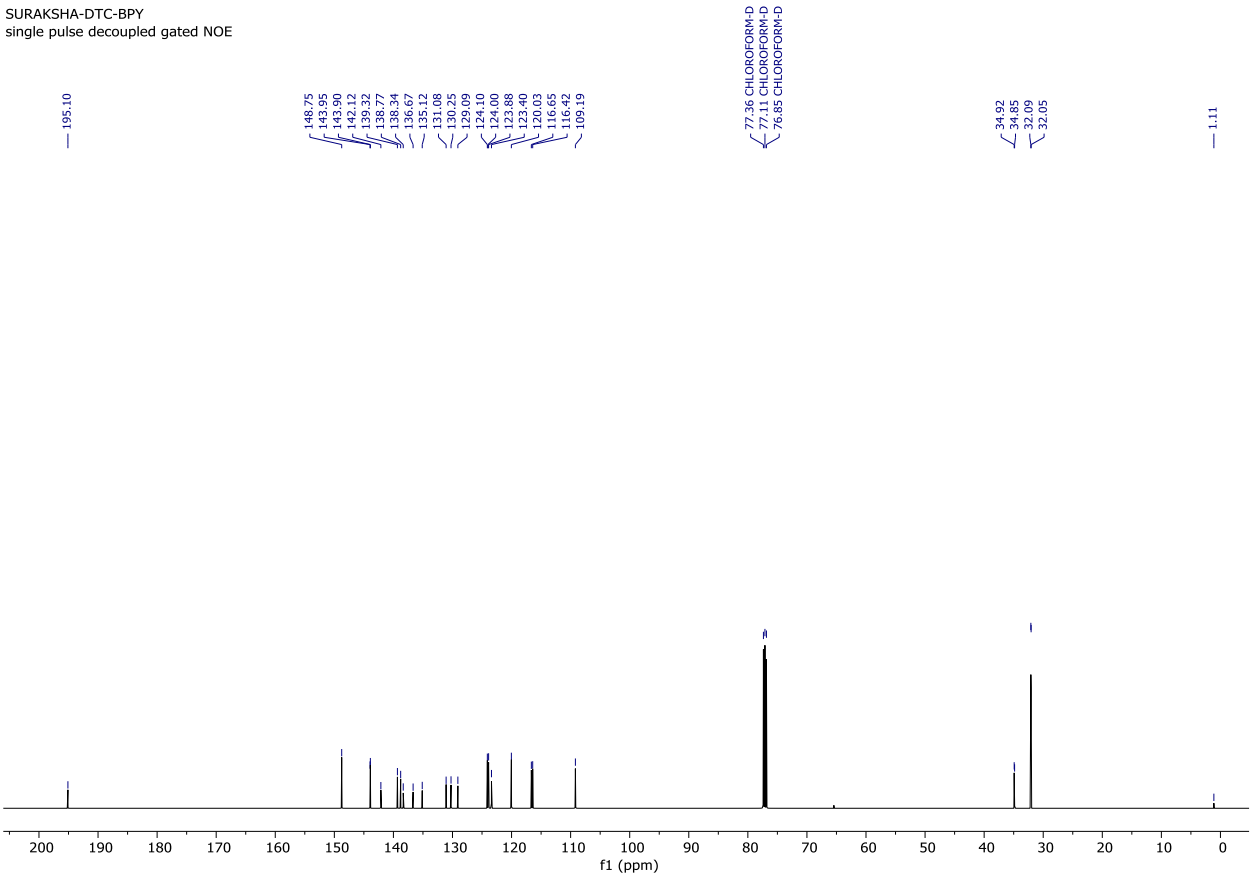


Fig. S5 ^{13}C NMR of BPy-DTC in $CDCl_3$

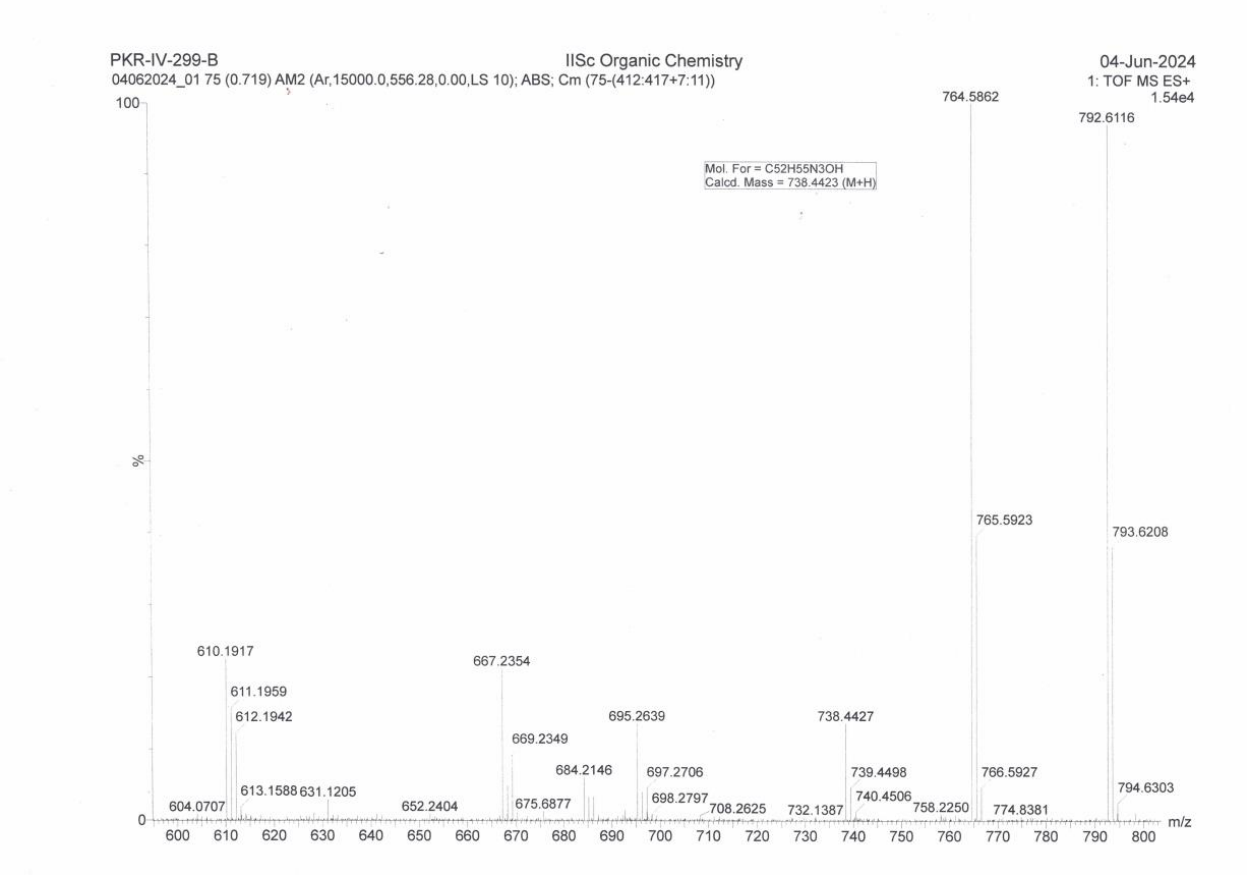


Fig. S6 HRMS of BPy-DTC.

4. Gelation study

To prepare the gel, 4 mg of 4BPy-*m*DTC was taken in a clean vial and was dissolved in 200 µl dichloromethane (DCM). To this solution, methanol (CH_3OH) was added drop wise followed by sonication, giving intense green emissive fibres. The gelation property of 4BPy-*m*DTC and BPy-DTC in different solvent combinations were checked, and observation are summarised in **Table S1**.

Table S1. Gel formation study of 4BPy-*m*DTC and BPy-DTC in different solvents.

Solvent-1	Solvent-2	4BPy-*m*DTC	BPy-DTC
Dichloromethane	Methanol	Stable gel	No gel
Dichloromethane	Ethanol	Stable gel	No gel

Dichloromethane	Isopropanol	Stable gel	No gel
Dichloromethane	Nitromethane	Not stable gel	PPT
Dichloromethane	Acetonitrile	No gel	PPT
Dichloromethane	Dimethyl sulfoxide	No gel	PPT
Dichloromethane	Dimethyl formamide	No gel	PPT
Ethyl acetate	Methanol	Stable gel	No gel
Ethyl acetate	n-Hexane	No gel	No gel
Ethyl acetate	Aniline	No gel	No gel
Tetrahydrofuran	Methanol	Not stable gel	PPT
Tetrahydrofuran	Ethanol	Not stable gel	PPT
Tetrahydrofuran	Water	Not stable gel	PPT
Acetone	Methanol	Not stable gel	No gel
Dimethyl sulfoxide	Methanol	PPT	No gel
Dimethyl formamide	Dimethyl sulfoxide	PPT	No gel

5. Rheology study

Theological studies of 4BPy-*m*DTC gel were performed in DCM+ CH_3OH solvent mixture. The viscosity vs shear stress plot shows a gradual decrease in the viscosity with increasing the stress (Fig. S7a). The amplitude sweep experiment shows that at lower shear strain range, storage modulus (G') shows higher value than the loss modulus (G''), representing the dominance of elastic nature of the gel.[3] At 8.71% shear strain, G' intercept G'' and this point corresponds to gel to sol phase transition point (Fig. S7b).

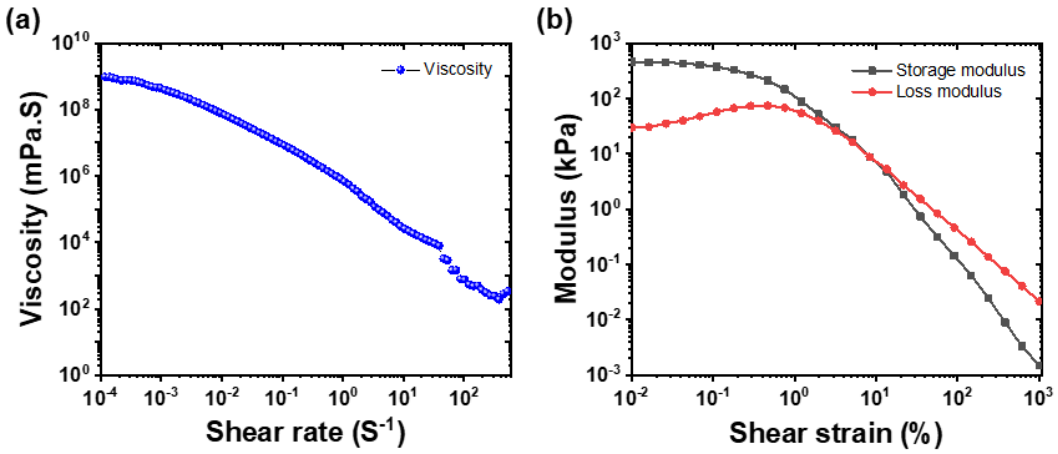


Fig. S7 (a) Viscosity vs shear stress plot; (b) amplitude sweep measurement plot of 4BPy-*m*DTC organogel in DCM+ CH_3OH.

6. CSLM images

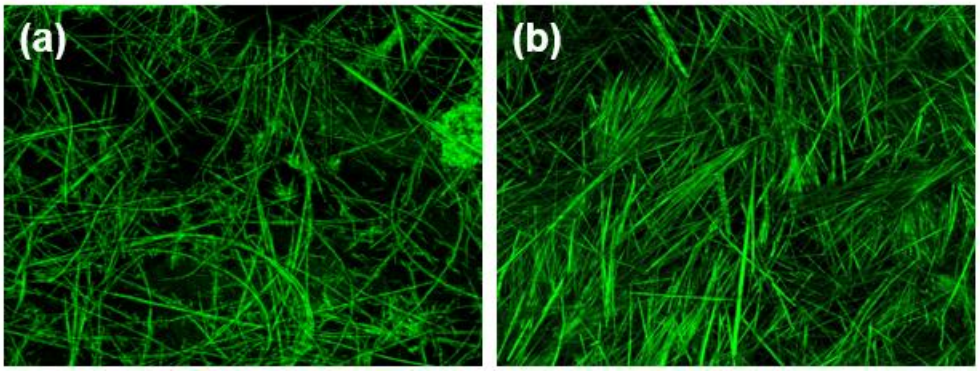


Fig. S8 Confocal scanning laser microscopic images of 4BPy-mDTC gel (a) in DCM + CH_3OH solvent mixture at CGC; (b) in diluted DCM + CH_3OH solvent mixture.

7. Single crystal XRD

While solving the crystal structures for 4BPy-*m*DTC, there are some B-level alerts remains, which are mainly coming from solvent disorder.

Table S2. Crystal data and structure refinement for 4BPy-*m*DTC

Identification code	4BPy-*m*DTC
Empirical formula	C52 H55 N3 O

Formula weight	855.11
Temperature	120 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1 P -1
Unit cell dimensions	a=12.2185(17) Å, b=12.7948(17) Å, c=16.259(2) Å
	α =95°, β =93°, γ =102°
Volume (Reported)	2466.1(6)
Z (Reported)	2
Density (Reported)	1.152 gcm^{-3}
Absorption coefficient	0.070 mm^{-1}
F(000)	916.0
Crystal size	0.30 x 0.15 x 0.15 mm3
Theta range for data collection	2.61 to 27.50°
Index ranges	$-14 \leq h \geq 15$, $-16 \leq k \geq 16$, $-21 \leq l \geq 21$
Reflections collected	47148
Independent reflections	11327 [R(int) = 0.0309]
Completeness to theta = 27.598	99%
Absorption correction	Multi-scan
Maximum and minimum transmission	0.7455 to 0.6965
Refinement method	Full-matrix least-squares on F2
Data/ restraints/ parameters	11327/ 0/ 597
Goodness- of- fit on F2	0.944

Final R indices [I>2sigma(I)]	R1 = 0.0590 and wR2 = 0.1644
R indices (all data)	R1 = 0.0696 and wR2 = 0.1742
Largest diff. peak and hole	0.564 and -0.619 e Å^3
CCDC	2329995

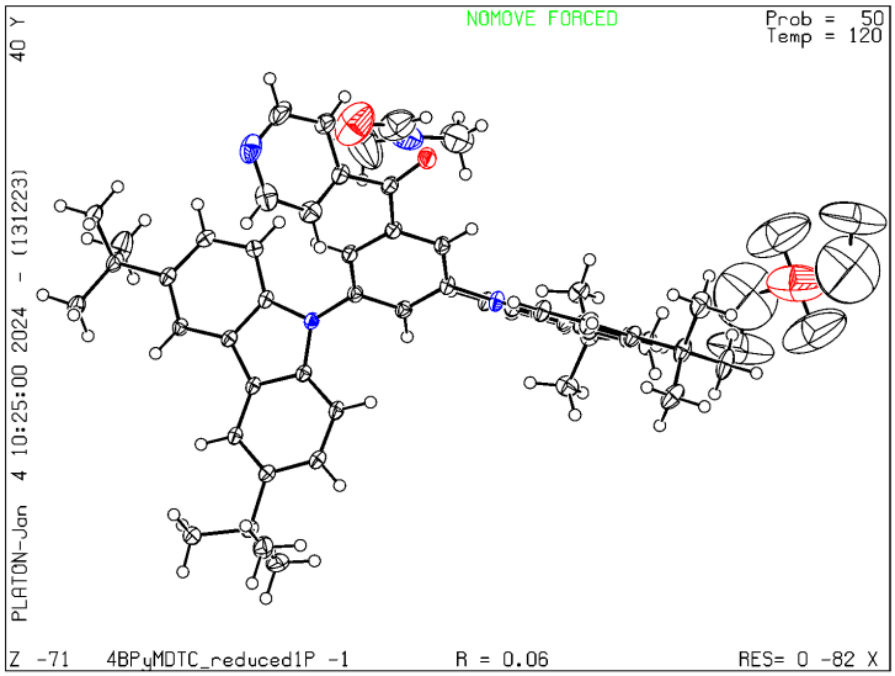


Fig. S8 View of 4BPy-*m*DTC obtained from single crystal XRD analysis (CCDC: 2329995). Displacement ellipsoid representation for 4BPy-*m*DTC (ellipsoids are drawn at 50% probability).

Table S3. Crystal data and structure refinement for BPy-DTC[2]

Identification code	BPy-DTC
Empirical formula	C52 H55 N3 O
Formula weight	737.99
Temperature	296 K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P 21/c

Unit cell dimensions	a=16.3143(3) Å, b=19.5553(4) Å, c=13.7512(2) Å
	α =90°, β =93°, γ =90°
Volume (Reported)	4380.94(14)
Z (Reported)	4
Density (Reported)	1.119 gcm^{-3}
Absorption coefficient	0.505 mm^{-1}
F(000)	1584.0
Crystal size	0.30 x 0.15 x 0.15 mm3
Theta range for data collection	2.7123 to 66.2445°
Index ranges	$-19 \leq h \geq 19$, $-23 \leq k \geq 23$, $-7 \leq l \geq 16$
Reflections collected	29531
Independent reflections	7571 [R(int) = 0.0322]
Completeness to theta = 66.660	97.6%
Absorption correction	Multi-scan
Maximum and minimum transmission	0.9492 and 0.8437
Refinement method	Full-matrix least-squares on F2
Data/ restraints/ parameters	7571/ 522/ 678
Goodness- of- fit on F2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0529 and wR2 = 0.1454
R indices (all data)	R1 = 0.0703 and wR2 = 0.1605
Largest diff. peak and hole	0.233 and -0.178 e $Å^3$
CCDC	1419353

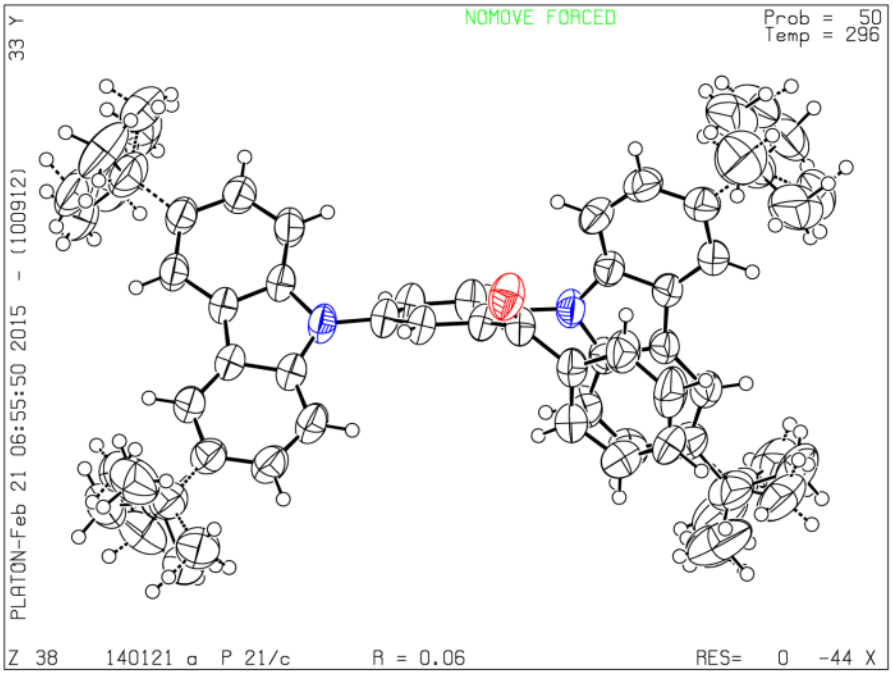


Fig. S9 View of BPy-DTC obtained from single crystal XRD analysis (CCDC: 1419353). Displacement ellipsoid representation for BPy-DTC (ellipsoids are drawn at 50% probability).

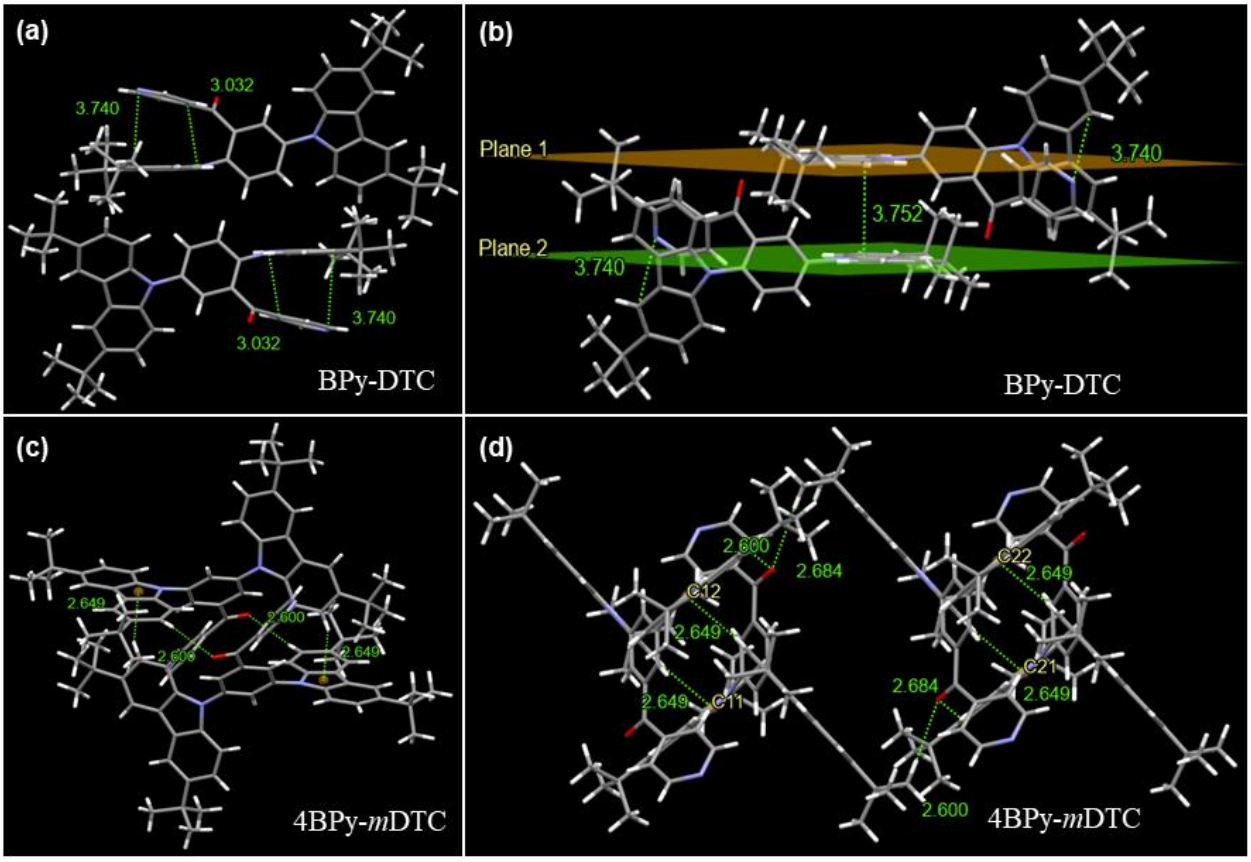


Fig. S10 (a) BPy-DTC dimer showing intramolecular interaction; (b) BPy-DTC dimer with π·π stacking; (c) 4BPy-mDTC dimer interacting through CH···π and CO···H interactions; (d) two dimers of 4BPy-mDTC interacting through CH···π interaction; [Colour code; grey = carbon; white = hydrogen; blue = nitrogen; red = oxygen].

8. Thin film XRD

For the small angle thin film XRD analysis the wavelength (λ) of the X-ray used was 1.54 Å.

d-spacing was calculated using the equation.[4]

$$n\,\lambda = 2d \times \sin\theta \qquad (1)$$

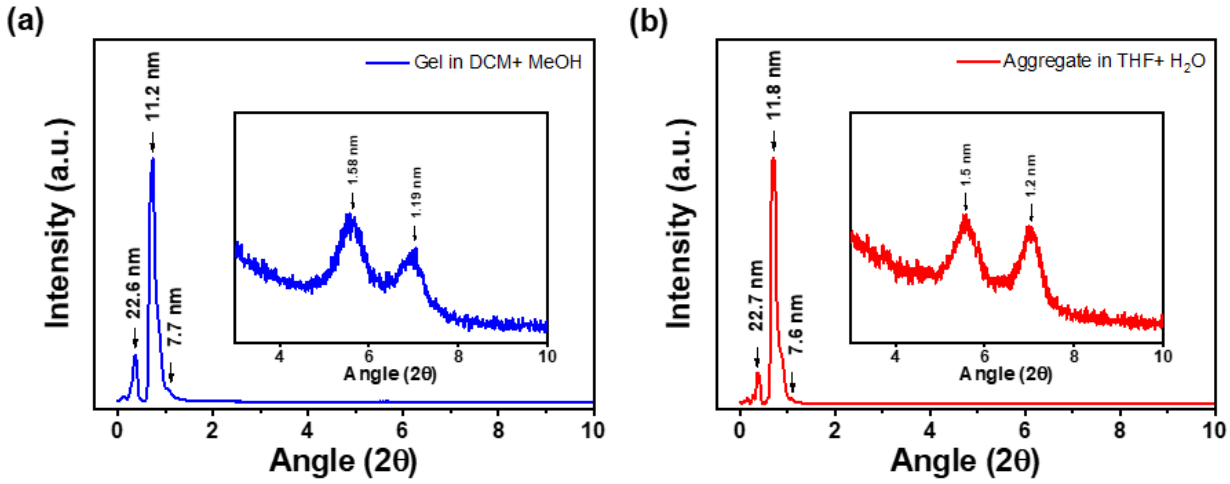


Fig. S11 Small angle thin film XRD of (a) 4BPy-*m*DTC fibrous gel obtained in DCM+ CH_3OH solvent fixture; (b) Fettuccine aggregate obtained in THF+ H_2O solvent mixture.

9. Photophysical studies

Absorbance and PL measurement of 4BPy-*m*DTC. In toluene solution emitter shows a broad absorption band at 370 nm. The emission maxima (λ_{max}) of toluene solution and gel film is nearly same, but the gel film has shorter FWHM due to enhanced rigidity.

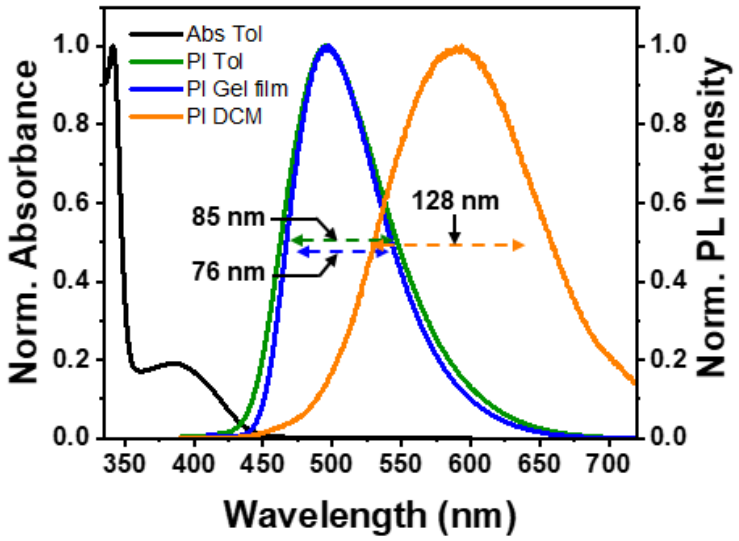
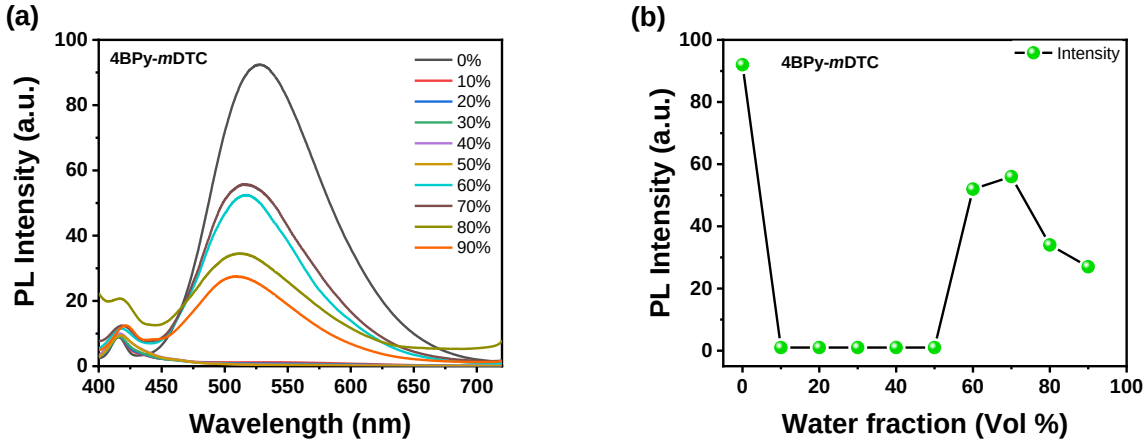


Fig. S12 Absorbance of 4BPy-*m*DTC in toluene solution; PL of 4BPy-*m*DTC in toluene, dichloromethane, and in gel film.

AIE study of 4BPy-*m*DTC in THF+ H_2O solvent mixture with varying water volume fraction. Clearly the PL intensity of initial THF solution is more than the aggregated solution.



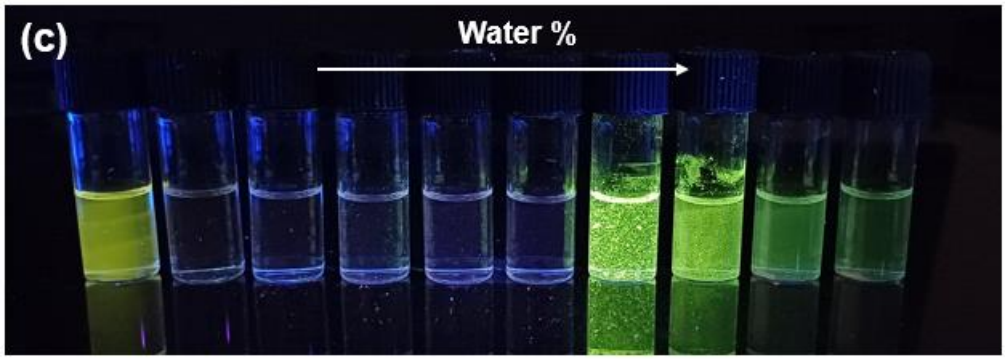


Fig. S13 AIE study of 4BPy-*m*DTC in THF+ H_2O solvent mixture with increasing water volume fraction; (a) PL intensity of 4BPy-*m*DTC in THF solution with different water volume fraction; (b) water volume fraction Vs PL intensity plot; (c) digital photograph of AIE study.

Absorption band of 4BPy-*m*DTC fibrous gel formed in DCM+ CH_3OH solvent mixture and toluene solution were compared.

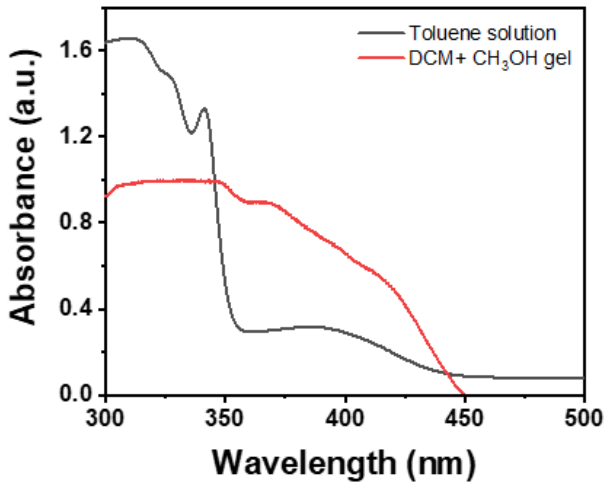


Fig. S14 Absorbance comparison of 4BPy-*m*DTC in toluene solution and in DCM+ CH_3OH fibrous gel.

10. Powder XRD

For the powder XRD analysis the wavelength (λ) of the X-ray used was 1.5406 Å.

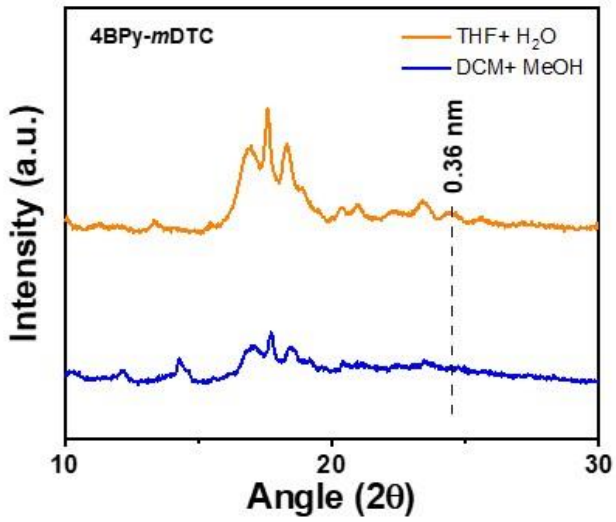


Fig. S15 Powder XRD of 4BPy-*m*DTC self-assembly formed in DCM+ CH_3OH and in THF+ H_2O solvent mixture.

11. Lifetime measurement

Ignoring the non-radiative decay from T_1 to S_0, the rate constants of all transitions were calculated using below equations (I to VII).[5, 6] The rate constant values are mentioned in **Table S4**.

$$K_p(R) = \varphi_p / \tau_p \quad \text{(I)}$$

$$K_p(T) = 1 / \tau_p \quad \text{(II)}$$

$$K_D(R) = \varphi_D / \tau_D \quad \text{(III)}$$

$$K_D(T) = 1 / \tau_D \quad \text{(IV)}$$

$$K_{IC} = K_p(T) - [K_p(R) + K_{ISC}] \quad \text{(V)}$$

$$K_{ISC} = [\varphi_D + K_{ISC}] / \varphi_T \quad \text{(VI)}$$

$$K_{RISC} = [K_D(T) \times K_P(T) \times \varphi_D] / [\varphi_T \times K_{ISC}] \quad \text{(VII)}$$

Where,

φ_T is the total PLQY under inert condition

φ_P is the PLQY under air

τ_p and τ_d are the prompt and delayed lifetimes, respectively

$K_P(R)$ is the prompt radiative rate constant

$K_P(T)$ is the total prompt rate constant

$K_D(R)$ is the delayed radiative rate constant

$K_D(T)$ is the total delayed rate constant

K_{IC} is the internal conversion rate constant

K_{ISC} is the intersystem crossing rate constant

K_{RISC} is the reverse intersystem crossing rate constant.

Table S4. Transient lifetime measurement of 4BPy-*m*DTC.

Emitter	φ_T /%	φ_P /%	τ_p /ns	τ_D /us	$K_{p(R)}$ /s^{-1}	$K_{p(T)}$ /s^{-1}	$K_{D(R)}$ /s^{-1}	$K_{D(T)}$ /s^{-1}	K_{IC} /s^{-1}	K_{ISC} /s^{-1}	K_{RISC} /s^{-1}
Gel	36.0	22.0	10.5	41.7	2.1 x 10^7	0.9 x 10^8	0.3 x 10^4	2.4 x 10^4	3.7 x 10^7	3.7 x 10^7	0.4 x 10^5
Tol	7.5	1.7	2.0	0.5	0.8 x 10^7	5.0 x 10^8	1.3 x 10^5	2.2 x 10^6	1.0 x 10^8	3.8 x 10^8	12.4 x 10^6

12. Electrical conductivity measurement

For electrical conductivity measurement, on a grass plate two strips of silver (Ag) layers were deposited. The Ag layer is used as electrode and the distance between them was maintained as 3 mm. On top of the electrode, gels were drop casted. By applying voltage (from -20 V to + 20V) across the electrode the corresponding current values were recorded.[7, 8]

$$R = V/I = \rho\,(L/A) = 1/G$$

$$\sigma = 1/\rho$$

$$R = 1/\text{ slop}$$

Table S5. Conductivity measurement parameters for 4BPy-*m*DTC self-assembly

Parameters	Assembly in DCM+ CH_3OH	Assembly in THF+ H_2O
Slop from linear fitting of I-V curve	4.45833×10^{-7}	2.52254×10^{-6}
Resistance (R)	0.222429×10^{7} Ω	0.39642×10^{6} Ω
Length between two electrodes (L)	0.003 m	0.003 m
Cross sectional area of gel film (A)	0.00000166 m^2	0.00000125 m^2
Conductance (G)	4.45833×10^{-7} S	2.52254×10^{-6} S
Resistivity (ρ)	1241.07 Ω m	165.175 Ω m
Conductivity (σ)	8.05×10^{-4} S/m	6.05×10^{-3} S/m

13. Reference

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