Electronic Supplementary Information

Enhanced Light Harvesting Through Förster Resonance Energy Transfer in Polymer-Small Molecule Ternary System

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Experimental details

The experimental setup used in this work is equipped with a water cooled planar magnetron fitted with a titanium target along with an RF electrode mounted just below the magnetron thus maintaining a gap of 10 cm. The magnetron is connected to a pulsed DC power supply for sputtering of titanium. The RF electrode is powered by a RF power supply for plasma polymerization of aniline. The gap between the magnetron and lower RF electrode is fixed at 10 cm in order to minimize the effect of magnetic field on the RF electrode. The RF electrode also serve the purpose of a substrate holder where various substrates silicon, quartz, glass, ITO coated glass are positioned for deposition. Prior to deposition, a turbo molecular pump supported by a roots dry pump is used to achieve a base pressure of 4×10^{-5} Torr. At first, Ar and O₂ gases (gas flow rates for Ar and O₂ are 10 and 2 sccm, respectively) are introduced into the plasma reactor at a partial pressure of 12×10^{-3} Torr, where argon acts as a feed gas for sputtering of titanium and oxygen acts as a reactive gas. Finally, the precursor with Aniline/Rubrene (flow rate = 20 sccm) is injected into the reactor in the vapour form such that the final partial pressure of the reactor is maintained at 5×10^{-2} Torr. RF generator operating at 13.56 MHz is used to facilitate the polymerization process in combination with pulsed DC magnetron sputtering of titanium. The various plasma controlling variables for the deposition of PPA/Rubrene/TiO₂ ternary blend are summarized in Table S1.

Table S1 Discharge controlling parameters during the deposition of PPA/Rubrene/TiO ₂ ternary
samples prepared using reactive magnetron sputtering and plasma polymerization combined
process.

PPA/Rubrene/TiO ₂
5×10^{-2}
8
55
100
7
45
64
200
28.57

Materials: Aniline ($C_6H_5NH_2$) monomer (Merck, India), guaranteed reagent G. R. grade with 99 % purity, Rubrene ($C_{42}H_{48}$) (Sigma, Aldrich) with GC > 99 % are used without further purification and Titanium target (Kurt J. Lesker, Clairton, PA) with 99.995 % purity is used as received. Propanol (Merck, India, 99 % purity), Acetone (Merck, India, 99.5 % purity) and de ionized water are used for cleaning purpose as received from the commercial sources. Aluminium wires (Alfa Aesar) of 0.5 mm diameter with 99.999 % purity are used as received.

Characterizations: The prepared samples are characterized using by Fourier Transform Infrared (FTIR) Spectrometer (Nicolet 5700 FT-IR) to investigate the chemical structure. The spectra are obtained in the transmission mode from the samples deposited on silicon substrate in the range 500 - 4000 cm⁻¹ over 32 scans. The UV-Visible study is done using Shimadzu UV spectrophotometer (UV-2600) to examine the absorbance of the samples. For photoluminescence (PL) measurements of the samples, a JASCO spectrofluorometer (FP-8300) is used with an excitation wavelength of 350, 530 nm. The time resolved photoluminescence (TRPL) measurements are performed using TCSPC fluorescence lifetime instrument (LifeSpec-II, Edinburgh Instruments). The electrochemical analysis id done using cyclic voltammetry (CV, Gamry Instruments, USA). Morphological features of the samples are examined using Field Emission Scanning Electron Microscope (FESEM) (*ZIGMA VP, Carl* Zeiss,) and Transmission Electron Microscope (TEM) (JEM 2100F). The current-voltage (I-V) characteristics under dark/white light and spectral response of the photodetectors are measured using a keithley electrometer (Keithley 6517B) at room temperature. All the material and electrical measurements are carried out after exposure of the samples to the atmosphere.



Fig. S1 FTIR transmittance spectra of (a) PPA and PPA/TiO₂ (b) PPA/Rubrene and PPA/Rubrene/TiO₂.

Materials	Wavenumber (cm ⁻¹)	Assignments ¹⁻⁵
	3367	Secondary amine N–H str vibration
	3027	C-H str vibration of aromatic ring
	2927	Saturated C-H str vibration
	2215	C≡N str of nitrile group
PPA	1600	C=C str vibration of quinoid ring
	1496	C=C str vibration of benzenoid ring
	1376	C–N str of QBQ
	1310	C–N str mode of QBB, BBQ
	828	1,4 di substituted aromatic ring
	752	1,2 di substituted aromatic ring
	696	1,3 di substituted aromatic ring
	3370	Secondary amine N–H str vibration
	3033	C-H str vibration of aromatic ring
	2915	Saturated C-H str vibration
	2210	C≡N str of nitrile group
PPA/TiO ₂	1602	C=C str vibration of quinoid ring
	1498	C=C str vibration of benzenoid ring
	1316	C–N str mode of QBB, BBQ
	842	1,4 di substituted aromatic ring
	752	1,2 di substituted aromatic ring
	554	O-Ti-O

Table S2 Assignment of peaks appeared in the FTIR spectra of PPA, PPA/TiO₂, PPA/Rubrene and PPA/Rubrene/TiO₂.

Q- Quinoid unit, B- Benzenoid unit

Table S3 Peak positions of the FTIR bands from the PPA/Rubrene and PPA/Rubrene/TiO₂ along with the peaks of previously reported Rubrene single crystals. Only Rubrene peaks are distinguished and compared here.

Rubrene Single	PPA/Rubrene	Observed shift
Crystal ^{6.7} (cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
616.4	613.25	3.15
650.1	668.83	18.73
889.1	896.73	7.63
977	975.80	1.2
1114.5	1108.86	5.64
1457	1446.35	10.65
3050.8	3045.12	5.68



Fig. S2 FESEM and TEM morphologies of PPA, PPA/TiO_2 , PPA/Rubrene and $PPA/Rubrene/TiO_2$ samples.



Fig. S3 FESEM morphologies of (a,b) PPA/Rubrene (c,d) PPA/Rubrene/TiO₂. TEM images of (e,f) PPA/Rubrene, the inset shows the SAED pattern (g) PPA/Rubrene/TiO₂ (h) lattice fringes of TiO₂ and the corresponding SAED pattern.



Fig. S4 (a) Large particle size distribution of Rubrene in PPA/Rubrene sample from FESEM image (b,c) FESEM morphology of PPA and PPA/TiO₂.



Fig. S5 EDX spectra and EDX mapping images of: Series A: PPA, Series B: PPA/Rubrene, Series C: PPA/TiO₂ and Series D: PPA/Rubrene/TiO₂. The scale of mapping images are 3 μm.



Fig. S6 (a) Small particle size distribution of Rubrene in PPA/Rubrene sample from TEM images (b,c) TEM images of PPA and PPA/TiO₂.

Calculation of Förster radius

The expression for the rate of energy transfer (k_T) from the excited donor to the acceptor as derived by Förster is given as⁸:

$$k_T = const J n^{-4} R^{-6} \kappa^2 \tag{1}$$

where, *R* is the distance between the donor and acceptor, *J* is the spectral overlap which is proportional to the overlap of donor emission and acceptor absorption spectrum, *n* is the refractive index and κ is the orientation factor. Two different molecules participating in FRET are described as coupled dipole oscillators by FRET theory.⁸ The probability of energy transfer is the highest when participating dipoles have parallel orientation but drops to zero when the dipoles are perpendicular. For random orientation κ value is estimated as 2/3.

As mentioned, the process (FRET) arises due to the dipole-dipole interaction and thus strongly dependent on the separation distance between the donor and acceptor. The resultant distance is referred as the Förster radius denoted by R_o which is a critical parameter in explaining the FRET mechanism.⁸⁻¹⁰ Traditionally, FRET can occur between two components only when the Förster radius falls within 1 – 10 nm.¹¹ The Förster radius is expressed using the following equation:

$$R_o^6 = \frac{9000(\ln 10)Q_D \kappa^2}{128\pi^5 n^4 N_A} J$$
(2)

where, Q_D is the donor PL quantum efficiency, κ is the relative orientation of the donor and acceptor dipole, *n* is the refractive index, N_A is the Avogadro's number and *J* is the spectra overlap integral between the donor emission and acceptor absorption expressed as:

$$J = \frac{\int F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda}{\int F_D(\lambda)d\lambda}$$
(3)

where, F_D is the normalized emission spectrum of the donor and ε_A is the acceptor molar extinction coefficient. The overlap integral *J* expresses the degree of spectral overlap between the donor emission and the acceptor absorption. $F_D(\lambda)$ is dimensionless. If $\varepsilon_A(\lambda)$ is expressed in units of M⁻¹ cm⁻¹ and λ is in nanometres, then *J* is in units of M⁻¹ cm⁻¹ nm⁴. If λ is in centimetres then *J* is in units of M⁻¹ cm³.

Förster radius calculations are done by using MATLAB software.

Component	$\tau_1(ns)$	τ_2 (ns)	$ au_{avg}(ns)$
Pristine Rubrene	12.778 (100 %)	-	12.778
PPA	0.649 (52.96 %)	1.921 (47.04 %)	1.285
PPA/TiO ₂	0.271 (70.88 %)	0.811 (29.12 %)	0.514
PPA/Rubrene	0.0671 (67.76 %)	0.846 (32.24 %)	0.456
PPA/Rubrene/TiO ₂	0.052 (61.32 %)	0.721 (38.68 %)	0.3865

Table S4 Fitted decay times of pristine Rubrene, PPA, PPA/Rubrene, PPA/TiO₂ and PPA/Rubrene/TiO₂. The excitation wavelength is 375 nm.

Electrochemical determination of the band alignment using cyclic voltammetry

Cyclic voltammetry is conducted with a potentiostat/galvanostat (Gamry Instruments, USA) for electrochemical analysis which are carried out in a standard three electrode cell consisting of a ITO working electrode, a platinum counter electrode and a Ag/AgCl reference electrode using a sweep rate of 100 mVs⁻¹. PPA is studied in the film form, which are prepared by plasma polymerization of aniline monomer on ITO electrode. The supporting electrolyte is KCl in acetronitrile and ferrocene is used for calibration.

Efficient charge transfer from donor to acceptor component, effective charge transport and charge injection into the electrodes are important parameters for design and optimization of hybrid photodetectors. In this regard electrochemical data allow the estimation of the relative position of Highest Occupied Molecular Orbital / Lowest Unoccupied Molecular Orbital (HOMO/LUMO) levels of the investigated materials. The redox couple ferrocene/ferricenium ion (Fc/Fc⁺) is used as external standard. The corresponding HOMO and LUMO levels are calculated using $E_{1/2}^{red}$ and E_{onset}^{ox} / E_{onset}^{red} for experiments in PPA films. The estimations are done with the empirical relation:^{2,12}

$$E^{HOMO/LUMO} = \left[-\exp\left(E_{onset(vs Ag/AgCl)} - E_{onset(Fc/Fc + vs Ag/AgCl)}\right)\right] - 4.8 eV$$

including standard ferrocene value of -4.8 eV with respect to vacuum level. The HOMO level as calculated from CV and optical band gap based on tauc's plot from UV-Vis spectra of PPA are 5.92 eV and 3.51 eV, respectively. Therefore, the LUMO level of PPA is deduced to be 2.41 eV. Here, the optical band gap is used to calculate LUMO level of PPA. However, the

LUMO level can also be calculated from the reduction onset potential in CV measurements. The optical band gap E_g can be determined from the optical absorption coefficient (α) calculated as a function of incident photon energy (hv) and is expressed by the tauc's relation:²

$$\alpha$$
 hv = B (hv - E_g)^m

where, B is an energy independent constant. The fundamental absorption edge in PPA is formed by direct allowed transition where $m = \frac{1}{2}$. The index 'm' is a constant that determines the type of optical transition. The value of 'm' can also be determined by the procedure described by Yakuphanoglu et al. The optical band-gap is obtained from the extrapolation of the linear part of the plot $(\alpha h \upsilon)^2$ versus h υ at $(\alpha h \upsilon)^2$ equals zero.

The HOMO and LUMO levels of TiO₂ have the values 7.34 eV and 4.23 eV, respectively.² In addition the HOMO and LUMO levels of Rubrene have the values 5.4 eV and 3.2 eV, respectively.¹³ The relative position of donor LUMO (PPA and Rubrene) and acceptor LUMO (TiO₂) is crucial for the efficient charge transfer. The HOMO/LUMO level of PPA/Rubrene are aligned in a cascade manner with respect to HOMO/LUMO of TiO₂. At these conditions it is energetically favorable for the photoexcited PPA/Rubrene to transfer electrons to TiO₂. Therefore, PPA/Rubrene can be used as the two donors and TiO₂ as the electron acceptor to be used in the fabrication of hybrid photodetectors.



Fig. S7 *I-V* characteristics of the PPA/TiO₂ hybrid photodetector (controlled device) under dark and (a) UV light (b) white light.

Bias	Wavelength	\mathbf{R}_{λ}	G	D*
(V)	(nm)	(AW-1)		Jones
	254	0.7656	3.7302	6.27×10^{11}
1.5	365	2.0653	7.0024	1.69×10^{12}
	570	0.3381	0.7340	2.76×10^{11}
	254	0.0582	0.2837	1.79×10^{11}
0	365	0.5625	1.9071	1.73×10^{12}
	570	0.0349	0.0759	1.07×10^{11}

Table S5 Typical response parameters of PPA/TiO₂ hybrid photodetector.



Fig. S8 Stable and reproducible on/off switching of the ternary hybrid photodetector (PD-2) for hundreds of consecutive cycles.

PD ^{a)}	Туре	V _{OC} ^{b)}	D* c)	G ^{d)}	R _{λ} ^{e)}	$\tau_r^{f)}$	$ au_d{}^{g)}$	Ref.
		(V)	(Jones)		(AW ⁻¹)	(ms)	(ms)	
CuO/Si	P - n	0.16	3 × 10 ⁹	0.0016	3.98 × 10 ⁻⁴	0.06	0.08	2014 ¹⁴
ZnIn ₂ S ₄ / agarose gel	Hybrid	0.63	-	1	1.65 × 10 ⁻²	25	120	201315
MoS_2	Transistor	0.48	-	-	107	260	267	201516
Graphene/ MoS ₂	Transistor	0.012	-	-	0.6	0.13	0.13	201517
MoS ₂ /Si	Hetero- junction	0.21	~ 10 ¹³	-	0.3	0.003	0.04	201518
ZnO/Spiro- MeOTAD	Hybrid	0.1	-	-	0.017	0.2	0.95	201419
ZnO NR	MIS	-	$7.99 imes 10^7$	-	$1.78 imes 10^{-6}$	100	100	2014 ²⁰
CH ₃ NH ₃ PbI ₃	Hybrid	-	3.29×10^{12}	-	0.284	0.02	0.017	2015 ²¹
PPA/TiN	Hybrid	0.78	1.92×10^{11}	1.24	0.57	9.23	18.12	2016 ²²
PPA/Rubrene/ TiO ₂	Hybrid (PD-3)	0.94	9.2×10^{12}	24.34	11.21	88	95	Present work

Table S6 Comparison of the characteristic photoresponse parameters for the present ternary hybrid photodetector (PD-3) and other organic / inorganic based self-powered photodetectors.

a) Photodetector; ^{b)} Open-circuit voltage; ^{c)} Detectivity; ^{d)} Photoconductive gain; ^{e)} Responsivity; ^{f)} Rise time; ^{g)} Decay time



Fig. S9 Schematic of the energy level diagram of ternary hybrid photodetector showing the common charge transfer process.

References

- 1 A. A. Hussain, S. Sharma, A. R. Pal, H. Bailung, J. Chutia and D. S. Patil, *Plasma Chem. Plasma Process.*, 2012, **32**, 817–832.
- 2 A. A. Hussain, A. R. Pal and D. S. Patil, *Org. Electron.*, 2014, **15**, 2107 2115.
- A. R. Pal, B. K. Sarma, N. C. Adhikary, J. Chutia and H. Bailung, *Appl. Surf. Sci.*, 2011, 258, 1199 1205.
- 4 L. Dong, M. Li, L. Dong, M. Xhao, J. Feng, Y. Han, J. Deng, D. Li and X. Sun, *Int. J. Hydrogen Energy*, 2014, **39**, 16116 16122.
- 5 J. T. Last, *Phys. Rev.*, 1957, **105**, 1740 1750.
- 6 J. Weinberg-Wolf, Optical characterization of organic semiconducting single crystals, Dissertation, University of North Carolina, Chapel Hill, 2006.
- 7 K. P. Dhakal, H. Lee, J. Lee, S. H. Lee, J. Joo and J. Kim, *J. Mater. Chem. C*, **2014**, *2*, 1830 1835.
- 8 A. R. Clapp, I. L. Medintz, J. M. Mauro, B. R. Fisher, M. G. Bawendi and H. Mattoussi, *J. Am. Chem. Soc.*, 2004, **126**, 301 – 310.
- 9 V. Gupta, V. Bharti, M. Kumar, S. Chand and A. J. Heeger, *Adv. Mater.*, 2015, **27**, 4398 4404.
- 10 W. –L. Xu, B. Wu, F. Zheng, X. –Y. Yang, H. –D. Jin, F. Zhu and X. –T. Hao, *J. Phys. Chem. C*, 2015, **119**, 21913 21920.
- 11 V. V. Didenko, *Biotechniques*, 2001, **31**, 1106 1121.
- 12 M. Al-Ibrahim, H.-K. Roth, M. Schroedner, A. Konkin, U. Zhokhavets, G. Gobsch, P. Scharff and S. Sensfuss, *Org. Electron.* 2005, **6**, 65.
- 13 A. K. Pandey and J.-M. Nunzi, *Appl. Phys. Lett.* 2007, **90**, 263508.
- Q. Hong, Y. Cao, J. Xu, H. Lu, J. He and J. –L. Sun, ACS Appl. Mater. Interfaces, 2014, 6, 20887 – 20894.
- L. Mandal, N. S. Chaudhari and S. Ogale, *ACS Appl. Mater. Interfaces*, 2013, **5**, 9141 9147.
- 16 X. Zhong, W. Zhou, Y. Peng, Y. Zhou, F. Zhou, Y. Yin and D. Tang, *RSC Adv.*, 2015, **5**, 45239–45248.
- 17 X. Li, J. Wu, N. Mao, J. Zhang, Z. Lei, Z. Liu and H. Xu, *Carbon*, 2015, **92**, 126–132.
- 18 L. Wang, J. Jie, Z. Shao, Q. Zhang, X. Zhang, Y. Wang, Z. Sun and S. -T. Lee, Adv. Funct. Mater., 2015, 25, 2910–2919.
- O. Game, U. Singh, T. Kumari, A. Banpurkar and S. Ogale, *Nanoscale*, 2014, 6, 503 513.
- 20 Z. Zhang, Q. Liao, Y. Yu, X. Wang and Y. Zhang, *Nano Energy*, 2014, **9**, 237 244.
- 21 D. Li, G. Dong, W. Li and L. Wang, *Sci. Rep.*, 2015, **5**, 7902 7909.
- A. A. Hussain, B. Sharma, T. Barman and A. R. Pal, ACS Appl. Mater. Interfaces, 2016, 8, 4258 – 4265.