Electronic Supplementary Information (ESI)

Palladium-induced transformation of nematic liquid crystals to robust metallogel comprising self-assembled nanowires

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1. Physical Measurements and Instrumentation.

Materials and Methods. All required chemicals were obtained from commercial sources and solvents were dried properly whenever it was necessary. FT-IR spectra of the compounds were recorded in Perkin Elmer Spectrum BX FT-IR system. Mass spectra were measured on a MicroMass ESI-TOF spectrometer. ^1H -NMR (400 MHz) and ^{13}C -NMR (100 MHz) spectra were recorded in Bruker-400 Avance NMR spectrometer. Elemental analysis was performed on a Carlo Erba elemental analyzer model 1106.

Gelation Studies. A certain amount of **1** had been added into a properly capped glass vial containing appropriate solvent with heating and sonication to get a clear solution. After that, the solution was cooled and left for 0.5 h. The gelation test was performed using the inverse flow method. Upon gelation, the gel was further characterized quantitatively by determining the critical gelator concentration (CGC). CGC is defined as the minimum amount of compound required to form gel in 1 mL of solvent. For compound **2**, **1** and $\text{PdCl}_2(\text{PhCN})_2$ (2:1 molar ratio) were mixed in DCM/CHCl_3 and kept at room temperature to form gel.

Differential Scanning Calorimetry (DSC). Differential Scanning Calorimeter (DSC; Perkin-Elmer, Model Pyris 1D) was used to record thermotropic phase transition behavior of **1** in solid phase. During the experiments, the heating and cooling rates were fixed at $2\text{ }^\circ\text{C min}^{-1}$.

UV-Vis Spectroscopy. UV-Vis spectra **1** and **2** in solution were recorded on Shimadzu model 2600 spectrophotometer.

Inverted Phase-contrast Optical Microscopy: Gel of compound **1** in ethanol was taken in a properly cleaned glass slide and covered with a coverslip. The images were recorded in phase contrast mode (Olympus CX 81).

Scanning Electron Microscopy (SEM). The gel samples (**1** and **2**) were drop-coated onto a cover-slip which was glued on brass stubs. Then samples were kept for drying. Before experiments, samples were coated with platinum vapor. JEOL JSM-7500F (Field Emission Scanning Electron Microscope) operated at 1-10 kV was used to record images for this experiment.

Atomic Force Microscopy (AFM). A diluted solution of the gelator (**2**) has been drop-coated on freshly cleaved mica and then dried in open air. The microscopic measurements were performed in tapping mode (JPK instruments, NanoWizard JPK00901 software).

Transmission Electron Microscopy (TEM). The aggregates of the gelators (**2**) were examined under a transmission electron microscope. A solution of **2** (10 μL) sample was drop coated onto a 400 mesh copper grids and allowed to dry. Then, the sample was observed under TEM (JEOL2100F) with an acceleration voltage of 200 kV.

Polarized Optical Microscopy (POM). Birefringence at different temperatures of the sample (**1**) had been followed under polarized optical microscope (Olympus BX 51) which was equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90).

Powder X-ray Diffraction (PXRD). Both gels (**1** and **2**) were scooped onto a properly cleaned glass slide. After that samples were freeze-dried under vacuum before PXRD measurements. XRD measurements were performed in a Bruker D8 Advance instrument. X-ray beam for this experiment was generated by rotating Cu anode at the wavelength of $1.5418\text{ \AA}$ and the sample was scanned from 1 to 30° (2θ). Variable temperature XRD experiments of **1** (solid) were performed in a properly sealed capillary.

Rotating-frame Overhauser Spectroscopy (ROESY).

The ROESY experiment was performed in 700 MHz Bruker-Avance instrument with a mixing time of 250 ms and ROESYPH pulse sequence at 293 K. During this measurement, a ROESY continuous-wave spin-lock of 1.5 KHz was applied to collect 2k points and 512 points in the f_2 and f_1 domain respectively. Bruker TOPSPIN 2.1 software was used for processing data.

2. Synthesis and Characterization:

Synthesis of 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzohydrazide (**5**) was carried out based on reported procedures^{S1}. Synthetic scheme of compound (**1**) and palladium-complex (**2**) is shown below.

Synthetic Scheme 1^a

^a**Reagents, conditions and yields:** (i) Tosyl Chloride, NaOH-THF-H₂O, 0 °C-rt, 6h, 90%; (ii) Ethyl gallate, K₂CO₃, CH₃CN, reflux, 12h, 75%; (iii) Hydrazine hydrate, methanol, reflux, 12h, 95%; (iv) Dry DMF, 140 °C, 12h, 20%. (v) PdCl₂(PhCN)₂, dry DCM, rt, 1h, quantitative.

Synthesis of Compound 1:

1,4,5,8-naphthalene tetracarboxylic dianhydride (1.3 g, 4.84 mmol), 4-picolylamine (0.52 g, 4.8 mmol) and 3,4,5-tris(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzohydrazide^{S1} (3 g, 4.82 mmol) were mixed together and dry

DMF was added to it. The solution was refluxed for 12h in N₂ atmosphere at 140 °C. After that, the organic solvent was removed in vacuum with heating. The compound was purified by column chromatography using chloroform and methanol (v/v 100:2) as solvent. The purified yield was 0.93 g, 20%.

FT-IR (Neat, cm⁻¹): 2873, 1696, 1664, 1582, 1492, 1421, 1329, 1243, 1204, 1102, 991, 848, 794, 759; ¹H NMR (400 MHz, CDCl₃, ppm): δ 3.26 (s, 6H), 3.38 (s, 3H), 3.5 (t, 4H, 4 Hz), 3.55 (t, 2H, 4 Hz), 3.62-3.73 (m, 18H), 3.80-3.85 (m, 6H), 4.27- 4.28 (m, 6H), 5.40 (s, 2H), 7.4 (d, 2H, 5.2 Hz), 7.45 (s, 2H), 8.58 (d, 2H, 5.2 Hz), 8.82 (s, 4H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 43.1, 58.9, 59.0, 69.1, 69.7, 69.7, 70.2, 70.43, 70.45, 70.51, 70.54, 70.59, 71.84, 71.90, 72.31, 108.3, 123.4, 126.3, 126.5, 126.8, 126.9, 127.0, 131.41, 131.53, 142.05, 145.5, 149.89, 152.33, 160.85, 162.7, 165.6; ESI-MS (HRMS): Calcd. for [C₄₈H₅₈N₄O₁₇ + Na]⁺ 985.3695; Found 985.3695; Anal. Calcd for C₄₈H₅₈N₄O₁₇.H₂O: C 58.77, H 6.17, N 5.71. Found: C 58.72, H 6.19, N 5.68.

Synthesis of palladium complex (2):

In a mixture of compound **1** (200 mg, 0.207 mmol) and palladium Bis(benzonitrile)palladium(II) chloride (39 mg, 0.103 mmol) was dissolved in dry DCM. The homogenous mixture was stirred for one hour. After that DCM was evaporated in vacuum to get the pure metal complex without any column chromatographic separation.

FT-IR (Neat, cm⁻¹): 2873, 1670, 1619, 1580, 1522, 1489, 1425, 1329, 1244, 1190, 110, 1022, 995, 936, 851, 760; ¹H NMR (400 MHz, CDCl₃, ppm): δ 3.24 (s, 12H), 3.38 (s, 6H), 3.48 (m, 8H), 3.55 (m, 4H), 3.61-3.72 (m, 36H), 3.83 (m, 12H), 4.72 (m, 12H), 5.38 (s, 4H), 7.45 (s, 4H), 7.47-7.48 (d, 4H, 6 Hz), 8.74-8.75 (d, 4H, 6.4 Hz), 8.78-8.84 (m, 8H), 9.6 (s, 2H); Anal. Calcd for C₉₆H₁₁₆Cl₂N₈O₃₄Pd: C 54.82, H 5.56, N 5.33. Found: C 54.87, H 5.60, N 5.29.

References.

S1. S. Bhattacharjee and S. Bhattacharya, *Chem. Asian. J.* **2015**, *10*, 572–580.

Characterization of **1**:

Mass Spectrum

¹H NMR

^{13}C NMR

Table S1. Summary of the gelation test of **1** in different solvents at ~22 °C. The CGC is written in the parenthesis when gelation is observed.

Solvent	State
Water	Sol
Methanol	Sol
Ethanol	Gel (10.4 mM)
Dichloromethane	Sol
Chloroform	Sol
THF	Sol
Acetonitrile	Sol
Methylcyclohexane	Insoluble
Benzene	Sol
Toluene	Sol

Table S2. Summary of the gelation test of metallogel **2** in different organic solvents at ~22 °C. The CGC is written in the parenthesis when gelation is observed.

Solvent	State
Dichloromethane	Gel (3.8 mM)
Chloroform	Gel (14 mM)
THF	Precipitate
Acetonitrile	Precipitate
Benzene	Precipitate
Toluene	Precipitate

Fig. S1. DSC thermogram of **1** (2nd heating/cooling cycle).

Fig. S2. The appearance of the nematic LC phase of **1** during heating cycle. Scale bar represents 50 μm. Liquid-like nature or mobility of the LC phase was confirmed by pressing the top coverslip gently with a tong.

Fig. S3. The appearance of the nematic LC phase of **1** during cooling cycle. Scale bar represents 50 μm . Liquid-like nature or mobility of the LC phase was confirmed by pressing the top coverslip gently with a tong.

Fig. S4. Energy minimized structure of **1** has been obtained using B3LYP/6-31 G* level of theory.

Fig. S5. (a) Concentration-dependent UV/Vis spectra of **1** (slit width 1mm/1mm) in EtOH. (b) CAC of **1** in EtOH has been determined to be ~1.2 mM by plotting ratios of absorbance at 376 nm and 356 nm in different concentrations.

Fig. S6. SEM image of the gel of **1** (EtOH).

Fig. S7. Plausible schematic illustration of the probable molecular packing of **1** in the gel phase in EtOH.

Fig. S8. Comparison of **1** and its' Pd-complex (**2**) in (a) TLC plate, running solvent MeOH-CHCl₃ (v/v 4:100) (b) Comparison of ^1H NMR spectra of **1** and its discrete Pd-complex **2** respectively. After complexation, the downfield shift of the pyridyl protons (H_c and H_d) were observed.

Fig. S9. (a) Concentration-dependent UV/Vis spectra of metallogel **2** in DCM (slit width 1mm/1mm). (b) Plot of the ratio of absorbance at 378 nm and 358 nm vs concentration of **2** in DCM. (c) TEM images of the metallogel of **2** ([**2**] = 0.3 mM) from DCM. (d) SEM image of the metallogel (**2**) from DCM.

Fig. S10. Selected area ROESY NMR spectrum (CDCl_3 , 700 MHz, 10 mM, 293 K) of the metallogel of **2**. The black circles highlight intramolecular through-bond coupling signals.

Fig. S11. Energy minimized structure of **2** has been obtained using B3LYP/LAN2DZ level of theory.

Fig. S12. Snapshots of **2** at different temperatures under POM. Scale bar represents 50 μm.