

## Supporting Information

### **Polythiophene-g-Poly (methacrylic acid) and Perylene Diimide Appended Peptide Conjugates with Tuneable Photoluminescence, OMEIC and Photo-switching Properties**

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## **1. Detailed Synthesis procedure of PTMA:**

### **1.1 Preparation of Thiophene Initiator (TI):**

Thiophene-3-ethanol (20 mmol) and triethylamine (22 mmol) were dissolved at 0°C in anhydrous DCM (40 ml) under nitrogen atmosphere. Then 2BIB (22 mmol), dissolved in 10 ml anhydrous DCM, was added drop wise into the reaction mixture over 30 mins and was stirred for another 4 h at 0°C. The reaction mixture was then allowed to stir for overnight at room temperature. It was then filtered and repeatedly washed with 1% HCl, saturated NaHCO<sub>3</sub>, NaCl solution and distilled water using a separating funnel. The organic layer was then passed through anhydrous Na<sub>2</sub>SO<sub>4</sub> to remove the water and then through silica column in a solvent mixture of hexane / ethyl acetate (95/5, in volume ratio) for further purification. After solvent evaporation, a brown liquid (yield 75%) is collected as a final product, denoted as TI.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>):** 1.9 (6H, s), 3.0 (2H, t), 4.3 (2H, t), 6.9-7.2 (aromatic ring protons).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>):** 29.4, 30.9, 55.9, 65.9, 121.9, 125.8, 128.4, 137.8, 171.8.

**HRMS (ESI, m/z):** 277. 979

### **1.2 Preparation of Polythiophene Macro-Initiator (PTI):**

In a 100 ml round-bottom flask 15 mmol of anhydrous FeCl<sub>3</sub> was dispersed in 30 ml of freshly distilled chloroform (CHCl<sub>3</sub>) under N<sub>2</sub> atmosphere. Then 3.5 mmol of TI, dissolved in 25 ml of anhydrous chloroform, was added drop wise into that with vigorous stirring and left for overnight stirring. Then the reaction mixture was poured into a large amount of methanol (1L). The precipitate was separated by filtration, washed with methanol and soxhlet extracted with methanol to remove FeCl<sub>3</sub> and then dried under vacuum at 30°C. The brown powder was then dissolved in 100 ml CHCl<sub>3</sub> and then refluxed with 100 ml of concentrated ammonia

solution to remove any trace amount of FeCl<sub>3</sub>. After solvent evaporation, a brown powder was dried and was collected as a final product, denoted as PTI.

**Yield:** 65%.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>):** 1.9 (6H), 3.2 (2H), 4.4 (2H), 6.9-7.2 (aromatic proton).

### **1.3 Synthesis of polythiophene-g-poly(tert-butyl methacrylate) (PT-g-TBMA):**

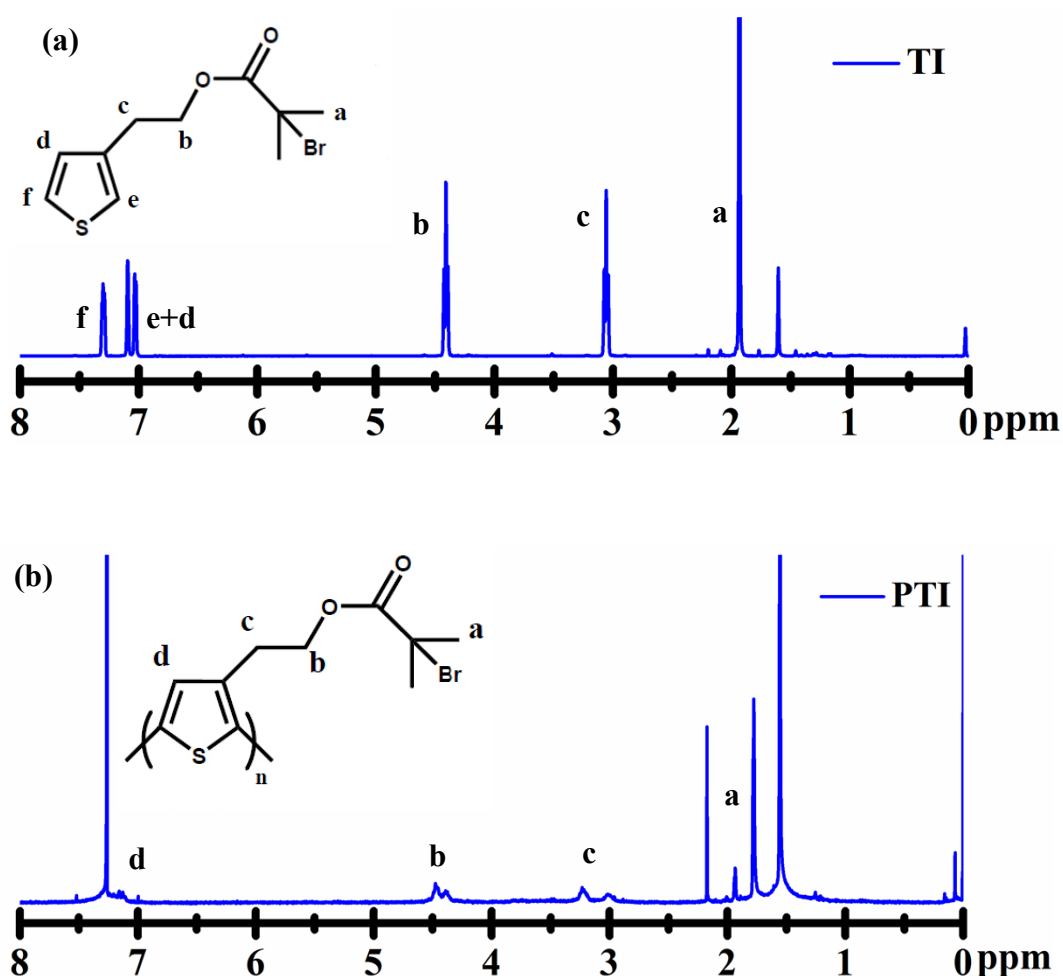
30 mg of PTI was dissolved in 3 ml anisole in a N<sub>2</sub> purged reaction vessel. Then 10 mg cuprous chloride (CuCl) was added into that solution. 1 mL nitrogen purged TBMA was next injected into the reaction vessel with constant stirring, and nitrogen purging was continued for 20 min. Then 40 μL HMTETA was injected into the reaction vessel and was sealed with a rubber septum. The reaction mixture was kept for stirring for another 12 h at 30<sup>0</sup>C. It was then poured into excess methanol. The separated polymer was re-dissolved in THF and was again poured into methanol to remove any trace amount of monomer entrapped within the polymer. Next the polymer was dissolved in the THF and passed through a silica column followed by solvent evaporation to remove the catalyst and to obtain copper free PT-g-TBMA graft copolymer.

**Yield:** 50%

### **Synthesis of polythiophene-g-poly(methacrylic acid) (PTMA):**

In a 100 ml round-bottom flask, 500 mg of PT-g-TBMA was dissolved into 30 ml dry DCM under N<sub>2</sub> atmosphere. Then 1 ml CF<sub>3</sub>COOH (TFA), diluted by 10 ml dry DCM, was added drop wise into the reaction mixture, and kept for overnight stirring at 30<sup>0</sup>C. The reaction mixture was then dried in a rotary evaporator to remove excess TFA and washed several times with DCM to obtain pure PTMA.

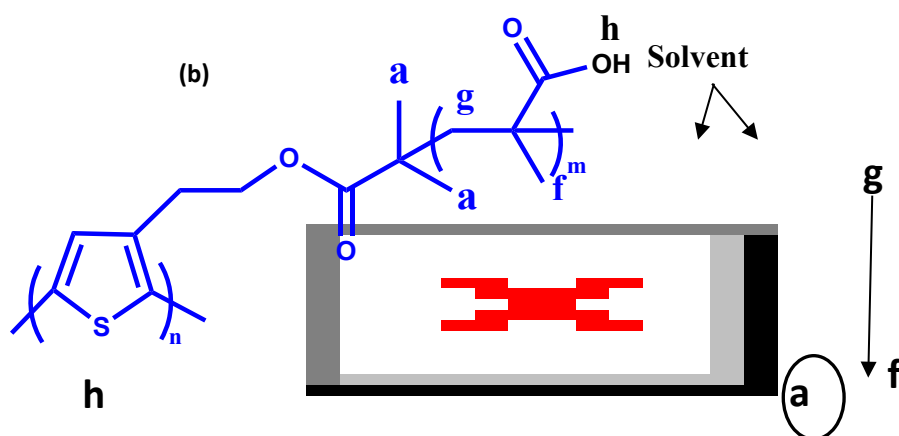
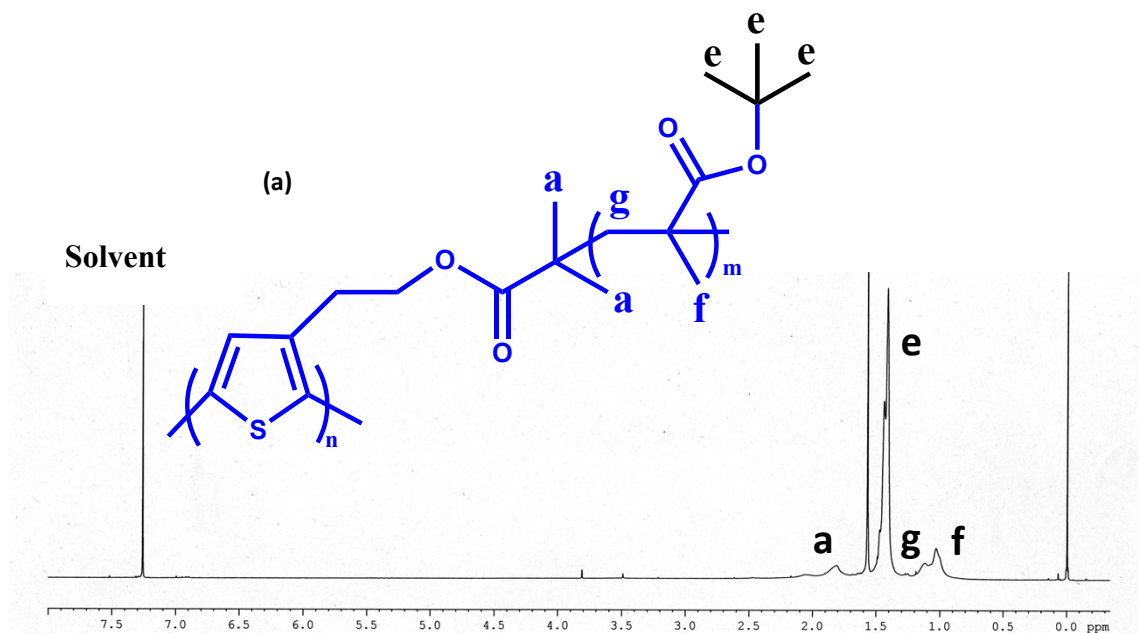
## 2. Characterization of PTMA:



<sup>1</sup>H NMR spectrum of (a) TI and (b) PTI polymer in CDCl<sub>3</sub>

### <sup>1</sup>H NMR analysis of TI and PTI with their peak assignments.

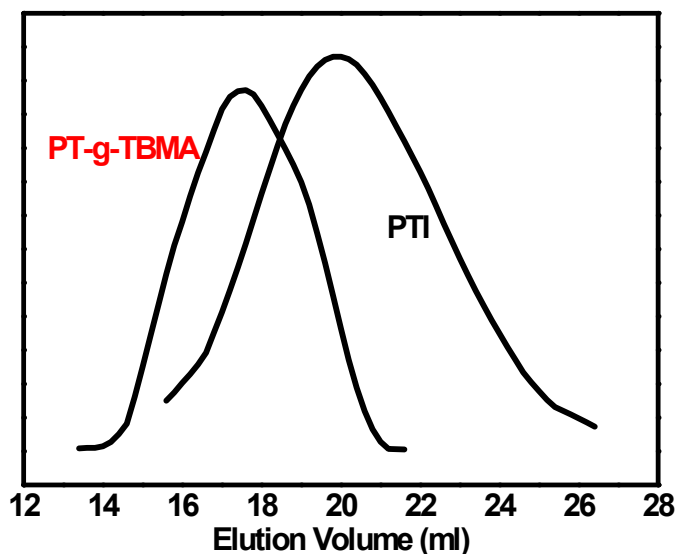
The <sup>1</sup>H NMR spectra of TI shows 'a', 'b', 'c', 'd'+ 'e', and 'f' protons are resonated at  $\delta$  values of 1.9, 4.4, 3.1, 7.0 and 7.3 ppm, respectively. In case of PTI peak 'b' and 'c' ( $\delta$ = 4.4 and 3.1 ppm, respectively) becomes broader and splitted than those of TI. This broadness arises due to the polymerization and the splitting indicates the presence of regio-irregularity (found to be 65%) in the linkages of thiophene moieties. Due to polymerization, the 'e' and 'f' protons also disappeared.



$^1\text{H}$  NMR spectra of (a) PT-g-TBMA and (b) PTMA in  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  solvent, respectively.

$^1\text{H}$  NMR spectra of PT-g-TBMA and PTMA and the signals corresponding to 'a', 'e', 'f' and 'g' protons of the grafted TBMA segments are observed at  $\delta = 1.8, 1.43, 1,$  and  $1.1$  ppm. Protons correspond to 'a', 'f' and 'g' of PTMA are observed at  $\delta = 12.3, 1.8, 1$  and  $1.1$  ppm, respectively, however, on hydrolysis the tertbutyl groups of grafted TBMA chains ("e")

protons) at  $\delta$  1.49 ppm disappears and a new peak appears at  $\delta = 12.3$  ppm for the -COOH proton (h) of PTMA which successfully confirms conversion of PTMA from PT-g-TBMA.



**Figure S1.** GPC traces of PT-g-TBMA and PTI, Eluent: THF, Flow rate: 1ml/min.

Figure S1 shows the GPC traces of PTI and PT-g-TBMA and the GPC analysis gives the  $\bar{M}_n$  of PTI  $\sim 40\,000$  with dispersity 2.8 and that of PT-g-TBMA are found to be  $\sim 200\,000$  with dispersity 1.6. The hydrodynamic volume of PT-g-TBMA is higher than that of PTI due to the growth of the grafted chains from the polythiophene backbone and consequently, the GPC trace of PT-g-TBMA shows a clear sweep towards lower elution volume. However, for PT-g-TBMA it may be very approximate as the molecular weight is calculated using linear polystyrene as the calibration standard due to the non-availability of any grafted/branched copolymer as the GPC standard.

**3.1 Detailed synthetic procedure of PBI-F-ED-Boc:** In a 100 mL round bottom flask 1.37g (2 mmol) of N, N'-di (2-(L-phe)-perylene-3, 4:9, 10- tetracarboxylic acid bisimide) and 0.80 gm (5 mmol) Boc-ED-NH<sub>2</sub> was dissolved in 5 mL of dry DMF 0.618 g (3 mmol) of dicyclohexylcarbodiimide (DCC) and 0.459 g (3 mmol) of HOBt, H<sub>2</sub>O. The reaction mixture was heated at 140°C for an hour then 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 brine (1 × 30 mL) and dried over anhydrous sodium sulphate and evaporated in a vacuum to obtain the crude reddish material as product. The crude product was purified by silica gel column chromatography (chloroform /methanol).

**Yield:** 1.26 gm (1.3 mmol).

**MALDI-TOF:** Calculated 994 for [M+Na<sup>+</sup>], found 997

**(<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C):** δ = 8.57-8.33 (m, H's of perylene); 7.52-6.99 (m, ring H's of L-phenyl alanine, 10H); 6.01-5.99 (m, NH, 2H); 3.70-3.68 (br, L-phenyl alanine C<sub>α</sub> H, 2H); 3.53-3.40 (m, 4CH<sub>2</sub> of Ethylene Di amine, 8H); 2.88-2.85 (br, L-phenyl alanine C<sub>β</sub>H, 4H); 1.54 (s, Boc CH<sub>3</sub>, 18H).

**<sup>13</sup>C NMR:** Due to the insufficient solubility of the compound <sup>13</sup>C NMR spectrum of the compound did not appear.

**3.2: Detailed synthetic procedure of PBI-F-ED or PBI-NH<sub>2</sub>:** 5 ml of Trifluoroacetic Acid was added to 900 mg (1mM) of PBI-F-ED-Boc and the removal of the Boc group was monitored by TLC. After 6 h, TFA was removed under a vacuum. The residue has been 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<sub>3</sub>. The aqueous portion has been evaporated in vacuum to yield the powdered products. It was then dried in air and used for our study.

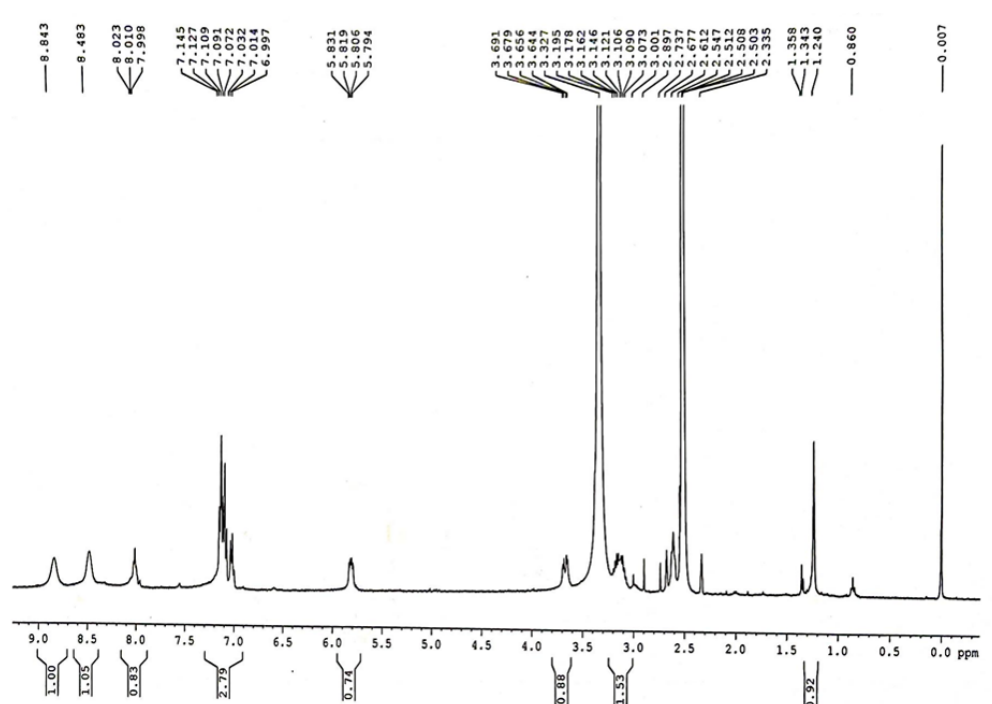
**(Scheme 2b)**

**Yield:** 426 mg. (0.6 mmol).

**MALDI-TOF:** Calculated 794 for [M+Na<sup>+</sup>], found 796.

**<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C):** d = 8.84-8.48 (br, 4H's of perylene); 8.02-7.99 (m, NH, 2H); 7.14-6.99 (m, ring H's of L-phenyl alanine, 10H); 5.83- 5.79 (m, L-phenyl alanine C<sub>α</sub> H, 2H); 3.69-3.64 (m, L-phenyl alanine C<sub>β</sub>H, 4H); 3.32-3.07 (m, 4CH<sub>2</sub> of Ethylene Di amine, 8H); 2.89-2.73 (m, NH<sub>2</sub>, 2H).

**<sup>13</sup>C NMR:** Due to the insufficient solubility of the compound <sup>13</sup>C NMR spectrum of the compound did not appear.



<sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, 25 °C) spectra of PBI-F-ED or PBI-NH<sub>2</sub>

#### 4. Instrumentation:

**NMR experiments:** All NMR studies were carried out on a Bruker DPX400 MHz or Bruker DPX500 MHz spectrometer at 300 K. Concentrations was in the range 5–10 mmol in DMSO-d<sub>6</sub> and CDCl<sub>3</sub>.

**Mass spectrometry:** Mass spectra were recorded on a Q-ToF microTM (Waters Corporation) mass spectrometer by a positive mode electrospray ionization process.



**MALDI-TOF:** MALDI-TOF MS analysis was performed using an Applied Biosystems MALDI-TOF analyser with dithranol as a matrix.

**Fourier Transform Infrared (FTIR) study:** All FT-IR spectra were recorded using the KBr pellet technique in a Nicolet 380 FT-IR spectrophotometer (Thermo Scientific).

**X-ray diffraction study:** X-ray diffraction study of PTMA, PBI-NH<sub>3</sub><sup>+</sup> and the hybrid materials 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 K $\alpha$  radiation and was calibrated with a standard silicon sample. Samples were scanned from 5° to 50° (2 $\theta$ ) at the step scan mode (step size 0.016, pre-set time 2s) and the diffraction patterns are recorded using a scintillation scan detector.

**UV/Vis spectroscopy:** UV/Vis absorption spectra were recorded on a Hewlett-Packard (model 8453) UV/Vis spectrophotometer (Varian Carry 50.bio) at 0.05mM concentration.

**PL spectroscopy:** The photoluminescence (PL) spectra of the PTMA, PBI-NH<sub>3</sub><sup>+</sup> 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 385 and 420 nm. Emission scans were documented by using a slit width of 2 nm.

**TCSPC study:** TCSPC measurements have been performed by means of Horiba Jobin Yvon IBH having MCP PMT Hamamatsu R3809 detector instrument and all data were fitted using Data Station v2.3.

**Transmission Electron Microscopy:** The morphology of the PTMA, PBI-NH<sub>3</sub><sup>+</sup> and hybrid were 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.

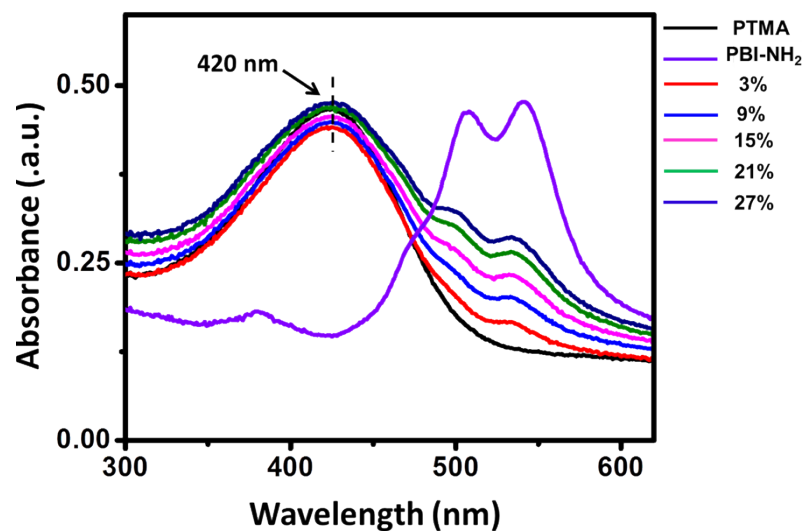
**I-V measurements:** For I-V measurements, the DC currents were measured using Keithley source meter (model 2410). The dark I-V characteristic has been performed after keeping the samples in dark for several hours. For **photocurrent transient measurement**, a xenon light source (model no. 66902; Newport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

### **Impedance Spectra (IS):**

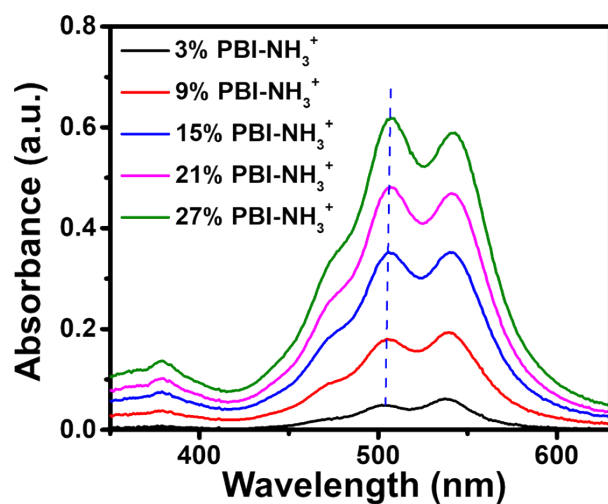
Impedance spectroscopic analyses of the samples were performed using the drop casted films on a 2 mm ITO electrode and sandwiched with another same ITO electrode. Electrical data of these materials were obtained with the help of an LCR meter (Hioki, model IM 3536) where the frequency range was 4 Hz-8 MHz at room temperature (303K).

**Table S1:** Average lifetime data of PTMA, PBI-NH<sub>3</sub><sup>+</sup> and hybrids.

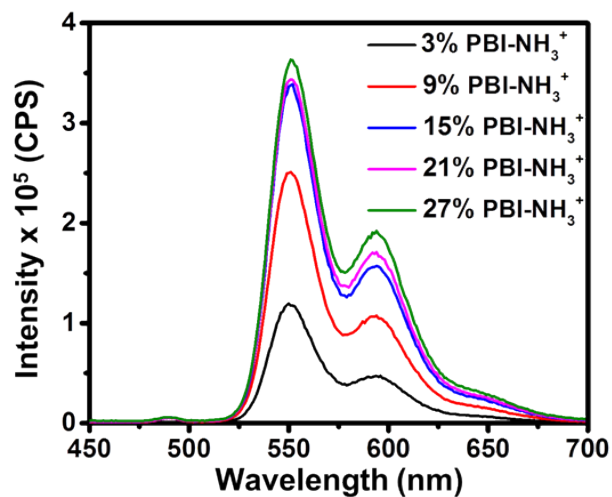
Sample	Decay profile						
	Lifetime [ $\tau_1$ (ns)]	Relative Amplitude [ $a_1$ ]	Lifetime [ $\tau_2$ (ns)]	Relative Amplitude [ $a_2$ ]	Lifetime [ $\tau_3$ (ns)]	Relative Amplitude [ $a_3$ ]	Average fluorescence lifetime ( $\langle\tau\rangle$ ) (ns)
PTMA	0.184	0.94	0.916	0.059	—	—	0.23
PBI-NH <sub>3</sub> <sup>+</sup>	0.08	0.91	4.16	0.09	—	—	0.41
3%	0.79	0.06	4.31	0.07	0.155	0.859	0.50
9%	0.70	0.08	3.99	0.05	0.157	0.864	0.40
15%	0.77	0.049	4.55	0.045	0.114	0.905	0.34
21%	0.43	0.015	4.55	0.013	0.027	0.97	0.09
27%	0.432	0.014	4.50	0.016	0.037	0.969	0.11



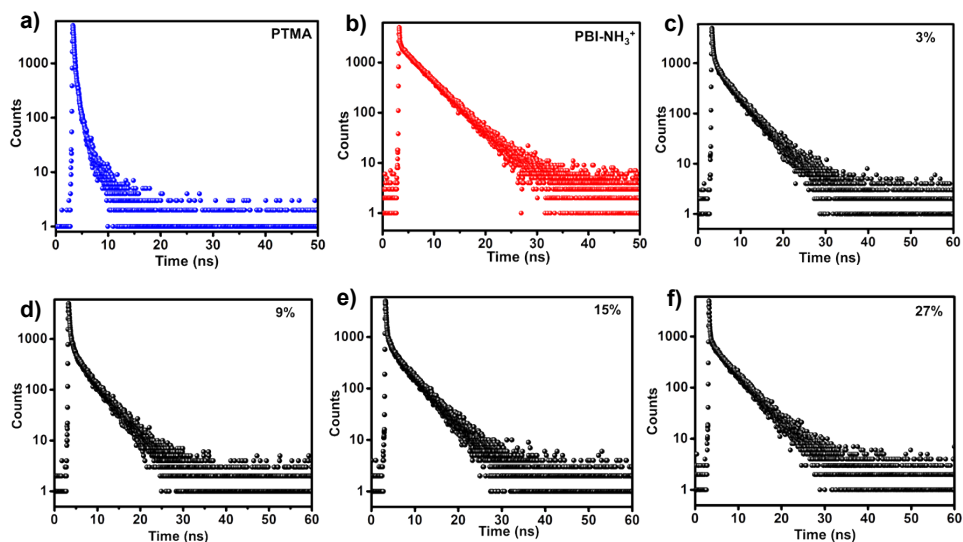
**Figure S2:** UV-Vis spectra of PTMA solution on the addition of PBI-NH<sub>2</sub> at the indicated weight percentage.



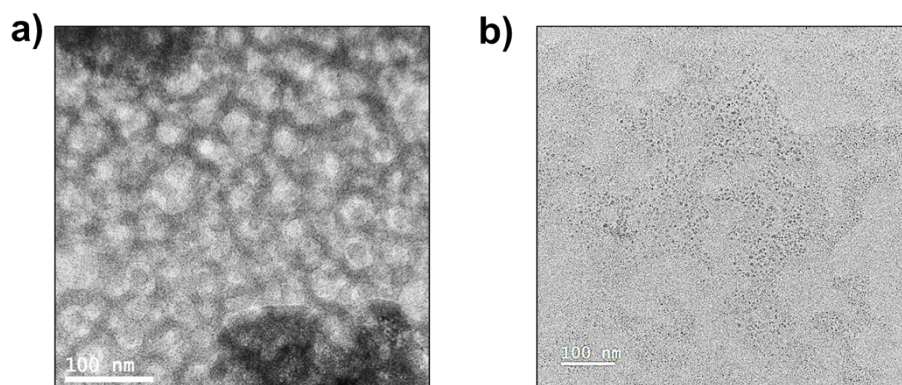
**Figure S3:** UV-Vis spectra of pristine PBI-NH<sub>3</sub><sup>+</sup> in aqueous solution at the indicated weight percentage.



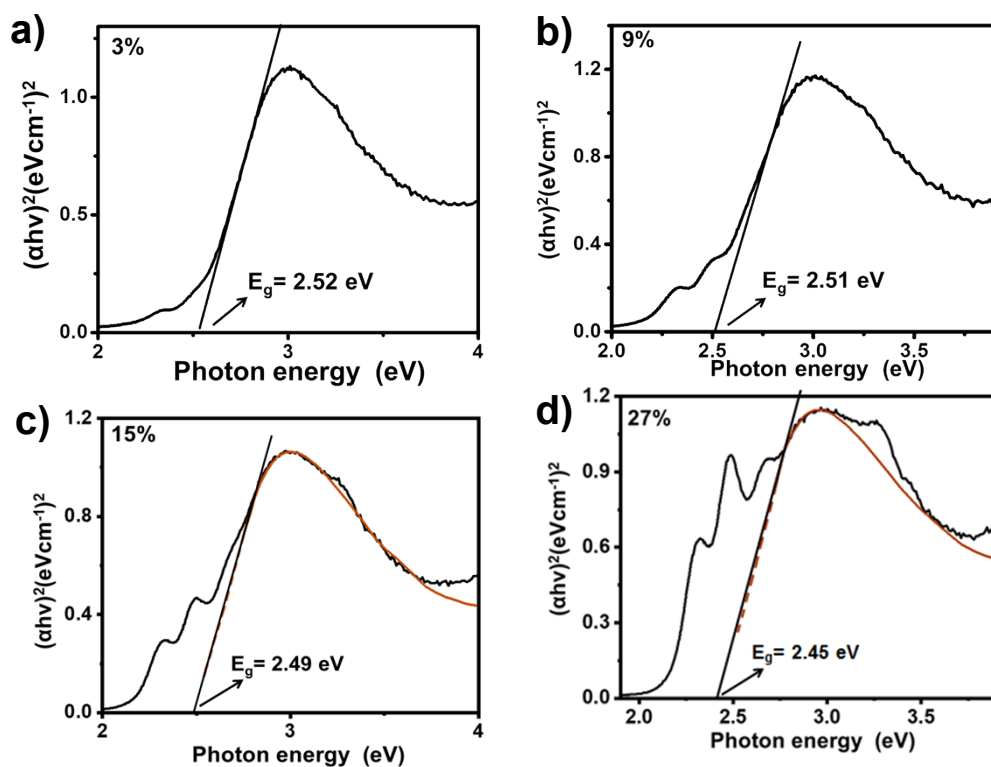
**Figure S4:** Fluorescence spectra of pristine PBI-NH<sub>3</sub><sup>+</sup> in aqueous solution at the indicated weight percentage.



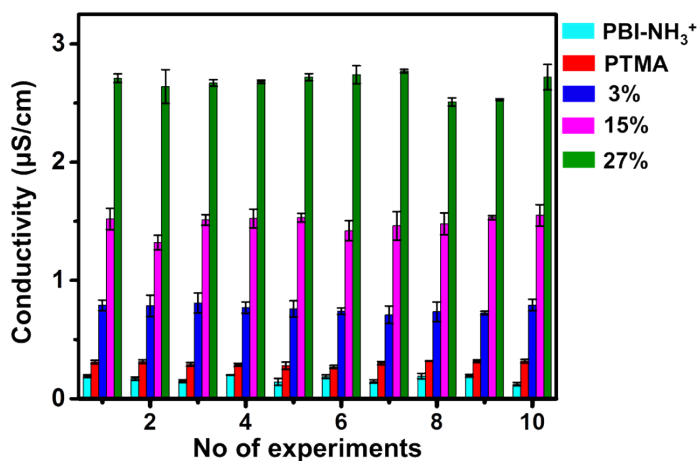
**Figure S5.** Time-correlated Single Photon Counting (TCSPC) spectra of the PTMA solution ( $0.05 \text{ mg mL}^{-1}$ ) on addition of  $\text{PBI-NH}_3^+$  at the indicated weight percentage.



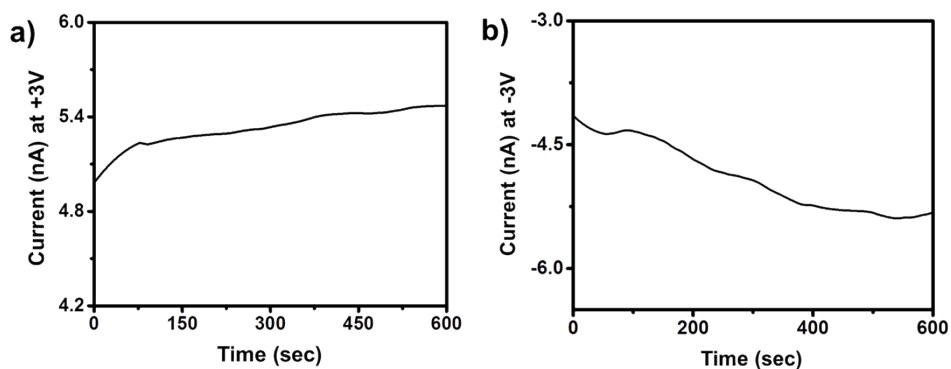
**Figure S6:** HR-TEM images of (a) PTMA-  $\text{PBI-NH}_3^+$  hybrid containing 27 wt%  $\text{PBI-NH}_3^+$  drop casted from dilute hybrid solution and b) layer by layer deposition of  $\text{PBI-NH}_3^+$  and PTMA solutions on TEM grid.



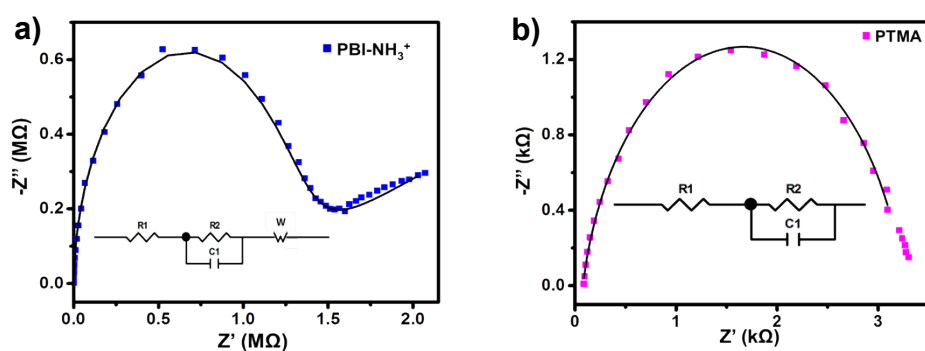
**Figure S7:** Tauc's plot of Hybrids of PTMA for a) 3 wt%, b) 9 wt% c)15% and d) 27% of PBI-NH<sub>3</sub><sup>+</sup>.



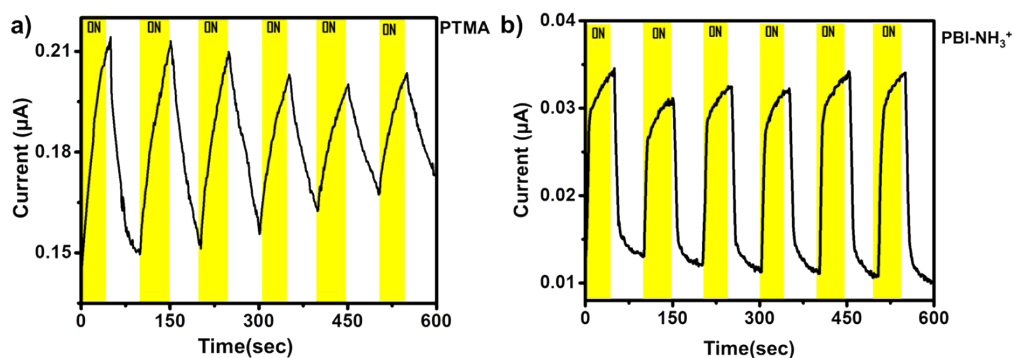
**Figure S8:** Statistical analysis of DC-conductivity studies of PTMA, PBI-NH<sub>3</sub><sup>+</sup> and hybrids containing at different wt% ratio (3%, 15%, 27%).



**Figure S9:** Current (I) vs. time (t) plots of the PBI-NH<sub>3</sub><sup>+</sup> at (a) +ve voltages and (b) -ve voltages.



**Figure S10:** Nyquist plots from the impedance spectra of a) PBI-NH<sub>3</sub><sup>+</sup> and b) PTMA.



**Figure S11:** Photoresponse behaviour by turning on/off white light on devices made of a) PTMA and b) PBI-NH<sub>3</sub><sup>+</sup>.