First Report of Charge-Transfer Induced Heat-set Hydrogel. Structural Insights and Remarkable Properties

Subham Bhattacharjee, a Bappa Maiti, b and Santanu Bhattacharya*bc

aPresent address: The Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.
bDepartment of Organic Chemistry, Indian Institute of Science, Bangalore, Karnataka 560012, India.
cDirector’s Research Unit, Indian Association for the Cultivation of Science, Kolkata 700032, India. E-mail: sb@orgchem.iisc.ernet.in, director@iacs.res.in; Tel: +91 (0)33 2473 4688.

1. Physical Measurements and Instrumentation.

Materials and Methods: All chemicals, solvents and silica gel for TLC were obtained from well-known commercial sources and were used without further purification, as appropriate. Solvents were distilled and dried by standard procedure before use. Melting points was measured in open capillaries and were uncorrected. 1H-NMR and 13C-NMR spectra were recorded in Bruker-400 Advance NMR spectrometer. Chemical shifts were reported in ppm downfield from the internal standard tetramethylsilane (TMS). Mass spectrometry of individual compounds was performed using a MicroMass ESI-TOF MS instrument. Elemental analysis was recorded in Thermo Finnigan EA FLASH 1112 SERIES.

Gelation Studies. A detailed procedure leading to the formation of RT-gels as well as the heat-set gels is presented in the main paper. The formation of the gel was confirmed using a tube inversion method. If a gel was formed, it was evaluated quantitatively by determining the critical gelator concentration (CGC) which is the minimum amount of gelator required to immobilize 1 mL of a particular solvent or solvent mixtures.

FT-IR Spectroscopy. Solution of the compounds were drop-cast on the CaF₂ cell and dried under vacuum and the spectra were recorded in Perkin Elmer Spectrum BX FT-IR system.

UV-Vis absorption and Fluorescence Spectroscopy. The UV-Vis and fluorescence spectra of various solution and gel were recorded on a Shimadzu model 2100 spectrophotometer and Hitachi F-4500 spectrofluorimeter respectively, both equipped with a temperature-controller bath.

Scanning Electron Microscopy (SEM). The gels were carefully drop-coated onto the brass stubs and were allowed to freeze-dry overnight. The freeze-dried samples were then coated with gold vapor and analyzed on a Quanta 200 SEM operated at 10-15 kV.

Transmission Electron Microscopy (TEM). Solutions of the gelator were drop-casted on carbon-coated copper grid and then carefully air-dried. Samples were stained with 0.1% uranyl acetate solution. TEM image were taken at an accelerating voltage of 200 kV using a TECNAI F30.

Dynamic Light Scattering (DLS). DLS measurements were performed at room temperature using a Malvern Zetasizer Nano ZS particle sizer (Malvern Instruments Inc., Westborough, MA). Samples were prepared and
examined under dust-free conditions. Average hydrodynamic diameters ($D_h$) reported were obtained from the Gaussian analysis of the intensity-weighted particle size distributions.

$^1$H NMR Spectroscopy of the CT Hydrogel. In order to avoid DMF for the $^1$H-NMR study, the solvents in the hydrogel were removed using high vacuum pump to yield a film of a dark colored solid. Dispersion of the solid in D$_2$O by both sonication and vortexing afforded a deep violet colored, hydrogel instantaneously, which was used for the $^1$H NMR spectroscopic studies.

Rheological Studies. For rheology experiment of the gels, an Anton Paar 100 rheometer with a cone and plate geometry (CP 25-2) having an adjustable peltier temperature controlling system was used. All the measurements were done fixing the gap distance between the cone and the plate at 0.05 mm. The gels were scooped on the plate of the rheometer. An oscillatory strain amplitude sweep experiment was performed at a constant oscillation frequency of 1 Hz for the applied strain range 0.001-400 % at 20 °C. The software US-200 converted the torque measurements into either $G'$ (the storage modulus) and $G''$ (the loss modulus) and represent $G'$ and $G''$ with either strain or shear stress. Oscillatory frequency sweep experiments were performed in the linear viscoelastic region (strain 0.01%) to ensure that calculated parameters correspond to an intact network structures.

A thixotropic loop test has been carried out by applying a successive low-high strain separated by sufficient time interval to ensure a complete gel-to-sol and sol-to-gel transition. Interestingly the sol obtained after applying high strain, transforms into a robust gel on relaxing the high strain. This provides a concrete evidence of the thixotropic behavior of the halogel.

Differential Scanning Calorimetry (DSC). Solid phase DSC experiment of Py-D was performed using a differential scanning calorimeter (DSC; Perkin-Elmer, Model Pyris 1D) with heating and cooling rate fixed at 2 °C min$^{-1}$. This technique was used to detect the thermal transitions and to monitor the rate of heat flow from the sample during phase change.

Polarized Optical Microscopy (POM). The change in the birefringent texture of Py-D during thermal phase transition was followed under polarized optical microscope (Olympus BX51) equipped with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90). Before experiment, ~0.2 mg sample was placed on a glass slide and covered with a piece of cover slip. The sample was heated (~80 °C) until it reached the isotropic state and then it was cooled slowly to 25 °C with a cooling rate of 1 °C min$^{-1}$. Repeated heating and cooling cycles were performed to confirm the reproducibility of the phases appeared under POM.

X-ray Diffraction. Gels were scooped onto glass slide and dried under vacuum for the corresponding XRD measurement. For the solid sample of Py-D, the compound was annealed at its associated isotropic temperature and subsequently used for the XRD measurement. These samples were analyzed using a Bruker D8 Advance instrument (θ, 20 geometry with scintillation detectors). The X-ray beam generated with rotating Cu anode at the wavelength of KR beam at 1.5418Å was directed toward the film edge and scanning was done up to a 2θ value of 30°. Data were analyzed and interpreted using the Bragg equation.

Single Crystal X-ray Diffraction. Single crystal X-ray data for NDI-A and 1:1 Pyrene:NDI-A co-crystal was collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software$^{51}$ at 293 K and 100 K respectively. Intensity data were collected using graphite-monochromatized Mo-Kradiation (0.71073 Å) at 293 K. The structures were solved by direct methods using the SHELX-97$^{52}$ program incorporated into WinGX.$^{53}$ Empirical absorption corrections were applied with SADABS.$^{54}$ Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were performed using the full-matrix least-squares method.

It is important to note that the R-Factor (%) of the 1:1 Pyrene:NDI-A co-crystal was 14.17. Our impression is that the co-crystal contains solvent molecules in its unit cell. We have attempted to assign those solvent molecules during solving the crystal structure using WinGX software. However, we have failed to do the same
even after several attempts. We have also grown the co-crystal several times and subsequently collected the data at 100 K. Despite all these attempts the R-Factor of the co-crystal could not be reduced.

2. Synthesis and Characterization. The synthesis of compound 1 was carried out according to a reported procedure. Synthetic scheme of Py-D, NDI-A and NDI-A 1 are shown below.

Synthetic Scheme.

Reagents, reaction conditions, and yields: (a) 1-Pyrenecarboxaldehyde, 1, 1:1 MeOH/THF, reflux, 4 h, yield = 95%; (b) 1,4,5,8-naphthalenetetracarboxylic dianhydride, isoniazid, DMF, 140 °C, 12 h, yield = 90%; (c) 1,4,5,8-naphthalenetetracarboxylic dianhydride, 4-aminopyridine, DMF, 140 °C, 12 h, yield = 81%

Synthesis of Py-D: A mixture of 1-Pyrenecarboxaldehyde (1g, 4.3 mmol) and compound 1 (2.7 g, 4.3 mmol) in dry MeOH/THF (30 ml, 1:1 v/v) was heated at 70 °C for 4 h under nitrogen atmosphere. The crude product was purified using silica column chromatography using 3% MeOH/CHCl₃ and pure Py-D has been obtained in 95 % yield as a light yellow wax like solid. IR (Neat, cm⁻¹) 3517, 2877, 1645, 1581, 1517, 1498, 1440, 1332, 1215, 1112, 1052, 944, 851; ¹H NMR (400 MHz, CDCl₃) δ 3.31 (m, 6H), 3.37 (m, 3H), 3.54 (m, 6H), 3.62 (m, 18H), 3.77 (m, 6H), 4.18 (m, 6H), 7.39 (s, 2H), 7.99 (m, 7H), 8.67 (m, 2H), 9.55 (s, 1H), 10.99 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 58.83, 58.92, 68.85, 69.61, 70.38, 70.42, 70.53, 70.57, 70.58, 70.67, 70.81, 71.85, 72.31, 107.84, 122.06, 124.44, 125.07, 125.4, 125.73, 125.97, 126.81, 127.38, 128.21, 128.38, 129.42, 130.40, 131.13, 132.49, 141.69, 152.37, 164.08; HRMS: m/z calcd. for C₃₅H₂₆N₂O₁₆ (M+Na)⁺: 857.39, found: 857.3838; Elemental analysis: calcd. for C₃₅H₂₆N₂O₁₆: C, 64.73; H, 7; N, 3.36; found: C, 64.41; H, 7.41; N, 3.21.

Synthesis of NDI-A: A mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1 g, 3.73 mmol) and isoniazid (1.02 g, 7.46 mmol) in dry DMF (20 ml) was heated at 140 °C for 12 h under nitrogen atmosphere. A crystalline solid which was obtained on cooling, was filtered and purified by repeated washing with DMF. The pure product was obtained in 90% yield as an off-white solid. m.p. > 275 °C; IR (Neat, cm⁻¹) 3578, 3479, 3191, 2850, 1732, 1698, 1582, 1527, 1291, 1240, 1198, 1126, 984, 846, 757, 584; ¹H NMR (400 MHz, DMSO-d₆) δ 7.97 (d, J = 5.6 Hz, 4H), 8.89 (s, 4H), 8.92 (d, J = 5.2 Hz, 4H), 11.97 (s, 2H); ¹³C NMR (100 MHz, DMSO-d₆) δ 122.48, 127.43, 127.51, 132.59, 139.30, 151.66, 161.63, 164.95; HRMS: m/z calcd. for C₂₆H₁₄N₆O₆ (M+Na)⁺: 529.1, found: 529.0873; Elemental analysis: calcd. for C₂₆H₁₄N₆O₆: C, 61.66; H, 2.79; N, 16.59; found: C, 61.93; H, 2.71; N, 16.74.
Synthesis of NDI-A 1: NDI-A 1 was synthesized following a reported procedure. The pure product was obtained in 81% yield as an off-white solid. m.p. > 275 °C; IR (Neat, cm⁻¹) 3578, 3479, 3191, 2850, 1732, 1698, 1582, 1527, 1412, 1291, 1240, 1198, 1126, 984, 846, 757, 584; ¹H NMR (400 MHz, DMSO-d₆) δ 7.61 (d, J = 5.2 Hz, 4H), 8.79 (s, 4H), 8.85 (d, J = 5.2 Hz, 4H); HRMS: m/z calcd. for C₂₄H₁₂N₄O₄ (M+H)⁺: 421.09, found: 421.0937; Elemental analysis: calcd. for C₂₆H₁₄N₆O₆: C, 68.57; H, 2.88; N, 13.33; found: C, 68.61; H, 2.77; N, 13.24.
$^1$H-NMR spectra of NDI-A in d$_6$-DMSO

$^{13}$C-NMR spectra of NDI-A in d$_6$-DMSO
HRMS of NDI-A

Mol. For. = C26H14N6O3Na
Calcd Mass = 529.0873 (M+Na)

1H-NMR spectra of Py-D in CDCl₃
HRMS of Py-D

1H-NMR spectra (only aromatic region) of NDI-A 1 in d$_6$-DMSO
Table S1. Crystal data of NDI-A and co-crystal of 1:1 Pyrene:NDI-A.

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Figure S1. Packing arrangement of NDI-A in the single-crystal (viewed along the b-axis).

Figure S2. (a) UV-Vis spectra of NDI-A:Ag⁺ (at different molar ratios) at a fixed total concentration of 50 μM. (b) Job’s plot of NDI-A with Ag⁺ in 2:1 v/v DMSO:H₂O; For Job’s plot the total concentration of [NDI-A] + [Ag⁺] is kept at 0.5 x 10⁻⁴ M. (c) UV-Vis titration of NDI-A (25 μM) in 2:1 v/v DMSO:H₂O with the gradual addition of Ag⁺.
Figure S3. SEM images of 1:2 NDI-A:AgOTf at [NDI-A] = 25 mM from 2:1 v/v DMSO:H₂O solution at different magnifications.

Figure S4. (a,b) Comparison of the UV/Vis absorption and fluorescence emission spectra of Py-D in THF (good solvent) and in water (bad solvent) respectively.
Figure S5. (a) Py-D remains as a monomeric form in THF alone. (b) Schematic illustrations of the aggregation mode of Py-D in H₂O at different concentrations. Only a part of the truly existing superstructures i.e, spherical aggregates has been shown in figure c and d for clarity. The slipped π-π stacking among the Py-D scaffolds in the aggregates is maintained in the schematic diagrams.

Figure S6. (a) Temperature-dependent transmittance of Py-D solutions at different concentration. (b) Reversibility of the LCST phenomena of solution of Py-D at a concentration of Py = 2.4 mM. (c) Temperature-dependent emission spectroscopy of a solution of Py-D at a concentration of Py-D = 0.2 mM below the phase transition temperature. (d) Temperature-dependent measurement of average hydrodynamic diameter (Dₜ) of a solution of Py-D at a concentration of Py-D = 2.4 mM.
Figure S7. Variable temperature $^1$H-NMR spectra (upper panel: aromatic region; lower panel: aliphatic region) of Py-D at a concentration of Py-D = 2.4 mM. Chemical shift of HDO as a function of temperature has been assigned following a reported literature.\textsuperscript{57}

Figure S8. Energy minimized structure of Py-D using B3LYP/6-31 G* level of computation.
**Figure S9.** POM images of Py-D were captured during heating (upper panel) and cooling (lower panel) cycle respectively (sweep rate = 2 °C/min).

**Figure S10.** Analysis of the data of figure 4b in the manuscript; Conc. (M)/A vs. $1/A^{1/2}$ has been plotted and the association constant (K) was estimated using the following equation as shown below:

$$C/A = 1/(K\epsilon l)^{1/2} \times 1/A^{1/2} + 1/\epsilon l$$

Where C, A, K, $\epsilon$ and l denote concentration, absorbance of the CT-band, association constant, extinction coefficient and path length (1 cm) of the cuvette respectively.
Figure S11. Photographs showing abolition of the RT-gel of 2:1 Py-D:NDI-A ([Py-D] = 6 mM) to a clear transparent solution on shaking (Path a). The resultant sol again turns into the native RT-gel on resting (Path b). The resultant sol, on the other hand, directly transform into the heat-set gel on heating (Path c). Abolition of the heat-set gel on shaking and reformation of the heat-set gel on cooling of the heated sol and subsequent heating of the cooled sol has been also demonstrated (Path d,e). The heat-set gel or the heated sol again transformed into the RT-gel on cooling and rest (Path f,g). (h) Demonstration of LCST transition of 2:1 Py-D:NDI-A solution by heating the lower part of the solution above the clouding point ([Py-D] = 3 mM).
Figure S12. (a) Variable temperature concentration dependence of transmittance of 2:1 Py-D:NDI-A. (b) Hysteresis (1 °C) of LCST transition between the heating and cooling processes. (c) Reversibility of LCST phenomena of solution of 2:1 Py-D:NDI-A at a concentration of Py-D = 3 mM. (d) Variable temperature (VT) DLS measurement of 2:1 Py-D:NDI-A and its comparison with VT transmittance of 2:1 Py-D:NDI-A ([Py-D] = 1.5 mM). (e) Size distribution of the globular aggregates of the 2:1 Py-D:NDI-A before phase transition (25-47 °C), during phase transition (48 °C and 49 °C) and after phase transition (50-70 °C); ([Py-D] = 1.5 mM).
Figure S13. Variable temperature $^1$H-NMR spectra of 1:1 Py-D:NDI-A in D$_2$O at a concentration of Py-D = 10 mM. In order to avoid DMF for the $^1$H-NMR study, the solvents in the hydrogel were evaporated using high vacuum pump to yield a film of a dark colored solid. Dispersion of the solid in D$_2$O by both sonication and vortexing afforded a deep violet colored, hydrogel instantaneously, which was used for the $^1$H NMR spectroscopic studies. The $^1$H-NMR signals at around 8, 2.9 and 3 ppm have appeared due to the presence of residual DMF in the hydrogel. Chemical shift of HDO as a function of temperature has been assigned following a reported literature.$^{37}$

Figure S14. DSC studies of the solution of Py-D ([Py] = 2.4 mM) alone in water as well as 1:1 Py-D:NDI-A ([Py-D] = 2.4 mM) and 2:1 Py-D:NDI-A ([Py-D] = 6 mM) CT hydrogels.
Figure S15. Frequency-sweep rheology data of 1:1 and 2:1 Py-D:NDI-A CT gels ([Py-D] = 10 mM). Oscillatory frequency sweep experiments were performed in the linear viscoelastic region (strain 0.01%) to ensure that calculated parameters correspond to an intact network structures. The results indicate that $G'$ remains always greater than $G''$ and both of them are invariant to the applied angular frequency range.

Figure S16. (a,b) SEM images of 2:1 Py-D:NDI-A system dried below the clouding point of the solution, ([Py-D] = 0.3 mM). (c) TEM images of the 2:1 Py-D:NDI-A system at [Py-D] = 0.2 mM.

Figure S17. An energy minimized structure of 1:1 Py-D:NDI-A based on B3LYP/6-31 G* level of computation.
Figure S18. Unit cell of the co-crystal of 1:1 Pyrene:NDI-A viewed along the a-axis showing the long axis of pyrene molecule (represented with green bonds) was placed between the two NDI-A molecules in a diagonal fashion. H-atoms are omitted for clarity.

Figure S19. Space-filling diagram of the co-crystal showing the molecular channels along the b-axis.

References:

(S1) SMART/SAINT; Bruker AXS, Inc.: Madison, WI, 2004.


(S4) Sheldrick, G. M. SADABS; University of Göttingen, Göttingen, Germany, 1999.

