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Supporting Information for

Optoelectronic, Femtosecond Nonlinear Optical Properties and Excited State Dynamics of a Triphenyl Imidazole Induced Phthalocyanine Derivative

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Table of Contents

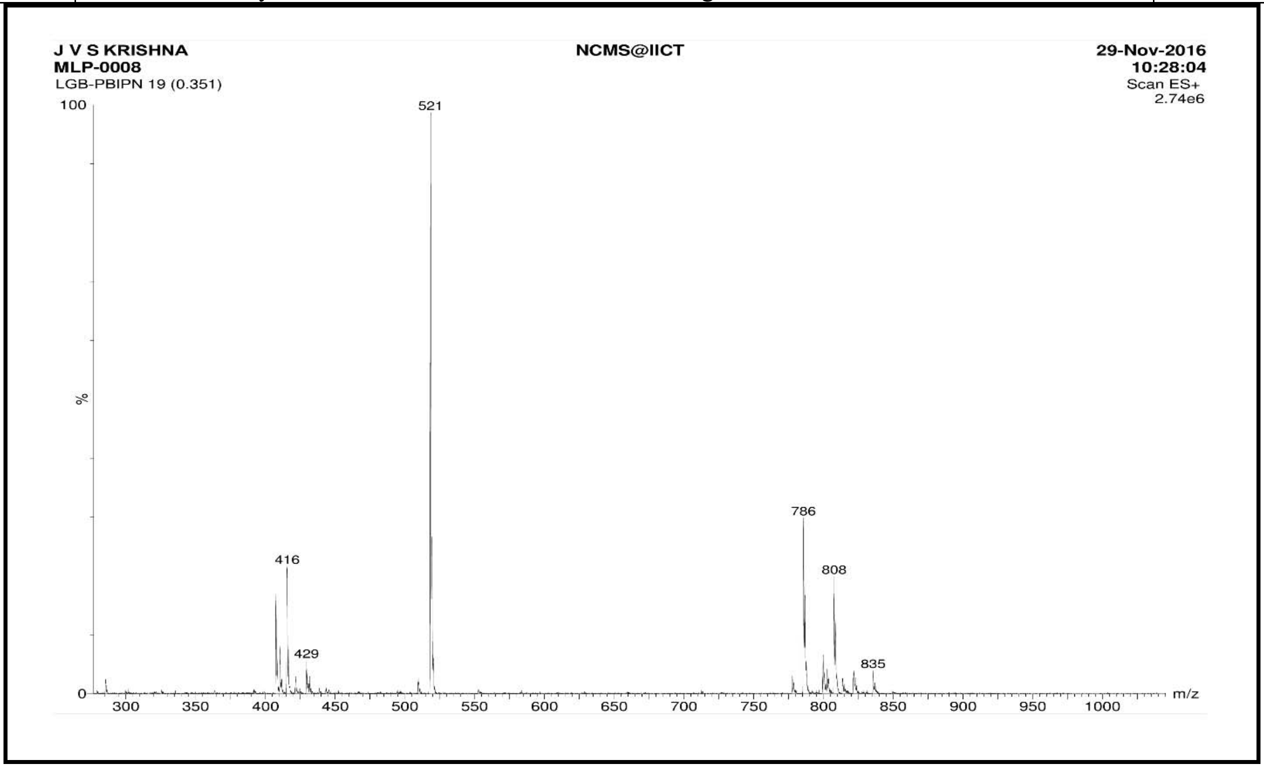

Figure S1. ESI-MS of **PBIPN**

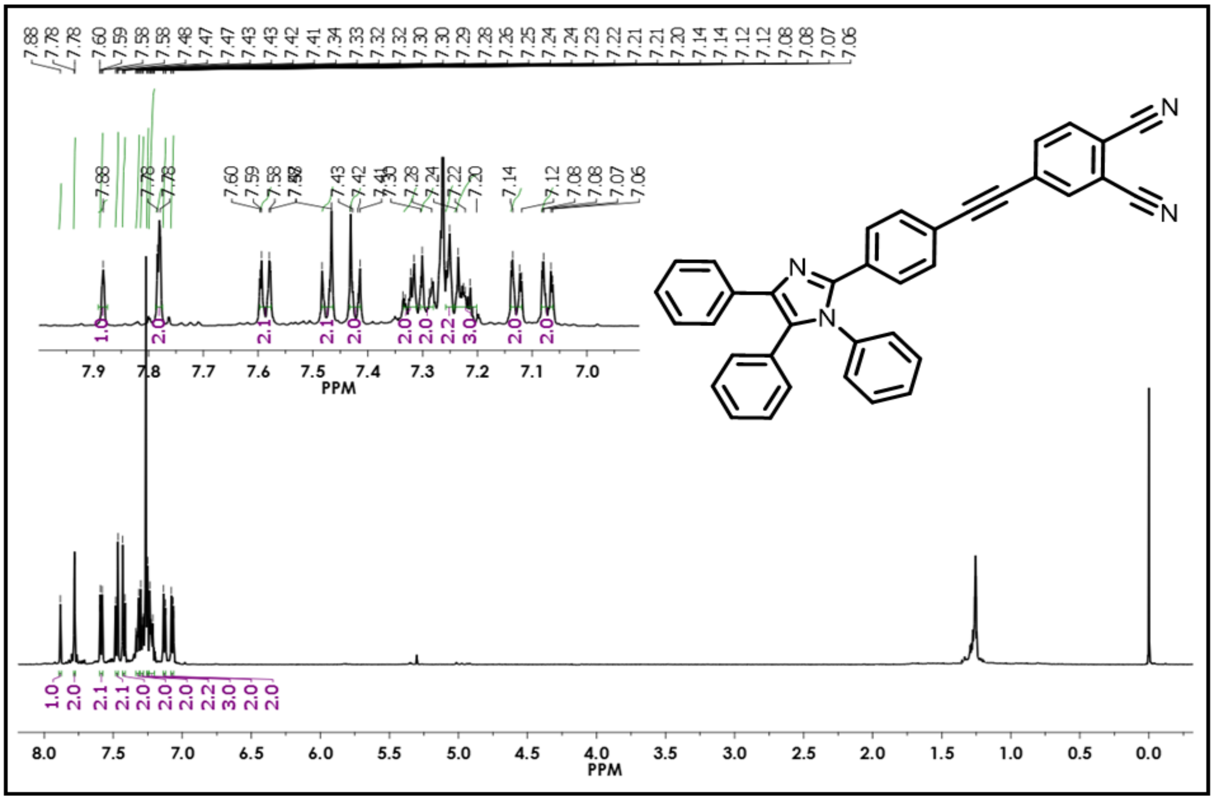

Figure S2. 1H NMR of **PBIPN**

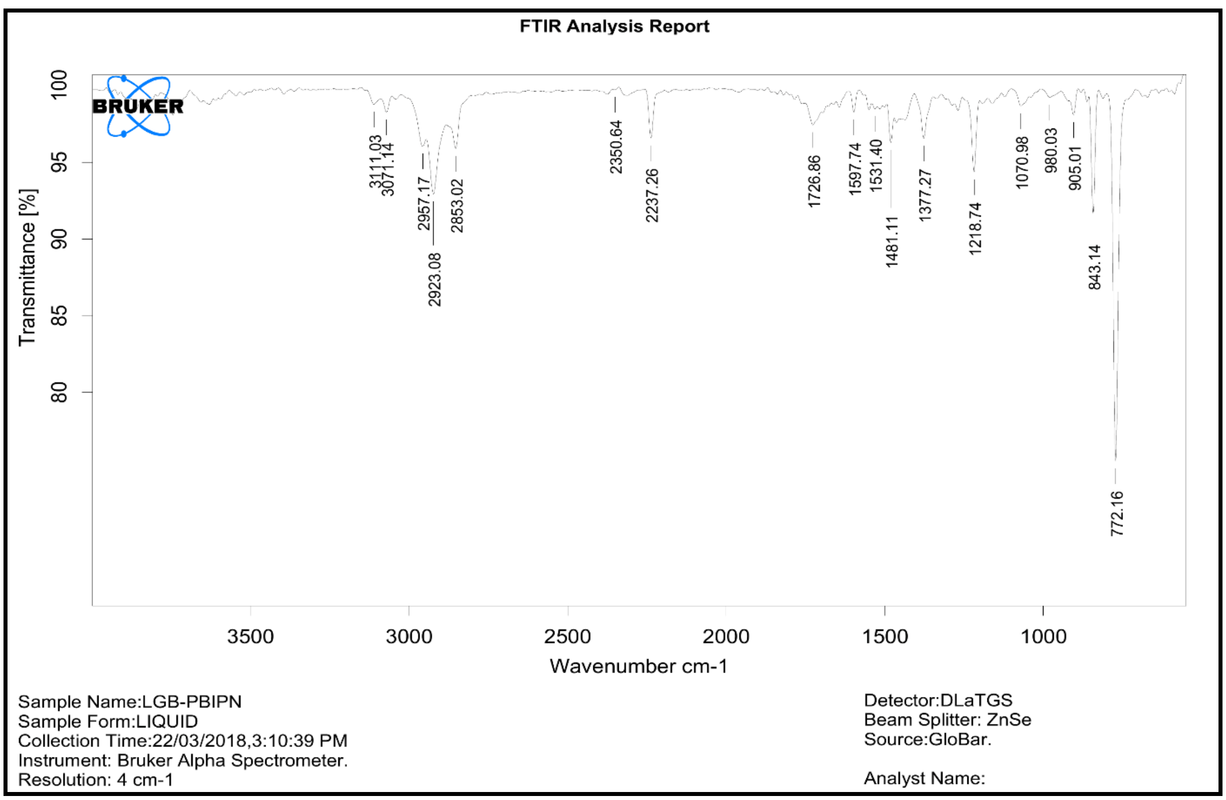

Figure S3. FT-IR of **PBIPN**

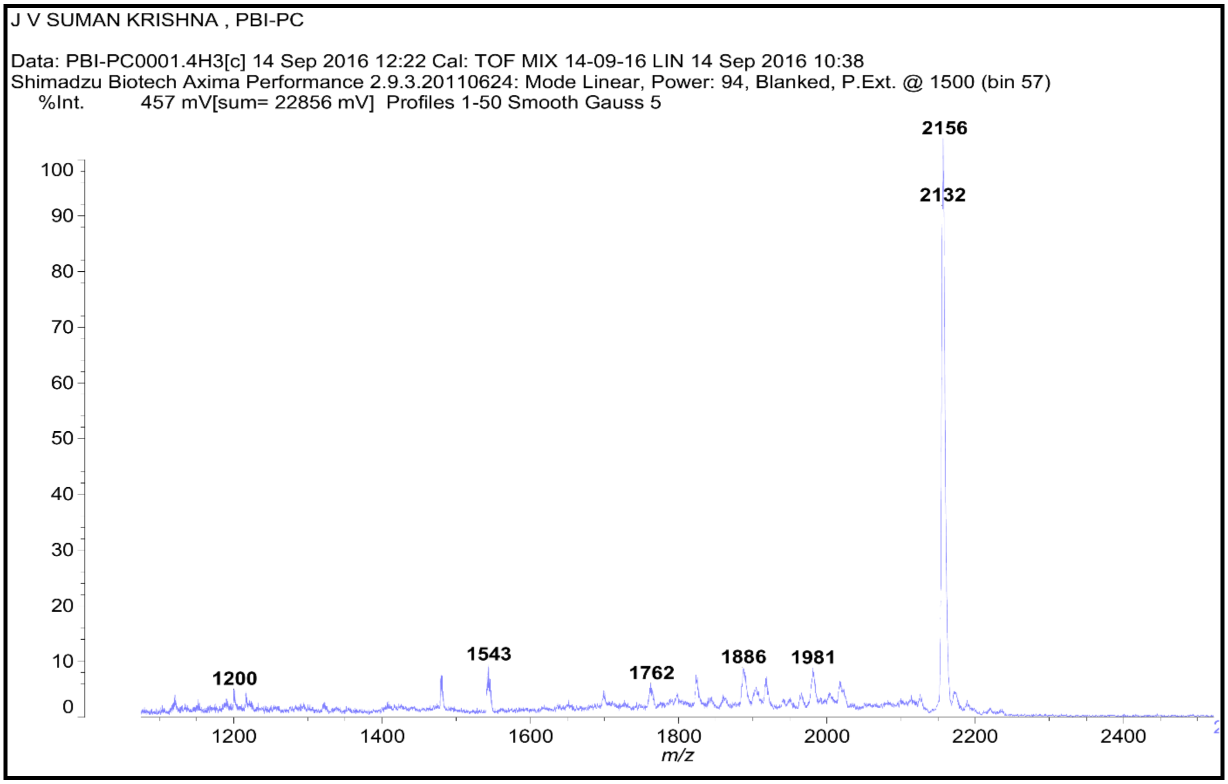

Figure S4. MALDI-TOF of**PBIPC**

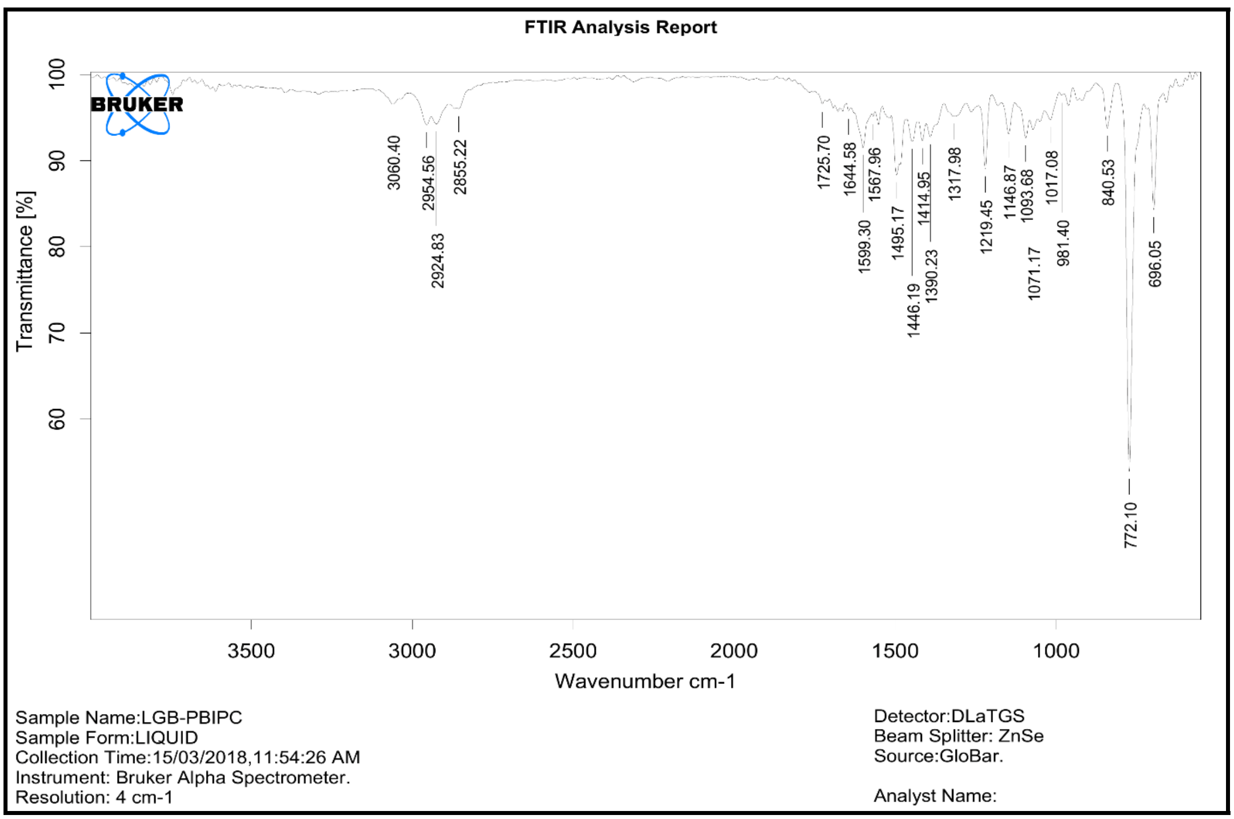

Figure S5. FT-IR of **PBIPC**

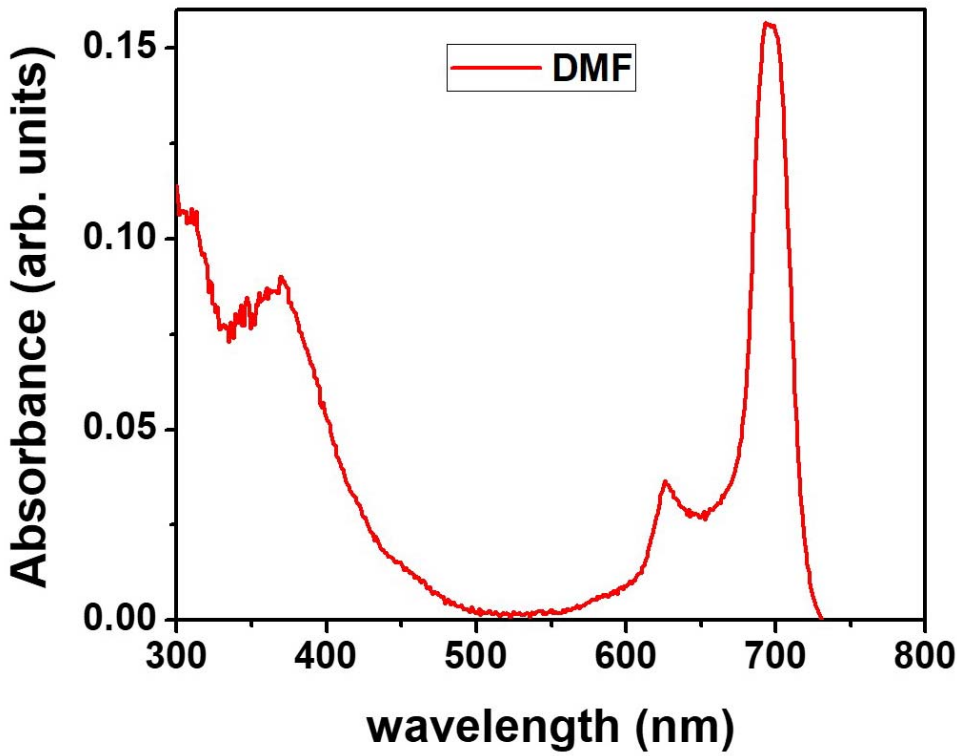

Figure S6. Absorption spectrum of PBIPC in DMF solvent (low concentration).

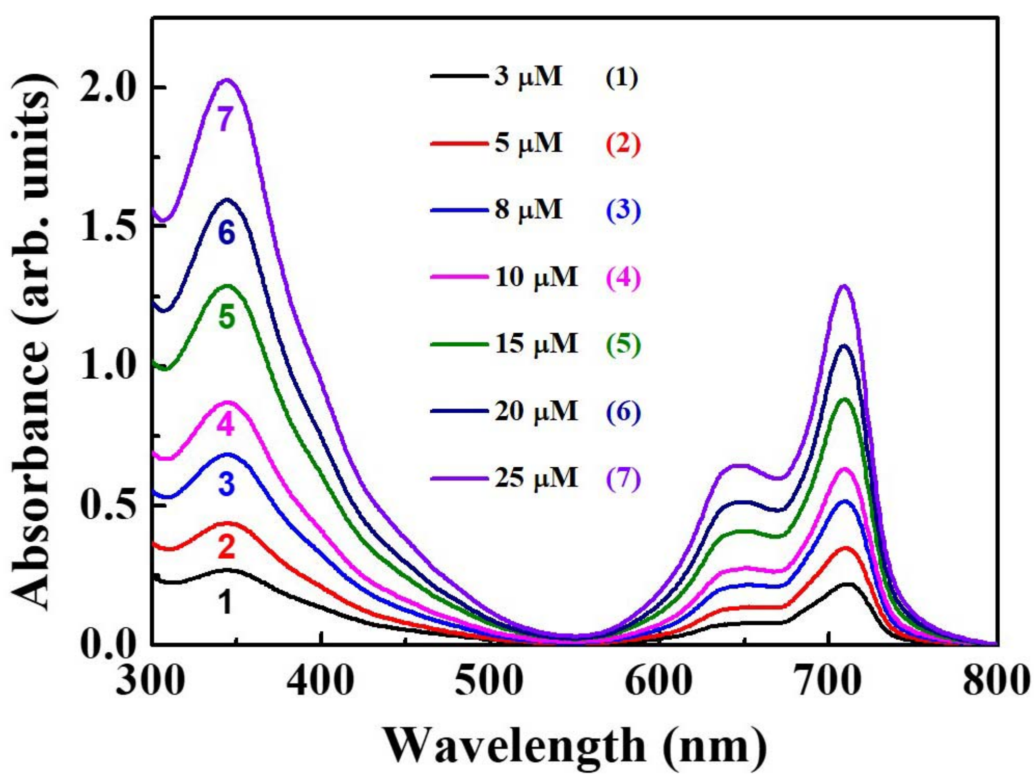

Figure S7. Absorption spectral changes of **PBIPC** in DCM at different concentrations: 3 μM (b) 5 μM (c) 8 μM (d) 10 μM (e) 20 μM (f) 25 μM

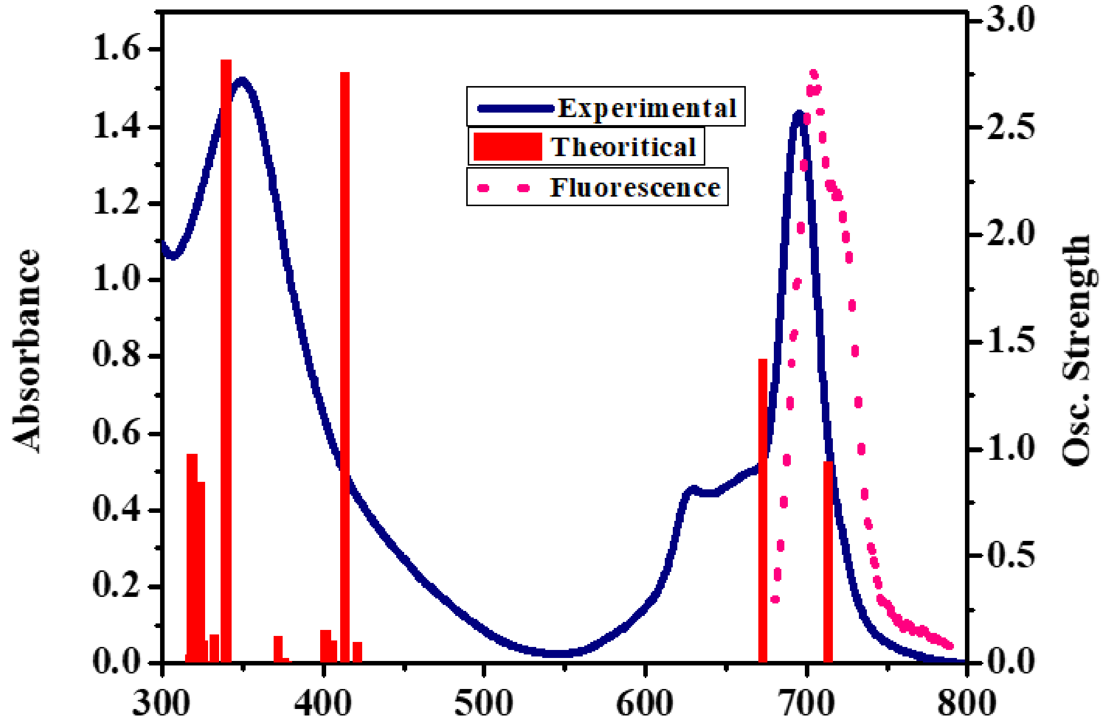

Figure S8. Absorption (left) and emission (right) spectra of **PBIPC** in the THF solvent. Simulated absorption bands are shown as vertical bars.

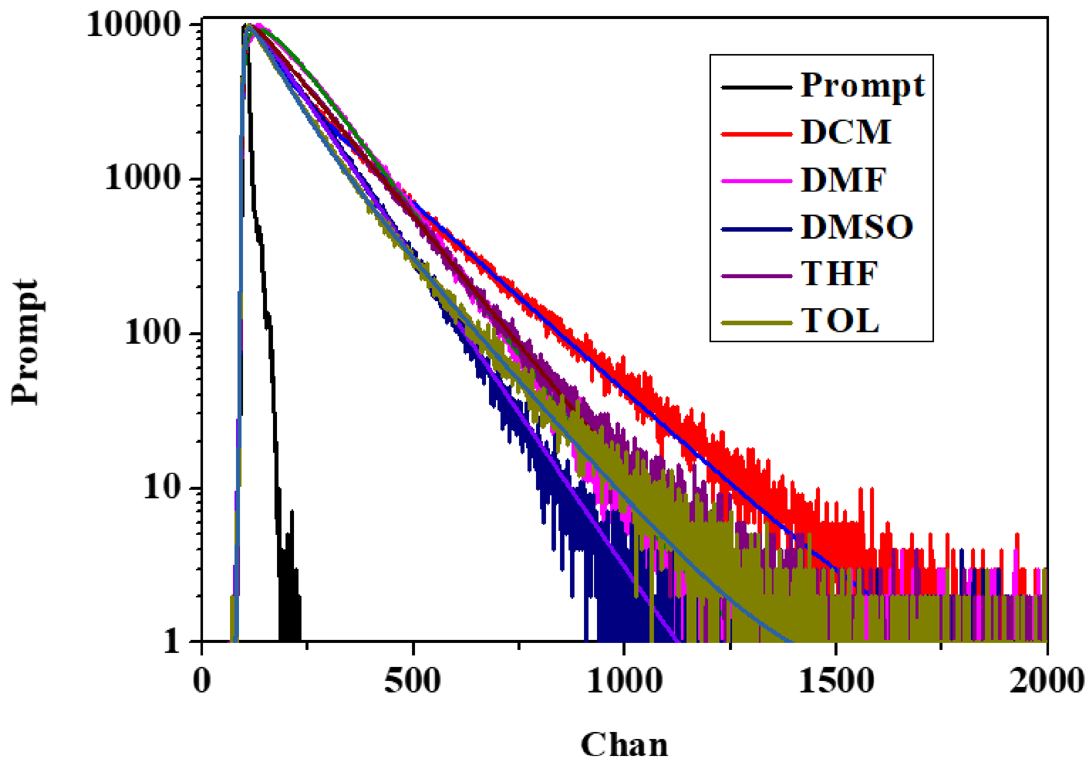

Figure S9. Fluorescence decay signals of **PBIPC** in different solvents. Solid lines are fits to the experimental data.

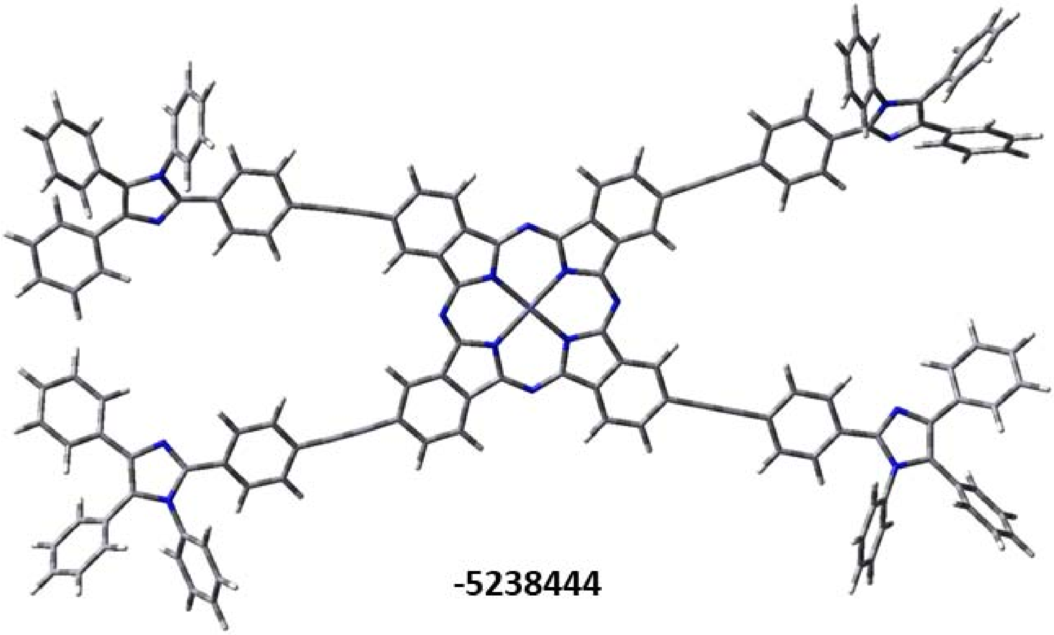

Figure S10. Optimized structure of **PBIPC** and minimum energy in kcal/molby using B3LYP method6-31G(d,p).

Table S1. Optimized energies, HOMO-LUMO energies and ground state dipole moment by DFT studies by using B3LYP/6-31G (d,p) in vacuum.

Sample	**E Kcal/mol**	**HOMO (H) eV**	**LUMO (L) eV**	**H-L gap eV**	**μ**
PBIPC	-5238444	-4.830	-2.871	-1.959	7.7584

Table S2. Singlet excited state properties of **CBZPC1**and **CBZPC2** obtained by B3LYP method and M06-2X function in tetrahydrofuran solvent in PCM model.

Dye	$^{a}\lambda_{max}$	^{b}**f**	^{c}**E (eV)**	**% of Molecular Orbital Contribution**
PBIPC	677 622 392	0.9429 1.4177 0.1049	1.867 1.974 3.156	HOMO->LUMO (95%) HOMO->L+1 (94%) H-18->LUMO (2%) H-3->LUMO (52%) H-7->LUMO (7%), H-6->LUMO (5%), H-6->L+1 (4%), H-5->LUMO (2%), H-2->L+1 (4%), H-1->LUMO (5%), H-1->L+1 (5%)

[a]Theoretical absorbance in nm, [b]Oscillator strength, and [c]Excited state energy in eV.

Z-scan data fit formulae:

Open aperture transmittance:

$$T_{nOA} = \frac{1}{\left[1 + (n-1)\alpha_n L' \left[\frac{I_0}{\left(1+\frac{z}{z_0}\right)^2}\right]^{(n-1)}\right]^{\frac{1}{(n-1)}}} \quad \textbf{Eqn. 1}$$

Where n = 1, 2 ,….,n; α_n = n photon absorption co-efficient; Effective length, $L' = 1 - \frac{e^{-(n-1)\alpha_0 L}}{(n-1)\alpha_0}$

I_0 = input peak intensity; z_0 = Rayleigh range at wavelength λ (nm).

Closed aperture transmittance:

$$T_{CA} = 1 \pm \frac{4\Delta\phi\left(\frac{z}{z_0}\right)}{\left[\left(\frac{z}{z_0}\right)^2 + 9\right]\left[\left(\frac{z}{z_0}\right)^2 + 1\right]} \quad \textbf{Eqn. 2}$$

Δφ is obtained from fitted curve and then nonlinear refractive index n_2 is calculated as:

$$n_2 = \frac{\Delta\phi\lambda}{2\pi L' I_0} \quad \textbf{Eqn. 3}$$

The third order non linear susceptibility, $\chi^{(3)} = [(\chi_R^{(3)})^2 + (\chi_I^{(3)})^2]^{1/2}$

$$\chi_R^{(3)} = 2cn_0^2\varepsilon_0 n_2 \quad \textbf{Eqn. 4}$$

$$\chi_I^{(3)} = \frac{c^2\varepsilon_0 n_0^2 \alpha_2}{\omega}$$

Where, $c = 3 \times 10^8$ m/s; ε_0 = absolute permittivity; ω = frequency of laser radiation. The n-photon absorption cross-sections are calculated as:

$$\sigma_n = \frac{(\hbar\omega)^{n-1}}{N}\alpha_n \quad \textbf{Eqn. 5}$$

N = solute molecule concentration.

Example: For **800 nm**, the average power used was 0.4 mW with beam radius of 1 mm and focusing lens of 10 cm focal length. Thus, the Rayleigh range, Z_0 was calculated to be 2.54 mm.

Effective length, $L' = \frac{1 - e^{-0\cdot 354}}{0\cdot 354} cm = 0\cdot 084$

Peak intensity,

$$I_0 = \frac{0\cdot 4 \times 10^{-3}}{\pi \times (0.0025)^2 \times 70 \times 10^{-15} \times 10^3}\frac{w}{cm^2} = 2.8 \times 10^{11} \quad W/cm^2$$

For 800 nm, we observe two-photon absorption hence, n = 2. Putting above parameters in Eqn. 1, we fit it with experimental open aperture z-scan data to obtain NLO absorption coefficient, $\boldsymbol{\alpha_2}$ to be **12.0×10^{-11} cm/W**. Similarly, from Eqn. 2, we can obtain the value of $\Delta\Phi$ which was obtained to be 0.17. Putting this value to Eqn. 3, the nonlinear refractive index obtained was:

$$n_2 = \frac{0\cdot 17 \times 8 \times 10^{-5}}{2\pi \times 0.084 \times 2\cdot 8 \times 10^{11}} = 0\cdot 92 \times 10^{-16} \quad \text{cm}^2/\text{W}$$

Using Equation 4 the value of NLO susceptibilities were calculated and tabulated in Table 2.

The two-photon absorption cross-section was calculated using equation 5 where no. of molecules in 0.07 mM of sample is given by,

$$N = 0.07 \times 10^{-3} \times 6.02 \times 10^{23} = 4\cdot 21 \times 10^{19} \quad \text{Molecules.}$$

Thus, 2PA cross-section was calculated as,

$$\sigma_2 = \frac{6\cdot 62 \times 10^{-34} \times 3 \times 10^{8} \times 12 \times 10^{-11}}{8 \times 10^{-7} \times 4\cdot 21 \times 10^{14} \times 10^{-3}} = 7.08 \times 10^{-47} \quad \text{cm}^4\,\text{s photon}^{-1}\,\text{molecule}^{-1}$$

$$= 7080 \text{ GM}$$

1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}

For **λ= 1000 nm,** the average power taken was 0.75 mW with Rayleigh range of 3.18 mm. This effective length calculated was 0.072 cm. Rest of the parameters were same as λ=800 nm.

Peak intensity,

$$I_0 = \frac{0\cdot 75 \times 10^{-3}}{2\pi \times 70 \times 10^{-15} \times 10^{3} \times \pi \times (0.0038)^2} = 3\cdot 36 \times 10^{11} \quad \text{W/cm}^2$$

For 1000 nm, we observe three-photon absorption hence, n = 3. Putting above parameters in Eqn. 1, we fit it with experimental open aperture z-scan data to obtain NLO absorption coefficient, $\boldsymbol{\alpha_3}$ to be **2.7×10^{-21} cm^3/W^2**. Similarly, from Eqn. 2, we can obtain the value of $\Delta\Phi$ which was obtained to be 2.8. Putting this value to Eqn. 3, the nonlinear refractive index obtained was:

$$n_2 = \frac{2\cdot 8 \times 10^{-4}}{2\pi \times 3\cdot 36 \times 10^{11} \times 0.072} = 18\cdot 4 \times 10^{-16} \quad \text{cm}^2/\text{W}$$

The three-photon cross section obtained using equation 5 was,

$$\sigma_2 = \frac{(6\cdot 62 \times 10^{-34} \times 3 \times 10^{8})^2 \times 2\cdot 7 \times 10^{-21}}{(10^{-6})^2 \times 4\cdot 21 \times 10^{19}} \quad \text{cm}^6\text{s}^2$$

$$= 2\cdot 53 \times 10^{-78} \quad \text{cm}^6\text{s}^2$$

For **λ= 1500 nm,** the average power taken was 0.7 mW with Rayleigh range of 4.7 mm. This effective length calculated was 0.08 cm. Rest of the parameters were same as λ=800 nm.

Peak intensity,

$$I_0 = \frac{0 \cdot 75 \times 10^{-3}}{\pi \times (0.0047)^2 \times 70 \times 10^{-15} \times 10^3} = 1 \cdot 4 \times 10^{11} \quad \text{W/cm}^2$$

For 1500 nm, we observe four-photon absorption hence, n = 4. Putting above parameters in Eqn. 1, we fit it with experimental open aperture z-scan data to obtain NLO absorption coefficient, $\boldsymbol{\alpha_4}$ to be $\mathbf{2.2\times10^{-32}}$ $\mathbf{cm^5/W^3}$. Similarly, from Eqn. 2, we can obtain the value of $\Delta\Phi$ which was obtained to be 1.35. Putting this value to Eqn. 3, the nonlinear refractive index obtained was:

$$n_2 = \frac{1 \cdot 35 \times 1500 \times 10^{-7}}{2\pi \times 0.08 \times 1 \cdot 4 \times 10^{11}} = 28.9 \times 10^{-16} \quad \text{cm}^2/\text{W}$$

The four-photon cross section obtained using equation 5 was,

$$\sigma_2 = \left(\frac{6 \cdot 62 \times 10^{-34} \times 3 \times 10^8}{1500 \times 10^{-9}}\right)^3 \times \left(\frac{2 \cdot 2 \times 10^{-32}}{4 \cdot 21 \times 10^{19}}\right) \qquad \text{cm}^8/\text{s}^3$$
$$= 12 \cdot 13 \times 10^{-108}$$

Femtosecond Transient Absorption Spectroscopy experimental schematic:

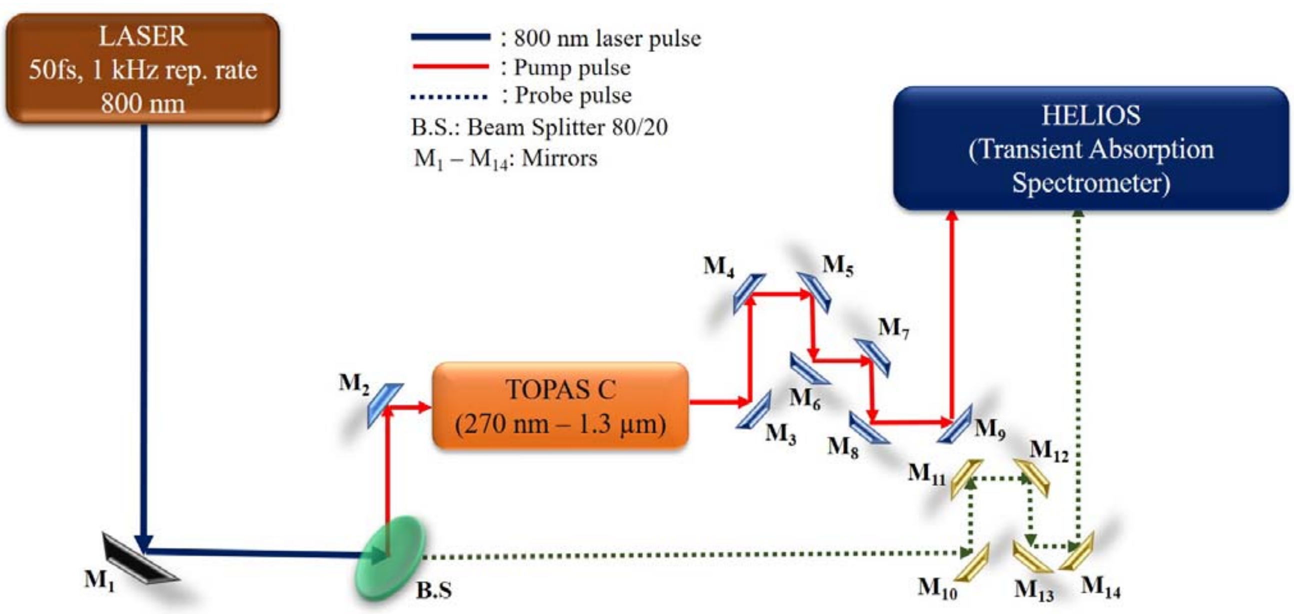

Figure S11. Schematic of the fs-TAS setup used for photophysical studies of PBIPC at ACRHEM, University of Hyderabad, India.

Table S3. Decay lifetimes of relaxation dynamics in PBIPC for different wavelengths.

Excitation wavelength	**Peak maxima**	**τ_R (ps)**	**τ_1 (ps), τ_2 (ps)**	**τ_3 (ps)**
400 nm	532 nm	0.131	5.59, 333.9	1300
	640 nm	0.123	21.02	346
	700 nm	0.241	8.60	1286
650 nm	532 nm	1.36	8, 216.3	1403
	640 nm	1.39	3.62	408
	698 nm	1.32	142	1340

τ_R: Rise time; τ_1 /τ_2: shorter decay component showing IC and/ or VC; τ_3: longer decay component showing ISC. Error involved is ±10%.