Electronic Supplementary Information

A terpyridine based hydrogel system for reversible transmissive-to-dark electrochromism and bright-to-quenched electrofluorochromism

Sayan Halder,[a] Susmita Roy,[a] Mudit Dixit[a,b] and Chanchal Chakraborty[a,b,*]

[a] Department of Chemistry, Birla Institute of Technology & Science (BITS) Pilani, Hyderabad Campus. Jawaharnagar, Samirpet, Hyderabad, Telangana 500078, India

[b] Materials Center for Sustainable Energy & Environment (McSEE), Birla Institute of Technology and Science, Hyderabad Campus, Hyderabad 500078, India

*Corresponding Author: Chanchal Chakraborty

E-mail: chanchal@hyderabad.bits-pilani.ac.in

ORCID ID: https://orcid.org/0000-0002-4829-1367

[†]Electronic Supplementary Information (ESI) available.

Contents

Fig. S9. (a) Cyclic voltammogram of TPPCA solution based EC device in 0.1 M Nacl-water solution at scan rate of 100 mV/s. (b) Corresponding optical color change of the EC device.

Fig. S10. Scan rate dependent study of TPPCA hydrogel.

Fig. S11. Chronoamperometric performance of the device.

Fig. S12. Measurement of electrochromic parameters of the gel based ECD.

Fig. S13. CV and EC study of TPPCA hydrogel (10 mg/mL).

Supplementary methods

Chemicals. Commercially available chelidamic acid, potassium pentabromide (PBr_5), potassium hydroxide (KOH), potassium carbonate (K_2CO_3), bis(triphenylphosphine)palladium(II) dichloride and sodium chloride (NaCl) were purchased from Sigma Aldrich Co. Ltd, while the solvents like methanol (MOH), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO) and hydrochloric acid were bought from Sisco Research Laboratories (SRL) Pvt. Ltd. – India and used as received. 4'-(4-pinacolatobororonphenyl)-2,2':6',2"-terpyridine was prepared according to previous reported protocol. Indium tin oxide (ITO)-coated glass slides (R ≈ 20 Ω) were obtained from Shilpa Enterprises. Millipore Milli-Q water (18 MΩ cm) was utilized for solution preparation and spectroscopic investigations.

Synthesis process.

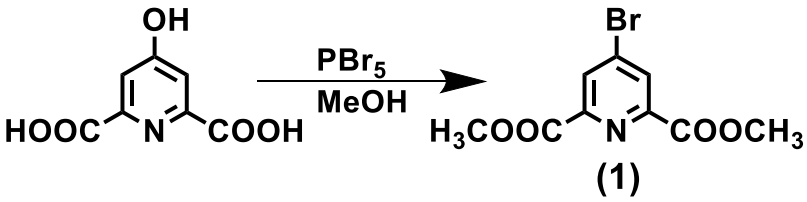

Fig. S1. Synthetic step for the preparation of compound 1.

Synthesis of Dimethyl-4-bromo-2,6-pyridinedicaboxylate (1):

Chelidamic acid monohydrate (1.5 g, 7.48 mmol) and PBr_5 (15.0 g, 36.01 mmol) was taken in a Schlenk tube and heated to 120 ^oC in inert atmosphere. The reaction mixture was stirred at 100 ^oC for another 3h under inert atmosphere. Finally, the solution was cooled down at room temperature, solubilized in $CHCl_3$ and again cooled to 0 ^oC. Dry methanol was added to it and stirred overnight. The reaction mixture was concentrated in vacuum and recrystallized from methanol to provide white needle shaped castral as the title product. (1.53 g, 75%).

^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 8.3 (s, 2H, Ar-H), 4.1 (s, 6H, -OCH_3), ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 164.1, 149.5, 135.43, 128.3, 53.4. MS (MALDI-TOF) m/z: [(M + H)$^{+}$] calcd for $C_9H_8{}^{79}BrNO_4$ 273.97, found 274.53; [(M + H)$^{+}$] calcd. for $C_9H_8{}^{81}BrNO_4$ 275.97, found 276.10.

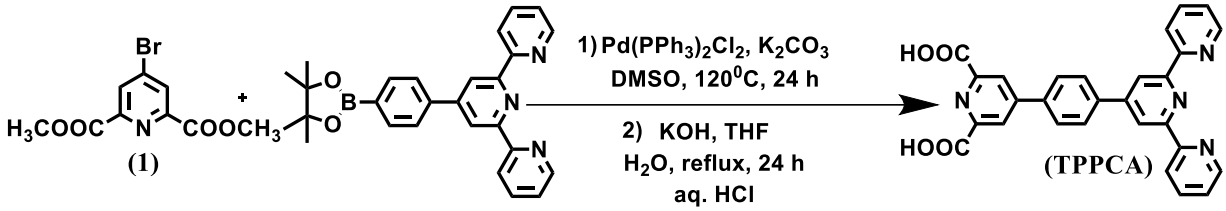

Fig. S2. Synthetic route for the preparation of gelator TPPCA.

Synthesis of 4-(4-([2,2':6',2''-Terpyridin]-4'-yl)phenyl)-pyridine-2,6-dicarboxylic acid (TPPCA):

In a 100 mL round-bottom flask, 4'-(4-pinacolatoboronphenyl)-2,2':6',2''-terpyridine (0.65 g, 1.50 mmol), 1 (0.40 g, 1.04 mmol) and $PdCl_2(PPh_3)_2$ (0.12 g, 0.16 mmol) was dissolved in 25 mL dry DMSO under inert condition. The mixture was degassed for 15 min. K_2CO_3 (0.45 g, 3.27 mmol) in 1 M water solution was taken and degassed through N_2 air passing. The aq. K_2CO_3 solution was added to the mixture by syringe. Then the reaction mixture was stirred for 24 h at 100 ^{o}C. After the reaction mixture was cooled to room temperature, the mixture was filtered and worked-up with $CHCl_3$. The organic layer was separated and dried over Na_2SO_4. The crude product was purified by column chromatography. Further the purified product was refluxed overnight in 50 mL THF-water mixture (1:1) with KOH (0.35 g, 6.20 mmol). Then the mixture was cooled and neutralized with 1 M HCl solution. Finally, the precipitation was filtered and thoroughly washed with water and diethyl ether, and dried overnight as yellowish white solid. (0.6 g, 83%)

^{1}H NMR (300 MHz, d_6-DMSO) δ ppm: 8.9 (m, 2H), 8.9 (s, 2H), 8.8 (m, 2H), 8.5 (s, 2H), 8.3 (t, 2H, J= 7.2 Hz), 8.2 (d, 2H, J= 8.4 Hz), 8.1 (d, 2H, J= 8.4 Hz), 7.8 (t, 2H, J= 5.7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 165.7, 154.8, 153.7, 149.3, 149.2, 148.9, 148.5, 139.1, 138.6, 136.8, 128.3, 128.1, 125.3, 124.6, 121.9, 118.7. HRMS (ESI-TOF) m/z: [(M + H)$^{+}$] calcd for $C_{28}H_{18}N_4O_4$ 475.1408, found 475.1180.

Experimental Section

Characterization of hyrdogelator: ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL AL 300/BZ instrument at 300 and 75 MHz, respectively. Mass spectra were recorded using a Shimadzu LCMS-IT-TOF spectrometer or AXIMA-CFR, Shimadzu/Kratos TOF mass spectrometer.

Preparation of Hydrogel: The measured amount of TPPCA was taken in deionized water with different concentrations. The mixture was sonicated for 15 min and kept undisturbed for 3 h to settle as a self-assembled gel. The gelation was started from a 2 mg/mL concentration of TPPCA. In presence of 0.1 M NaCl, a similar procedure was adopted for gelation and the stable gel formation was started from a 5 mg/mL of TPPCA concentration. For further characterizations, we have used the 5 mg/mL TPPCA hydrogel.

ECD fabrication: ITO coated glass ($R \approx 20\ \Omega$, from Shilpa Enterprises) was washed with soap water, distilled water, acetone, and isopropyl alcohol with sonication. The cleaned ITOs were dried overnight in the oven. The sandwich-shaped cells were prepared by two ITO glass slides, attaching the conducting side by double tape and pasting with silicone sealant to prepare the box size of 1 cm × 1.2 cm × 1 mm. Three sides of the cells were sealed by this method and the remaining was used to inject the gelator solution inside the cell. One end side of the cell was clipped with the working electrode, whereas the other was attached with reference and counter electrodes, making it a two-electrode system.

FT-IR spectroscopy: The FTIR spectroscopic data were collected using a JASCO/FTIR-4200 instrument by preparing KBr pellets of TPPCA and its dried gel. The experimental spectra were measured at 64 scans with a resolution of 2 cm^{-1} in between 4000 and 400 cm^{-1}.

UV-Vis and Florescence spectroscopy: The UV−vis spectra and emission spectra of the TPPCA sol, hydrogel state, and the change of absorption spectra in presence of voltage were

investigated by an Ocean Optics UV-vis spectrophotometer (USB4000, Ocean Optics). For measurement purposes, we used sandwich-shaped cells prepared by ITOs.

Rheology Study: All the rheological measurements were conducted using a rheometer (Anton Paar MCR 302, Graz, Austria), using a gap distance of 0.5 nm in between the bottom of the cup and gel surface. A zero force of 0 N was maintained throughout the experiment. All the measurements were performed at 25 ^{0}C maintaining the concentration of hydrogel as 5 mg/ mL.

FESEM study: Morphological Studies of the hydrogel in water and 0.1 m NaCl-water solution were performed by a field emission scanning electron microscopy (FESEM) study using an FEI, Apreo SEM instrument with an operating voltage of 30 kV. A small portion (10 μL) of prepared gel was placed on a glass coverslip and dried overnight at 75 ^{o}C before SEM analysis.

Electrochemical studies: CV and chronoamperometry data were collected using an Autolab PGSTAT128N potentiostat with an ITO sandwiched two-electrode cell. The scan-rate dependent CV study was executed in various scan rates from 50 to 200 mV. The EC performance of the ECDs was carried out by chronoamperometry studies with an interval time of 10 s and in a potential window of -3.5/0 V.

Table S1. Formation of hydrogel in water with different concentration of L resulting the stability of hydrogel from bottle inversion test.

Sample name	Concentration of solution (mg/mL)	Hydrogel formation
A1	1	not formed
A2	2	formed
A3	3	formed
A4	4	formed
A5	5	formed
A6	6	formed
A7	7	formed
A8	8	formed

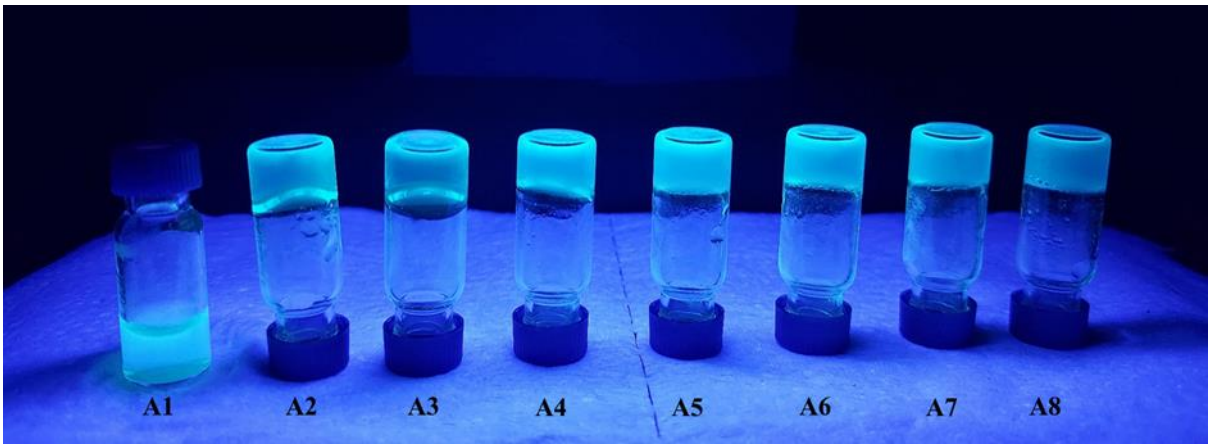

Fig. S3. Photographs of the prepared hydrogel in water under UV lamp.

Tables S2. Formation of hydrogel in 0.1 M NaCl- water for electrochemical use.

Sample name	Concentration of solution (mg/mL)	Hydrogel stability
B1	3	not formed
B2	4	not formed
B3	5	formed
B4	6	formed
B5	7	formed
B6	8	formed

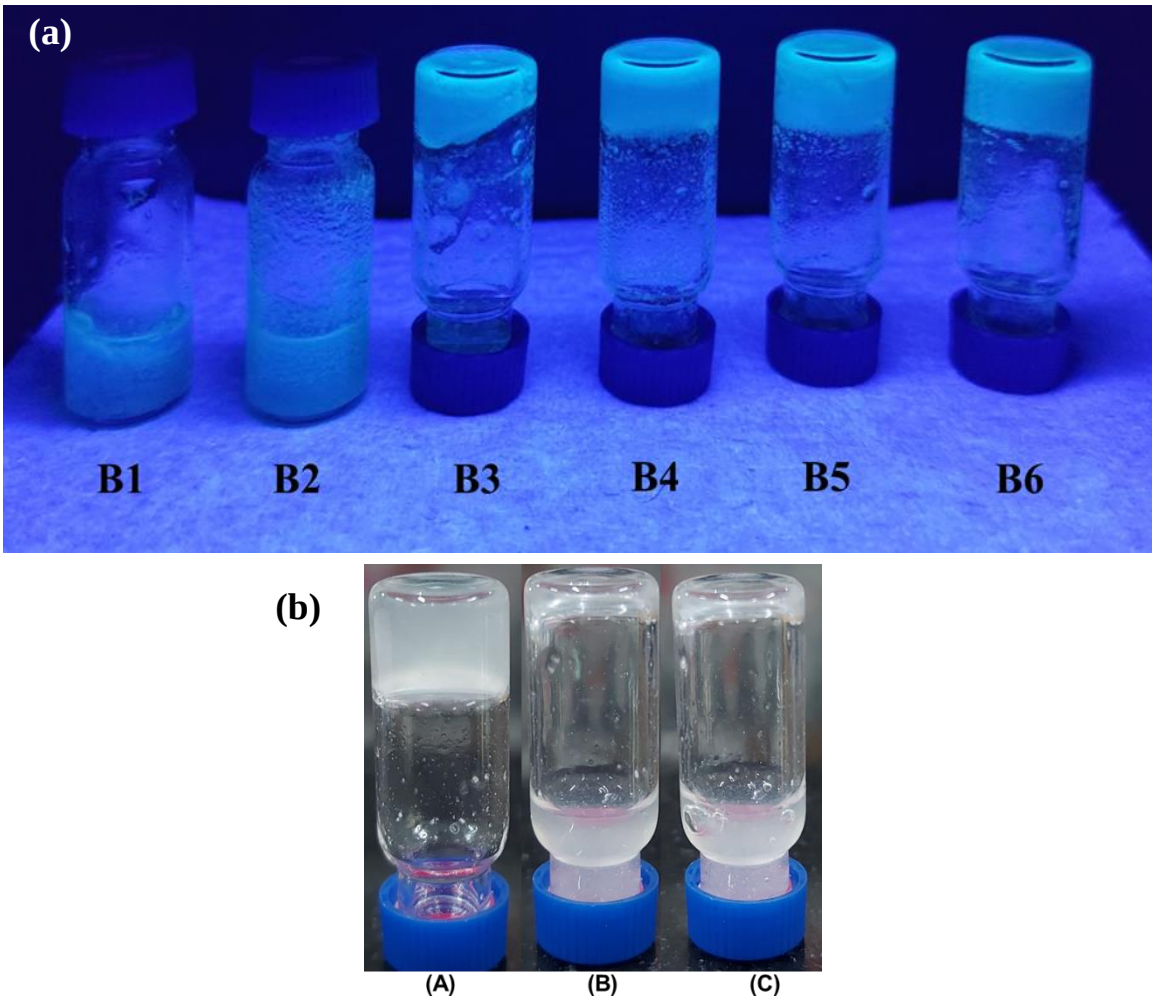

Fig. S4. (a) Photographs of the hydrogel in 0.1 M NaCl-water under UV light. (b) Photograph of gel and sol state of TPPCA (5 mg/mL) in a diiferent Nacl concentration of (A) 0.1 M, (B) 0.5 M and (C) 1.0 M in aqueous NaCl.

Computational Methods

DFT calculations were performed using the REV-PBE[1] exchange-correlation functional with Grimme's D3 method[2] using the CP2K package.[3] The DZVP basis with the Goedecker, Teter, and Hutter (GTH) pseudopotentials was used with a kinetic energy cutoff of 500 Ry for DFT calculations, The minimum energy pathways for alkane DH were investigated using climbing image nudged elastic band (CI-NEB) calculations[4] with a kinetic energy cutoff of 450 Ry. Excitation energies were computed with Time-Dependent Density Functional Perturbation Theory (TDDFPT) method as implemented in the CP2K package.

Aggregation energy is calculated as

$E_{Agg} = E_{Aggregated} - nE_{monomer}$

Where E_{Agg} is the aggregation energy, $E_{Aggregated}$ is the energy of aggregated structure containing n monomers, and $E_{monomer}$ is the energy of monomer unit.

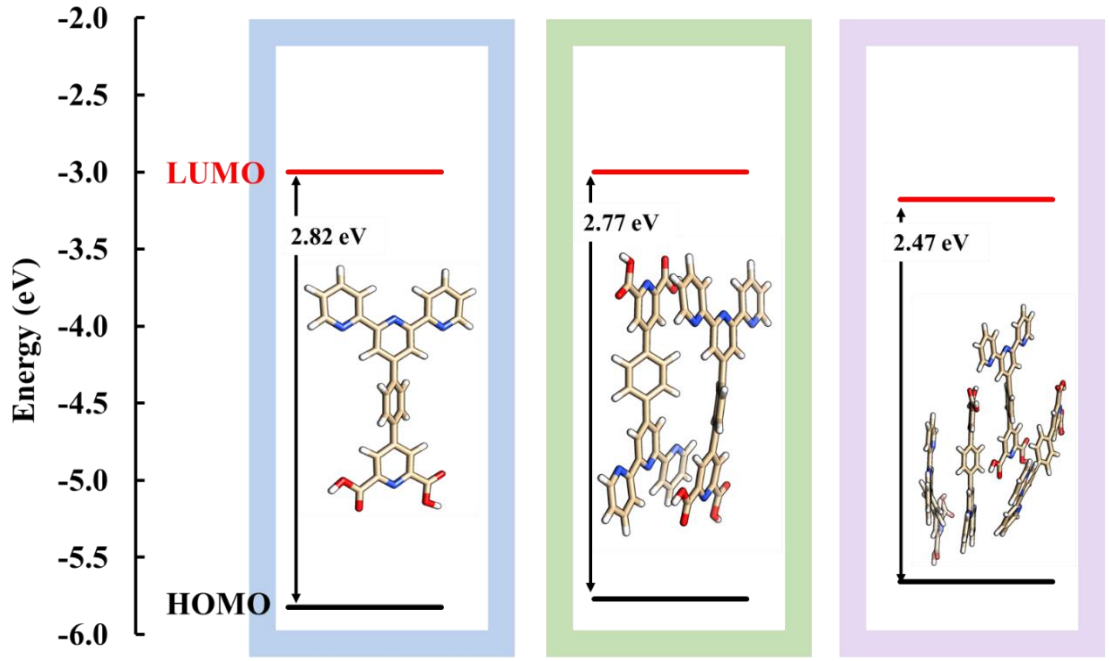

Fig. S5. Energy diagram with HOMO LUMO gaps for monomer, dimer, and tetramer of TPPCA. Color codes for spheres, O – red, N – blue, H – white, and C – copper gold.

Table S3. HOMO- LUMO gap computed with DFT and excitation energies computed with TDDFPT.

System	HOMO-LUMO gap (eV)	TDDFPT Excitation Energy (eV)
TPPCA monomer	2.82	2.87
TPPCA dimer	2.77	2.79
TPPCA tetramer	2.47	2.49

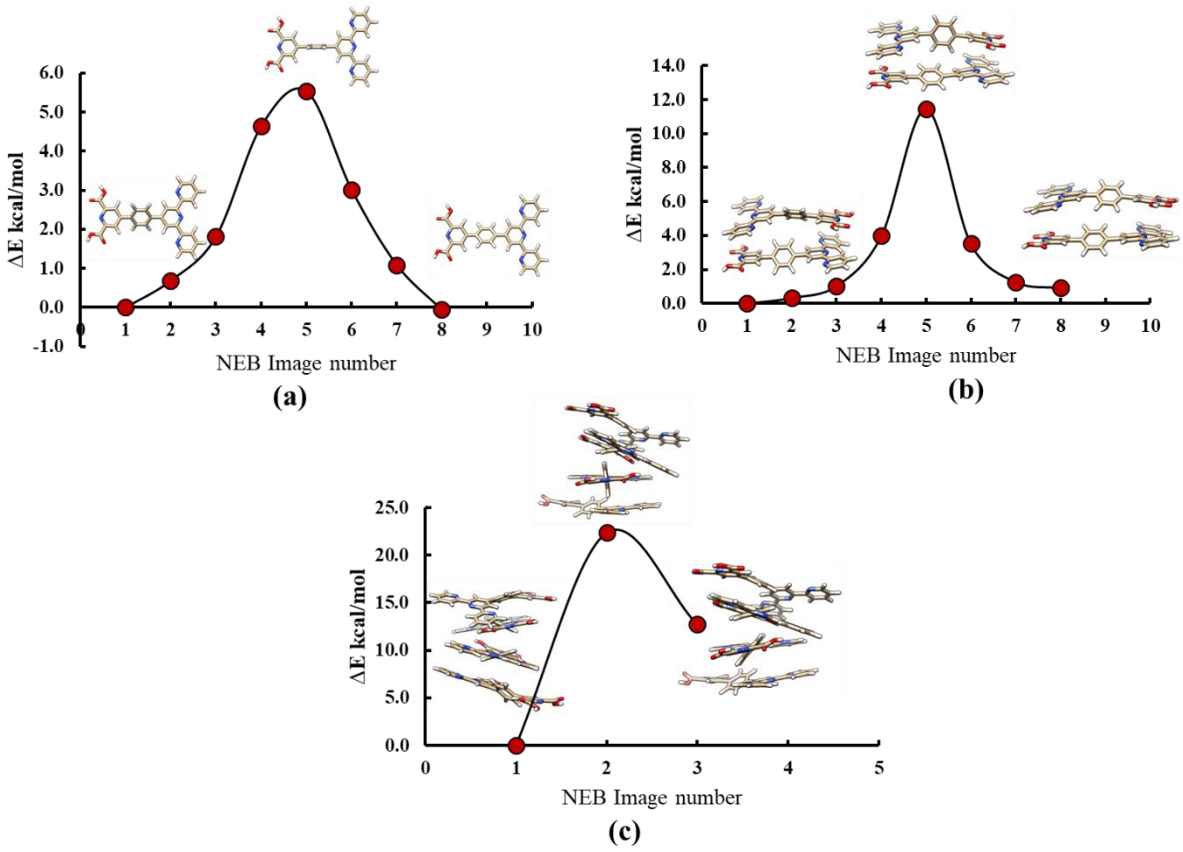

Fig. S6. NEB Energy profiles for intermolecular rotation of a phenyl group of TPPCA (a) monomer (b) dimer (c) tetramer. Color codes for spheres, O – red, N – blue, H – white, and C – copper gold. The final state energy becomes endothermic on aggregation due to asymmetry in the structure on aggregation.

To elucidate the aggregated states and the effect of aggregation of TPPCA on the free rotation of the phenyl group, we computed the barrier for phenyl group rotation on the monomer, dimer, and tetramer of TPPCA using Density Functional Theory (DFT) and Nudged Elastic Band (NEB) calculations. It was noted that the aggregation energies for TPPCA were favorable (12.4 and 32.9 kcal mol^{-1} for dimer and tetramer, respectively), suggesting that the aggregation was thermodynamically feasible. Again, the HOMO–LUMO gap (and TDDFPTexcitation energies, Table S3, ESI) was decreased with aggregation (Fig. S5, ESI), rationalizing the experimentally observed red-shift on aggregation. It was noted that the barrier for phenyl group rotation was increased on increasing the aggregation (5.58 kcal mol^{-1} for

monomer, 11.45 kcal mol^{-1} for dimer, and 22.38 kcal mol^{-1} for tetramer, Fig. S6, ESI†), suggesting that the aggregation of TPPCA hindered the free intramolecular rotations of the phenyl group. Generally, free intramolecular rotations are known for quenching the emission of a chromophore through the dissipation of the excitation energy. The observed hindrance of free rotation of phenyl groups through aggregation provided the enhancement of the emission as AIE.

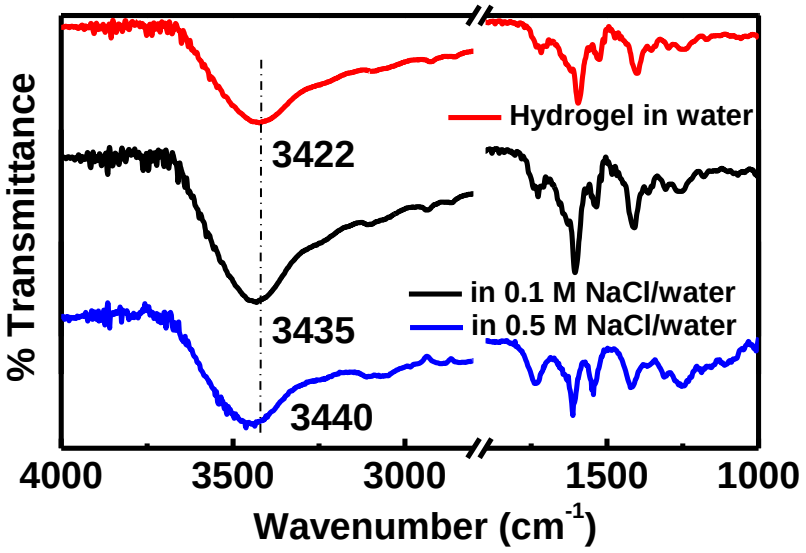

Fig. S7. FTIR spectra of dried TPPCA hydrogel in water, in 0.1 M NaCl-water and in 0.5 M NaCl-water

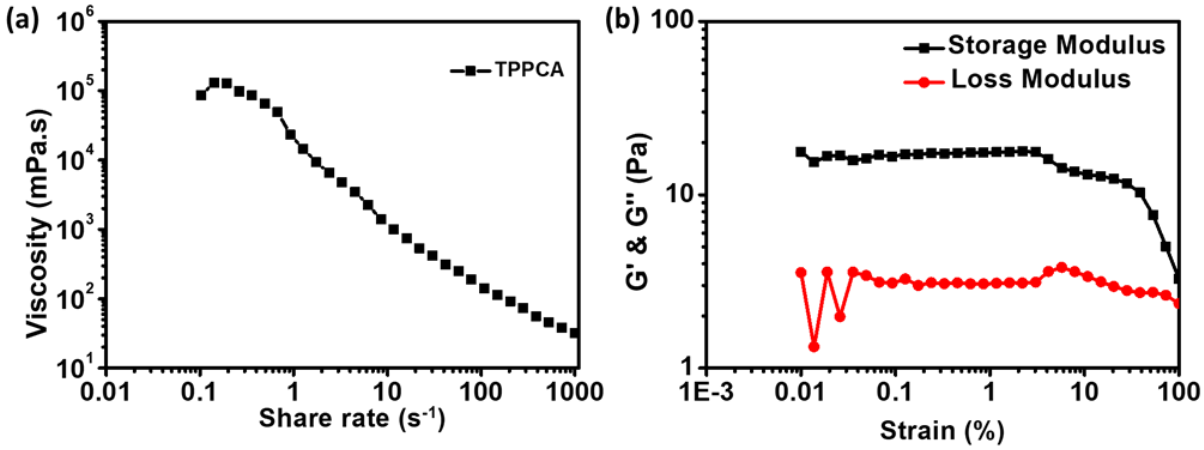

Fig. S8. Rheological measurement of hydrogel prepared (5 mg/mL in water) with (a) viscosity curve and (b) strain sweep measurement**.** A reversible viscoelastic was plotted with the increment and decrement of shear strain. The strain sweep measurement showed the storage modulus (G') is greater than loss modulus (G") in the entire strain region.

The rheology experiment suggested at lower shear rates, the hike in viscosity was mainly due to the closeness of the aggregated molecules by the intermolecular hydrogen bonding with π-π interaction. However, with the increment of shear rate, viscosity was decreased steeply, as the gel structure was destroyed. In a strain sweep measurement, *G'* was always higher than *G''* in the entire strain sweep range, indicating the viscoelastic behaviour of the gel was elevated by elastic nature.

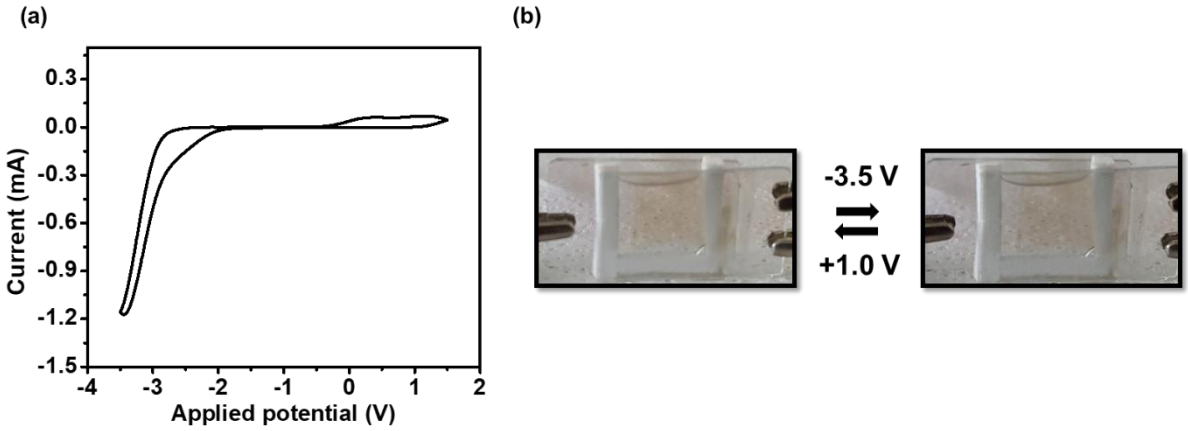

Fig. S9. (a) Cyclic voltammogram of TPPCA solution based EC device in 0.1 M Nacl-water solution at scan rate of 100 mV/s. (b) Corresponding optical color change of the EC device.

The CV study revealed no such prominent reduction peaks present in +1.5 to -3.5 V voltage window, and as a consequence the solution based EC device exhibited no colour change upon applied external voltage as shown in following figures. Probably, the voltage window is not suffies for the reduction in solution state. However, we can not put more voltage beyond -4 V as the ITO was making the irreversible and permanent coloration above -4 V in that condition.

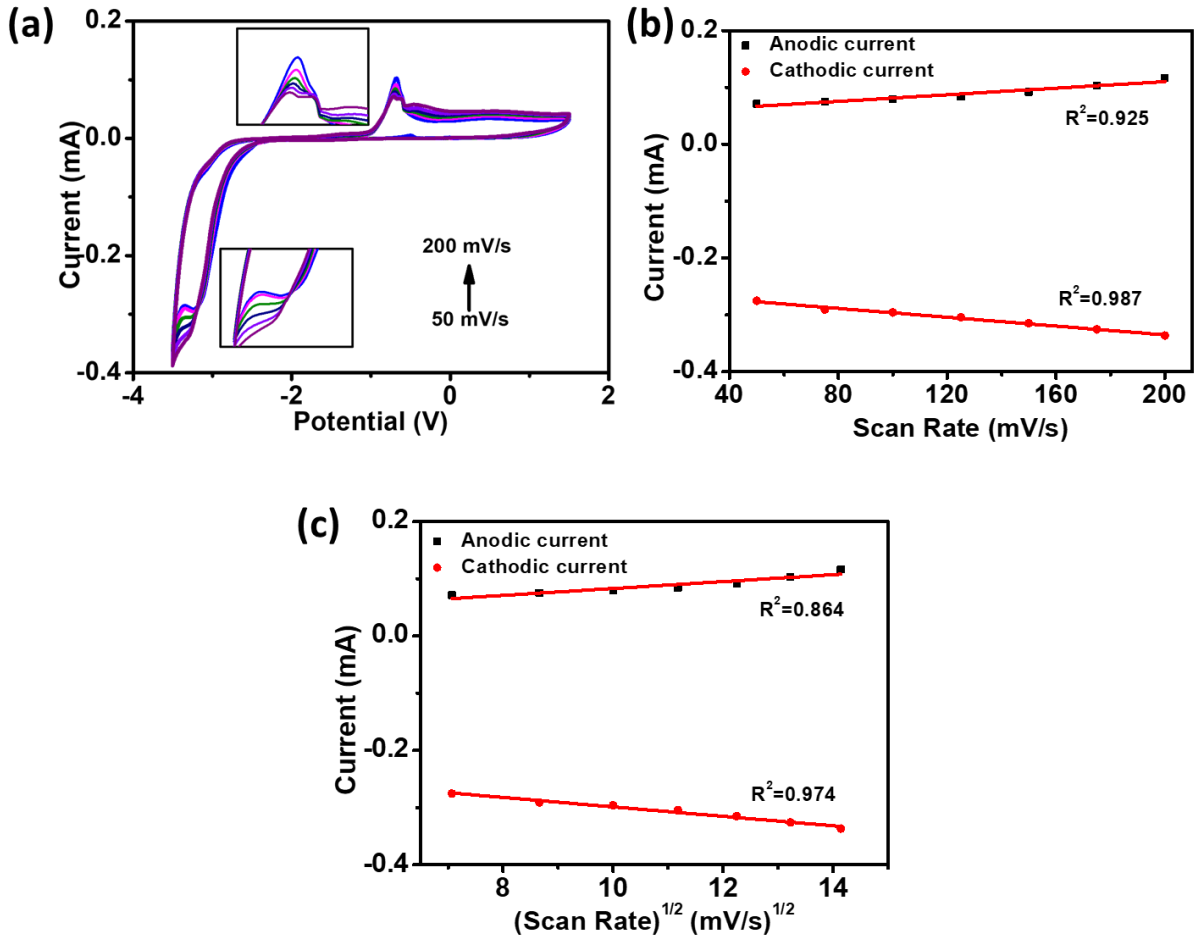

Fig. S10. Scan rate dependent CV study of TPPCA hydrogel.

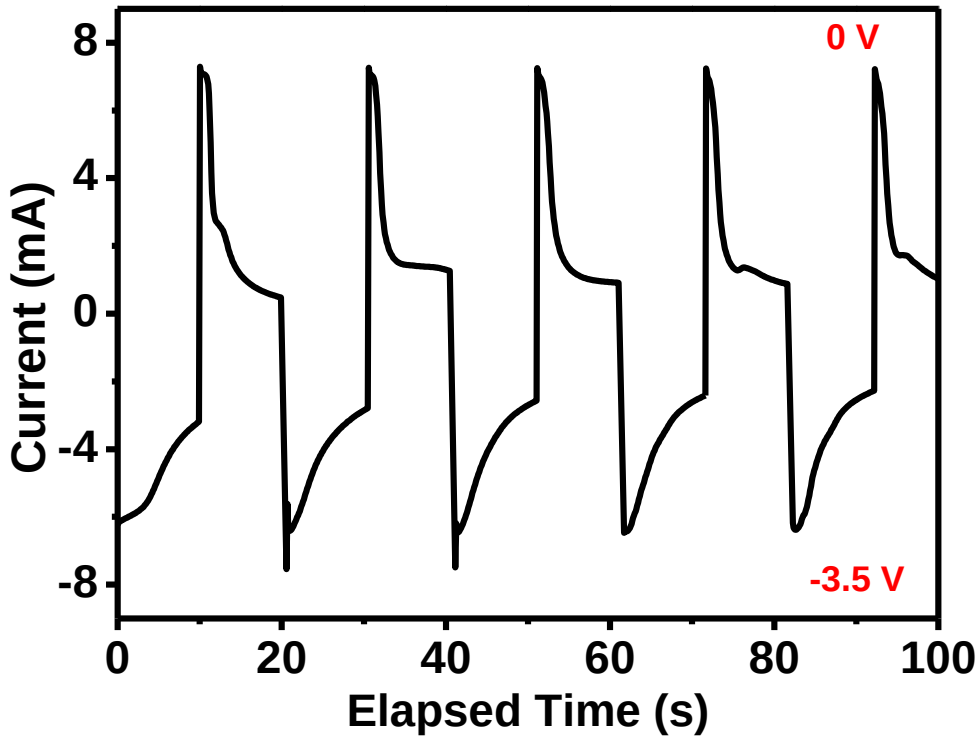

Fig. S11. Chronoamperometry of the gel at a potential sweep between -3.5 V and 0 V with a pulse width 10s.

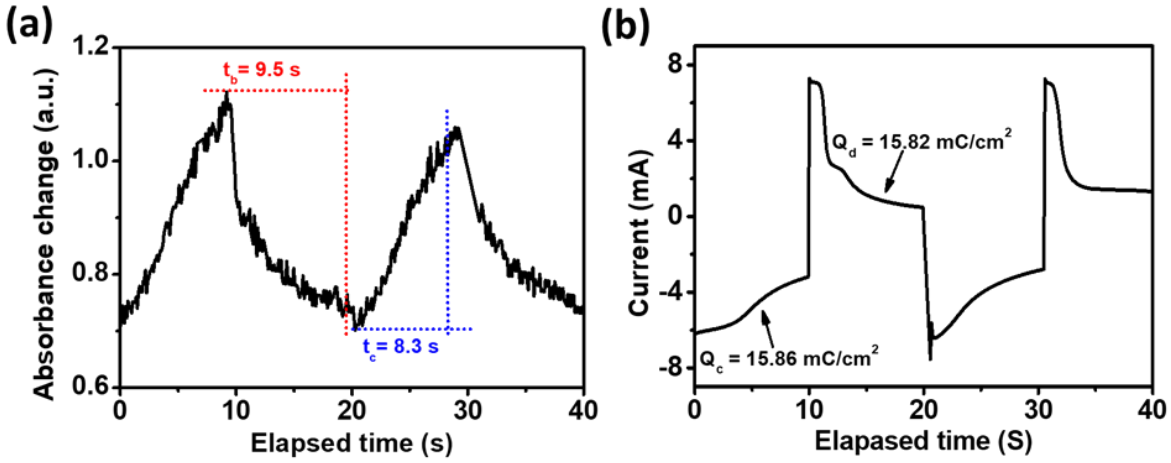

Fig. S12. (a) The first two cycles of absorbance change with time upon chronoamperometric potential switching between 0 V and -3.5 V of the hydrogel. Corresponding bleaching time (t_b) and colouration time (t_c) (time needed for 95% change of absorbance change) for the for formation of neutral and radical anion formation in ECD. (b) Double potential chronoamperometric switching between -3.5 V and 0 V with corresponding calculated charges.

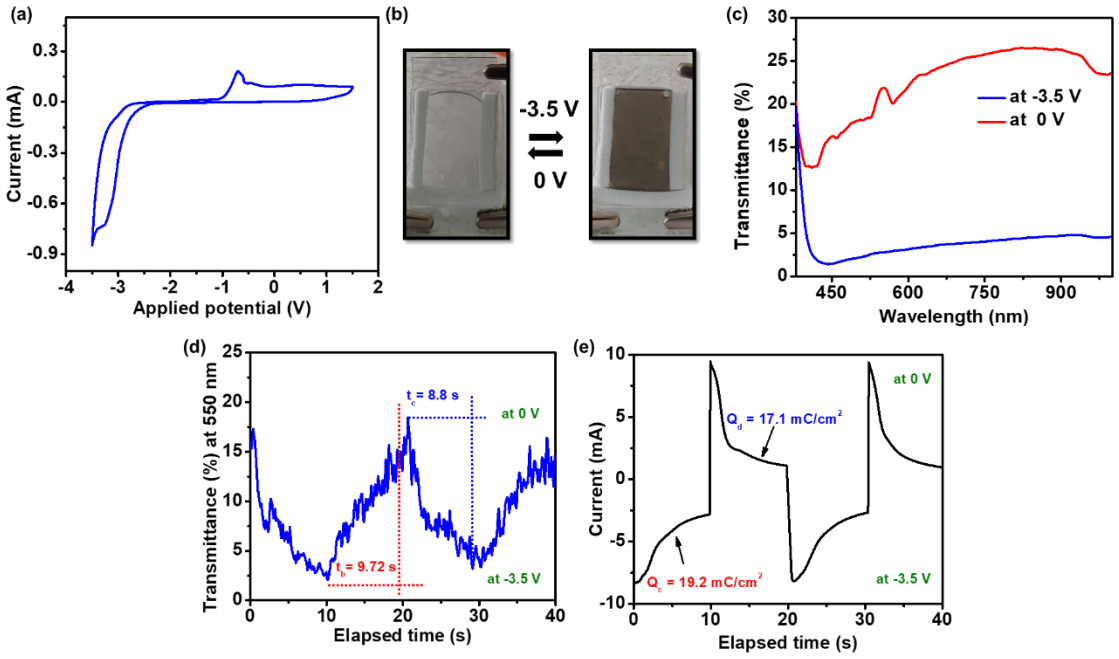

Fig. S13. (a) Cyclic voltammogram of TPPCA hydrogel at a geletor concentration of 10 mg/mL in 0.1 M NaCl at 100 mV/s. (b) Optical color change of the gel based ECD (c) Change of transmittance spectra on applying voltage in between 0 and -3.5 V. (d) Change of transmittance spectra of the ECDs at 550 nm during potential sweep in between 0 and -3.5 V at 10 s elapsed time. (e) change dischange (chronoamperometry) of the hydrogel based ECDs with calculated amount of charges.

To compare the EC parameters with gelator concentration, we have prepared an hydrogel of 10 mg/mL TPPCA gelator concentration and studied the EC properties exclusively by keeping the gel in box-type EC device. The CV study revealed the similar profile as the 5 mg/mL gel system. The gel demonstrated similar transparent to dark EC behaviour in 0 V to -3.5 V bias range. The After reduction the transparent gel gained a more blackish state which was also reflected by the larger decrement in absorption. Finally the EC response times i.e., average bleaching (t_b), and the colouration (darkening) time (t_c) of highly concentrated (10mg/mL) TPPCA hydrogel were determined as 9.72 and 8.80 s, respectively. The times are little higher due to the higher loading of the hydrogeltor between two electrodes during EC process. Aslo, the chronoamperometry study suggested the requirement of higher amount charges for charging a discharging compared to the gel with lower gelator concentration.

The photopic colouration efficiency:

The $T_{Photopic}$ can be calculated using the following formula and denotes the integral response over 380 to 780 nm wavelength range.

$$T_{Photopic} = \frac{\int_{380}^{780} T(\lambda).S(\lambda).P(\lambda)d\lambda}{\int_{380}^{780} S(\lambda).P(\lambda)d\lambda} \qquad (1)$$

Where, $T(\lambda)$ is the spectral transmittance of the EC gel, $S(\lambda)$ is the normalized spectral emittance of the light source, and $P(\lambda)$ is the normalized spectral response of the eye. T_{Photopic} for colouring and bleaching can be calculated using the EC transmittance spectra in coloured and bleached states and the values are summarized in Table S3. The photopic coloration efficiency was calculated to be 65.8 cm^2/C.

Table S4. Summary of EC parameters of TPPCA hydrogel.

Sample	Discharging/charging current density Q_d/Q_c (mC/cm^2)	t_b (s)	t_c (s)	Transmittance	T_b (%)	T_c (%)	Coloration Efficiency (η) (cm^2/C)
TPPCA (hydrogel)	15.8/15.8	9.5 ± 0.08	8.3 ± 0.02	at 550 nm	21	5.8	37.2 ± 1
				Photopic transmittance	68	6.2	65.8 ± 2

References:

(1) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77* (18), 3865-3868. Zhang, Y.; Yang, W. Comment on ``Generalized Gradient Approximation Made Simple". *Physical Review Letters* **1998**, *80* (4), 890-890.

(2) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* **2010**, *132* (15), 154104.

(3) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Computer Physics Communications* **2005**, *167* (2), 103-128.
(4) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *The Journal of Chemical Physics* **2000**, *113* (22), 9901-9904.