

Hydrogen bond cross-linked luminescent supramolecular network polymer and its application for detection of alkyl iodide with differentiation capabilities from aromatic iodide.

Ravi Prakash Behere¹, Rajlaxmi¹, Neelam Gupta¹, Susmita Roy², Ramnayan Gautam¹, Manoj Kumar Bharty¹, Chanchal Chakroborty², Biplab Kumar Kuila^{1,*}

¹Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi Uttar Pradesh 221005, INDIA, Email: bkkuila.chem@bhu.ac.in

²Department of Chemistry, BITS Pilani, Hyderabad Campus, Jawahar Nagar, Shameerpet Mandal, Hyderabad-500078

Experimental:

Materials. All the chemicals like 4-vinyl pyridine (4VP), CuCl, Me₆-TREN, perylene-3,4,9,10-tetracarboxylicdianhydride, imidazole, 6-Aminocaproic acid, etc. were purchased from Sigma Aldrich. Other solvents like ethanol, chloroform, etc., were obtained from Rankem. 4VP was purified by vacuum distillation before polymerization.

Synthesis of P4VP

Poly(4-vinyl pyridine) (P4VP) was synthesized by atom transfer radical polymerization 4VP in 2-propanol using PECl as the initiator and CuCl / tris[2-(dimethylamino)ethyl]amine (Me₆-TREN) at 40 °C.^[S1] A dry schlenk flask was first charged with CuCl (0.078 mMol, 7.6 mg) and stir bar. The flask was sealed with rubber septum, evacuated and back filled with argon atmosphere for several cycles to remove oxygen. Degassed isopropanol (5 ml), 4-vinyl pyridine (1 ml, 9.3 mMol), and Me₆-TREN (0.078 mMol, 17.9 mg) were added to the reaction mixture using a degassed syringe. The sealed flask was then immersed in oil bath maintained at 40°C. Initiator 1-phenyl ethyl chloride (0.078 mMol, 10.9 mg) was added and kept for 14 hours. The polymer was recovered by precipitation in hexane and purified by passing through basic alumina

column. The polymer was further characterized by GPC. The molecular weight of the polymer as determined by GPC (DMF as solvent) was $M_n = 10,510$ with $PDI = 1.17$

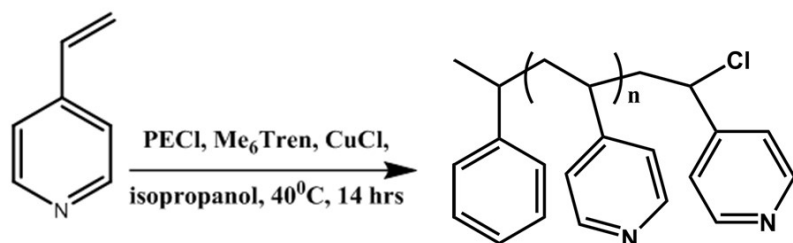


Figure S1 synthesis scheme of P4VP through ATRP.

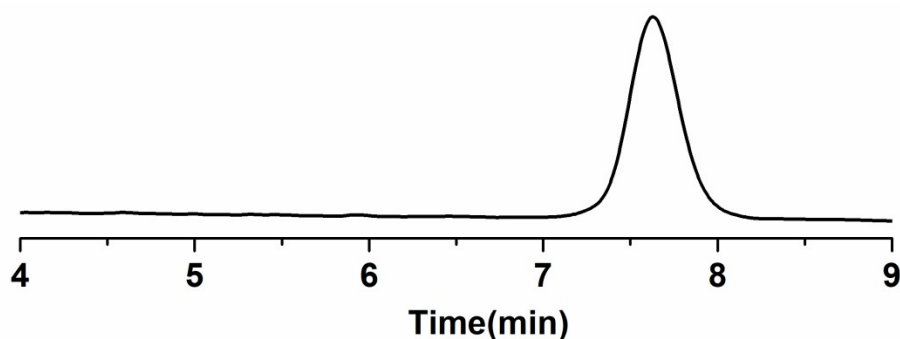


Figure S2 GPC trace of synthesized P4VP

Synthesis of N, N'-bis(6-caproic acid)-3,4:9,10 -perylene diimide (PDI):

In a 100 mL round bottom flask, 1.0 g (2.5mmol) perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and 985 mg (7.5mmol) 6-Aminocaproic acid in 8.0 gm imidazole were stirred 12hrs at 120° C under nitrogen atmosphere. After completion of the reaction, the mixture was cooled to 90°C and deionized water (50 mL) was added. After stirring the solution for 2 hrs, it was filtered to remove the small amount of unreacted PTCDA (if any). The solution was further acidified with dilute HCl so that pH 3-4 value is maintained. The precipitate was collected by filtration and thoroughly washed with deionized water until the filtrate was neutral. Then the precipitate was further washed with ethanol and dried under vacuum to get the desired product (yield 75%).

^1H NMR (400 MHz, d_6DMSO) δ =7.64 (m, 8H), 3.76 (t, 4H), 2.26 (t, 4 H), 1.5-1.0 (m, 6H). The NMR results were compared with the literature data, which confirmed that the correct structure was obtained.^[S2]

Sample preparation: The supramolecular polymers (SPMs) of varying compositions were prepared by dissolving desired amount of P4VP and PDI in dry DMF and heated to 60°C for 4 hours. The final concentration of the solution was maintained 0.25% (wt%). The resulting solution was kept overnight under stirring condition for complete hydrogen-bond formation. Bulk samples were prepared by drying the solution taken in Petri dish at 60°C. The resulting solid was further kept in vacuum oven for two days at 60°C for complete removal of solvent. The dried samples are then kept in desiccator for further experiments. Homogeneous thin film of the SPMs for AFM and optical studies were prepared by drop casting of DMF solution of the SMPs on cleaned quartz or silicon substrate from 0.1% solution. The solutions were filtered through PTFE (0.45 μm) membrane before drop cast and substrates were put on hot plate at 60°C.

Instrumental Characterization: For FTIR study, pallet made from KBr and bulk samples were directly used. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrometer (spectrum-II). Nuclear magnetic resonance spectra were recorded on 400 MHz JEOL instrument. UV-vis spectra in solution and thin film state were taken UV-vis spectrometer (Hewlett-Packard, model 8453) at room temperature. For the solution state measurement, SMP solutions in DMF (10 $\mu\text{M/L}$ with respect to PDI) were taken in a quartz cell. In case of thin film measurement, the thin films were deposited on quartz substrate by simple drop cast from DMF solution as discussed above. AFM imaging of the thin film deposited of silicon substrate was performed using AFM NT-MDT, SolverNext in the tapping mode. Analysis of the AFM images was performed with the WSxM software (Nanotec Electronica). The crystallographic structures of the bulk materials

were determined by a wide-angle X-ray diffraction system (Panalytical High Resolution XRD-I, PW 3040/60), Cu K α radiation (40 kV, 30 mA, $\lambda = 0.1540598$ nm). Fluorolog-HORIBA was used for absolute quantum yields and solid state emission studies. The fluorescent data for sensing measurement were collected at room temperature on “Agilent Technologies CaryEclipse” Fluorescence Spectrophotometer. For this, the solution of P4VP2025 (685 nM) is prepared in ethanol. The 3ml of P4VP2025 solution were added with CH₃I (10 μ M-133.23 mM) and other halides (20 μ L) followed by incubation at 50 $^{\circ}$ C for 30 min prior to collection of data. For addition of methyl iodide in lower concentration, diluted methanol iodide solution in ethanol was used and the total volume of the solution was maintained constant for all experiments to rule out the effect of dilution.

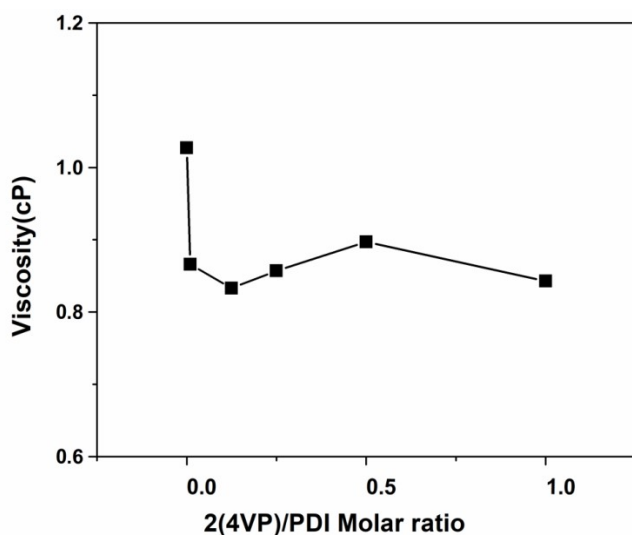


Figure S3 Viscosity as a function of 2(4VP)/PDI molar ratio for pure P4VP and different supramolecular polymer solution (0.1% in DMF).

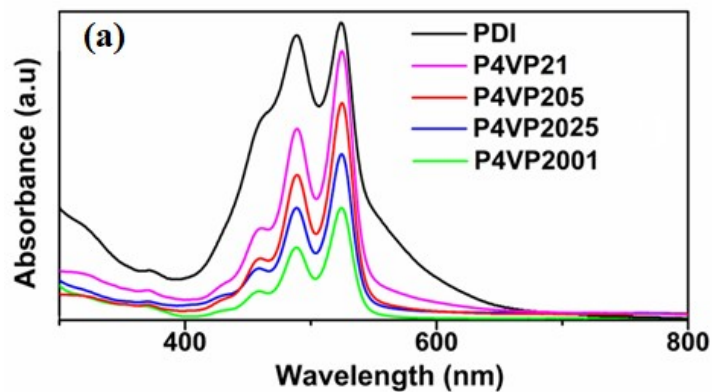
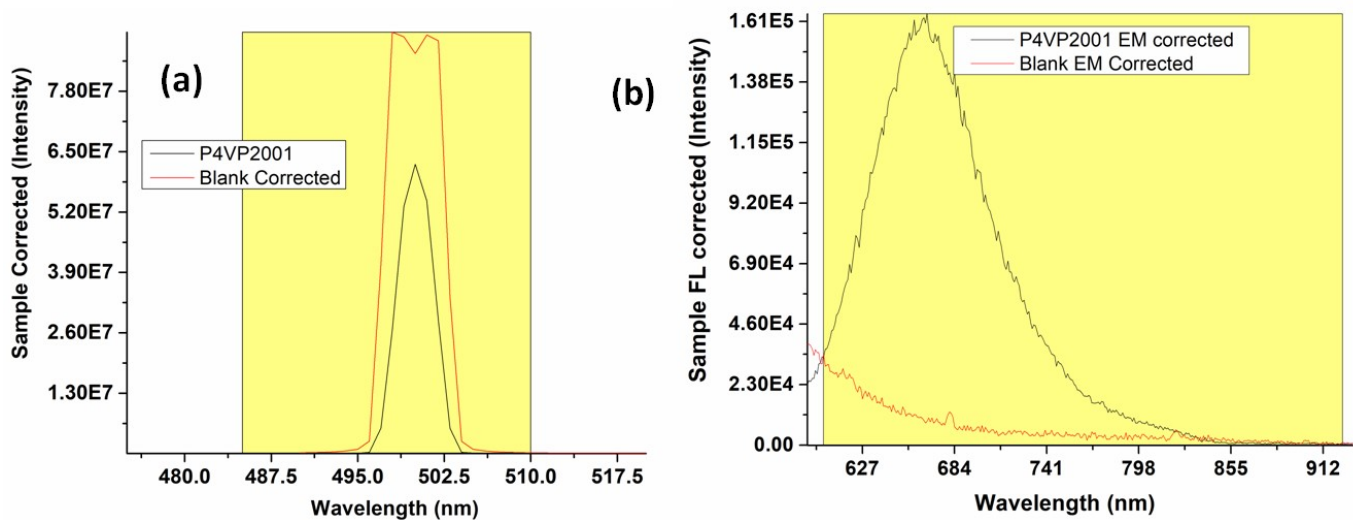


Figure S4 UV-vis spectra of PDI and SMPs in solution (1 μ M with respect to PDI).



Quantum Yield	4.47
Abs Error \pm	0.005
Relative Err \pm	0.00118

Figure S5 Fluorescence quantum yield data of P4VP2001 in solid state, (a) excitation spectra (b) emission spectra

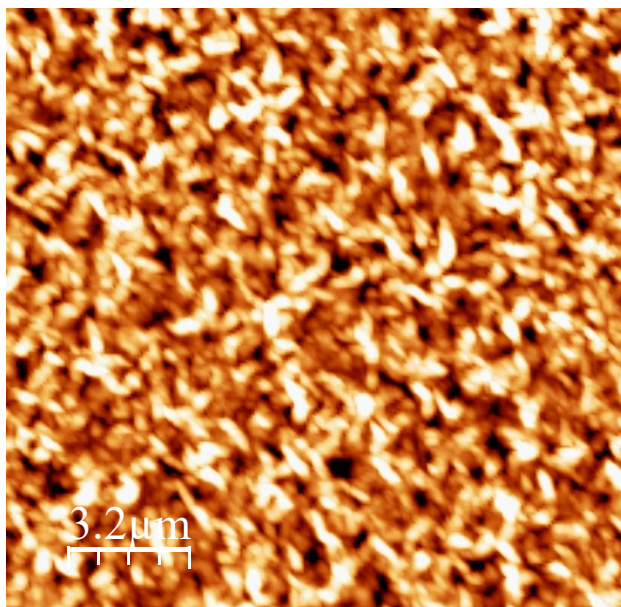


Figure S6 lower magnification AFM height image of PDI thin film deposited on silicon wafer.

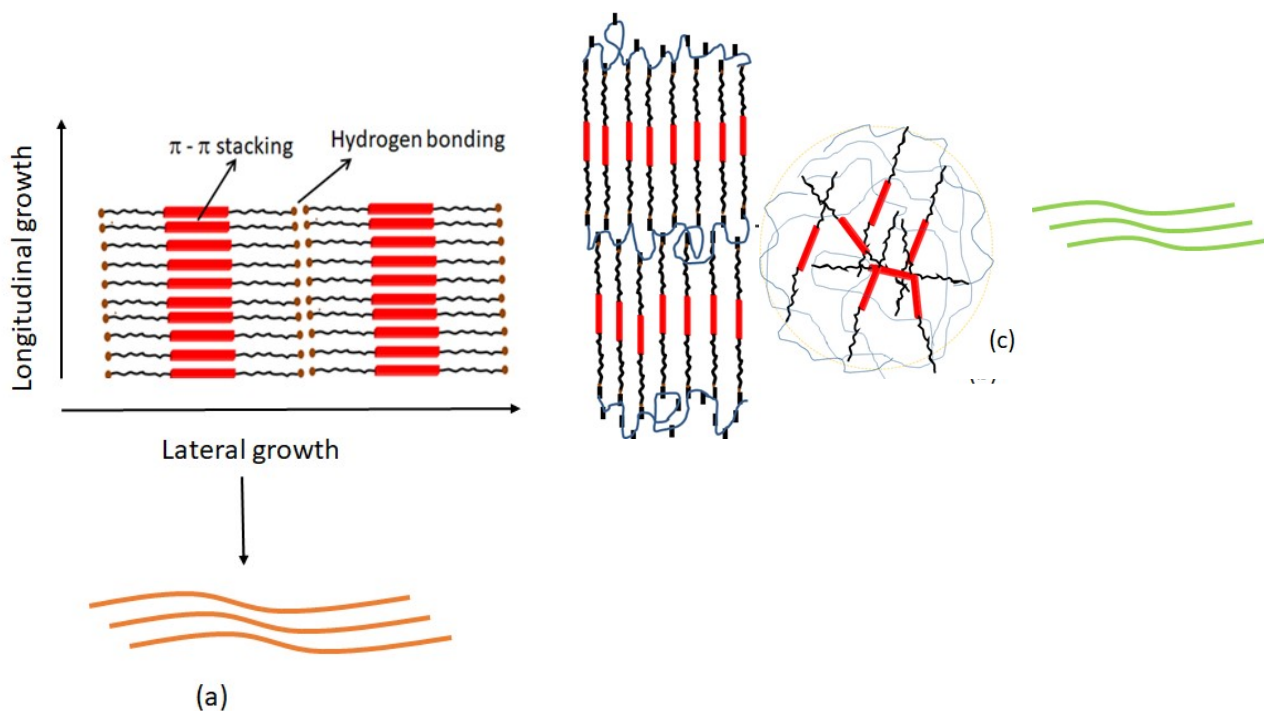


Figure S7 schematic diagram showing mechanism of different structure formation (a) fibrillar structure for pristine PDI (b) fibrillar structure for P4VP21, P4VP205, P4VP2025 (c) spherical structure for P4VP20125

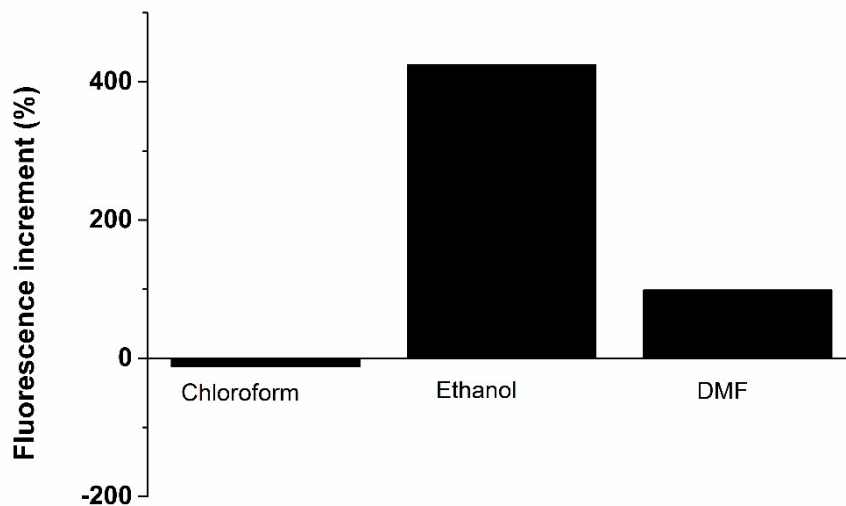


Figure S8 showing relative fluorescence intensity change $\{[(F-F_0)/F_0] \times 100\}$ of P4VP2025 solution in different solvents after adding (160 μmol) of CH_3I in 3 ml of solution

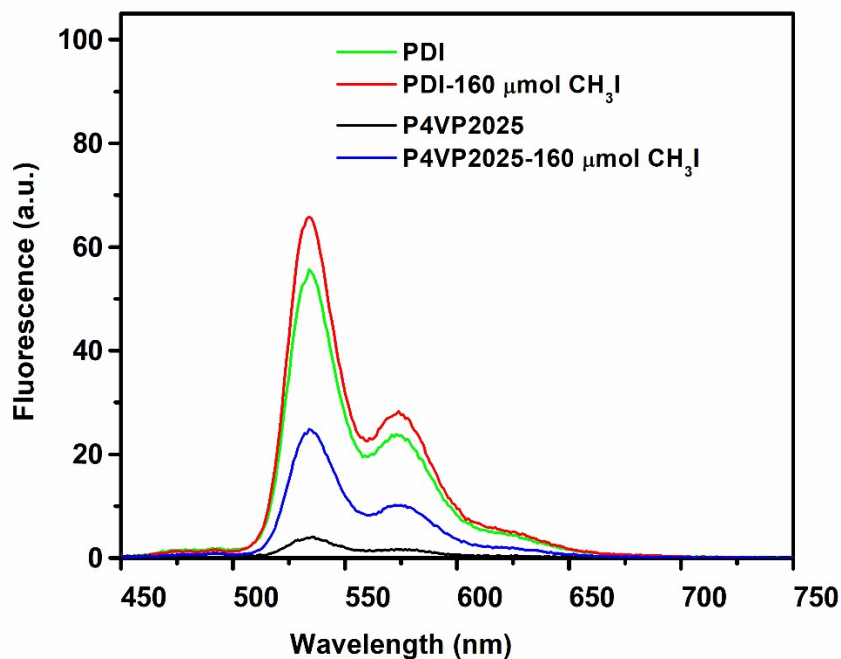


Figure S9 showing fluorescence of PDI and P4VP2025 solution (685 nM) after adding CH_3I .

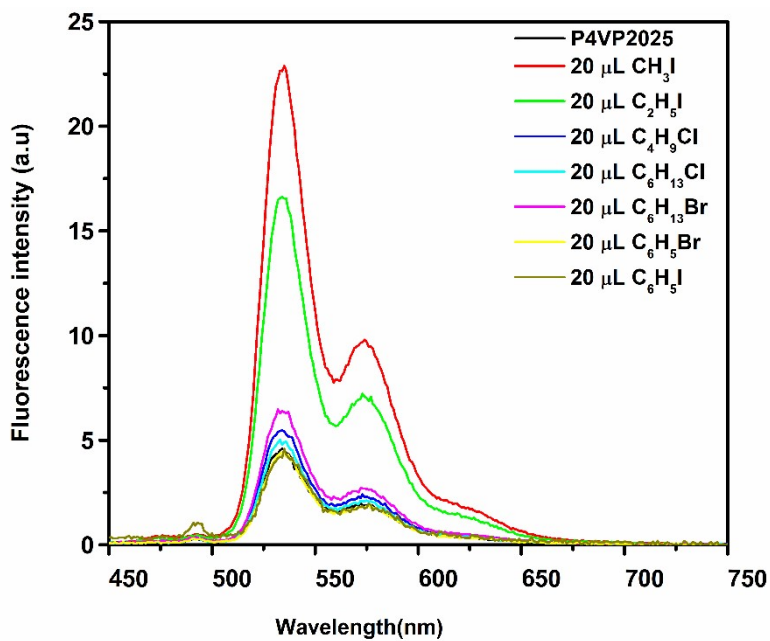


Figure S10 Fluorescence change on addition of aliquots of different alkyl and aryl halide (20μl) to a solution of P4VP2025 (3 ml).

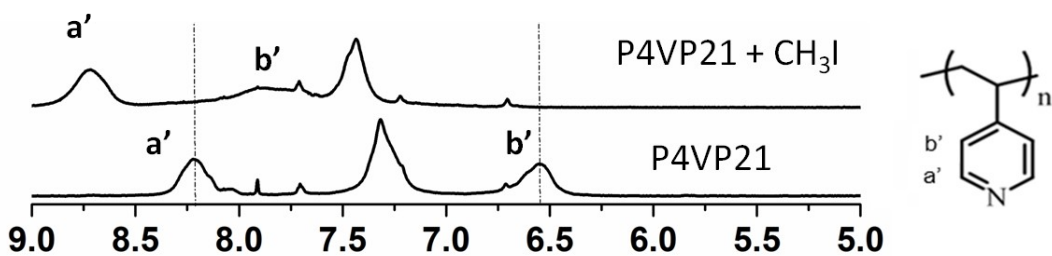


Figure S11 comparative ¹H NMR spectra of P4VP21 (10 mg/ml) and P4VP21 (10 mg/ml) after addition of 4μl of CH₃I in DMSO-d₆

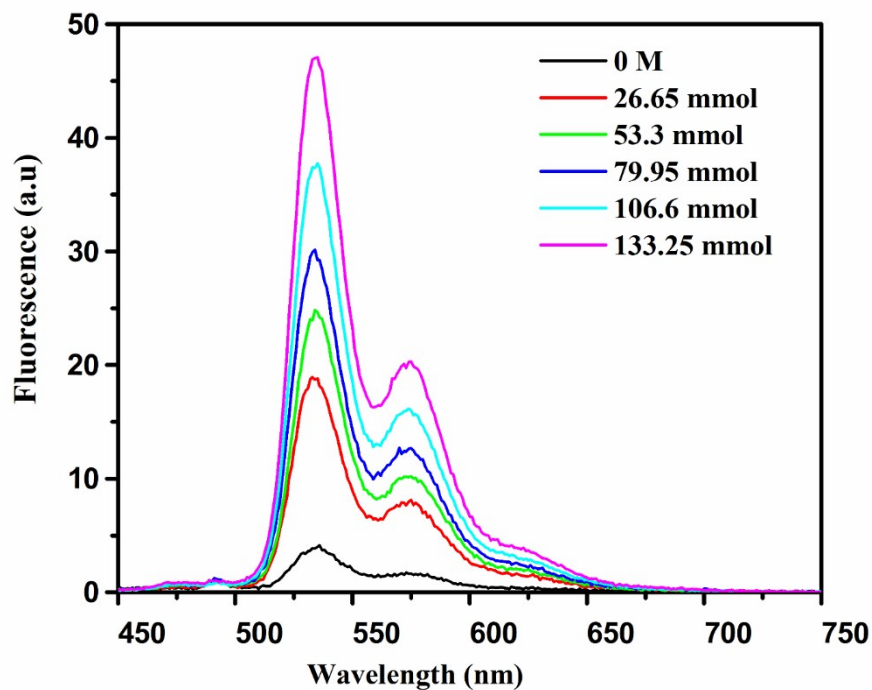


Figure S12 Fluorescence change on addition of aliquots of CH_3I to a solution of P4VP2025.

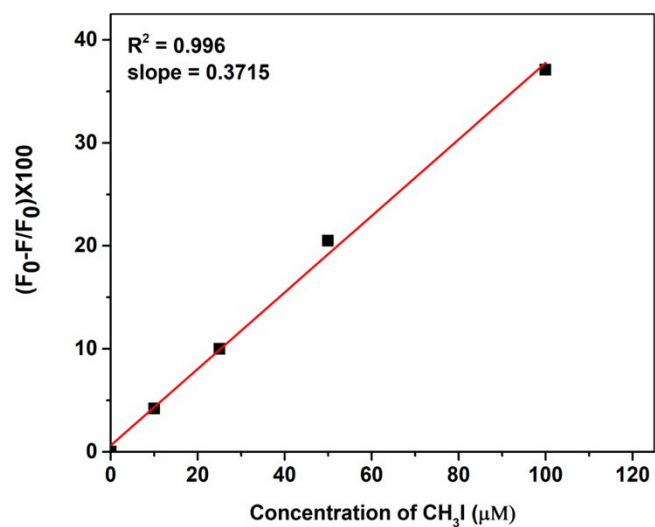


Figure S13 plot of fluorescence change vs. concentration of methyl iodide in the concentration range 10-100 μM .

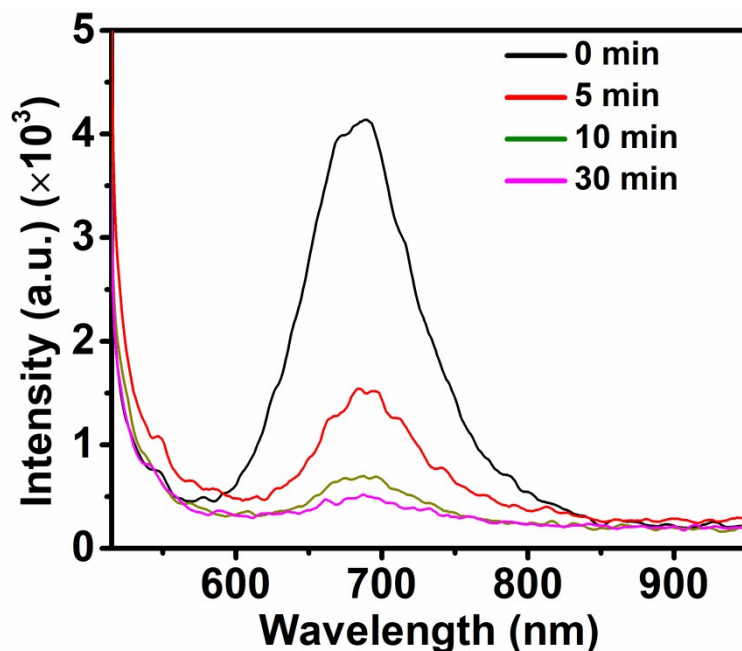


Figure S14 showing fluorescence intensity change of P4VP2025 thin film on quartz substrate after exposure to CH₃I vapor for different time

References:

S1 J. Xia, X. Zhang, and K. Matyjaszewski, *Macromolecules*, 1999, 32, 3531-3533.

S2 Y. Wang, J. Chen, H. Jiao, Y. Chen, W. Li, Q. Zhang, C. Yu, *Chem. Euro. J.*, 2013, 19, 12846-12852.