Electronic Supplementary Information

A new hydrogel from an amino acid based perylene bisimide and its semiconducting, photo-switching behaviour

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Instrumentation

NMR Spectroscopy

NMR studies were carried out on a Bruker dpx 500MHz spectrometer at 300 k. **PBI-Y** concentration was in the range 1–10 mg in $(CD_3)_2SO$.

UV/Vis Spectroscopy

UV/Vis absorption spectra were recorded on a Hewlett-Packard (model 8453) UV/Vis spectrophotometer (Varian carry 50.bio). The pH dependent UV-Vis studies were performed using the hydrogel into a thin film between two slides of glass at different pH.

Fluorescence Study

The fluorescence spectra were obtained using a Perkin-Elmer Spectrofluorimeter and excitation and emission wavelengths of 285 nm and 900 nm respectively.

Quantum yield have been generally measured relative to an optically dilute fluorophore standard solution that exhibits a well-known quantum yield (ϕ_s). The quantum yield of an unknown fluorophore (ϕ_u) has been determined using the parker-rees method[S1].

$$\phi_u = (A_s F_u n_u^2 / A_u F_s n_s^2) \times \phi_s$$

Where, A_u denotes the absorbance of the unknown sample at the excitation wavelength, F_u represents the total, integrated fluorescence intensity for the unknown sample when it is excited at the same excitation wavelength of the unknown sample, F_s is the integrated fluorescence intensity of the reference sample, when it is excited at the same excitation wavelength of the known sample. The refractive indices of solvents in which the unknown and the standard samples have been prepared, are given by N_u and N_s respectively. Here, in our study we have used rhodamine B in water as a standard and its quantum yield (ϕ_s) is known to be 31 % in water. The quantum yield of the **PBI-Y** has been determined to be 0.21 % with respect to rhodamine B.

TCSPC study

TCSPC measurements have been performed by means of Horiba Jobin Yvon IBH having MCP PMT Hamamatsu R3809 detector instrument and all data have been fitted using DataStation v2.3.

FT-IR Spectroscopy

The FT-IR spectra were taken using shimadzu (Japan) model FT-IR spectrophotometer. In

the solid state FT-IR studies, powdered and gummy peptides were mixed with KBr for preparing thin films.

MALDI-TOF MS

MALDI-TOF MS analysis has been performed by using Applied Biosystems MALDI TOF/TOF Analyzer in dithranol as a matrix.

X-ray Diffraction Study

For X-ray diffraction study of PBI-Y gelator, xerogel and wet gel were put on a glass slide. Samples were carried out by using an X-ray diffractometer (Bruker D8 Advance) with a parallel beam optics attachment. The instrument was operated at a 35 kV voltage and 30 mA current using Ni-filtered Cu Kα radiation and was calibrated with a standard silicon sample.

Field Emission Scanning Electron Microscopy (FE-SEM)

Morphologies of the hydrogel materials were investigated by FE-SEM. For the SEM study, the gel material was dried and coated with platinum. Then the micrographs were taken in a SEM apparatus (JEOL microscope JSM-6700F).

Transmission Electron Microscopic Study

The diluted hydrogel was first placed at carbon-coated copper grids (200mesh) and it was then allowed to dry by slow evaporation. Then it was dried under vacuum at 25°c for two days. TEM was recorded on a JEM 2010F electron microscope.

Rheology

Rheological experiments were performed with an AR 2000 advanced rheometer (TA Instruments) using cone plate geometry in a Peltier plate. The plate diameter has 40 mm, with a cone angle of 4 degrees.

Cyclic Voltametric (CV) analysis

The cyclic voltammetric (CV) measurements have been performed on a Princeton Applied Research potentiostat/galvonostat model 273A.

Energy Minimized Structure

We have studied the energy optimized electronic structure of the gelator molecule (PBI-Y) by employing the density functional theory (DFT) with hybrid function B3LYP using 6-31+G (d, p) basis set for all these elements involved here. Basically, the B3LYP function is a hybrid

function, which contains the Becke three-parameter exchange and Lee–Yang–Parr correlation function. All calculations have been performed in the Gaussian 03 suite of quantum chemistry program.

Photo-response study

The required light from a Xenon lamp (model no. 66902; Newport Corp. USA) is shined on the conductor area to measure the photo-response property. Xenon lamps emit "white light" with high luminance and high color temperature, which is close to that of sunlight and covers a broad continuous spectrum from the ultraviolet to infrared region (185 nm to 2000 nm). Therefore, the light of the xenon lamp used here is refereed as the white light and that after filtering the UV part, is called the visible light. The current between the two contacts were measured using a Keithley source meter (Model 2401).

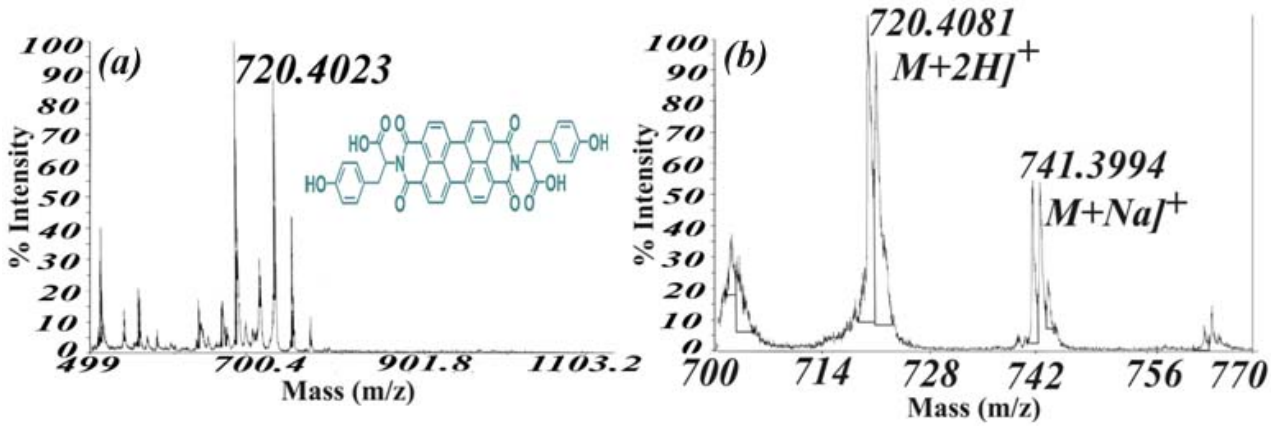


Fig. S1 (a) MALDI-TOF-MS spectrum of the **PBI-Y** Hydrogelator and (b) enlarged view of the spectrum (a) from m/z 700 to 770 showing the $[M+2H]^+$ peak.

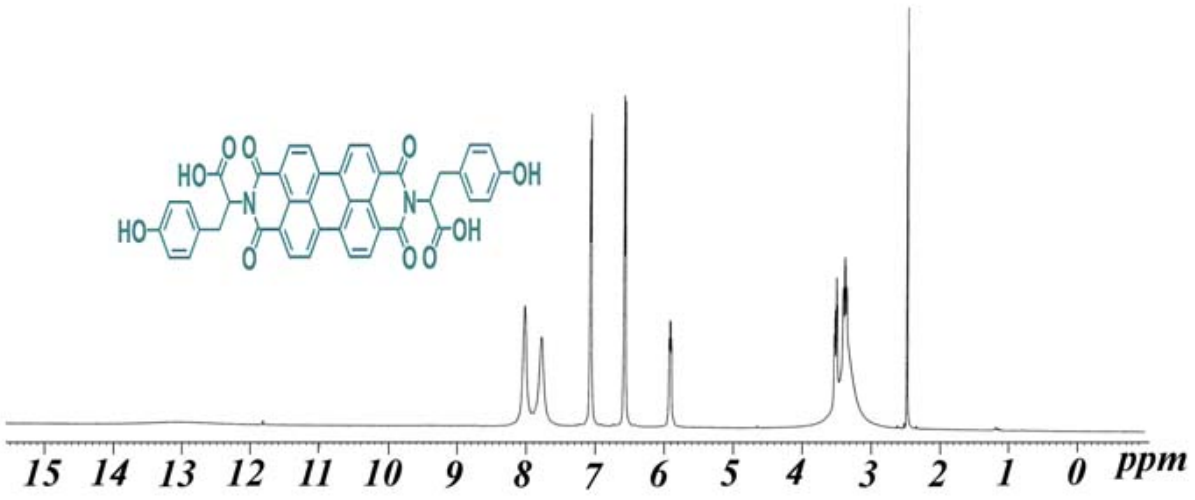


Fig. S2 ^{1}H NMR spectrum of the **PBI-Y** hydrogelator in DMSO-d_6.

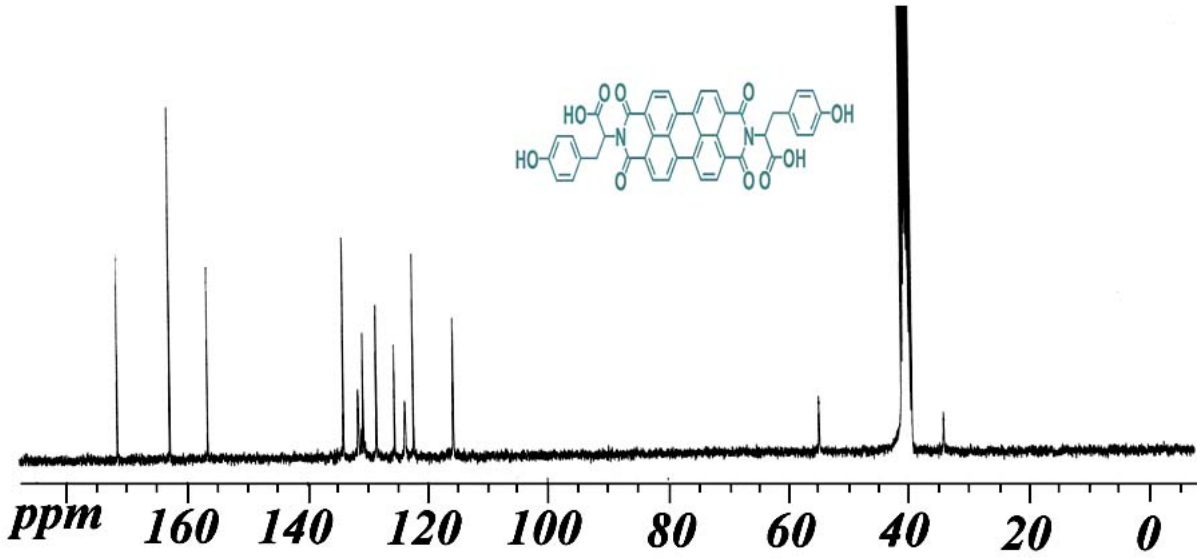
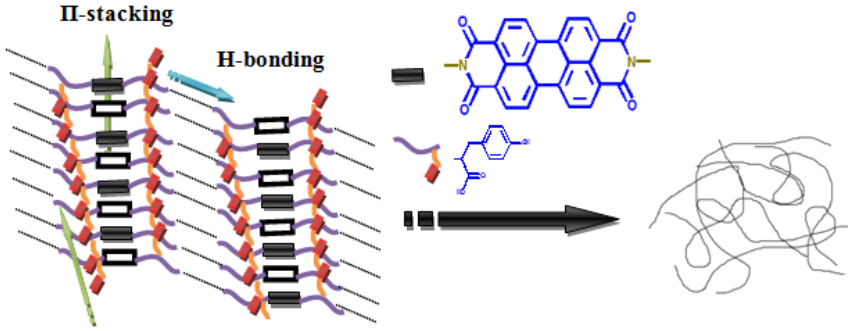


Fig. S3 ^{13}C NMR spectrum of the **PBI-Y** hydrogelator in DMSO-d_6.



Scheme S1. Probable schematic aggregation process of the **PBI-Y** gel fibrous network.

50 mM phosphate buffer	pH	MGC (% w/v)
1	5.00	0.27
2	6.00	0.54
3	7.00	2.83
4	7.46	3.5
5	9.00	3.8

Table S1 Hydrogelation characteristics of the **PBI-Y** hydrogelator at different pHs.

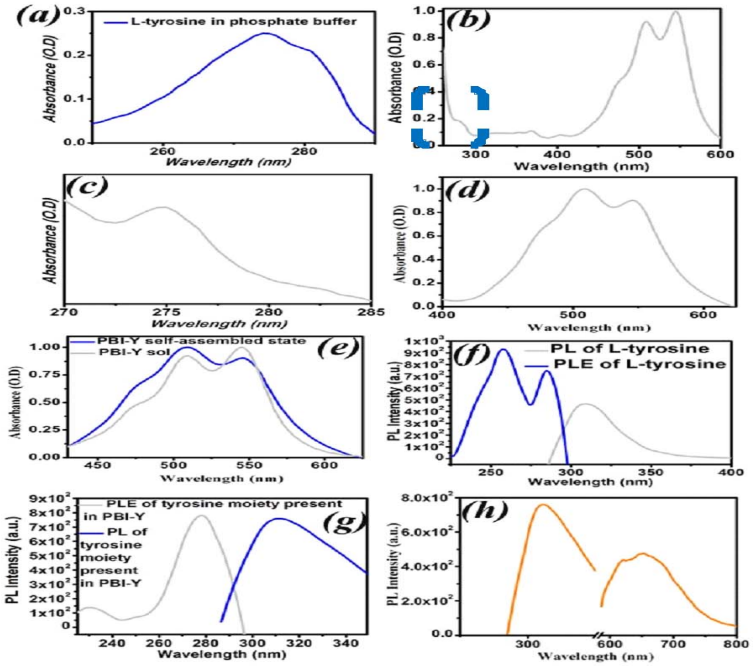


Fig. S4 (a) UV-Vis absorption spectrum of the L-tyrosine amino acid, (b) UV-Vis absorption spectrum of the **PBI-Y** hydrogelator in solution state**,** (c) Enlarge view of selected portion of the Fig. B (d) UV-Vis absorption spectrum of the **PBI-Y** diluted gel (sol state), (e) UV-Vis absorption spectra of the PBI-Y hydrogelator in solution (sol state) and in diluted gel state (self-assembled state), (f) fluorescence emission and fluorescence excitation spectra of the L-tyrosine amino acid, (g) fluorescence emission and fluorescence excitation spectra of the L-tyrosine moiety present in **PBI-Y** hydrogelator and (h) fluorescence emission of the PBI-Y hydrogel at an excitation of 275 nm showing the presence of L-tyrosine moiety as well as perylene core.

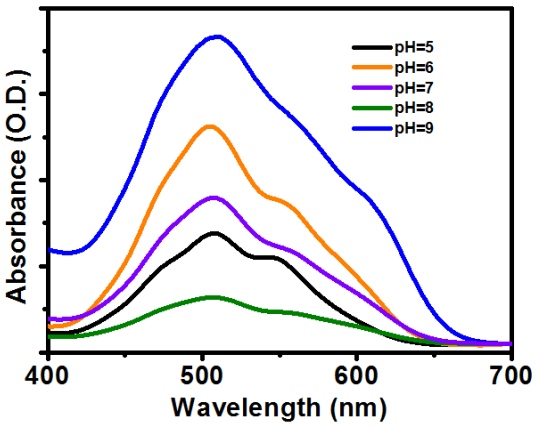


Fig. S5 pH dependent UV-Vis absorption spectra of the gelator in solution state.

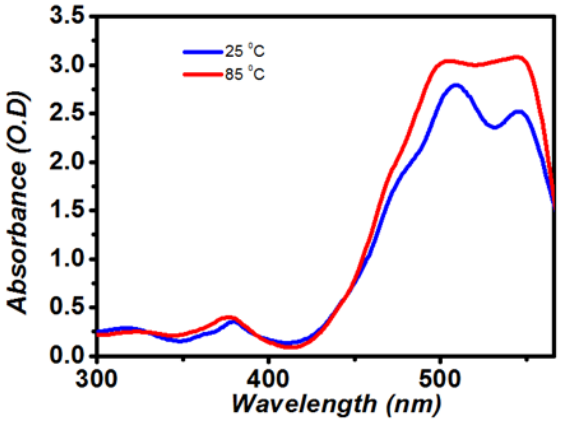


Fig. S6 Temperature dependent UV-Vis spectral study of the self-assembled diluted gel.

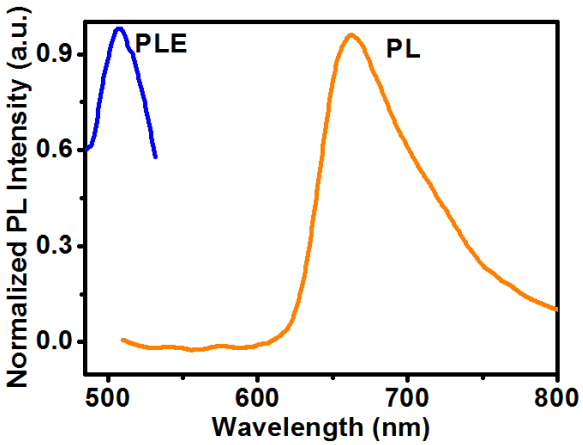


Fig. S7 Fluorescence emission and fluorescence excitation profile of the **PBI-Y** hydrogel at pH 5.00.

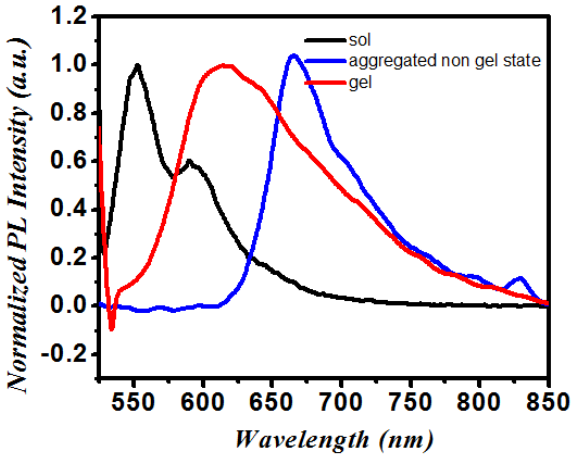


Fig. S8 Fluorescence emission of the **PBI-Y** gel in very dilute solution state (sol state), aggregated non-gel state and in gel state.

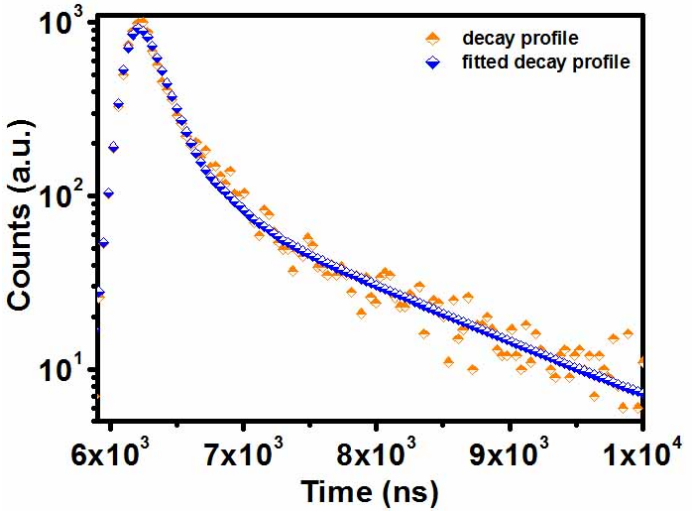


Fig. S9 Fluorescence decay profile of the **PBI-Y** hydrogel at pH 5.00.

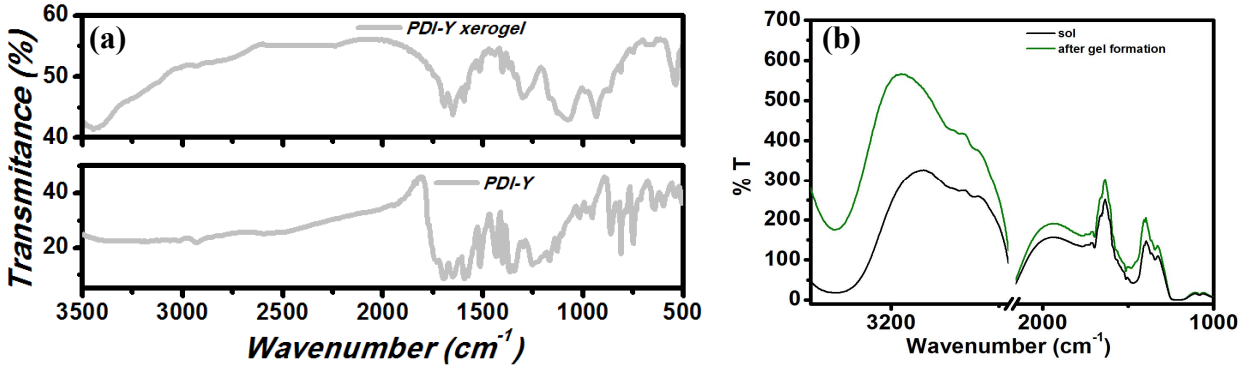


Fig. S10 (a) FT-IR spectra of the gelator in bulk and in xerogel state and (b) FT-IR spectra of the **PBI-Y** gelator during gel formation in D_20. The changes in absorption intensity around 3401 cm^{-1} and in carbonyl frequency region (1725 cm^{-1}) absorption intensity have also been changed suggesting the indirect proof of H-bonding during gel formation at pH 5.00.

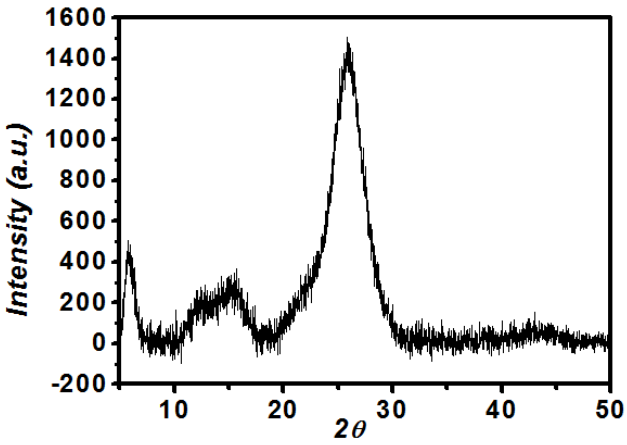


Fig. S11 X-ray diffraction pattern of the **PBI-Y** bulk material.

References

S1. J. N. Demas and G. A. Crosby, *J. Phys. Chem.,* 1971, **75**, 991-1024.