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Authors: Jay Shukla, Yeeshu Kumar, Manish Kumar Dixit, Mahendar Chinthakuntla, Vinay Kumar Sharma, Abul Kalam, and Mrigendra Dubey

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Investigation of mechanism behind conductive fluorescent and multi-stimuli responsive Li⁺-enriched metallogel formation

Jay Shukla,^[a] Yeeshu Kumar,^[a] Manish K. Dixit,^[a] Chinthakuntla Mahendar,^[a] Vinay K. Sharma,^[b] Abul Kalam^[c] and Mrigendra Dubey*^[a]

[a]	J. Shukla, Y. Kumar, M. K. Dixit, C. Mahendar, Dr. M. Dubey
	Soft Materials Research Laboratory, Department of Metallurgy Engineering and Materials Science
	Indian Institute of Technology Indore, Simrol, Indore 453552, India
	E-mail: mdubey@iiti.ac.in
[b]	V. K. Sharma

Indian Institute of Technology (BHU) Varanasi- 221005
 [c] Dr. A. Kalam
 Department of Chemistry,
 College of Science, King Khalid University, Abha 61413, KSA

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Abstract: A fluorescent metallogel (2.6% w/v) has been obtained from the two non-fluorescent components viz. phenyl-succinic acid derived pro-ligand H₂PSL and LiOH (2 equiv.) in DMF. Li⁺ ion not only plays a crucial role in gelation through aggregation, but it also contributed towards enhancement of fluorescence by imposing restriction over excited state intramolecular proton transfer (ESIPT) followed by origin of chelation enhanced fluorescence (CHEF) phenomenon. Further, the participation of CHEF followed by aggregation caused quenching (ACQ) and aggregation induced emission (AIE) in the gelation process have been well established by fluorescence experiments. Transmission electron microscopy (TEM) analysis disclosed the sequential creation of nanonuclei followed by nanoballs and its alignment towards the fibre creation of about 3, 31 and ~40 nm diameter, respectively. The presence of long-range fibrous morphology inside the metallogel was further attested by scanning electron microscopy (SEM). The rheological studies over metallogel proves its true gel phase material nature. Nyquist impedance study shows the resistance value 7.4 k Ω for metallogel which upon applying ultrasound increased to 8.5 k Ω , while at elevated temperature of 70 °C caused reduction in resistance value to 4.8 kΩ. The mechanism behind metallogel formation has been well established by using FTIR, UV-vis, SEM, TEM, PXRD, ¹H NMR, fluorescence and ESI-MS.

Introduction

Gels are well known smart materials, gathered alluring importance in the recent past due to their divergent and interdisciplinary applications.[1-6] Such smart materials, when subjected to external stimuli e.g. pH, temperature, light, sound and chemicals, usually undergo reversible gel-sol transition.[4-6] As a result of their responsiveness towards a variety of external stimuli, supramolecular gels find important applications in the field of catalysis, drug delivery, tissue engineering, sensing and light harvesting.^[7-9] Metallogels as an emerging subclass of the supramolecular gels find an increasing interest due to some additional enhanced properties such as conductance, optics, etc.^[10-15] catalysis. rheology, magnetism, Similar to supramolecular gels, metallogel formation also takes place with the help of H-bonding/ Van der Waals/ π - π stacking weak interactions in addition to characteristic driving forces such as metal-metal interactions, coordination complexation/ polymerization, *etc*.^[16-19]

Coordination of alkali/ transition/ lanthanide metal ions to appropriately designed ligands produces metallogels which may demonstrate the unique optical/fluorescent as well as other metal associated properties.^[20-26] Due to appearance of unique fluorescence property in metallogels, these materials could be utilized for sensing, cell imaging, security writing, *etc.*^[27-30] Involvement of CHEF, AIE and ACQ phenomenon towards generation of fluorescence in metallogels are well established in the recent past, but simultaneous occurrence and explanation of all the three phenomena in a single metallogel is hardly accomplished so far except our few reports.^[23, 25, 26]

Metallogels, by virtue of its electrically conducting behaviour, have gained substantial attention to be realized in the various electronic and electrochemical device applications.^[31, 32] Recently, Dey *et al.* developed a metallogel based semiconductive device, the conductivity of the metallogel was achieved to be 5.35×10^{-2} S/cm.^[31] Further, Bhattacharjee *et al.* synthesised zinc containing coordination driven metallogel and investigated its conducting property in order to develop gel electrolyte for supercapacitor application. The prepared metallogel exhibited very low resistance value of 26.3 Ω , hence claimed its suitability as an electrolyte for the targeted application.^[32] Thus, these reports suggest that the conductive properties of metallogels can be utilized for fabrication of gel phase-based devices.

Recently, we reported chiral tartaric acid/ citric acid derived ligands/ a series of bolamphiphiles including a succinic acid derived ligand H_2SL lead to formation of highly fluorescent metallogels either upon addition of requisite amount of LiOH or/and Zn(OAc)₂/Cd(OAc)₂.^[25,33] We also tuned the morphology from nanoball to twisted fibers, optical properties from CHEF to intramolecular charge transfer (ICT) upon incorporation of minor changes in molecular functionality in tartaric acid-based ligands.^[23] On the other hand, metallogels obtained from citric acid derived ligand showed morphological transformation from random to lucid nanofibrous morphology, 10 fold enhancement in conductance under influence of ultrasound.^[24] Inspired from all these findings, herein, we modified H₂SL ligand by incorporating additional benzene ring to obtain the chiral H₂PSL ligand which

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lead to formation of a multi-stimuli responsive, conductive and fluorescent metallogel upon treatment with 2 equivalents of LiOH.



Scheme 1. Representation of the steps involved in metallogel formation along with the changes in fluorescence.

Results and Discussion

With an objective to explore the effect of inclusion of an additional benzene ring to H_2SL ligand over metallogelation, we synthesized a phenyl-succinic acid derived ligand H_2PSL (Experimental



Figure 1. Stimuli-responsive behaviour of (A) metallogel towards (B) temperature, (C) UV light, (D) mechanical shaking and (E) resistant for ultrasound.

Sections and Scheme S1, Supporting Information). The phenyl group present in H₂PSL is expected to provide a platform for additional π - π stacking for aggregation and ONO' donor sites would accommodate Li⁺ ion to produce CHEF assisted fluorescent metallogel (Scheme 1). Further, it is also expected that metallogel enriched with Li⁺ ions would demonstrate the conductance property.

¹H NMR of synthesized **H**₂**PSL** ligand in *d*₆-DMSO displayed the existence of three conformers (syn/anti, anti/anti and syn/syn) which upon treatment with LiOH converted into a single conformer (syn/syn) as demonstrated in figure S1 (Supporting Information).^[25,25,33] The deprotonation of H_2PSL with 2 equivalents of LiOH in DMF followed by sonication for about 5 minutes led to the formation of blue fluorescent metallogel at 2.6% w/v, (Scheme 1 and Figure 1). The gelation was further confirmed by the conventional falling ball and inverted vial tests. The metallogel obtained was found to be stimuli-responsive towards heat, mechanical shaking, whereas, resistant against brief ultrasonication (Figure 1). Furthermore, H₂PSL alone or in presence of other alkali bases like NaOH, KOH, CsOH except LiOH failed to produce metallogel under aforementioned similar conditions implies the selectivity towards Li⁺ for gelation (Figure S3-S5, and Table S1, Supporting Information). Gelation test of H₂PSL with LiOH was also tested in presence of other common laboratory solvents such as CH₃OH/ DMSO/ CHCl₃, but except DMF, the compound failed to form a gel in other solvents tried. (Table S2, supporting information).

Morphological Characterization

To acquire the morphological insights, the metallogel was examined under field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). TEM disclosed an interesting mechanism behind fiber formation within the metallogel matrix. It revealed the formation of unique nanonuclei with average diameter of about ~3 nm which perhaps



Figure 2. TEM images of diluted metallogel (1x10 4 M) at four different magnifications.

aggregate into nanoballs of about ~31 nm average diameter (Figure 2).^[33] Moreover, these nanoball aggregates lead to fabrication of fibrous network (average fiber diameter ~40 nm) within metallogel matrix which was evident through FESEM analysis where we observed long range intermingled fibrous morphology (Figure 3).



Figure 3. FESEM images of the xerogel at different magnifications (A-B).

To investigate the packing of molecular aggregates and presence of weak interactions powder X-ray diffraction (PXRD) study performed on xerogel. High intensity peaks in the PXRD patterns of H₂PSL in the range $2\theta = 5^{\circ}-50^{\circ}$ indicative towards its crystalline nature while that of the xerogel showed broad peaks at 20 = 7.84°, 14.24°, 17.04°, 22.48° and 30.32° suggests amorphous nature of fibers (Figure 4). Three periodic diffraction peaks were obtained in the PXRD pattern of the xerogel at 2θ = 7.82°, 14.24° and 22.48° corresponding to *d*-values 11.29Å, 6.21Å and 3.95Å, respectively, with the sequential ratio close to d : d/2: d/3. The characteristic ratio of d-values advocates the presence of layered arrangement between molecular aggregates with the distance between layers equalling to 11.29Å.[25] Also, the existence of the diffraction peaks at $2\theta = 17.04^{\circ}$ and 22.48° corresponding to the *d*-values 5.19Å and 3.95Å, respectively, indicates the presence of $\pi-\pi$ stacking (Figure 4 and 8).^[24,25] Appearence of small peaks in the range of $2\theta = 30^{\circ}$ to 40° signifies the presence of H-bonding interaction in the gel network (Figure





Figure 4. PXRD pattern of the xerogel (H_2PSL/Li^* , black lines) and the ligand (H_2PSL , red lines).



Figure 5. ESI-Mass spectra show isotopic abundance pattern represented the simulated (red dotted line) and experimental (black line) for diluted metallogel.

Structural Analysis

To find out the chemical structure involved in formation of metallogel, we performed the FTIR, UV-vis and ESI-Mass studies. We could not observe the significant changes in FTIR spectra of ligand **H**₂**PSL** and xerogel **H**₂**PSL**/Li⁺ due to the only replacement of H⁺ with Li⁺ as demonstrated in scheme 1 and figure S6 (Supporting Information). Further, UV-vis spectra also did not display any kind of significant changes in two intense coupled π - π * transition and n- π * transition bands at 282, 291 and 323 nm, respectively, upon aliquot addition of LiOH (Figure S7, supporting information). FTIR and UV- vis spectra suggest the existence of weak interaction between **H**₂**PSL** and Li⁺.^[24,36] Moreover, to ascertain the adduct formation between **H**₂**PSL** and Li⁺, we recorded the ESI-MS spectra over diluted metallogel (Figure 5 and S8, Supporting Information). A molecular ion peak found to be at *m*/z 437.2 corresponding to the molecular formula

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 $[C_{24}H_{22}N_4O_4+Li]^+$, whereas the isotopic abundance pattern matches nicely with the simulated peak pattern which confirms the Li⁺ interaction with H₂PSL.

Aggregation Study

With an objective to explore the mechanistic steps involved in the gelation process, we performed various fluorescence experiments over H₂PSL and the freshly prepared metallogel. The weakly fluorescent gelator H₂PSL (λ_{ex} =320nm, λ_{em} =481nm, Stokes shift= 62112 cm⁻¹, 1x10⁻³ M, DMF, blue line) displayed a noticeable enhancement in the emission intensity upon aliquot addition of LiOH (1x10⁻¹ M, DMF, red line) along with blue shift of 9 nm (Figure 6).^[24-26] It might be because of the removal of ESIPT and origin of CHEF phenomenon, endorsed by the deprotonation followed by chelation of Li⁺ to the deprotonated species of gelator **PSL**² as well as the AIE phenomenon (*vide infra*, scheme 1).^[35, 37] Further, to ascertain the role of Li⁺ towards enhancement of fluorescence intensity of H₂PSL *via* CHEF phenomenon, we treated the diluted metallogel (H₂PSL/Li⁺, 10⁻⁴ M, DMF)



Figure 6. Fluorescence titration experiment of (A) H_2PSL (10⁻³ M, DMF, blue line) with LiOH (10⁻¹ M, DMF, red lines), (B) Fluorescence variable temperature experiment and (C and D) Fluorescence gel dilution experiment.



Figure 7. Fluorescence lifetime measurement of metallogel and its diluted conditions.

with [12]-crown-4 and observed the complete quenching of fluorescence intensity which is due to trapping of Li⁺ by [12]crown-4 or in other words removal of CHEF (Figure S9, supporting Information).^[26] Thermo-reversibility of the metallogel was further investigated by the variable temperature fluorescence experiment in the temperature range of 30-70°C. Upon increasing the temperature from 30 to 70°C, fluorescence intensity of metallogel decreased with red shift ($\Delta\lambda$ =6 nm) indicative towards the slight segregation of gel network (Figure 6). Further, upon cooling from 70 to 30°C, it regained 80% of its original fluorescence intensity supports the observation made about metallogel as stimuli-responsive towards heat (Figure 1 and 6).

In order to confirm the presence of CHEF, AIE and/or ACQ phenomena, we performed fluorescence dilution experiment on freshly prepared metallogel within the range from 10⁻² M to 10⁻⁴ M (Figure 6). Upon dilution of metallogel from 10⁻² M to 10⁻³ M concentration, the fluorescence intensity was decreased with a small blue shift of 5 nm suggests the presence of AIE phenomenon during the gelation process. Surprisingly, further dilution from 10⁻³ M to 10⁻⁴ M lead to the notable enhancement of fluorescence intensity with blue shift of 9 nm. This continuous enhancement in fluorescence intensity upon dilution 10⁻³ M to 10⁻ M advocates the involvement of ACQ phenomenon in the metallogelation. The occurrence of both quenching and enhancement of emission intensity with the dilution of the metallogel refers to the presence of AIE and ACQ, respectively, along with CHEF phenomena. Extreme dilution below 10⁻⁴ M concentration lead to usual decrease in emission intensity due to dilution effect.^[26] The fluorescence lifetime measurements were performed over the synthesized metallogel (H₂PSL/LiOH; ~10⁻² M) and its diluted conditions (10⁻³ and 10⁻⁴ M). A sequential increase in τ values 0.77 ns, 0.79 ns and 1.07 ns were observed the upon dilution from ${\sim}10^{\text{-2}}~\text{M}$ to $10^{\text{-3}}$ and $10^{\text{-4}}~\text{M}$ (diluted metallogel), respectively which supports the observation made from fluorescence gel dilution experiment (Figure 7).

Based on the observations drawn from the above experiments, we summarized a plausible mechanism of gel formation in figure 8.

Rheological Study

In order to establish the metallogel as true gel phase material and to explore its viscoelastic properties, we performed detailed rheological experiments over freshly prepared metallogel (2.6% w/v). Strain sweep experiment shows that in response to applied shear strain, the storage modulus (G') was found to be ~1 order magnitude higher than loss modulus (G") upto 4% strain value and beyond this value, they crossed each other which indicates the phase transition from gel to sol phase (Figure 9).^[38, 40] When the metallogel was subjected to dynamic shear stress, G' was found to be ~1 order magnitude higher than G" up to yield stress of 2.4 Pa, supporting the metallogel as true gel phase material, upon further application of shear stress beyond the yield stress point both G' and G" cross each other, indicating the deformation of the gel network (Figure 9).^[40] Dynamic frequency sweep measurements show that the predominantly unchanged behavior of the storage modulus (G') and the loss modulus (G'') within the applied frequency range (0.1 to 100 rad s⁻¹ at 25 °C) advocates the elastic nature of the metallogel (Figure 9). Moreover, logarithmic plot of complex viscosity (η^*) plotted against ω

provides a negative slope of ~1 suggesting constant declination of viscosity with respect to frequency. ^[38, 39] Effect of temperature

was again observed at about 80°C (Figure 9). This result was further attested by a curve of loss tangent (tan δ = G"/G') vs



Figure 8. A model representation for plausible mechanism of the gelation along with morphological changes.



on logarithmic plot of G' and G'' was recorded within the

temperature range 25°C-130°C (Figure 9). The plot shows

Figure 9. (A) Dynamic oscillation strain sweep, (B) Dynamic shear stress of G' and G'' at frequency of 10 rad s⁻¹ at 25°C, (C) Plot of Storage and loss modulus vs Temperature, (D) Plot of Storage and loss modulus over dynamic frequency ramp, (E) Plot of temperature vs complex viscosity and (F) Plot of temperature

vs tanδ.

that the metallogel can sustain temperature below 80°C, and beyond 80 °C, strong to weak gel transition has been observed.^[38] The phase transition temperature or strong to weak gel transition was further ascertained by the plot of complex viscosity over dynamic temperature ramp (25-130°C) where the gel transition temperature plot (Figure 9). An abrupt change in the curve at around 80°C confirms the phase transition temperature "T_{gel}" of the metallogel. Thus, the overall rheological results show that the present metallogel has characteristics of true gel phase materials.^[38, 40]



Figure 10. (A) Nyquist impedance plots, triangle points represent the best fit model. Equivalent circuit model for (B) metallogel (C) after ultrasound and (D) after heating the metallogel.

Conductance

The conductance property of the synthesised metallogel along with effect of temperature and ultrasound were explored using electrochemical impedance spectroscopic (EIS) measurements within the frequency range 10^6 to 10 Hz at an amplitude voltage of 10 mV. The Nyquist plots shown in figure 10, present a semicircle in high frequency region followed by a linear evolution in low frequency region for each plot. The semicircle can be fitted to a parallel circuit of a charge-transfer resistance and capacitance in each plot. The charge-transfer resistance (R_{ct1}, R_{ct2} and R_{ct3}) arises due to electrode-electrolyte interface, whereas the capacitance of the cell.^[24] The overall Nyquist plot has been fitted with the equivalent circuit models in each case of the metallogel (Heating and ultrasonication). At very high frequency (10^6 Hz) there is appearance of a series resistance (R_{s1}, R_{s2} and

R_{s3}) and the linear evolution could be fitted with a constant phase elements for each case accounting for the non-ideal behaviour of the electrode interface.^[24,32] The resistance was measured to be 7.4, 8.5 and 4.8 k Ω for metallogel, after sonication and after heating of the same metallogel, respectively, by extrapolating the straight line of the Nyquist plot from very low frequency (10 Hz) to an infinitely large frequency up to real axis (Z').[41] Notably, the resistance value of the metallogel obtained in various conditions is the sum of series resistance and charge transfer resistance. Initially, the metallogel shows resistance value of $R_1 = 7.4 \text{ k}\Omega$, however, upon sonication for 15 minutes resulted in the increased resistance value $R_2 = 8.5 \text{ k}\Omega$, this increment in the resistance, in other words, decrement in the conductivity of the metallogel perhaps attributed to the slight disorganisation caused in fibrous network of the metallogel, since conductance property is more dominant in highly organised system as compared to disorganised system.^[24,41] Furthermore, the metallogel was heated up to 70 °C, upon heating the resistance value significantly decreased to $R_3 = 4.8 \text{ k}\Omega$, this decrement in the resistance value caused by reduced viscosity of the metallogel at elevated temperature thereby increasing the mobility of ionic species inside the gel matrix (Figure 10).^[42] The effect of ultrasound and temperature on the conductance property of metallogels are in agreement with the observation made from rheology and stimuliresponsive behaviour explored in earlier sections (Figure 1 and 10).

Conclusion

In conclusion, we demonstrated the synthesis and properties of metallogel, obtained from phenyl ring containing succinic acidbased ligand and LiOH. The LiOH treatment with ligand H₂PSL not only contributed towards the metallogels formation, but also originate the intense fluorescence through the CHEF and AIE. In addition to the CHEF and AIE, another contradictory ACQ phenomenon was explored to be present in metallogel. Further, TEM and SEM analysis over diluted metallogel disclosed the steps involved in fiber formation in sequence of nanonuclei to nanoballs followed by nanofiber. Gelation mechanism is well established by UV-vis, PXRD, fluorescence, SEM, TEM and ESImass experiments. The true gel phase of the metallogel was proved by a detailed rheology experiment. Furthermore, we analyzed the external stimuli like ultrasound and thermal response over conductance property of metallogel. Ultrasound led to the disruption of metallogel network in turn increase in resistance value (8.5 k Ω) was observed whereas heating simply decreases the resistance value (4.8 k Ω) probably due to easy flow of ion in gel matrix. This concept of metallogel synthesis would be helpful to develop more stimuli responsive conductive fluorescent materials for electrolytic applications.

General Information, Material and Physical Methods

Common reagents and solvents were purchased from Avra, Merck, Qualigens or S.D. Fine Chem. Ltd., Mumbai, India and used as received without further purifications. The solvents were thoroughly dried and distilled by standard literature methods prior to their use. Phenylsuccinic acid, Hydrazine Hydrate, 2-hydroxybenzaldehyde and LiOH.H₂O were purchased from TCI chemicals Pvt. Ltd, Sisco Research Laboratories Pvt. Ltd., and Spectrochem Pvt. Ltd. Mumbai, India, respectively, and used as received without any purification.

PerkinElmer Spectrum two and UV 2600 Schimazdu spectrometers were used to obtain the FT-IR and electronic absorption spectra, respectively. Photoluminescence spectra were acquired on a Perkin Elmer FL8500 Fluorescence spectrophotometer. ¹H NMR spectra were obtained on a Bruker AVANCE III 400 Ascend Bruker BioSpin International AG spectrometer. Electrospray ionization mass (ESI-MS) spectra were recorded on a Waters (Micromass MS Technologies) QTof Premier. TEM images were captured using a JEOL JEM 2100. SEM images were recorded using JEOL 7610 F Plus. Rheology of metallogel was performed on Anton Paar MCR 102 Rheometer. Powder XRD data was collected on Rigaku Smart Lab between angle $2\theta = 5^{\circ}-50^{\circ}$. Melting point was obtained from MPA100 digital melting point apparatus.

UV-vis study

Stock solution of H_2PSL (10⁻⁵ M) was prepared in DMF for electronic absorption study. LiOH solution (10⁻³ M) was also prepared in DMF. As performed in a typical titration, solution of H_2PSL was taken in a quartz cuvette (3.0 mL; path length, 1 cm) and LiOH solution was added gradually with a micropipette. At each addition, proper mixing and sonication was performed, and spectra were recorded.

Rheological study

Rheological measurements were carried out using an MCR 102, Anton Paar rheometer equipped with stainless steel parallel plates (20 mm diameter, 1.0 mm gap). The instrument facilitated with a Peltier temperature control unit which was calibrated to give a temperature in the sample within 0.1 °C of the preset value. All the experiments were conducted over freshly prepared metallogel (2.6% w/v). Dynamic amplitude sweep experiments were conducted within stress and strain range of 1.2 to 2.8 Pa and 0.01% to 100%, respectively, at a constant frequency of 10 rad s⁻¹. Dynamic oscillatory frequency sweep was carried out at 25 °C (20 min and from 0.1 to 100 rad s⁻¹) at a constant shear strain of 1%. Dynamic temperature ramp experiment was performed within the temperature range of 25 to 130 °C at a constant frequency of 10 rad s⁻¹ and strain of 1%.

Conductance study

Electrochemical impedance spectroscopic (EIS) measurement were performed using a CH instruments electrochemical workstation CHI604E model within the frequency range 10⁶ to 10 Hz at a small perturbation voltage of 10 mV. To record Nyquist impedance plots for metallogel at different conditions, the experiment was conducted in a cylindrical shaped electrochemical cell with three electrodes system. Ag/AgCI reference electrode, glassy carbon working electrode and Pt wire counter electrode were used for the experiment. Further, Nyquist plot was fitted with a suitable equivalent electrical circuit model with the help of an inbuilt software provided by CH instruments.

FESEM and TEM sample preparation

A freshly prepared metallogel (1 mL) was dried inside vacuum desiccator at ambient room temperature in order to obtain the sample for FESEM analysis. The dried metallogel (xerogel) sample was gently removed out from the vial and transferred to the FESEM sample holder. Furthermore, gold coating was applied on the samples for reduction of the charging under an electron beam.

For TEM analysis, a sample was prepared by dilution of metallogel (DMF, 1×10^{-4} M) followed by drop casting on a carbon-coated copper grid (400 mesh) and dried in vacuum desiccator for 2 days.

Fluorescence lifetime measurements

TCSPC system from Horiba Yovin (Model: Fluorocube-01-NL) were used to perform the lifetime measurements. Excitation wavelength were fixed at 334 nm using a picoseconds diode laser (Model: Pico Brite-375L) for as synthesized metallogel and diluted metallogels at the concentration 10⁻³ and 10⁻⁴ M. Further, the data analysis was performed using IBH DAS (version 6, HORIBA Scientific, Edison, NJ) decay analysis software. The resulting decay was best fitted by a bi-exponential decay.

Synthesis of H₂PSL

To a methanolic solution of phenylsuccinic acid (1.00g, 5.1mmol) 2 or 3 drops of conc. sulphuric acid was added as a catalyst and the reaction mixture was refluxed for 18hrs at 70°C. In vacuo reduction in volume with mild heating was done to obtain dimethyl phenylsuccinate ester as an oily and sweet-smelling product. To the obtained dimethyl phenylsuccinate (1.00g, 4.5mmol) hydrazine hydrate (0.45g, 9mmol) was added in methanol and reaction mixture was stirred for 6 hours at room temperature. A white crystalline powder of phenylsuccinic hydrazide (PSAH) was obtained from above solution which was filtered, washed with methanol and diethyl ether and dried in desiccator. The compound PSAH (0.300g, 0.32mmol) was dissolved in 2mL of water and then mixed in 20mL methanol to obtain a clear solution. To this solution, 2-hydroxybenzaldehyde (0.329g, 0.64mmol) in methanol was added dropwise and solution was refluxed for 1 hours at 70°C. The white precipitate afforded from the solution was stirred for additional 2 hours at room temperature and then filtered, washed thoroughly with methanol and diethyl ether to afford a white solid (H₂PSL). Yield 1.74g (81 %). Mp 280°C; Anal. Calc. for C₂₄H₂₂N₄O₄: C, 66.95; H, 5.15; N, 13.02. Found C, 66.82; H, 5.09; N, 13.10. ¹H NMR [(CD₃)₂SO, 400 MHz]: δ (ppm) = 12.00+ 11.80+11.37+11.14 (3d+1t, 2H, NH), 10.19+10.09 (2s, 2H, OH), 8.43-8.27 (m, 2H, -CH=N), 7.55-7.32 (m, 8H), 6.94 (s, 5H, -Ph), 5.03 (s, 1H, CH-Ph), 4.20 (s, 2H, CH2); ¹³C NMR [(CD₃)₂SO, 400 MHz]: δ =168.79,163.25, 158.13, 132.48-128.15, 117.95 ppm; FTIR (KBr): v=3250, 3052, 1653, 1532 cm⁻¹; UV-vis (DMF), λ_{max} (ε:M⁻¹ cm⁻¹): 322 (26500), 291 (45000) and 282 (47500) nm.

Synthesis of Metallogel

H₂PSL 26mg was suspended in 0.5mL DMF and slow addition of 2 equivalents of LiOH solution (0.5mL, DMF) produced yellow suspension. Further, it was sonicated for 5 minutes to obtain an

opaque blue fluorescent metallogel (2.6% w/v) at room temperature. FTIR (KBr) v=3256, 3056, 1652, and 1532 cm⁻¹. Anal. Calc. for C₂₄H₂₁N₄O₄Li: C, 66.02; H, 4.85; N, 12.84. Found C, 65.93; H, 4.79; N, 12.89. ESI-MS *m/z*: calcd for [C₂₄H₂₂N₄O₄+Li]⁺: 437.18; found: 437.2.

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Author contributions

JS contributed in the synthesis of ligand, metallogel and preliminary characterization studies. YK helped in conductance measurements, formal analysis and investigation of results. MKD contributed to the fluorescence experiments and discussion. CM performed the rheology, UV-vis experiments and analysed the data. VKS and AK were involved in the TEM experiments, characterization, analysis and correction in the manuscript. All the authors analysed the experimental data, discussed the results, wrote and commented on the manuscript. MD had responsibility for funding acquisition, project administration, formal analysis, writing of original draft, validation and the overall project concept.

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A Li⁺-induced multi-stimuli responsive florescent metallogel (2.6% w/v) has been synthesized and explored the presence of ESIPT, CHEF, AIE and ACQ fluorescence phenomenon. The morphology, rheology and effect of ultrasound and heat was monitored on the conductance property of metallogel.

Twitter user name: mrigendra dubey @dubey_mrigendra

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