

Supporting Information

Photo-Modulated Wide-Spectrum Chromism in Eu^{3+} and $\text{Eu}^{3+}/\text{Tb}^{3+}$ Photochromic Coordination Polymer Gel: Application in Decoding Secret Information

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S1. Materials and physical measurements:

3,5-dibromo-2-methyl thiophene, octafluorocyclopentene, n-butyl lithium in hexane (2.5 M), triethyl orthoformate, 4'-chloro-2,2':6',2''-terpyridine, 1,3-diamino propane, Trichloroisocyanuric acid, Triphenylphosphine, Europium nitrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Terbium nitrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) were purchased from Sigma-Aldrich Chemical Co. Ltd. and used for synthesis as such. All the reagents were commercially available and used as supplied without further purification. All the synthesis and photophysical studies were carried out using HPLC grade solvents obtained from Sigma-Aldrich Chemical Co. Ltd. For column chromatography, solvents were purchased from Finar Ltd, India, and used as such. Deuterated chloroform (CDCl_3) and DMSO-D_6 were purchased from Sigma-Aldrich Chemical Co. Ltd and used for ^1H and ^{13}C -NMR as such. ^1H -NMR spectra were recorded in Bruker AV-400 spectrometer with chemical shifts recorded as ppm, and all spectra were calibrated against TMS. UV-Vis spectra were recorded in a Perkin-Elmer Lambda 900 spectrometer. For *in-situ* photoreaction study, ocean optic spectrometer was used (light source: DT-MINI-2-GS: 057781227; detector: Jaz spectral sensing suite: JAZA3265). The photoluminescence properties were performed in Fluorolog 3.21 spectrofluorimeter (Horiba Jobin-Yvon) instrument. Absolute quantum yield was measured in solution state using Edinburgh Instruments Steady State PL Spectrometer. Fluorescence decay profiles were recorded in a time-correlated single-photon counting spectrometer of Horiba-Jobin Yvon (Ti-sapphire laser with 310 nm). Hamamatsu (C11924-201) laser was used as UV light source ($365 \text{ nm} \pm 5 \text{ nm}$). Whereas, Schott KL 1600 LED light (1418057: $\lambda > 400 \text{ nm}$) was used as visible light source. Fourier transform infrared spectroscopy (FT-IR) was performed on a Bruker IFS 66v/S spectrophotometer. Morphological studies have been carried out using Lica-S440I Field Emission Scanning Electron Microscope (FE-SEM) by placing samples on a silicon wafer under a high vacuum with an accelerating voltage of 100 kV. Transmission electron microscopy (TEM) studies were performed in JEOL JEM -3010 with an accelerating voltage of 300 kV. Powder X-ray diffraction (PXRD) patterns were measured by a Bruker D8 Discover instrument using $\text{Cu-K}\alpha$ radiation. These measurements were carried out using a Thermo Scientific Flash 2000 CHN analyzer. The rheological study was done by Anton Paar Rheometer MCR 702.

S2. Experimental details:

Spectrophotometric studies: In a typical spectrophotometric titrations experiment, the UV-Vis absorption spectra was recorded upon gradual addition of methanolic solution of

Eu(NO₃)₃·6H₂O or Tb(NO₃)₃·6H₂O (stock solution=10⁻⁴ M) to the methanolic solution of TPY-DTE solution (c = 10⁻⁶ M, V= 3.0 ml) in a range of 0→2 equivalents. For *in-situ* photoisomerization study (Figure S8), a dilute dispersion of sample in methanol (10⁻⁴ M) was prepared and UV-Vis spectra were measured in a regular time-interval upon continuous UV as well as Visible light irradiation. Reaction kinetics of the photo-isomerization process was studied in the gel state. The sample was prepared by making a thin-film of gel sample over a glass plate.

Lifetime measurements: The excited-state lifetime measurement was performed for both, Eu-pcCPG and Tb-pcCPG by preparing a thin-film of gel sample over a glass plate. The decay spectra for photoisomers of Eu-pcCPG were collected at 615 nm upon exciting at 310 nm. Whereas, decay spectra for the photoisomers of Tb-pcCPG sample were collected at 546 nm upon exciting at 310 nm. Excited-state lifetime spectra for the photoisomers of both, Eu-pcCPG and Tb-pcCPG were fitted using biexponential decay.

FT-IR spectroscopy study: FT-IR study was performed in the region 4000–400 cm⁻¹ by making KBr pellets. FT-IR spectra for the photo-isomers of Eu-pcCPG and Tb-pcCPG were recorded by shining the UV as well as visible light on the prepared KBr pellets.

Sample preparation for FESEM and TEM studies: For FE-SEM measurement, xerogels of TPY-DTE organo gel, Eu-pcCPG-O and Tb-pcCPG-O were dispersed individually in ethanol and then drop-casted onto a small piece of silicon wafer. Next, the same samples which prepared for the FE-SEM was drop-casted on the carbon-coated copper grid and allowed to dry at room temperature for the TEM measurement. For analysis of close form (TPY-DTE-C and Eu-pcCPG-C), the ethanolic dispersion was irradiated under UV light followed by drop-casting on grid and dried under the dark condition at room temperature. To check the reversibility of morphology, the UV-irradiated ethanolic dispersion was further irradiated under visible light and then again drop-casted on the grid followed by drying at room temperature.

PXRD: PXRD pattern of samples was measured in the xerogel state.

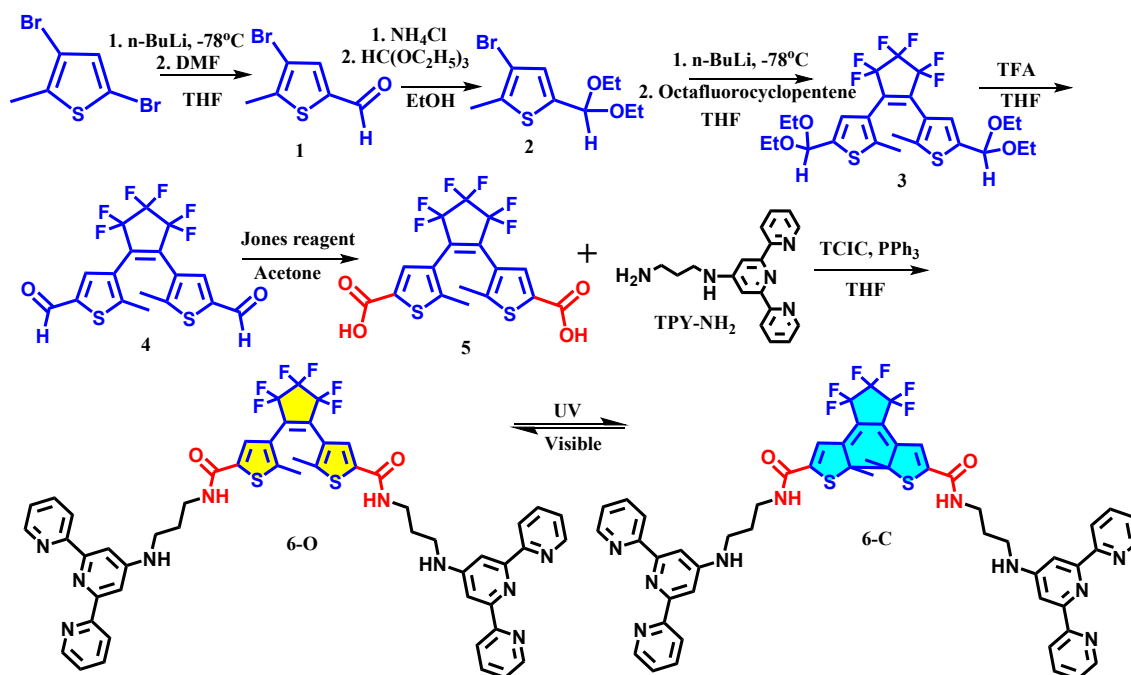
Rheological study: Rheology study was performed first with the gel sample (15 mg) in open form. Next, UV-light was irradiated to the sample without disturbing it in order to get the viscoelastic behaviour of the close form under similar condition as employed for the open form.

Encryption and decryption applications: For writing application, the photochromic sample (TPY-DTE-OG or Eu-pcCPG) (5 mg) was taken in the ethanol (5 ml). Next, we have used

ordinary A4 size paper for coating the organo gel sample. Whereas, Eu-pcCPG was coated on non-emissive paper in order to demonstrate secret writing application.

S3. Synthesis of TPY-DTE LMWG:

Synthetic scheme for the new low molecular weight gelator (LMWG) TPY-DTE is given in the scheme S1. The synthesis was carried out in four main steps as mentioned below.



Scheme S1. Synthetic scheme for TPY-DTE LMWG.

S3.1. Synthesis of 4,4'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-methylthiophene-2-carboxylic acid): [Compound 5: DTE(COOH)₂]: The synthesis of DTE(COOH)₂ was done by following a literature procedure.^[1] The stepwise synthesis is as follows:

1st Step: Synthesis of 4-bromo-5-methylthiophene-2-carbaldehyde [Compound 1]: To a solution of commercially available 3,5-dibromo-2-methyl thiophene (10 g, 39.1 mmol) in anhydrous THF (100 ml), n-butyl lithium in hexane (2.5 M, 19.5 ml, 48.7 mmol) was added dropwise at -78 °C and stirred for 1 hour at the same temperature. Next, DMF (3.9 ml, 50.7 mmol) was added to the reaction mixture and left on stirring further for 2 hours at the same temperature (-78 °C). The reaction mixture was allowed to attain room temperature and quenched with distilled water (100 ml). The compound was extracted with ethyl acetate (5×200 ml). The combined organic layer was washed successively with water (4×200 ml) and brine solution (500 ml). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography using silica gel (60-120 mesh size) and ethyl acetate-hexane mixture (4% ethyl acetate in hexane) as eluent to afford a

yellow solid crystalline compound of 4-bromo-5-methylthiophene-2-carbaldehyde (compound 1) (yield 5.8 g, 72.5 %). ¹H-NMR (400 MHz, CDCl₃): δ: 9.76 (s, 1 H), 7.59 (s, 1H), 2.49(s, 3H).

2nd Step: Synthesis of 3-bromo-5-(diethoxymethyl)-2-methylthiophene [Compound 2]:

To a solution of compound 1 (6.0 g, 29.3 mmol) in ethanol (120 ml), triethyl orthoformate (5.4 ml, 35.1 mmol) and NH₄Cl (780 mg, 14.6 mmol) were added at room temperature. The resulting reaction mixture was refluxed for 18 hours at 90°C. After that, the solvent was removed in a rotary evaporator under reduced pressure. The residue was solubilized in diethyl ether and subsequently washed with a saturated aqueous solution of sodium bicarbonate (500 ml) followed by distilled water (400 ml) and brine (200 ml). Next, the organic layer was evaporated in a rotary evaporator under reduced pressure and afforded yellowish liquid of 3-bromo-5-(diethoxymethyl)-2-methylthiophene (compound 2). The yield of pure product was found to be 93.5 % (7.6 g). ¹H-NMR (400 MHz, CDCl₃): 6.88 (s, 1H), 5.61 (s, 1H), 3.60 (m, 4H), 2.36 (s, 3H), 1.23 (t, *J* = 7.04 Hz, 6H).

3rd Step: Synthesis 4,4'-(Perfluorocyclopent-1-ene-1,2-diyl) bis(5-methylthiophene-2-carbaldehyde) [Compound 4]: To a solution of compound 2 (8.0 g, 28.7 mmol) in anhydrous THF (80 mL), n-butyl lithium in hexane (2.5 M, 14.9 mL, 37.3 mmol) was added dropwise at -78 °C and stirred for 1 hour at same temperature. Then, Octafluorocyclopentene (1.8 mL, 13.5 mmol) was added dropwise at -78 °C. The resulting mixture was stirred at -78 °C for 4 hours and subsequently allowed to stir at room temperature for 8 hours. The reaction mixture was quenched with distilled water (100 mL), and the organic product was extracted in diethyl ether (5 × 200 mL). The combined organic layer was washed with water (5 × 100 mL), brine (300 mL), and dried over anhydrous Na₂SO₄. The solvent was evaporated in rotary evaporator under reduced pressure to yielded 3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(5-(diethoxymethyl)-2-methylthiophene) (compound 3). Next, compound 3 was dissolved in THF (150 mL), and trifluoroacetic acid (6.7 mL, 87.5 mmol) was added to it, and the reaction mixture was stirred at room temperature for 2 hours. The reaction mixture was then concentrated under reduced pressure, and the residue was triturated with hexane (200 mL). The solid product (compound 4) was collected by filtration and washed with hexane (500 mL) under suction. The crude product was purified by column chromatography using silica gel 60-120 mesh size and ethyl acetate-hexane mixture (20 % ethyl acetate in hexane) as eluent to afford title compound 4 (4.1 g, 34 %) as pale-yellow solid. ¹H NMR (400 MHz, CDCl₃) δ: 9.89 (s, 2 H), 7.76 (s, 2H), 2.05 (s, 6H).

4th Step: Synthesis of 4,4'-(Perfluorocyclopent-1-ene-1,2-diyl) bis (5-methylthiophene-2-carboxylic acid) [compound 5: DTE(COOH)₂]: Freshly prepared John's reagent (16 ml) was added dropwise to an acetone solution of compound 4 (1.6 g, 3.8 mmol) at 0°C and the reaction mixture was stirred for 5 hours at room temperature. Next, the reaction mixture was quenched by iso-propyl alcohol (IPA) (5 ml) and diluted with water (50 ml). The desired product was extracted with diethyl ether (6 × 200 ml) and then the combined diethyl ether layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude organic product was purified by recrystallization in the mixture of ethyl acetate (5 ml)/hexane (15 ml) to afford compound 5 (1.5 g). The yield of pure product was found to be 87 %. ¹H NMR (400 MHz, DMSO-d₆) δ: 13.29 (s, 2H), 7.67 (s, 2H), 1.97 (s, 6H). Anal. calcd for C₁₇H₁₀F₆O₄S₂: C, 44.74; H, 2.21; S, 14.05 %. Found: C, 44.81; H, 2.63; S, 14.29 %. HRMS: calcd for C₁₇H₁₀F₆O₄S₂: 455.9925. Found: 455.9928 [M]⁺.

S3.2. Synthesis of 2,2':6',2''-terpyridin-4'-yl-propane-1,3-diamine (TPY-NH₂): Synthesis and characterization of 2,2':6',2''-terpyridin-4'-yl-propane-1,3-diamine (TPY-NH₂) is reported in the literature, and we have followed a similar procedure.^[2] In brief, 4'-chloro-2,2':6',2''-terpyridine, (300 mg, 1.12 mmol) was suspended in 1,3-diamino propane (2.16 ml) and refluxed at 120 °C for overnight. After cooling to room temperature, around 25 mL of distilled water was added, which yielded a white precipitate. The obtained precipitate was filtered and further washed with 100 ml of distilled water (4-5 times). The solid white precipitate was further dissolved in dichloromethane and washed twice with distilled water. The organic layer was dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure to yield a solid white product. The solid white product was dried under vacuum at 100°C for 12 hours and then characterized by ¹H-NMR. Yield: 82%. ¹H-NMR (400 MHz, CDCl₃): δ: 8.66 (d, *J* = 4.60 Hz, 2H), 8.60 (d, *J* = 7.81 Hz, 2H), 7.82 (t, *J* = 6.28 Hz, 2H), 7.66 (s, 2H), 7.29 (t, *J* = 6.16 Hz, 2H), 5.06 (m, 1H), 3.46 (m, 2H), 2.90 (t, *J* = 6.48 Hz, 2H), 1.83 (quint, *J* = 6.52 Hz, 2H), 1.25 (m, 2H). Anal. calcd for C₁₈H₁₉N₅: C, 70.80; H, 6.27; N, 22.93 %. Found: C, 70.90; H, 6.11; N, 22.83 %. HRMS: calcd for C₁₈H₁₉N₅: 305.1640. Found: 306.1715 [M+H]⁺.

S3.3. Synthesis of DTE integrated low molecular weight gelator (LMWG) (TPY-DTE): The new photochromic gelator (TPY-DTE LMWG) was synthesized via amide coupling between DTE(COOH)₂ and TPY-NH₂. In brief, compound 5 (400 mg, 0.87 mmol), trichloroisocyanuric acid (TCIC) (426 mg, 1.84 mmol) and triphenylphosphine (PPh₃) (482 mg, 1.84 mmol) were taken together in anhydrous THF (50 ml) and subsequently stirred for 2 hours under the inert condition at room temperature. Next, solution of TPY-NH₂ (561 mg, 1.84

mmol) in the mixture of anhydrous THF (8 ml) and triethylamine (514 μ l, 3.6 mmol) was added into it and stirred further for 8 hours under the same condition. Reaction progress was monitored by TLC analysis. After completion of the reaction, reaction mixture was filtered, and filtrate was evaporated under reduced pressure. The crude product was washed with 40 ml chloroform (4-5 times) followed by diethyl ether (10 ml) and resulted in the pure yellowish product (TPY-DTE LMWG Open form, i.e., compound **6-O**) (254 mg, 28 %). The characterization of compound (6-O), i.e., TPY-DTE LMWG in open form, is as follows. $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ : 8.66 (m, 4H), 8.55 (d, $J = 7.6$ Hz, 4H), 7.93 (t, $J = 8.6$ Hz, 4H), 7.69 (m, 4H), 7.43 (m, 4H), 7.28 (s, 2H), 7.05 (s, 2H), 3.79 (m, 2H), 3.32 (m, 4H), 2.97 (m, 4H), 1.94 (m, 4H), 1.78 (s, 6H). ^{13}C {H} NMR (150 MHz, $\text{DMSO-}d_6$): δ : 15.48, 26.70, 31.88, 63.22, 121.84, 125.06, 128.50, 138.23, 145.25, 150.12, 156.19, 156.66, 157.19, 164.83. Selected FT-IR data (KBr, cm^{-1}) for TPY-DTE LMWG (open form): 3462 (b), 2980 (m), 2920 (m), 1696 (s), 1549 (s), 1472 (s), 1387 (s), 1341 (s), 1273 (s), 1188 (s), 1120 (s), 1041 (s), 988 (s), 892 (m), 755 (m), 664 (m), 536 (m), 473 (m). Anal. calcd for $\text{C}_{53}\text{H}_{44}\text{F}_6\text{N}_{10}\text{O}_2\text{S}_2$: C, 61.74; H, 4.30; N, 13.58; S, 6.22 %. Found: C, 60.90; H, 4.11; N, 12.83, S, 6.98 %. HRMS: calcd for $\text{C}_{53}\text{H}_{44}\text{F}_6\text{N}_{10}\text{O}_2\text{S}_2$: 1030.2994. Found: 1031.3073 $[\text{M}+\text{H}]^+$.

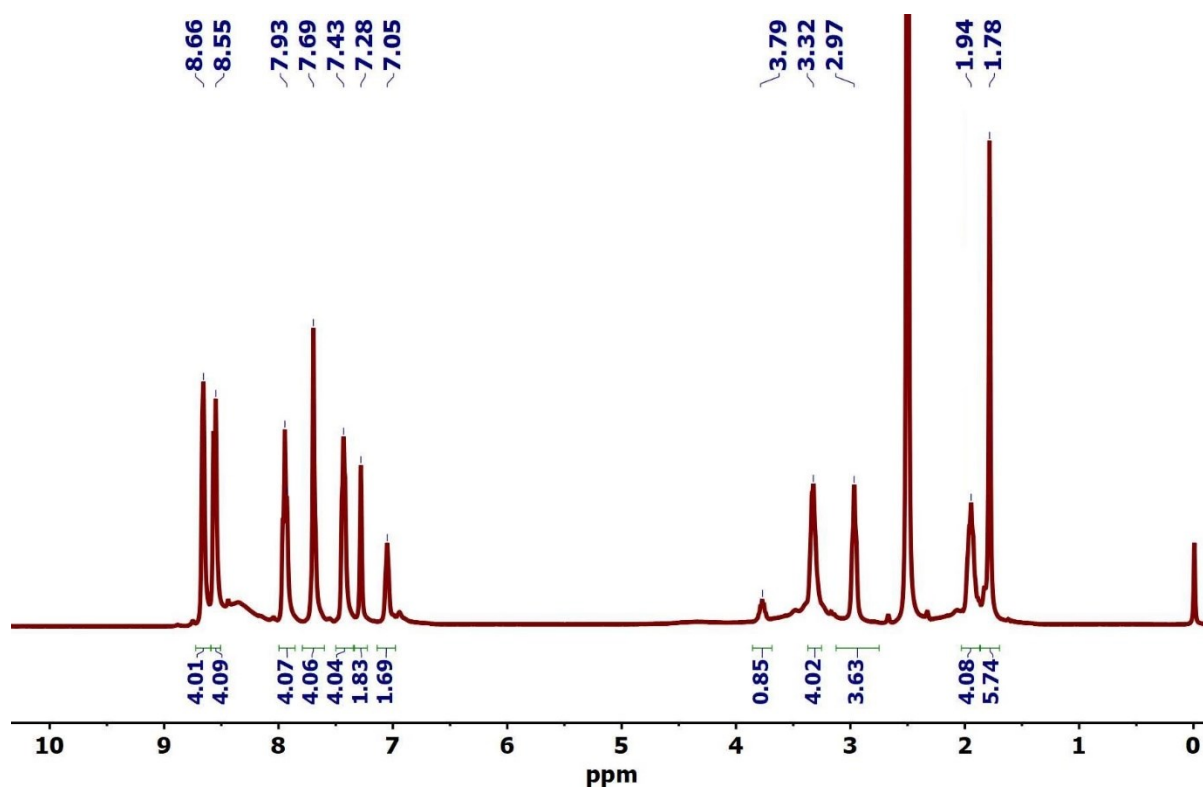


Figure S1: $^1\text{H-NMR}$ spectrum of TPY-DTE LMWG in $\text{DMSO-}d_6$.

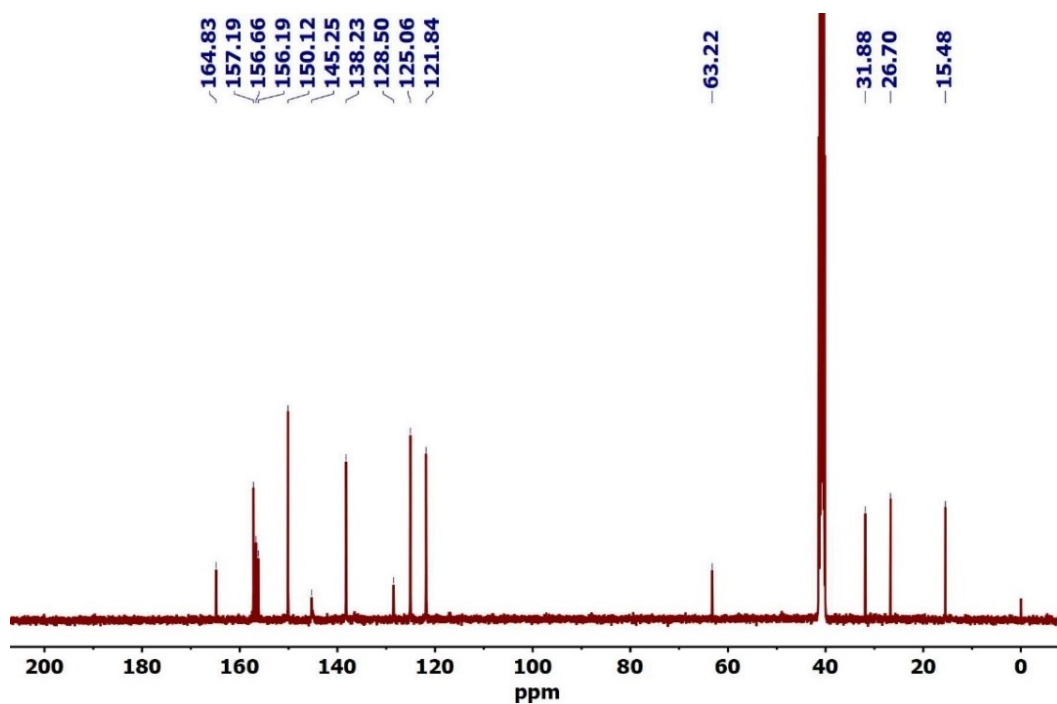


Figure S2: ^{13}C -NMR spectrum of TPY-DTE LMWG in DMSO-d_6 .

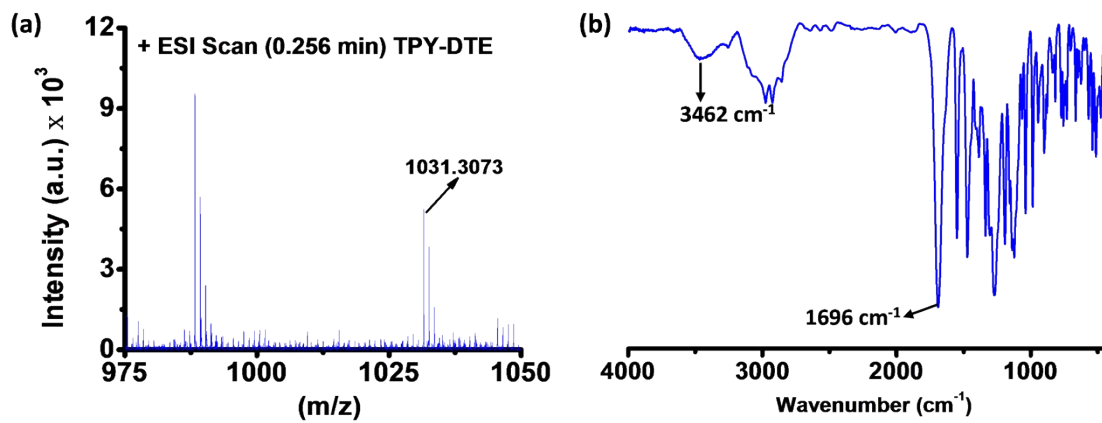


Figure S3. (a) HRMS and (b) FT-IR for TPY-DTE LMWG.

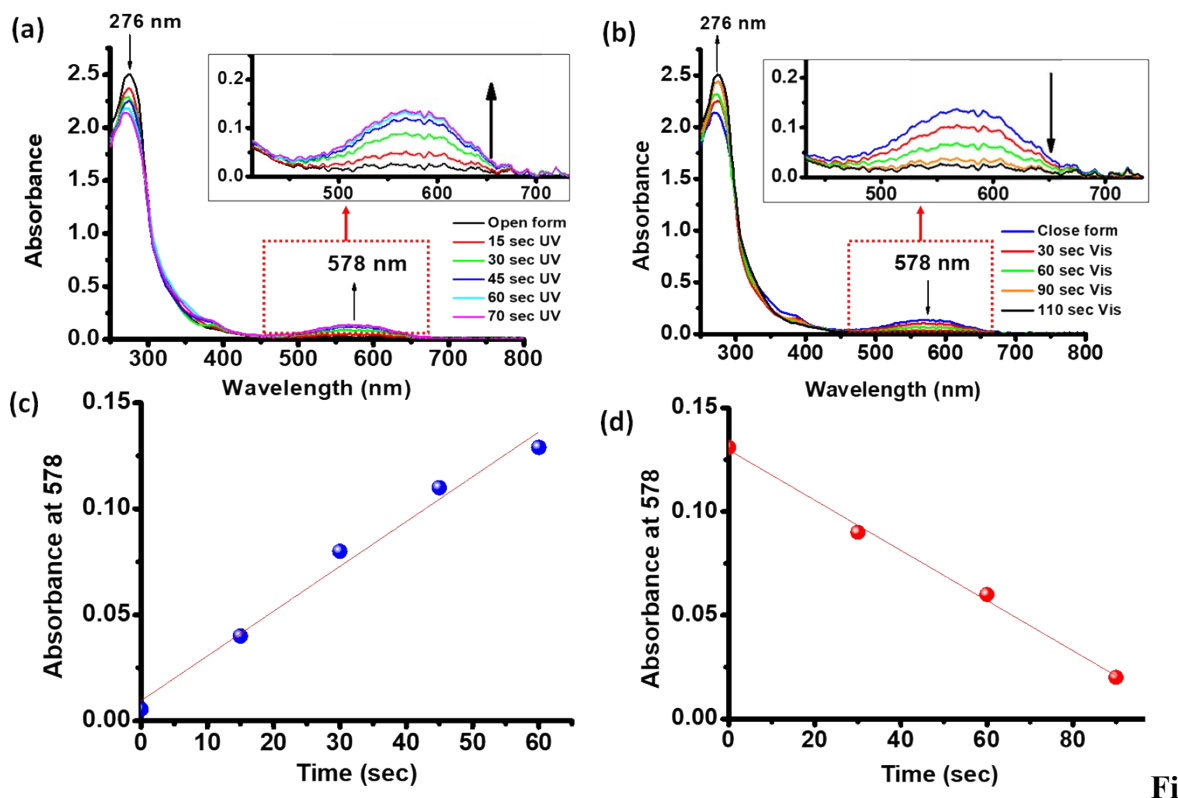


Figure S4. (a) Absorption spectra of TPY-DTE LMWG (6×10^{-5} M in methanol) were recorded at different time intervals upon UV irradiation (at 365 nm). (b) Absorption spectra of TPY-DTE LMWG (6×10^{-5} M in methanol) were recorded at different time intervals upon visible light irradiation ($\lambda > 400$ nm). (c) Plot for incremental absorbance at 578 nm wrt time upon UV irradiation time. (d) Plot for decremental absorbance at 578 nm upon visible light irradiation.

The calculation for TPY-DTE LMWG photocyclization (Φ_c) and photocycloreversion (Φ_o): The photoreaction quantum yields of TPY-DTE LMWG at 365 nm and >400 nm was calculated. The quantum yields for photocyclization and photocycloreversion were calculated based on the following equation [1]^[3]:

$$\Phi_x = \frac{\Delta A / \Delta t}{(Nh\nu/t) \times \epsilon_x \times F_x} \dots\dots\dots (1)$$

where $\Delta A / \Delta t$ is the change of absorbance upon irradiation at detective wavelength, ϵ_x is the molar extinction coefficient at detective wavelength and F_x is the mean fraction of light absorbed, the value of which is $1-10^{-A}$. For photocyclization quantum yields, it should be the absolute value of Φ_c . For photocycloreversion quantum yields, it should be the absolute value of Φ_o . $Nh\nu$ is the light intensity used for photocyclization (at 5 cm distance for 60 sec) and photocycloreversion (at 5 cm distance for 110 sec). Slope for photocyclization ($\Delta A / \Delta t = 0.002$) and for photocycloreversion ($\Delta A / \Delta t = 0.001$) from figure S4.

Photoreaction	Φ_x
TPY-DTE-O to TPY-DTE-C	$\Phi_c = 0.81$
TPY-DTE-C to TPY-DTE-O	$\Phi_o = 0.69$

Photocyclization conversion ratio measurement: The ratio of the equilibrium concentrations of the open form (Co) and closed forms (Cc) at a given photostationary state (PSS) is expressed as follows^[3]:

$$\frac{C_o}{C_c} = \frac{\varphi_{c \rightarrow o} \times \varepsilon_c}{\varphi_{o \rightarrow c} \times \varepsilon_o}$$

where ε_o and ε_c are the molar absorption coefficients of the open and closed forms, $\Phi_{c \rightarrow o}$ and $\Phi_{o \rightarrow c}$ are quantum yields of cycloreversion and cyclization, respectively.

Therefore, the conversion ratio at the photostationary state (PSS) was calculated to be ~72%.

S4. TPY-DTE-GO organogel synthesis and characterizations:

For the formation of photochromic organo-gel, the TPY-DTE LMWG (5 mg, 0.005 mmol) was dissolved in the 300 μ l solvent mixture of methanol (200 μ l), ethylene glycol (50 μ l) and water (50 μ l) and heated gradually from 60 °C to 120 °C in a closed vial to get a homogenous viscous yellow solution which was then left to stand for 1 hour and subsequently yielded a yellow colour gel material (TPY-DTE-GO). Further, this gel was gradually heated to above 80 °C, and the gel was converted to a solution, which again forms a gel within 30 minutes upon cooling down to room temperature. Further, to convert into the xerogel, the TPY-DTE-GO was kept under vacuum at 80°C for 8 hours. Selected FT-IR data for TPY-DTE-GO (KBr, cm^{-1}): 3436 (b), 3233 (b), 2971 (s), 2938 (s), 1750 (s), 1684 (s), 1640 (m), 1588 (s), 1472 (s), 1440 (s), 1403 (s), 1269 (m), 1168 (s), 1117 (s), 1036 (s), 985 (m), 849 (m), 794 (m), 761 (s), 697 (m), 543 (s), 459 (w).

Table S1: Gelation ability of TPY-DTE LMWG in different solvent:

No.	Solvent	Gelation ability	No.	Solvent mixture	Ratio	Gelation ability
1.	Ethanol (EtOH)	S	7.	MeOH +EG+ H ₂ O	(4:1:1)	G*
2.	Methanol (MeOH)	S	8.	MeOH +EG+ H ₂ O	(4:1:2)	S
3.	Tetrahydrofuran (THF)	S	9.	MeOH +EG+ H ₂ O	(4:2:2)	S
4.	Ethyl acetate (EtOAc)	S	10.	EtOH +EG+ H ₂ O	(4:1:1)	S
5.	Ethylene Glycol (EG)	S	11.	THF +EG+ H ₂ O	(4:1:1)	P
6.	Water (H ₂ O)	P	12.	EtOAc +EG+ H ₂ O	(4:1:1)	S

S = solution; P = precipitate; G = Gel; *CGC (Critical Gelator Concentration) = 0.005 mmol

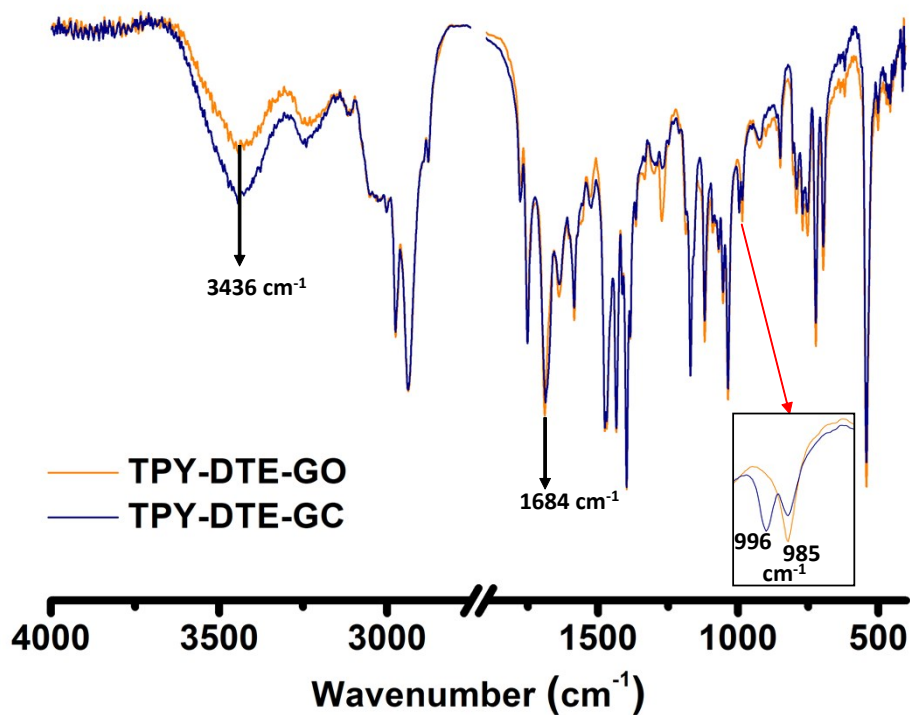


Figure S5. FT-IR for TPY-DTE-GO and TPY-DTE-GC.

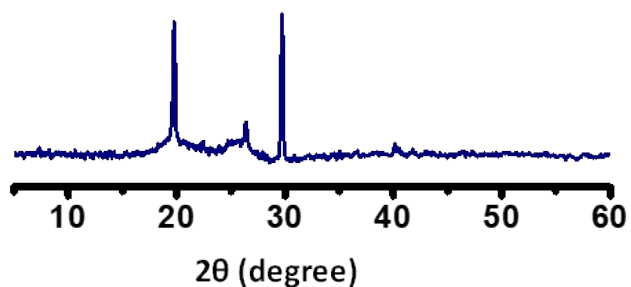


Figure S6. PXRD for TPY-DTE-GO.

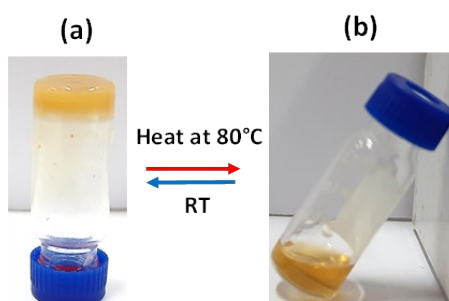


Figure S7. Reversible gel-sol transformation of TPY-DTE-GO upon heating/cooling. (a) Photograph of gel state and (b) Photograph of solution state.

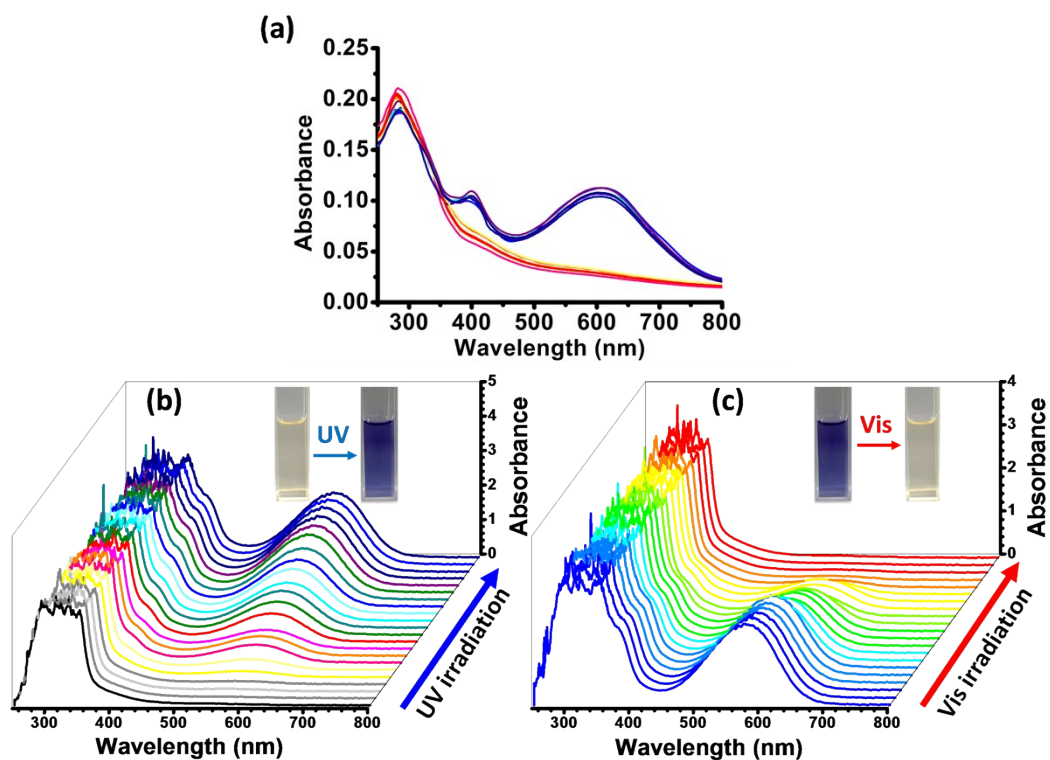


Figure S8. (a) UV-visible absorption spectra for TPY-DTE-GO and TPY-DTE-GC up to 10 cycles of photoconversion in the gel state. UV-visible absorption spectra recorded upon continuous UV-light irradiation for the methanolic dispersion of TPY-DTE-GO and TPY-DTE-GC (10^{-4} M); (b) UV-visible absorption spectra plotted in time interval of 3 sec upon UV-light irradiation. (c) UV-visible absorption spectra plotted in time interval of 6 sec upon visible light irradiation.

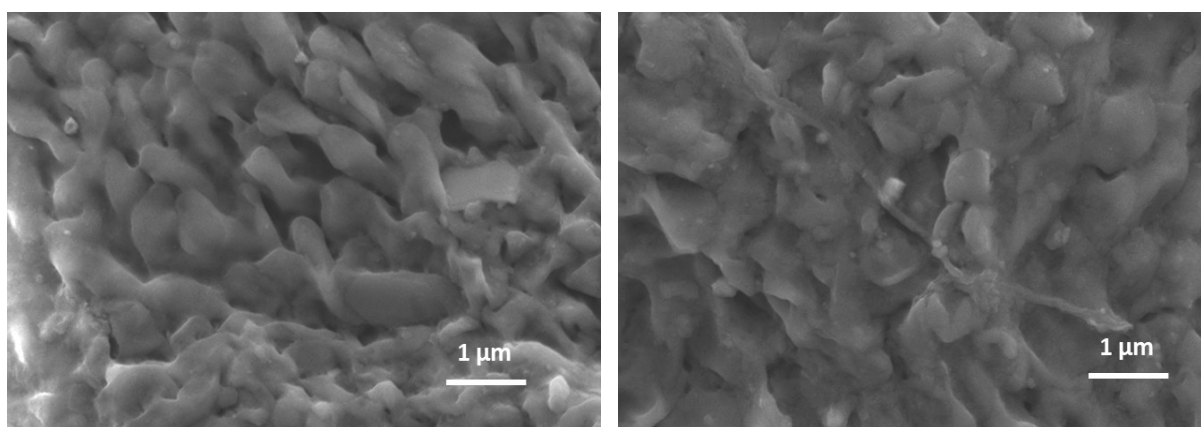


Figure S9. FESEM image (a) TPY-DTE-GO and (b) TPY-DTE-GC.

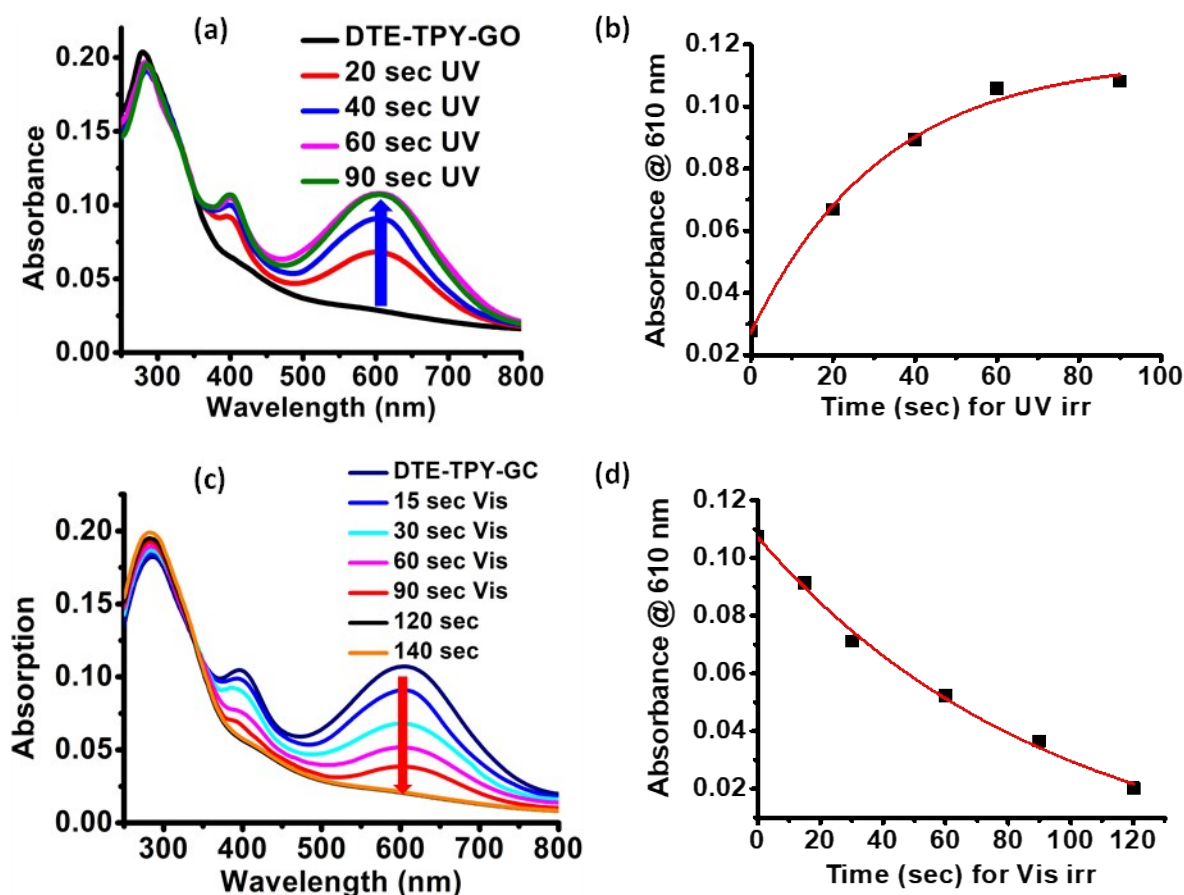


Figure S10. (a) Changes in the UV-visible absorption spectra for TPY-DTE-GO upon UV light irradiation. (b) Change in absorbance at 610 nm upon UV light irradiation (slope = 0.0019). (c) Changes in the UV-visible absorption spectra for TPY-DTE-GC upon visible light treatment. (d) Change in absorbance at 610 nm upon visible light irradiation (slope = -0.0012).

The calculation for TPY-DTE organogel photocyclization (Φ_C) and photocycloreversion (Φ_O): Similar to DTE-TPY LMWG, the slope for photocyclization ($\Delta A/\Delta t = 0.0019$) and photocycloreversion ($\Delta A/\Delta t = 0.0012$) was calculated from figure S10.

Photoreaction	Φ_X
TPY-DTE-GO to TPY-DTE-GC	$\Phi_C = 0.60$
TPY-DTE-GC to TPY-DTE-GO	$\Phi_O = 0.46$

Therefore, the conversion ratio at the photostationary state (PSS) was calculated to be ~71%.

S5. Synthesis and characterizations of Eu-TPY-DTE-GO pcCPG:

For photochromic coordination polymer gel (pcCPG) synthesis, yellow coloured TPY-DTE LMWG (5 mg, 0.005 mmol) was dissolved in the solvent mixture of methanol (200 μ l), and ethylene glycol (50 μ l) and Eu (NO_3)₃.6H₂O (0.005 mmol) in water (50 μ l) was added. This

gelator solution was heated gradually from 60°C to 90°C to get a homogenous viscous yellow solution and then left to stand for 30 min in a closed vial, which has resulted in a yellow coloured opaque gel. The gel formation was confirmed by the inversion test method. The Eu-pcCPG was kept under vacuum at 80°C for 8 hours to obtain the xerogel. Selected FT-IR data for Eu-pcCPG-O (KBr, cm^{-1}): 3455 (b), 3432 (b), 3378 (b), 3254 (s), 3055 (b), 2948 (b), 1642 (s), 1587 (s), 1557 (s), 1496 (s), 1466 (s), 1410 (s), 1292 (s), 1217 (m), 1181 (m), 1162 (m), 1142 (s), 1095 (w), 1065 (s), 1018 (s), 923 (w), 885 (m), 815 (s), 773 (s), 691 (m), 648 (m), 592 (w), 566 (w). Anal. calcd for TPY-DTE: $\text{Eu}(\text{NO}_3)_3$ in [1:1] ratio; C, 46.50; H, 3.24; N, 13.30; S, 4.68 %, Found: C, 45.12; H, 3.21; N, 13.69; S, 4.87 %.

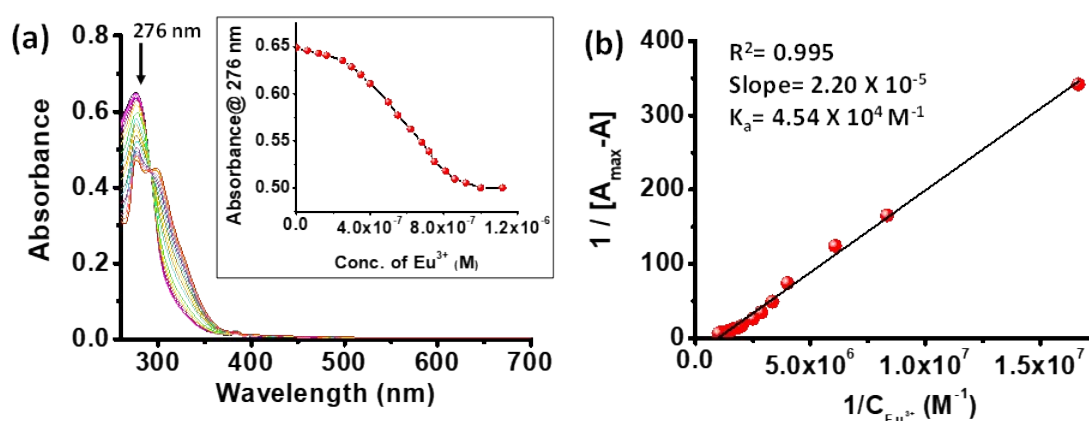


Figure S11. (a) Titration of TPY-DTE LMWG (10^{-6} M) with Eu^{3+} in methanol (inset: change in absorbance at 276 nm with the incremental addition of Eu^{3+} ion). (b) Benesi-Hildebrand plot of TPY-DTE with varied concentrations of Eu^{3+} .

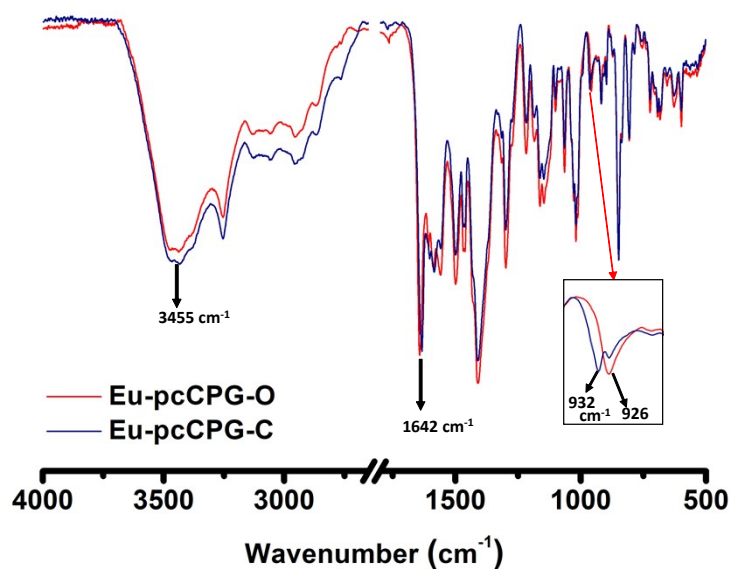


Figure S12. FT-IR for Eu-pcCPG-O and Eu-pcCPG-C.

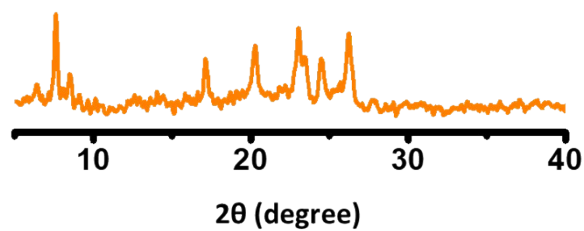


Figure S13. PXRD for Eu-pcCPG-O.

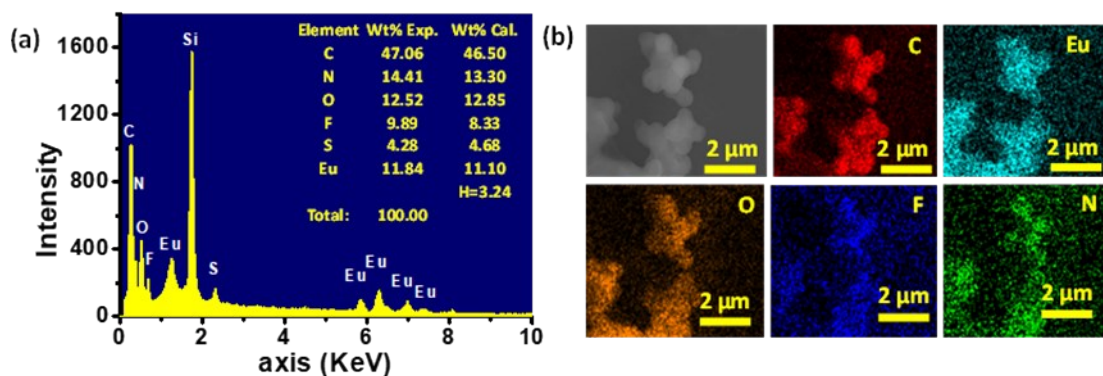


Figure S14. (a) EDAX analysis and (b) elemental mapping for Eu-pcCPG-O.

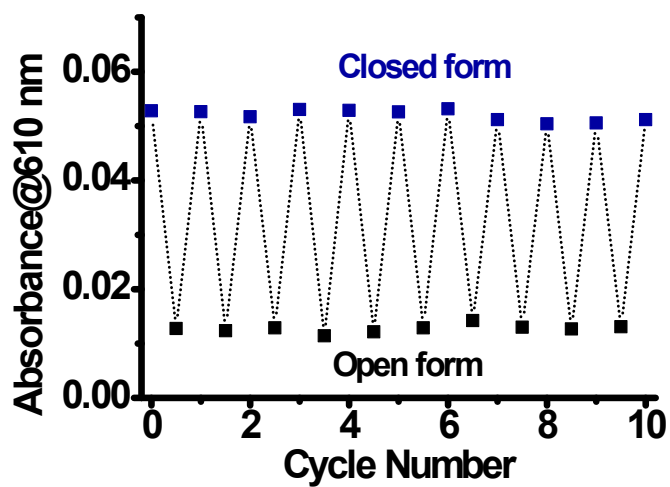


Figure S15. UV-Vis absorption spectra for Eu-pcCPG-O and Eu--pcCPG-C recyclability test for 10 cycles.

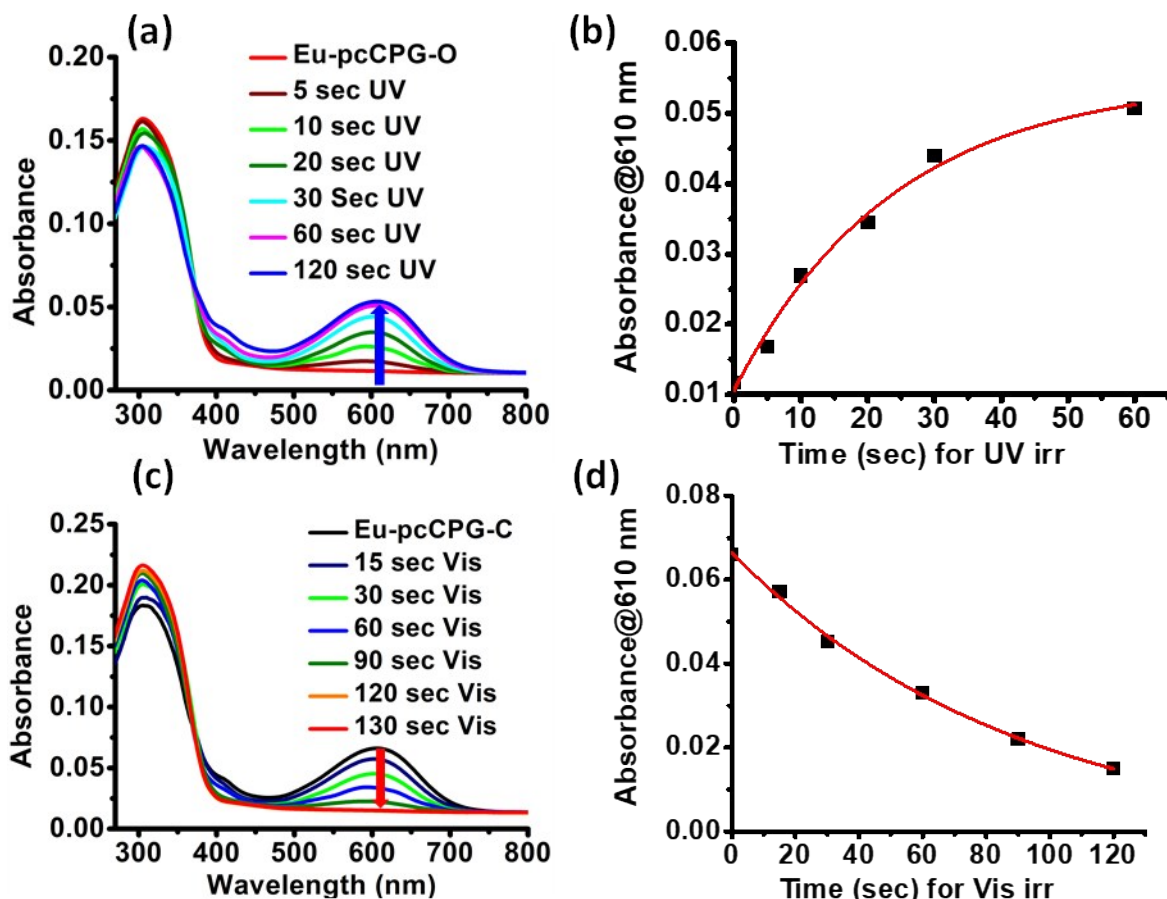


Figure S16. (a) UV-visible absorption spectra for Eu-pcCPG-O upon UV light irradiation. (b) Changes in absorbance at 610 nm upon UV light irradiation (slope = 0.00152). (c) UV-visible absorption spectra for Eu-pcCPG-C upon visible light irradiation. (b) Changes in absorbance at 610 nm upon visible light irradiation (slope value = -0.00069).

Photocyclization (Φ_C) and photocycloreversion (Φ_O) for Eu-pcCPG:

A similar calculation was employed here as discussed above for the calculation of quantum efficiency for Eu-pcCPG-O and Eu-pcCPG-C in equation [1]. Slope for photocyclization ($\Delta A/\Delta t = 0.0015$) and for photocycloreversion ($\Delta A/\Delta t = 0.0006$) as shown in figure S15.

Photoreaction	Φ_X
Eu-pcCPG-O to Eu-pcCPG-C	$\Phi_C = 0.70$
Eu-pcCPG-C to Eu-pcCPG-O	$\Phi_O = 0.57$

Therefore, the conversion ratio at PSS was calculated to be ~71%.

Kinetics and Energy transfer study:

Lifetime calculations: Lifetime data for Eu-pcCPG were collected upon exciting at 310 nm.

The average lifetime is calculated using the following formula:

$$\text{Average life time, } \tau_{\text{avg}}(\text{ns}) = (\Sigma A_i \tau_i^2 / \Sigma A_i \tau_i)$$

Where, τ_{avg} = average lifetime in nano-seconds, ΣA_i = sum of the percentage of all the components exists in the excited state, $\Sigma \tau_i$ = sum of excited-state lifetime of all the component.

Table S2: Lifetime data for Eu-pcCPG:

Catalyst	τ_1 (μs)	A_1	τ_2 (μs)	A_2	τ_{av} (μs)
Eu-pcCPG-O	108.7	46.39 %	456.2	53.61 %	397.0
Eu-pcCPG-C	36.6	11.99 %	5.1	88.01 %	20.7

Calculation of energy transfer efficiency: For Eu-pcCPG-O/ Eu-pcCPG-C in gel state:

$$\text{Energy transfer efficiency} = 1 - (\tau_{\text{Eu-pcCPG-C}} / \tau_{\text{Eu-pcCPG-O}})$$

$$= 1 - (20.7/397.0)$$

$$= 0.9479$$

Therefore, the percentage of energy transfer efficiency (φ_e) = **94.79 %**

Images for encryption and decryption:

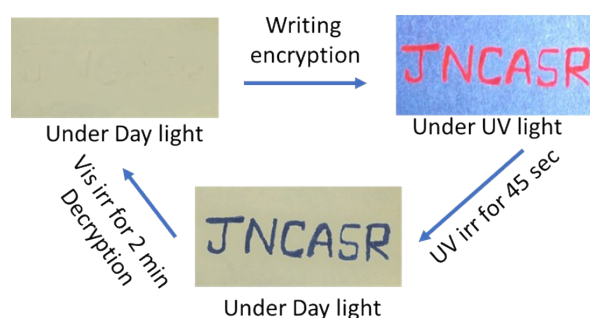


Figure S17. Coating of Eu-pcCPG-O in yellow paper followed by encryption under UV irradiation. Decryption was done by visible light irradiation.

S6. Synthesis and characterizations of Tb-TPY-DTE pcCPG:

For Tb-pcCPG synthesis, TPY-DTE LMWG (5 mg, 0.005 mmol) was dissolved in the solvent mixture of methanol (200 μ l) and ethylene glycol (50 μ l), and 50 μ l of an aqueous solution of Tb (NO₃)₃·6H₂O (0.005 mmol) was added into it. This gelator solution was heated gradually from 60°C to 120°C in a closed vial to get a homogenous viscous yellow solution, which was left to stand for 30 min. This resulted in a yellow opaque gel (Tb-pcCPG-O). The gel formation was confirmed by the inversion method. The Tb-pcCPG-O was kept under vacuum at 80°C for 8 hours and yielded the xerogel. Selected FT-IR data (KBr, cm⁻¹) for Tb-pcCPG-O: 3450 (b), 3256 (s), 2945 (m), 1652 (s), 1609 (s), 1519 (m), 1478 (m), 1427 (s), 1308 (s), 1233 (m), 1160 (m), 1074 (w), 1038 (m), 938 (w), 898 (w), 830 (s), 797 (m), 707 (m), 666 (m), 608 (w), 576 (m), 455 (w). Anal. calcd for TPY-DTE: Tb(NO₃)₃ in [1:1] ratio; C, 46.26; H, 3.22; N, 13.23; S, 4.66 %, Found: C, 46.39; H, 3.27; N, 13.11; S, 4.57 %.

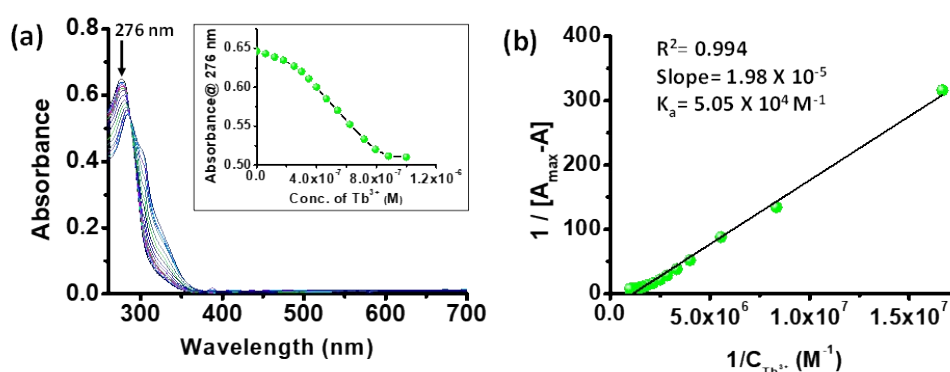


Figure S18. (a) Titration of TPY-DTE LMWG (10^{-6} M) with Tb³⁺ in methanol (inset: change in absorbance at 276 nm with incremental addition of Tb³⁺ ion). (b) Benesi-Hildebrand plot of TPY-DTE with varied concentrations of Tb³⁺.

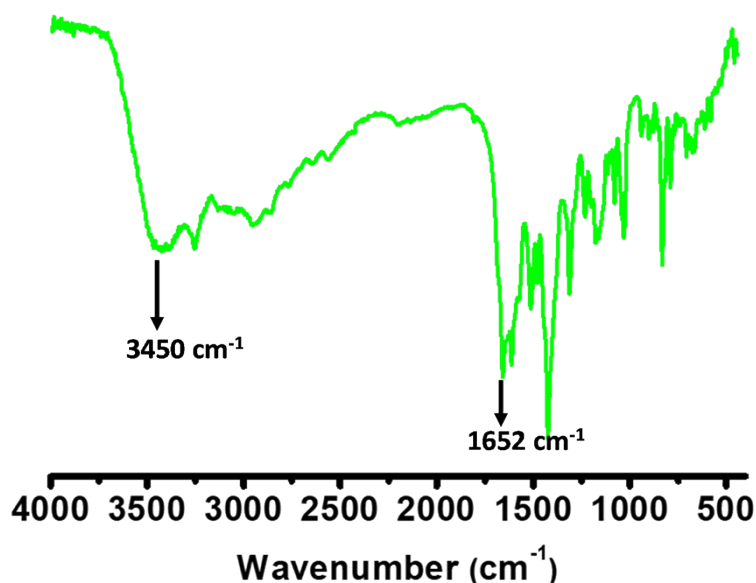


Figure S19. FT-IR for Tb-pcCPG-O.

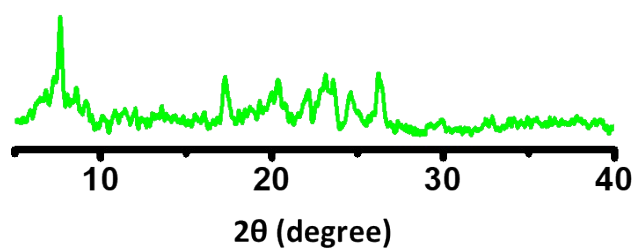


Figure S20. PXR D for Tb-pcCPG-O.

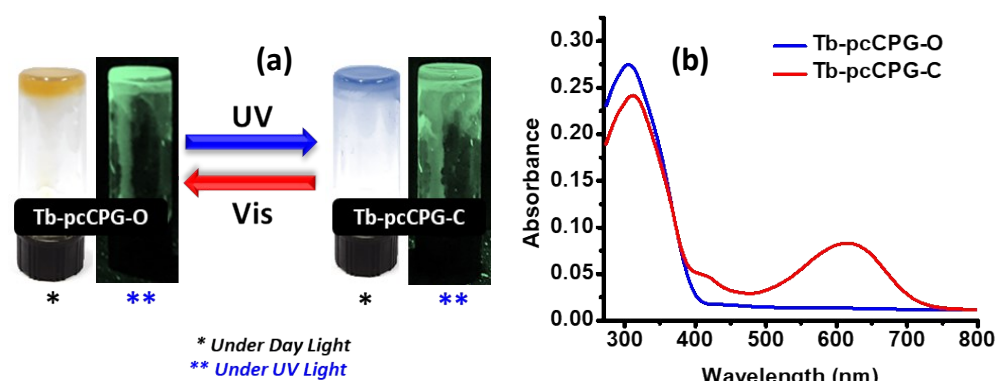


Figure S21. (a) Photographs of Tb-pcCPG-O and Tb-pcCPG-C. (b) UV-visible absorption spectra for Tb-pcCPG-O and Tb-pcCPG-C.

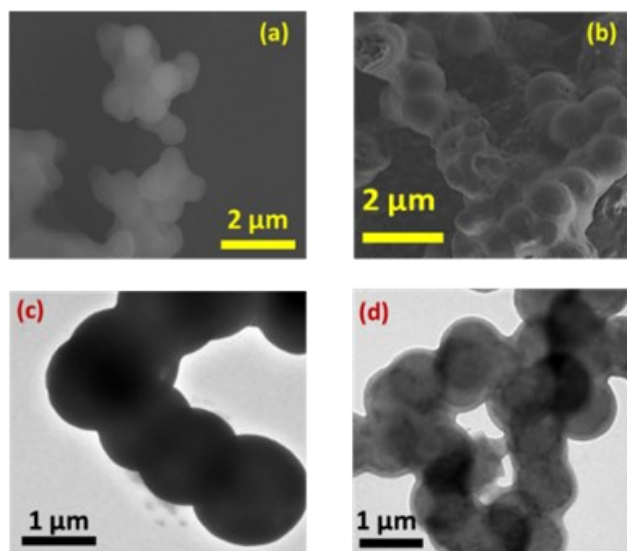


Figure S22. (a-b) FESEM images and (c-d) TEM images for Tb-pcCPG-O.

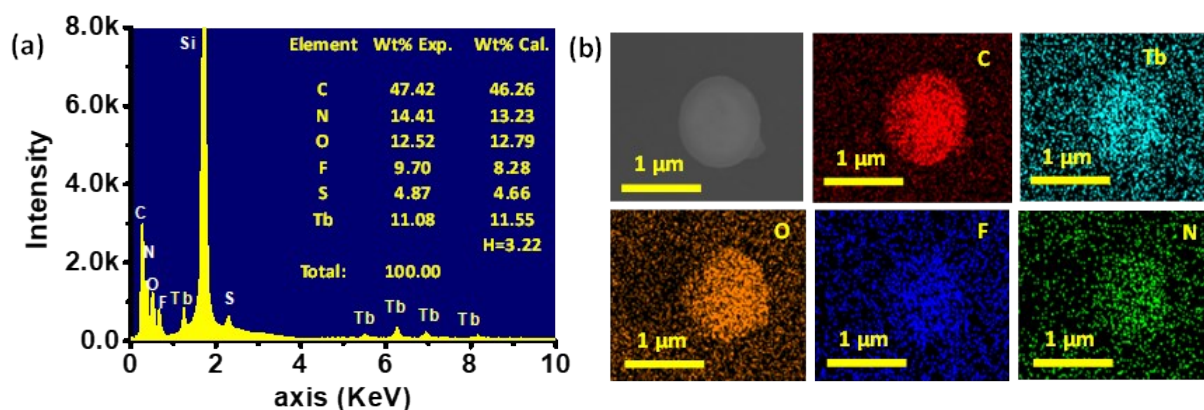


Figure S23. (a) Elemental mapping and (b) EDAX analysis for Tb-pcCPG-O.

Kinetics and Energy transfer study for Tb-pcCPG:

Table 3: Lifetime data for Tb-pcCPG:

Catalyst	τ_1 (μs)	A_1	τ_2 (μs)	A_2	τ_{av} (μs)
Tb-pcCPG-O	96.14	20.82 %	84.2	79.18 %	87.0
Tb-pcCPG-C	110.2	8.55 %	79.1	91.45 %	82.7

The excited-state decay plot of Tb-pcCPG was also found to be biexponential due to similar cause as mentioned for the Eu-pcCPG.

Calculation of energy transfer efficiency: For Tb-pcCPG-O/ Tb-pcCPG-C in gel state:

$$\begin{aligned} \text{Energy transfer efficiency} &= 1 - (\tau_{\text{Tb-pcCPG-C}} / \tau_{\text{Tb-pcCPG-O}}) \\ &= 1 - (82.7/87.0) \\ &= 0.0494 \end{aligned}$$

Therefore, the percentage of energy transfer efficiency (φ_e) = **4.94 %**

S7. Synthesis and characterization of mixed Eu/Tb-pcCPG:

For the synthesis of mixed metal gel, 7 mg of Eu-pcCPG-O and 3 mg of Tb-pcCPG-O was taken separately in a gel state and heated at 80°C for 2-3 min to convert into a solution state. Next, both the solution was mixed at 80°C and kept at room temperature for 30 min, which has resulted in the yellow coloured opaque gel. The formation of the gel was further confirmed by the inversion test method.

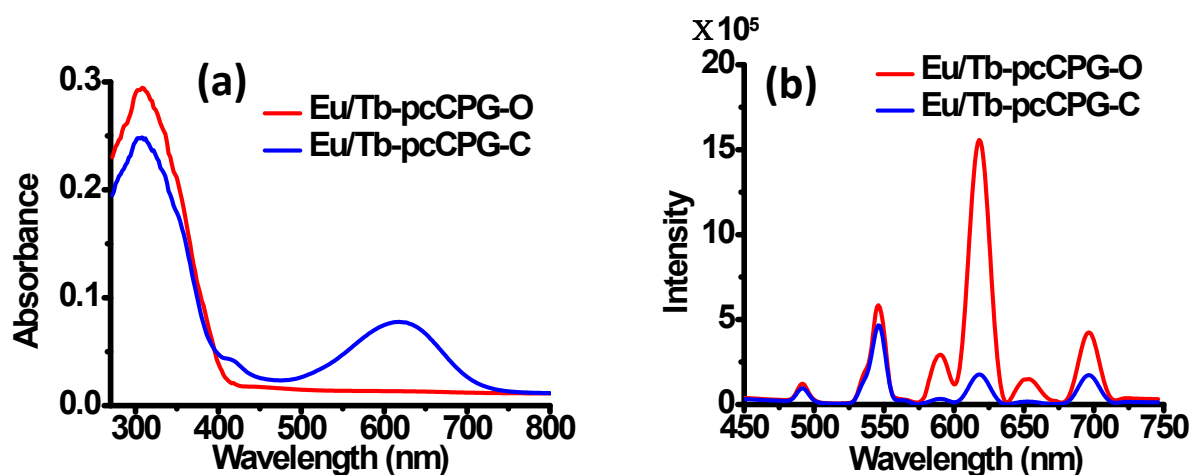


Figure S24. (a) UV-visible absorption spectra for mixed gel and (b) Emission for Eu/Tb-pcCPG-O and Eu/Tb-pcCPG-C.

S8. Supporting Video:

Video (VS1): This video shows the barcode scanning using a mobile phone under UV light. The Eu-pcCPG-O coated red emissive barcode was generated for our institute (JNCASR, Bangalore, India).

S8. References:

- [1] W. Jeong, M. I. Khazi, D. H. Park, Y. S. Jung, J. M. Kim, *Adv. Funct. Mater.* **2016**, *26*, 5230-5238.
- [2] P. Sutar, V. M. Suresh, T. K. Maji, *Chem. Commun.* **2015**, *51*, 9876-9879.
- [3] a) K. Shibata, K. Muto, S. Kobatake, M. Irie, *J. Phys. Chem. A* **2002**, *106*, 209-214; b) Z. Zhang, W. Wang, P. Jin, J. Xue, L. Sun, J. Huang, J. Zhang, H. Tian, *Nat. Commun.* **2019**, *10*, 4232 (1-9); c) A. R. Santos, R. Ballardini, P. Belser, M. T. Gandolfi, V. M. Iyer, L. Moggi, *Photochem. Photobiol. Sci.* **2009**, *8*, 1734-1742.