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Supporting information

Modulation of optoelectronic properties in a donor - acceptor conjugate between a cationic polythiophene and a peptide appended perylenebisimide ampiphile

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1. Materials:

3-thiophene ethanol and *N, N* dimethylaminoethyl methacrylate (DMAEMA) were purchased from Sigma Aldrich (USA) and it was purified by passing through a basic alumina column. 1, 1, 4, 7, 10, 10 - hexamethyl triethylene tetramine (HMTETA) was purchased from, Sigma Aldrich, USA) was used as received in the role of ligand. The catalyst CuCl (Loba Chemicals, Mumbai) was purified under nitrogen atmosphere by washing with 10% HCl in water followed by methanol and diethyl ether. The solvents dichloromethane (DCM), chloroform and anisole (Loba Chemicals, Mumbai) were purified by distillation.

3, 4, 9, 10-perylenetetracarboxyldianhydride and 12-Aminododecanoic acid (ADDA= NH_2-C_{11}-CO_2H=C_{12}) were acquired from Sigma-Aldrich chemicals. sodium dihydrogen phosphate, pH paper, and disodium hydrogen phosphate were purchased from Merck. L-Tyrosine(Y), imidazole, sodium chloride, sodium carbonate, liquid ammonia, sodium hydroxide, L-glutamic acid, 35 % hydrochloric acid, di-tert-butylpyrocarbonate(Boc-anhydride),methanol, DCC (dicyclohexylcarbodiimide) titanium isopropoxide, and 98% formic acid were bought from SRL. HOBt (1-hydroxybenzotriazole) in the form of monohydrate was purchased from Spectrochem chemicals.

2. Preparations of cationic polythiophene (CPT-I)

2.1 Preparation of thiophene initiator 3-[1-ethyl-2-(2-bromoisobutyrate)]thiophene (TI)

In a 100 ml flask thiophene-3-ethanol (20 mmol) and triethylamine (22 mmol) were dissolved in anhydrous DCM (40 ml) and stirred at 0 ^{0}C under nitrogen atmosphere Then 2-bromoisobutyryl bromide (BIB, 22 mmol) in 10 ml anhydrous DCM was added drop wise into the reaction mixture by a pressure-equalizer and the reaction mixture was then stirred for 24 hrs at 30 ^{0}C. Then the reaction mixture was filtered and the filtrate was washed repeatedly with 1% HCl, saturated NaHCO3, brine solution and distilled water. The organic layer was

separated by a separator funnel and was passed through anhydrous Na_2SO_4 to remove water. Silica column chromatography was performed in a solvent mixture of hexane / ethyl acetate (95/5, in volume ratio) for further purification. A brown colour liquid was obtained after solvent evaporation as final product (yield-70%).

^{1}H NMR ($CDCl_3$): δ= 1.9 (6H, s), 3.0 (2H, t), 4.3 (2H, t), 6.9-7.2 (aromatic ring protons); 13C NMR ($CDCl_3$) δ= 29.4, 30.9, 55.9, 65.9, 121.9, 125.8, 128.4, 137.8, 171.8. Molecular weight of TI obtained from high resolution mass spectra (HRMS) is 277.9.

2.2 Synthesis of polythiophene macro-initiator (2, 5-poly (3-[1-ethyl-2-(2- bromo isobutyrate)] thiophene (PTI))

Under nitrogen atmosphere, in a 250 ml round bottom flux anhydrous $FeCl_3$ (15 mmol) was dispersed in 25 ml anhydrous chloroform. Then TI (3.5 mmol in 25 ml of anhydrous chloroform) was drop wise added and was stirred for overnight. Then reaction mixture was added slowly into excess methanol (1 lit) with continuous stirring. The solid precipitate was separated by filtration, washed repeatedly with methanol and was soxhlet extracted with methanol for 24 h. The precipitate was then dried under vacuum at 30 0C. To remove the trace amount of $FeCl_3$ and the brownish-black solid product was dissolved in 125 ml $CHCl_3$ and was refluxed with additional 100 ml of concentrated ammonia solution. The organic layer was concentrated and precipitated into excess methanol. The precipitate was then separated and was washed thoroughly with methanol. After drying in vacuum at 30 ^{0}C for three days a red solid was obtained as a final product (yield-60%).

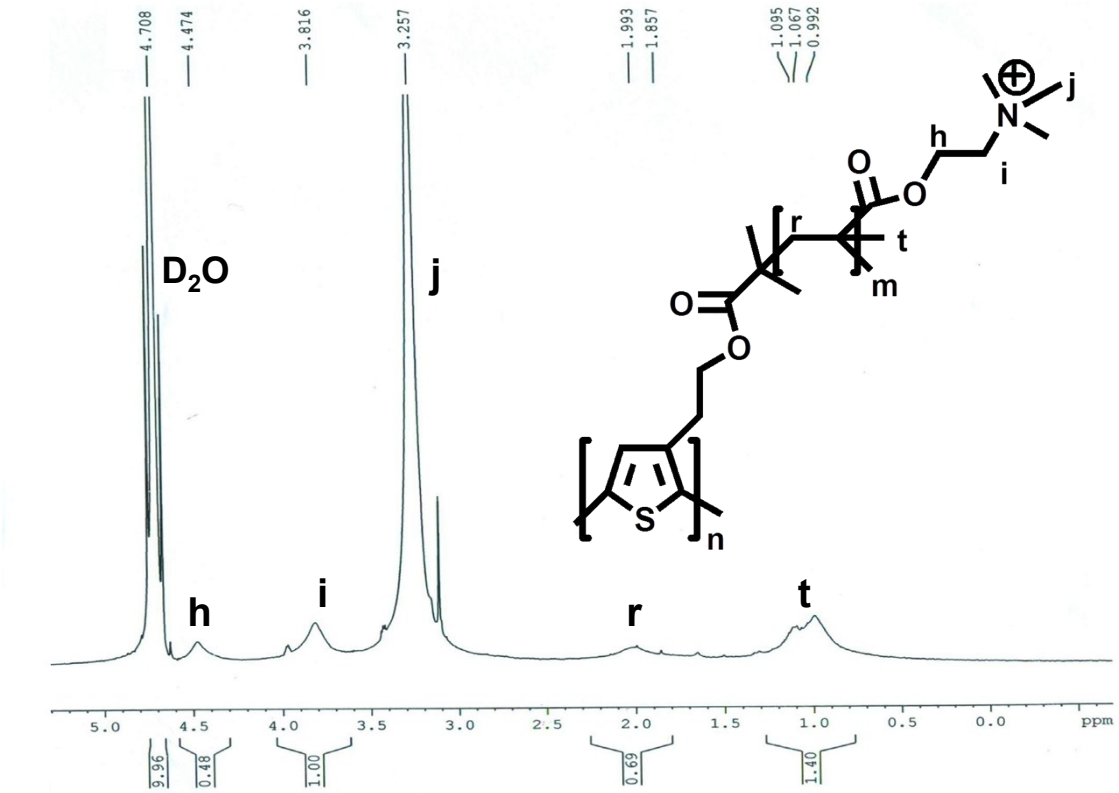
^{1}H NMR ($CDCl_3$): δ= 1.9 (6H), 3.2 (2H), 4.4 (2H), 6.9-7.2 (aromatic proton)

2.3 Synthesis of polythiophene-g-poly (N, N dimethylaminoethyl methacrylate)(PT-g-PDMAEMA)(PTDMA)

In a nitrogen purged tube PTI (30 mg), anisole (3 ml), CuCl (10 mg) were taken. The monomer DMAEMA (1 ml) was then injected into the reaction tube, and nitrogen purging was continued for 15 min. The tube was closed with a rubber septum and 40 μL HMTETA was injected into the reaction mixture and was stirred for 14 h at 30 ^{0}C. The reaction mixture was then precipitated into excess petroleum ether (60-80 ^{0}C). The separated polymer was precipitated by re-dissolving in THF, and precipitating into excess petroleum ether. The silica column chromatography was performed with THF solution of the polymer to remove the copper catalyst and finally we obtained copper free pure polymer ($\overline{M}_n$ =173000, PDI= 2.1).

2.4 Synthesis of cationic polythiophene-g-poly (dimethylaminoethyl methacrylate) (CPT-I)

In a nitrogen purged reaction vessel PTDMA (50 mg) and dry methanol (1 ml) were taken. 1 ml methyl iodide was then drop wise injected into the reaction mixture with continuous stirring. The reaction mixture was then stirred for 24 h and a yellow precipitate was produced. The solid precipitate was then separated by filtration and was washed repeatedly by methanol to remove trace amount of CH_3I. Then the product was dried under vacuum for 3 days and finally a yellow solid was collected as a pure product (Scheme 1).



^{1}H NMR spectra of CPT-I in D_2O with peak assignments

3. Synthesis of [N, N'-di (2-(12-aminododecanamido-L-tyrosine)-perylene-3,4:9,10-tetracarboxylic acid bisimide]-(PBI-DY)

The dipeptide (2-(12-aminododecanamido)-L-tyrosine) was synthesized by solution-phase methods. The the C-terminus of L- tyrosine was protected as a methyl ester and for N-terminal protection of 12-aminododecanoic acid, we have used Boc group. Couplings were mediated by dicyclohexylcarbodiimide/1-hydroxybenzotriazole monohydrate (DCC/HOBt. H_2O). Methyl ester deprotection has been performed by hydrolysis with 1(N) NaOH solution, and the Boc group was deprotected by 98% formic acid. All the intermediates were well characterized by 300 MHz and 500 MHz ^{1}H NMR and mass spectrometry. The 2-(12-aminododecanamido)-L-tyrosine based perylene bisimide derivative was synthesized by heating of 2-(12-aminododecanamido)-L-tyrosine, 3,4:9,10-

perylenetetracarboxyldianhydride and imidazole by mixing very well under inert N_2 atmosphere in silicon oil bath at 140 °C. The red product has characterized using MALDI-TOF MS and analyses ^{1}H NMR.

3.1 Synthesis of Boc- ADDA -OH

5.375 g (25 mmol) of 12-amino dodecanoic acid (ADDA) has been taken in a round bottomed flask. Then 25 ml 1(N) NaOH, 25 ml water and 50 ml 1, 4-dioxane were added to it and the solution was cooled to 0°C. After addition of 5.47 g (25.1 mmol) di-tert-butyl dicarbonate (Boc anhydride) the reaction mixture was allowed to stir for 10 hours at room temperature. The resulting mixture has been acidified with saturated $KHSO_4$ solution and the aqueous layer extracted with ethyl acetate (4 × 40 ml). The ethyl acetate extract was dried over anhydrous sodium sulfate and evaporated in vacuum to obtain the white powdered material. **Yield:** 7.87 g (21.5 mmol, 84 %).

3.2 Synthesis of Boc- ADDA (1)-Y (2)-OMe

6.2 g (20 mmol) of Boc- ADDA -OH was dissolved in 5 mL of dry DMF and retained it in an ice-water bath. H_2N-Y-OMe was isolated from the corresponding methyl ester hydrochloride by neutralization, subsequent extraction with ethyl acetate and the ethyl acetate extract was concentrated to 10 mL. It was then added to the reaction mixture, followed by the addition of 4.12 g (20 mmol) of dicyclohexylcarbodiimide (DCC) and 3.06 g (20 mmol) of HOBt, H_2O. The reaction mixture was allowed to come to room temperature and stirred for 1.5 days. The residue was taken up in ethyl acetate (40 mL) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1 (M) HCl (3 × 30 mL), brine (1 × 30 mL), 1 (M) sodium carbonate (3 × 30 mL) and brine (2 × 30 mL); dried over anhydrous sodium sulfate and evaporated in a vacuum to obtain the crude yellowish white material as product. The crude product was purified by silica gel column chromatography (ethyl acetate/petrolium ether).

Yield: 9.12 g (18.55 mmol, 83.7 %)

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): 6.93-6.74 (m, tyrosine ring Hs, 4H); 5.95 (d, J = 7.6, NH, 1H); 4.87-4.83 (m, Cα H of L- tyrosine, 1H); 4.59 (br, NH, 1H); 3.72 (s, -OCH3 of ester, 3H); 3.09-3.01 (m, 2CβHs of tyrosine and 2Cα Hs with respect to NH of DUNDA, 4H); 2.18-2.13 (m, 2CH2, 4H); 1.57 (br, 2CH2, 4H); 1.44 (s, Boc CH3,9H); 1.27 (br, 7CH2, 14H). **^{13}C NMR (100 MHz, $CDCl_3$):** d= 173.34, 172.47, 156.37,156.07, 130.27, 126.79, 115.69, 79.33, 53.28, 52.35, 40.72, 37.18, 36.67, 36.57, 30.05, 29.53, 29.48, 29.47, 29.38, 29.33, 29.27, 29.22, 29.15, 28.52, 26.76, 25.60.

HRMS (ESI, m/z): Calculated 515 for $[M+Na]^+$, found 515.31 .

3.3 Synthesis of Boc- ADDA (1)-Y-(2)-OH

To 7.38 g (15 mmol) of Boc- ADDA (1)-Y-(2)-OMe were added 70 mL of MeOH and 25 mL of 1 (M) NaOH. The reaction mixture was stirred for 12 hours and the progress of saponification was monitored by thin-layer chromatography (TLC). After 12 h, methanol was removed under a vacuum; the residue was taken in 70 mL of water, washed with diethyl ether (2 × 50 mL). Then the pH of the aqueous layer was adjusted to 2 using 1 (M) HCl and it was extracted with ethyl acetate (3 × 50 mL). The extracts was dried over anhydrous sodium sulfate and evaporated in a vacuum. A sticky material was obtained.

Yield: 4.818 g **(**10.08 mmol, 72.05 %).

^{1}H NMR (400 MHz, DMSO-d6, 25 °C): d = 12.58 (br, COOH, 2H); 8.00 (m, NH, 1H); 7.01-6.69 (m, tyroine ring H's); 4.35-4.31 (m, tyroine Cα H, 1H); 3.46-3.42 (m, 2Cβ Hs of tyroine and 2Cα Hs with respect to NH of DUNDA, 4H); 2.93-2.87 (m, $2CH_2$, 4H); 2.05-2.00 (m, CH_2, 2H); 1.33 (s, Boc CH_3, 9H); 1.16-1.11 (m, $7CH_2$, 14H). **^{13}C NMR (100 MHz, DMSO-d_6):** d= 173.26, 172.10, 155.82, 155.53, 129.87, 127.69, 114.86, 79.11, 77.21, 56.00, 53.57 36.03, 35.06, 29.44, 28.96, 28.93, 28.88, 28.77, 28.70, 28.48, 28.22, 26.23, 25.15, 20.95, 18.47.

HRMS (ESI, m/z): Calculated 501 for $[M+Na]^+$, found 501.25 .

3.4 Synthesis of H_3N+- ADDA (1)-Y-(2)-COO-

To 4.78 g (10 mmol) of Boc-ADDA (1)-Y-(2)-OH was added 5 ml of 98% formic acid and the removal of the Boc group was monitored by TLC. After 10 h, formic acid was removed under a vacuum. The residue has taken in water (20 ml) and washed with diethyl ether. The pH of the aqueous solution was then adjusted to pH=7 with 30% aqueous NH_3. The aqueous portion has been evaporated in a vacuum to yield the desired dipeptide.

Yield: 2.53 g (6.7 mmol, 67 %).

1H NMR (500 MHz, DMSO-d6, 25 °C): d = 7.27-7.25 (br, NH_3^+, 3H); 6.93 (d, J= 8.5 Hz, phenyl ring hydrogen, 2H), 6.60 (d, J= 8 Hz phenyl ring hydrogen, 2H); 4.08 (br, tyrosine Cα H, 1H); 3.22-3.14 (br, phenylalanine Cβ H, 2H) 2.95-2.92 (br, 2Cα Hs with respect to NH of DUNDA, 2H); 2.06 (br, 2 CH2, 2H); 1.99 (br, 2CH2, 4H); 1.52-1.23 (m, 7CH2, 14H). **^{13}C NMR (125 MHz, DMSO-d_6):** d= 170.96, 155.37, 130.04, 128.93, 114.48, 48.51, 36.57, 35.40, 28.25, 28.02, 27.91, 27.03, 25.39, 24.95.

HRMS (ESI, m/z): Calculated 379 for $[M+H]^+$, found 379.2604 and for $[M+2H]^+$ at 380.3050

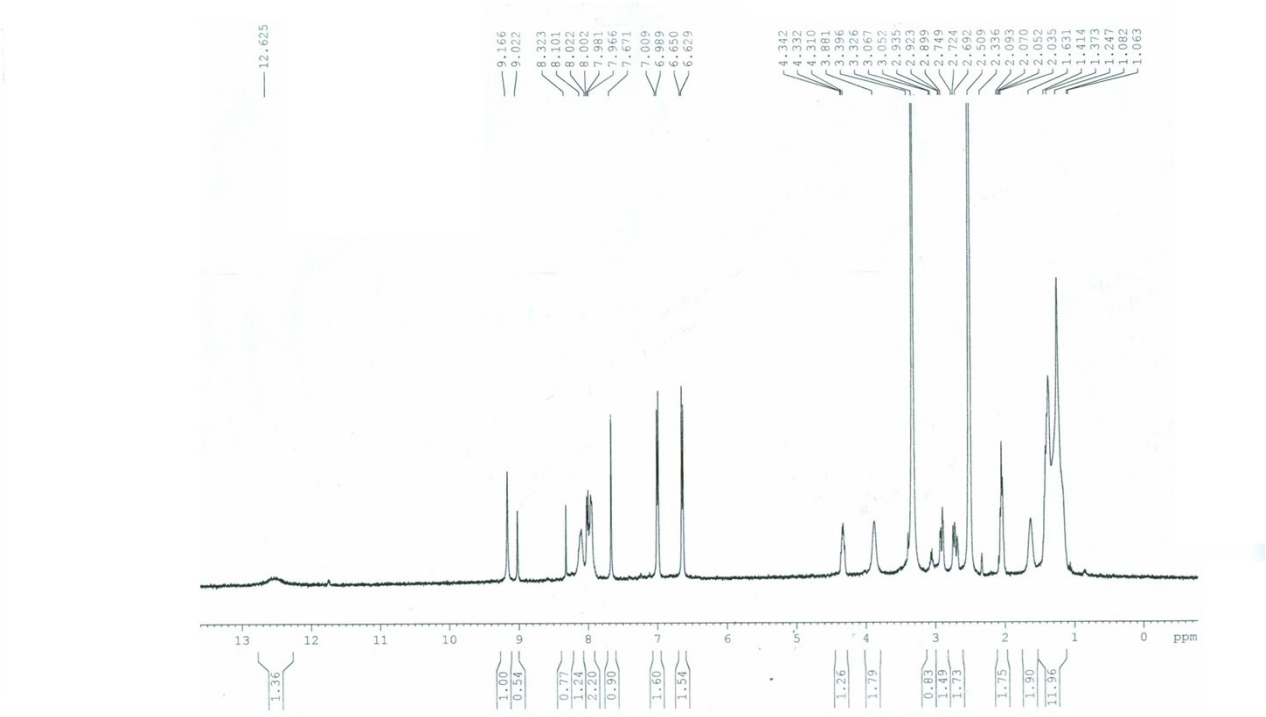
3.5 Synthesis of N, N′-di (2-(12-aminododecanamido-L-tyrosine)-perylene-3,4:9,10-tetracarboxylic acid bisimide]-(PBI-DY)

In a 100 mL round bottom flask 2-(12-aminododecanamido)-L-tyrosine 0.69 g (2 mmol), 3, 4, 9, 10- perylenetetracarboxyldianhydride (PTCDA) 0.392 g (1 mmol) and 1.36 g imidazole (20 mmol) were taken. The mixture was then purged with N_2 for 30 min before being heated at 140 ˚C until the reaction mixture was completely soluble in water. Consequently, the reaction mixture was cooled to 90 ˚C. Deionised water was then added under N_2 atmosphere and then it was allowed to keep for 1 h. The dark red solution was filtered to remove the trace

amount of un-reacted PTCDA. The solution was then acidified with 2 M HCl aqueous solution until the pH of the mixture was reached to pH 2, the precipitate was collected by suction-filtration method and was thoroughly washed with deionised water until the filtrate was neutral; the red solid was obtained. It was then dried in air and used for our study (Scheme-1b)

Yield: 0.678 g (0.61 mmol, 61%).

^{1}H NMR (400 MHz, DMSO-d6, 25 ºC): d = 12.625 (br, COOH, 1H); 9.16-9.02 (m, 4H's of perylene); 8.23-8.02 (m, NH, 2H); 7.98-7.67 (m, 4H's of perylene); 7.01-6.629 (m, ring H's of L-tyrosine, 8H); 4.34-4.31 (br, tyrosine Cα H, 2H); 3.89 (br, 2CH2, 4H); 3.07-3.04 (m, 2CH2, 4H); 2.93-2.89 (m, 2CH2, 4H); 2.74-2.69 (br, 2CH2, 4H); 2.09-2.03 (m, 2CH2, 4H); 1.60-1.06(m, 12CH2, 24H). **13C NMR:** Due to the insufficient solubility of the compound in DMSO-d6 13C NMR spectrum of the compound did not appear.



^{1}H-NMR spectrum of PBI-DY in DMSO-d6.

Maldi-TOF MS: Calculated 1112.51 for $[C_{66}H_{72}N_4O_{12}]$, found for $[M+H]^+$ m/z at 1113.797 and $[M+Na]^+$ m/z at 1135.61 and $[M+K]^+$ m/z at 1151.67.

4. Instrumentatal part:

NMR Experiments

All NMR studies have been carried out on a Brüker DPX 300 MHz and 500 MHz spectrometer at 300 K.

Mass Spectrometry

Mass spectra have recorded on a Q-tof Micro™ YA263 high-resolution mass spectrometer.

Transmission Electron Microscopy

The morphology of the CPT-I, PBI-DY, and hybrid was investigated by using a transmission electron microscope (JEOL, 2010EX). The samples were prepared by depositing of the highly diluted sample onto a TEM grid (300 mesh carbon coated Cu grid). Then, the grid was dried under vacuum at 30 ˚C for two days.

UV/Vis spectroscopy

The UV-vis spectra has been taken in buffer medium from 200 to 800 nm range using a UV-vis spectrophotometer (Hewlett-Packard, model 8453) at 30 ^{0}C. The aqueous solution of the components and mixture of different compositions were taken in quartz cell of 1cm path length. PBS buffer was used in a similar cell for background correction.

Fluorescence study

The photoluminescence (PL) spectra of the CPT-I, PBI-DY and hybrid were completed in a Fluoromax-3 instrument (Horiva Jovin Yvon). The quartz cell of 1 cm path length has been used for this experiment and the samples were excited at 420 nm. Emission scans were documented from 440 to 800 nm using a slit width of 2 nm.

Maldi-TOF MS

MALDI-TOF MS analysis has been performed by using Applied Biosystems MALDI TOF/TOF Analyzer in 2, 5-Dihydroxybenzoic acid matrix.

I-V measurements

For I-V measurements, the DC currents were measured using Keithley source meter (model 2410). The dark I-V characteristic has been performed after keeping the samples in dark for several hours. For photocurrent transient measurement, a xenon light source (model no. 66902; Newport Corp. USA) with power of 1 sun was used for the light illumination.

X-ray diffraction study:

X-ray diffraction study of CPT-I, PBI-DY and the hybrid material was carried out by using an X-ray diffractometer (Bruker D8 Advance) with a parallel beam optics attachment. The instrument was operated at a 30 mA and current 35 kV voltages using Ni-filtered Cu Kα radiation and was calibrated with a standard silicon sample. Samples were scanned from 5º to 50º (2θ) at the step scan mode (step size 0.016º, preset time 2 s) and the diffraction patterns are recorded using a scintillation scan detector.

Impedance Spectra (IS):

Impedance spectroscopic analyses of the samples were performed using the drop casted films on a 2 mm ITO electrode and sandwich with another same ITO electrode. The spectra were recorded using Impedance analyzer (Solartron 1260SI) within a frequency range of 100 kHz to 0.1 Hz at 0.2 V DC bias and 10 mV AC perturbation voltage. The experimental results were fitted and analysed using the Z-view software.

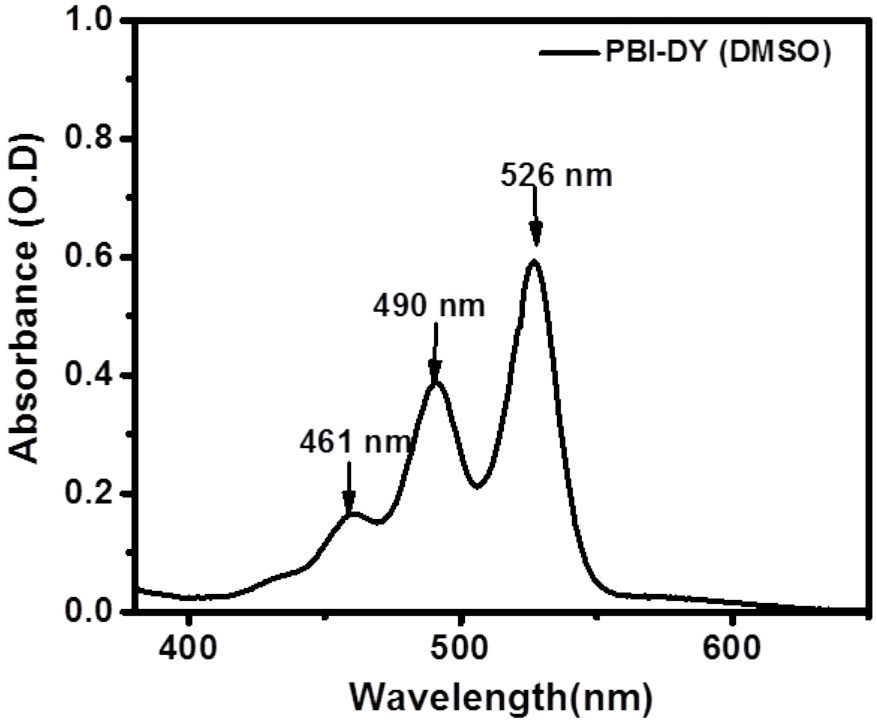


Figure S1: UV−Vis study of **PBI-DY** in dimethyl sulphoxide (DMSO).

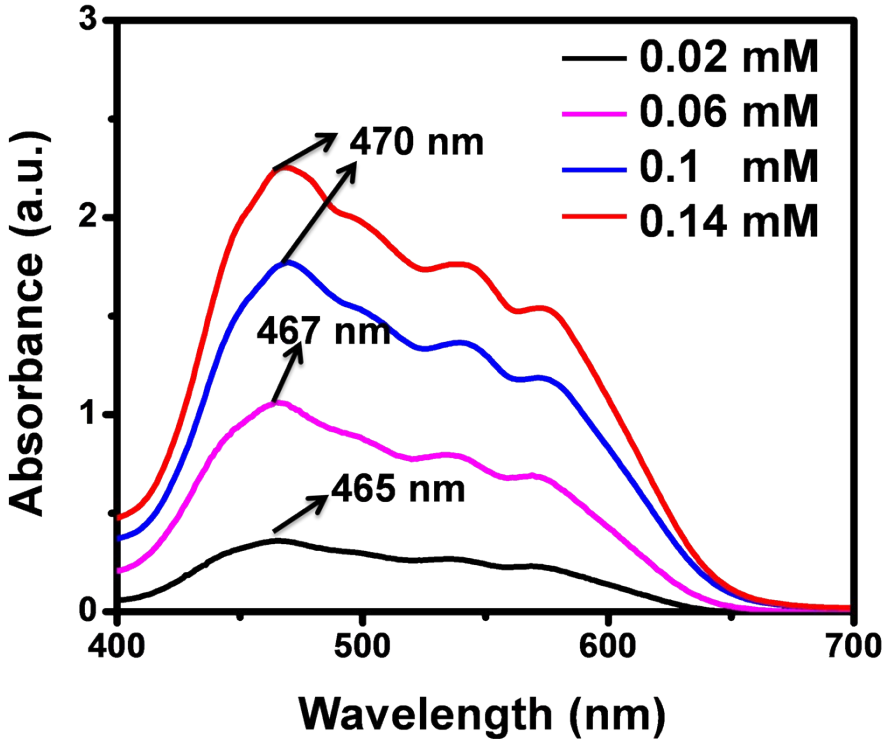


Figure S2. Change of UV-Vis Spectra of PBI-DY solution in PBS buffer at different molar concentration of PBI-DY.

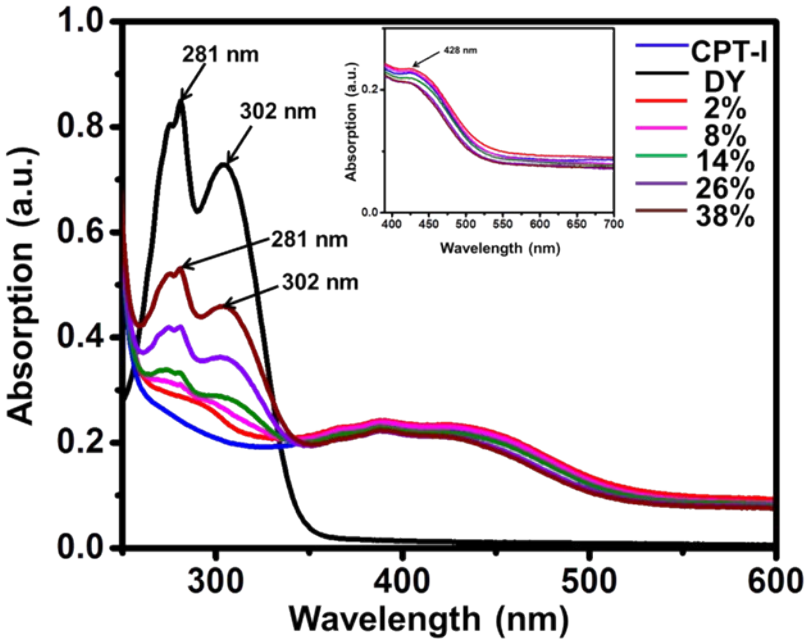


Figure S3. UV-Vis Spectra of CPT-I solution in PBS buffer on addition of DY at indicated weight percent. (Inset: no shift of CPT-I absorption peak at 428 nm with increasing DY concentration).

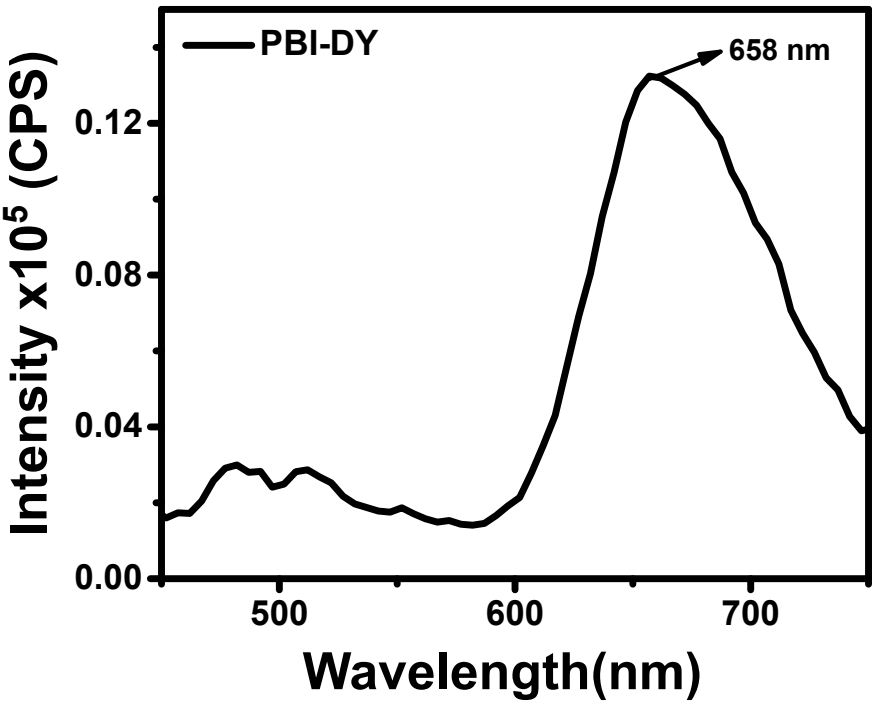


Figure S4: Enlarged photoluminescence spectra of PBI-DY in 7.4 PBS buffer. (Figure2)

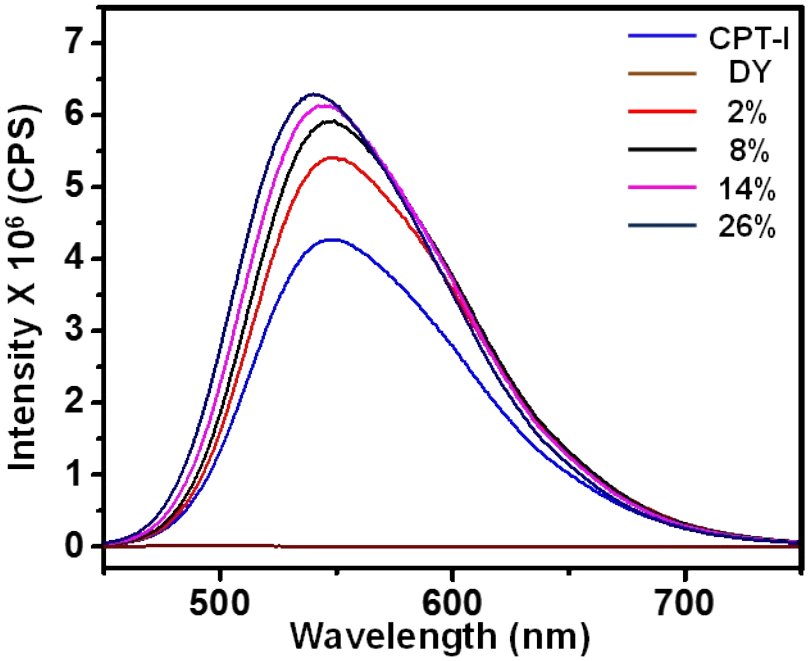
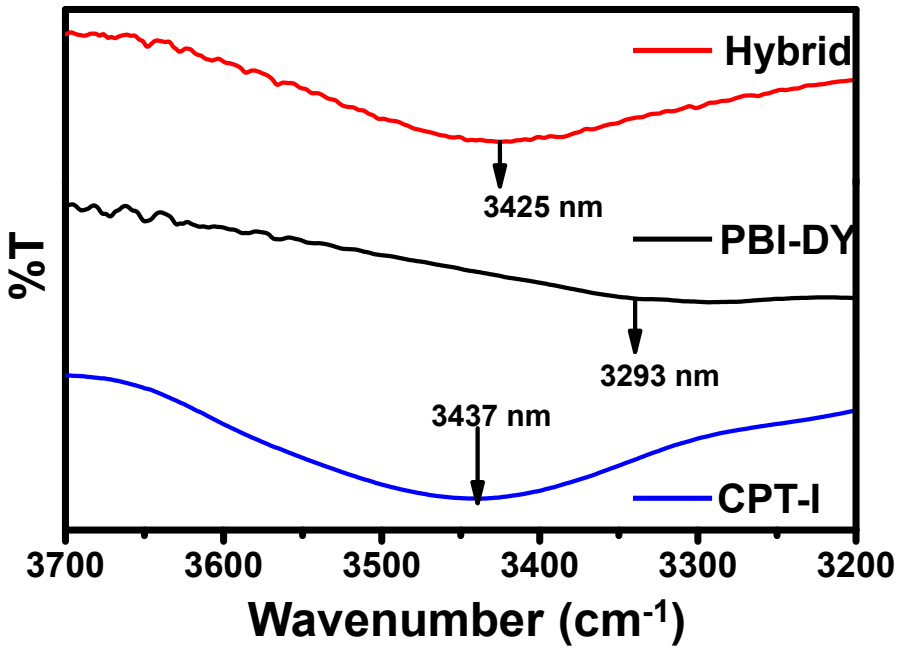


Figure S5. Photoluminescence spectra of CPT-I solution in PBS buffer on addition of DY at indicated weight percent.



FigureS6: FT-IR spectra CPT-I (blue); PBI-DY (black); Hybrid (red) range 3700 cm^{-1} to 3200 cm^{-1} .

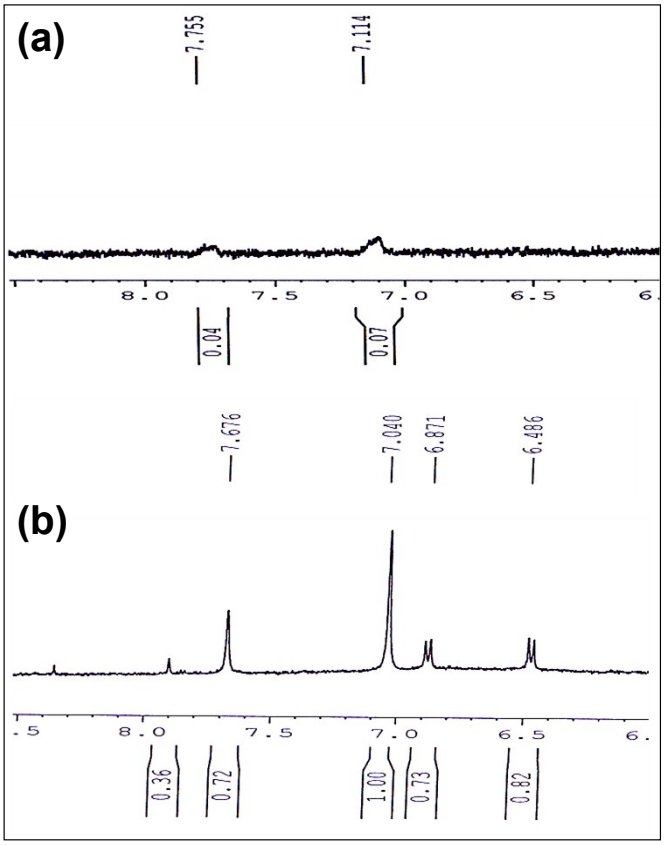


Figure S7. ^{1}H-NMR spectrum of (a) CPT-I- PBI-DY hybrid at 14 wt% PBI-DY composition (b) pure PBI-DY in D_2O .

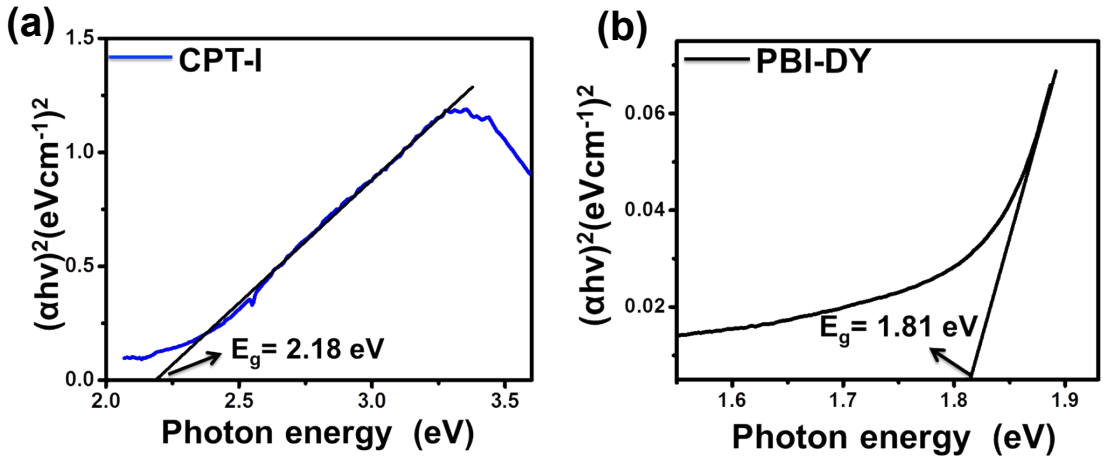


Figure S8: (a) Tauc's plot of CPT-I from the solid state UV-Vis spectra of CPT-I and (b) PBI-DY.

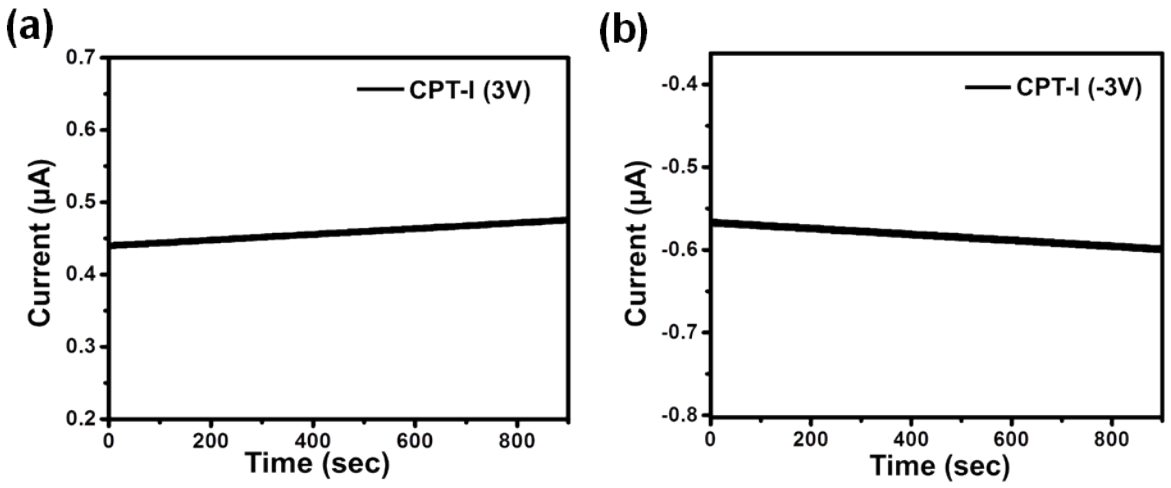
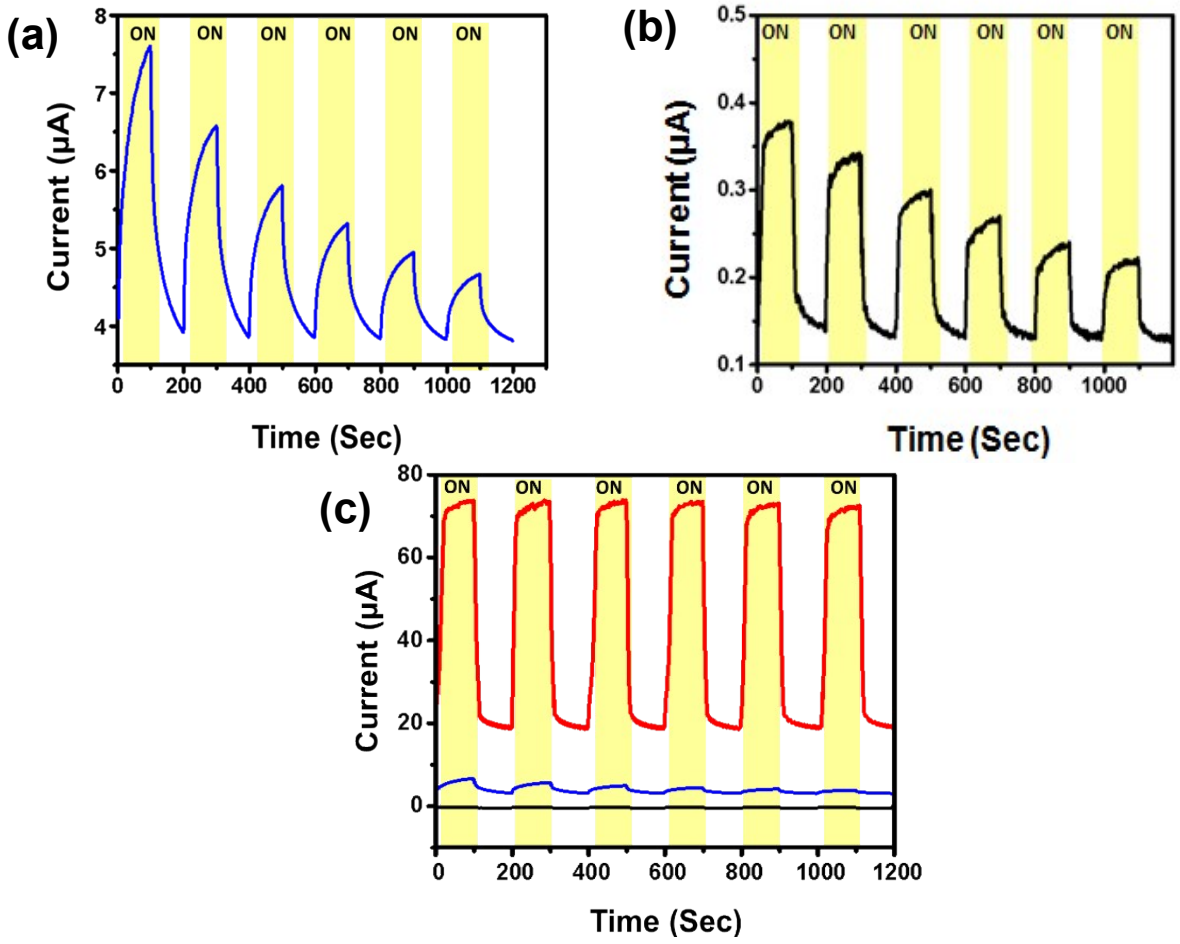
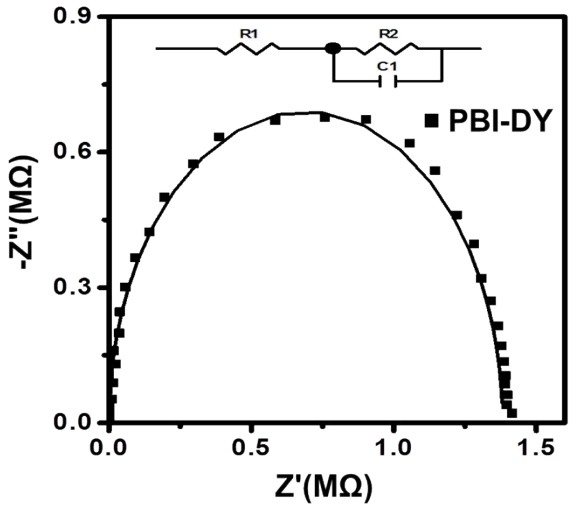


Figure S9. Current (I) vs time (t) plot of CPT-I at (a) +3V, (b) -3V


(a)
ON
Current (μA)
Time (Sec)
(b)
Current (μA)
Time (Sec)
(c)
Current (μA)
Time (Sec)

FigureS10: Photoresponse behaviour (on-off cycle) of (a) CPT-I, (b) PBI-DY and (c) the hybrid for repeated measurement on illumination with white light of 1 sun.



FigureS11 Enlarged Nyquist plot from impedance spectra of PBI-DY (Figure 8)