Supplementary Information

Facile synthesis and exploration of excited state assisted two–photon absorption property of D–A–D type thiophene–pyridine derivatives

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Characterization details

^{1}H NMR (Bruker, 400 MHz), ^{13}C NMR (Bruker, 100 MHz), ESI–Mass (Waters micro mass Q-Tofmicro), MALDI TOF–Mass (Autoflex speed MALDI TOF-MS) spectral techniques and gel permeation chromatography (GPC) (Perkin Elmer Series-200) techniques were utilized to elucidate the structures of all the intermediates and final compounds. A flash EA-112 CHNS analyzer (Thermo electron corporation) was used for the elemental analysis. The UV–Vis spectral data were collected from Analytik jena SPECORD S600 spectrometer and photoluminescence (PL) spectra were recorded using a Fluoromax Horiba Jobin Yuan spectrometer. IVIUM (Vertex-V55610) electrochemical work station was used to carryout cyclic voltammetric (CV) measurements of the compounds using three electrode system wherein the CVs of the molecules were measured in solution state (chloroform) and that of the polymer was dissolved in chloroform and drop casted on glassy carbon electrode which was taken as working electrode, Platinum (Pt) wire as a counter electrode and saturated calomel electrode (SCE) as a reference electrode and the electrolyte used was 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in acetonitrile. All the solutions used were degassed for 20 min before the usage. Ferrocene/ferrocenium (Fc/Fc$^+$) was used as an internal standard for all the electrochemical measurements and the scan rate used was 100 mV s^{-1}. Gaussian 09 software with B3LYP functional 6-31G(d,p) level basis set was used for the density functional theory (DFT) and time–dependent density functional theory (TD-DFT) studies of the compounds. Thermogravimetric analysis (TGA) were carried out using Seiko Instruments TGA/DTA Exstar 6300, Japan at a heating rate of 10°C min^{-1} under nitrogen atmosphere.

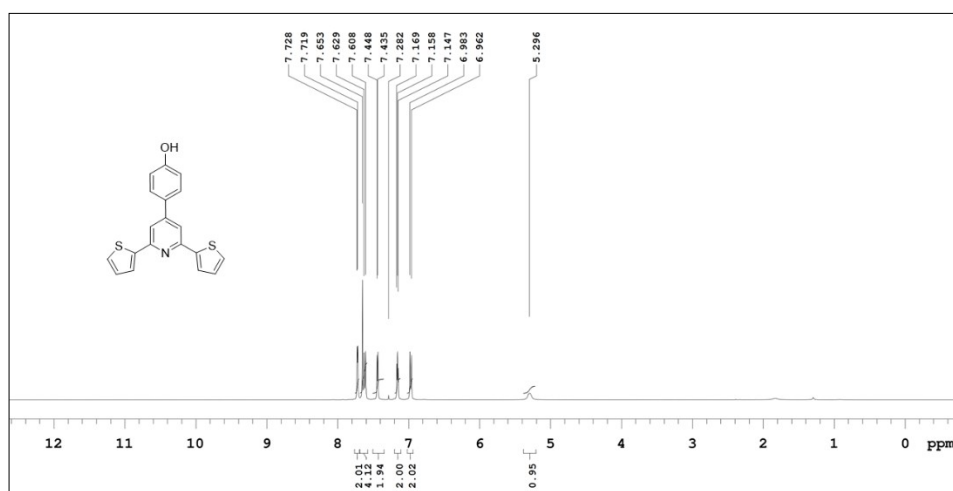**Spectral characterizations of intermediates and final compounds**
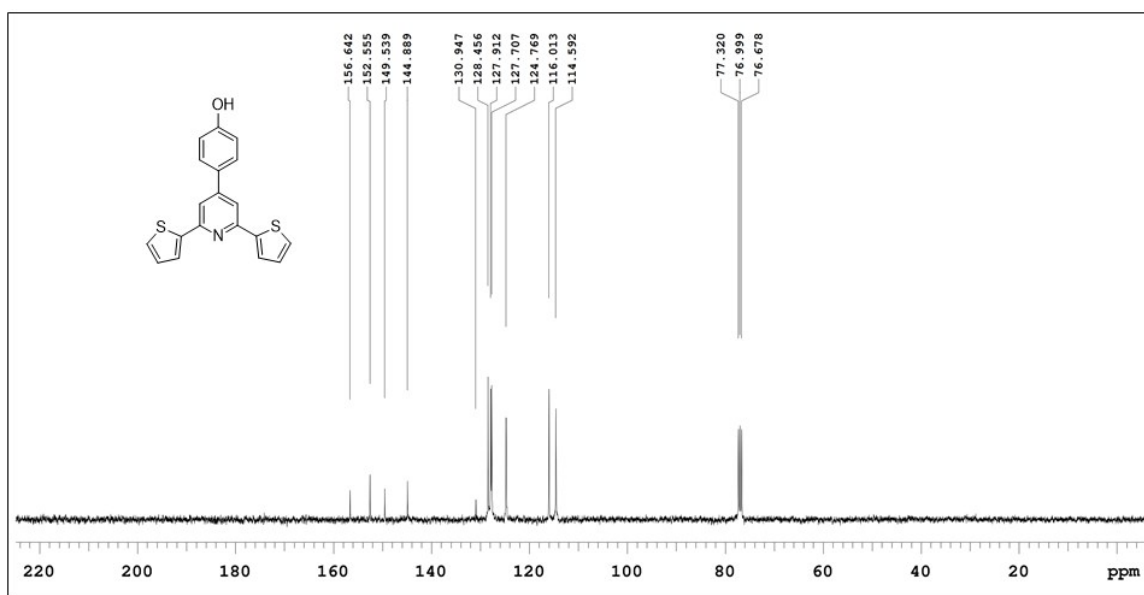

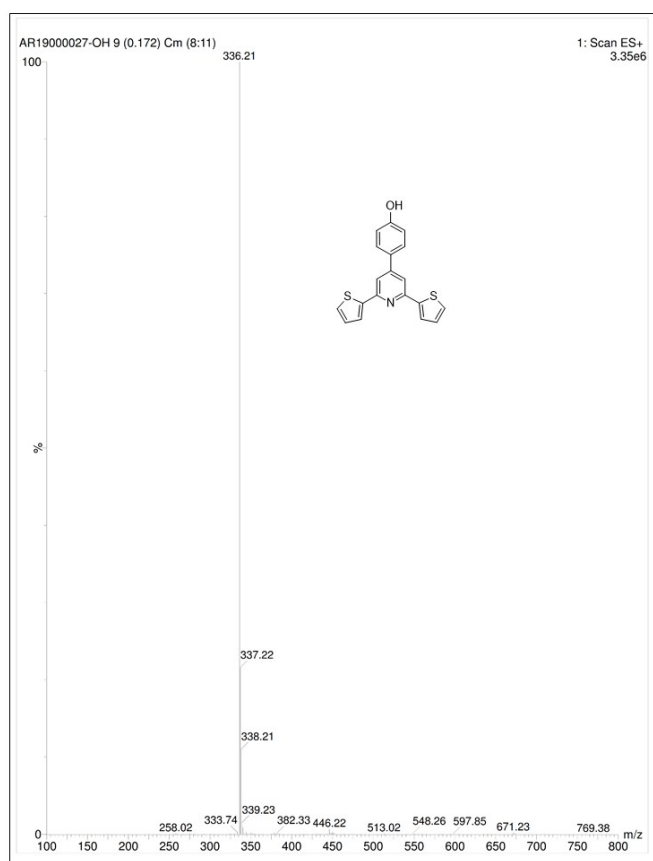**Fig. S1.** ^{1}H NMR spectrum of **(3)**

Fig. S2. ^{13}C NMR spectrum of **(3)**

Fig. S3. Mass spectrum of **(3)**
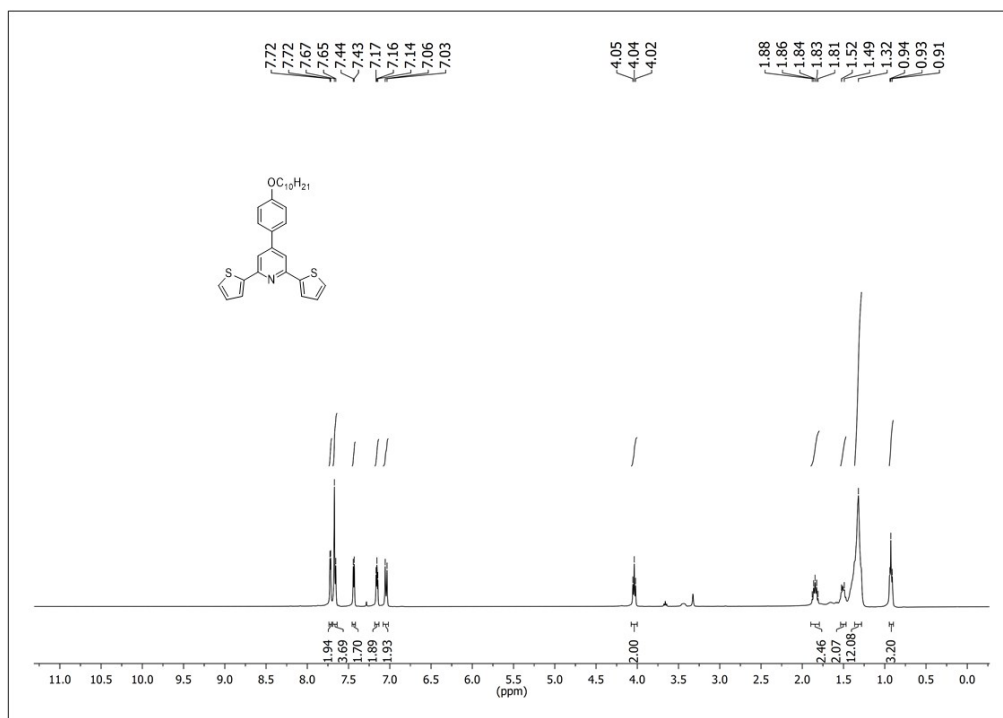
Fig. S4. ^{1}H NMR spectrum of **(4)**
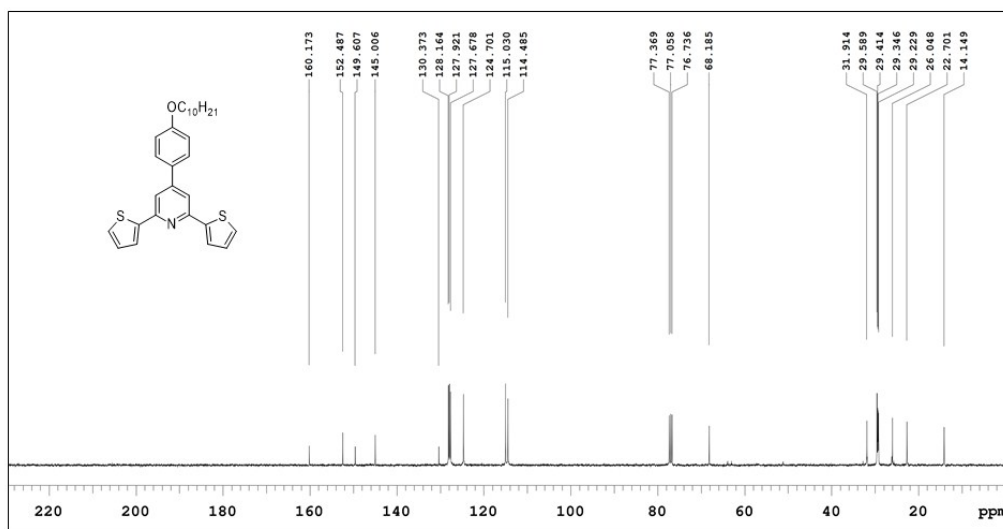
Fig. S5. ^{13}C NMR spectrum of **(4)**
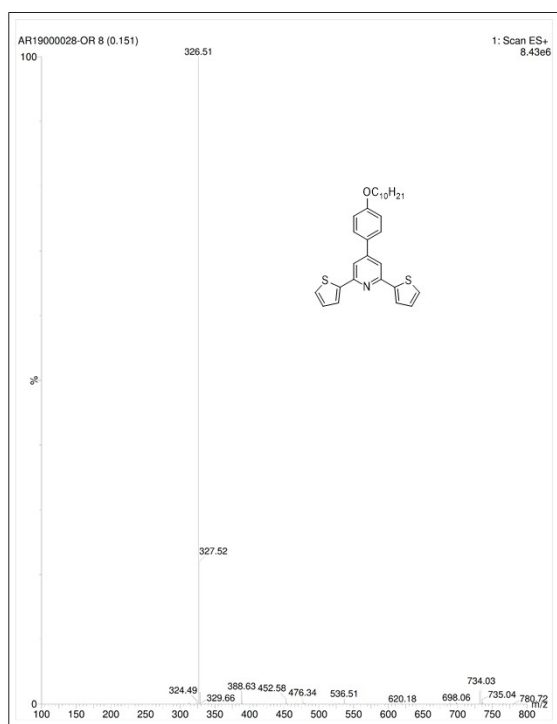
Fig. S6. Mass spectrum of **(4)**
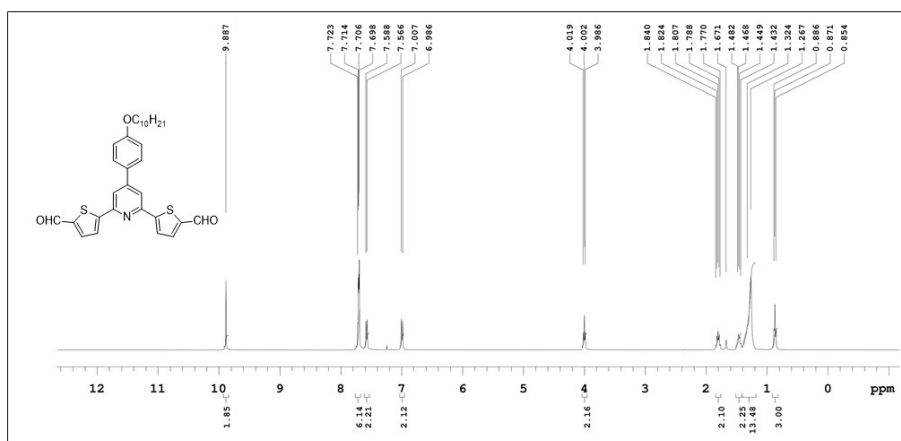
Fig. S7. ^{1}H NMR spectrum of **(5)**
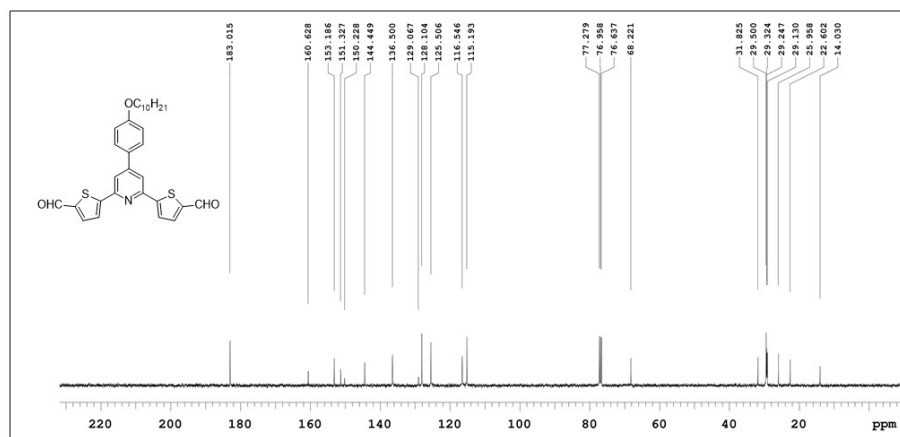
Fig. S8. ^{13}C NMR spectrum of **(5)**
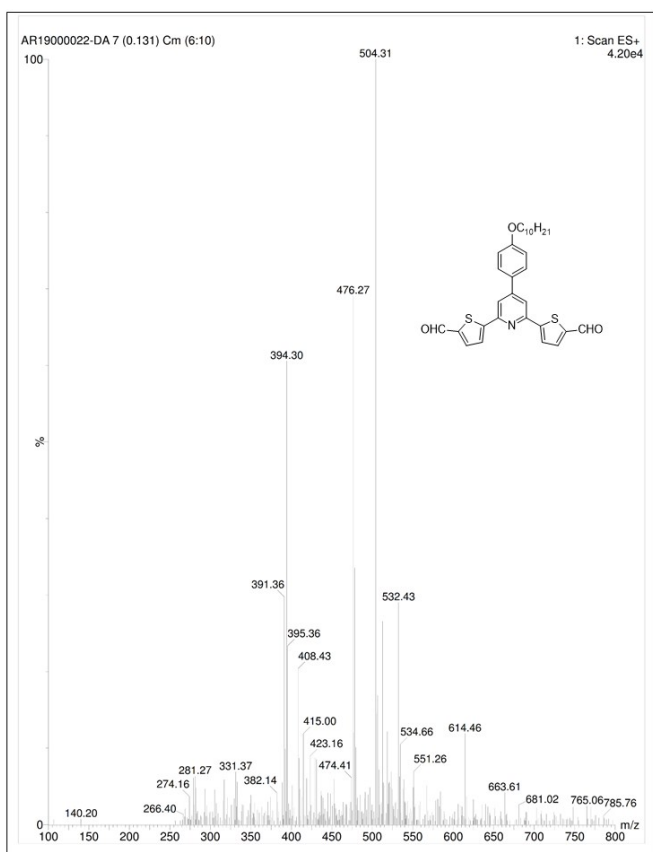
Fig. S9. Mass spectrum of **(5)**
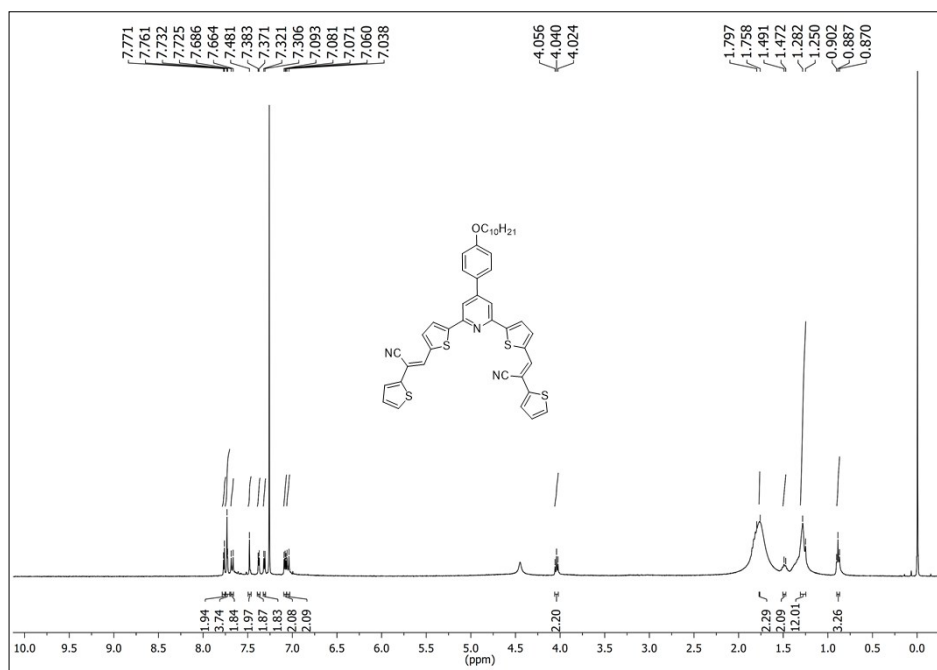
Fig. S10. ^{1}H NMR spectrum of **TPyT**
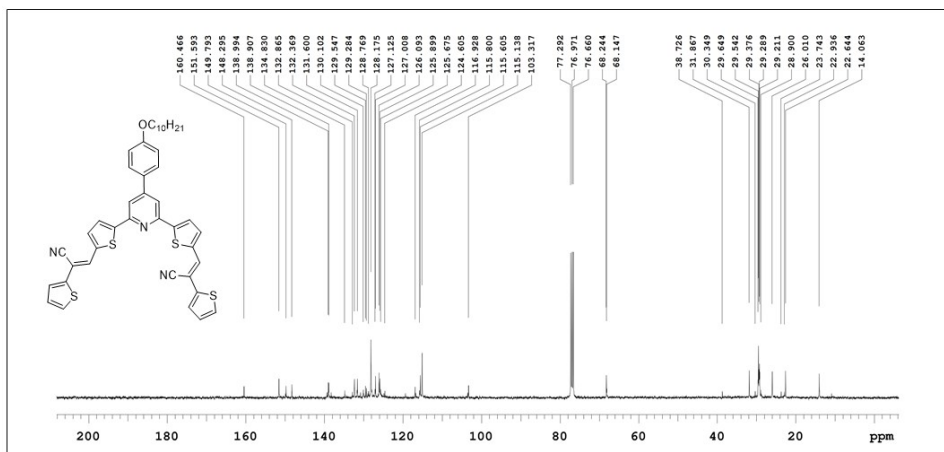
Fig. S11. ^{13}C NMR spectrum of **TPyT**
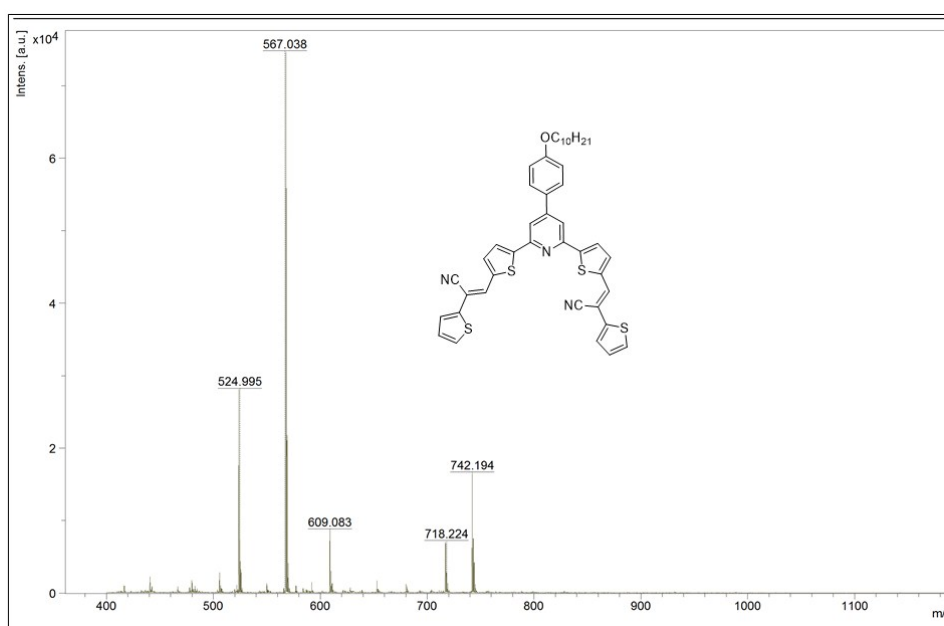
Fig. S12. MALDI-TOF Mass spectrum of **TPyT**
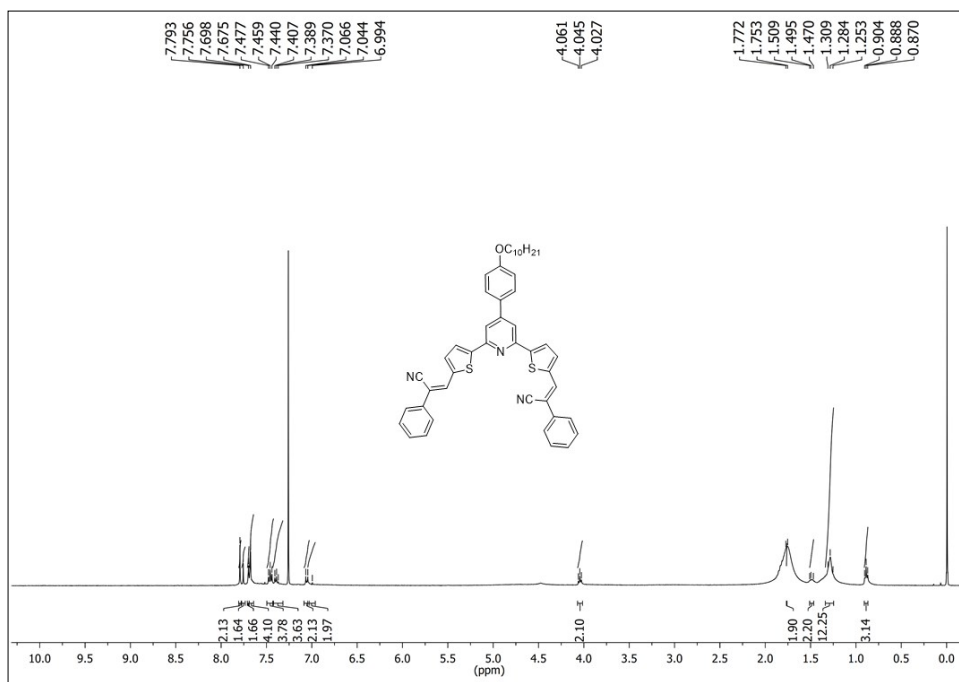
Fig. S13. ^{1}H NMR spectrum of **TPyP**
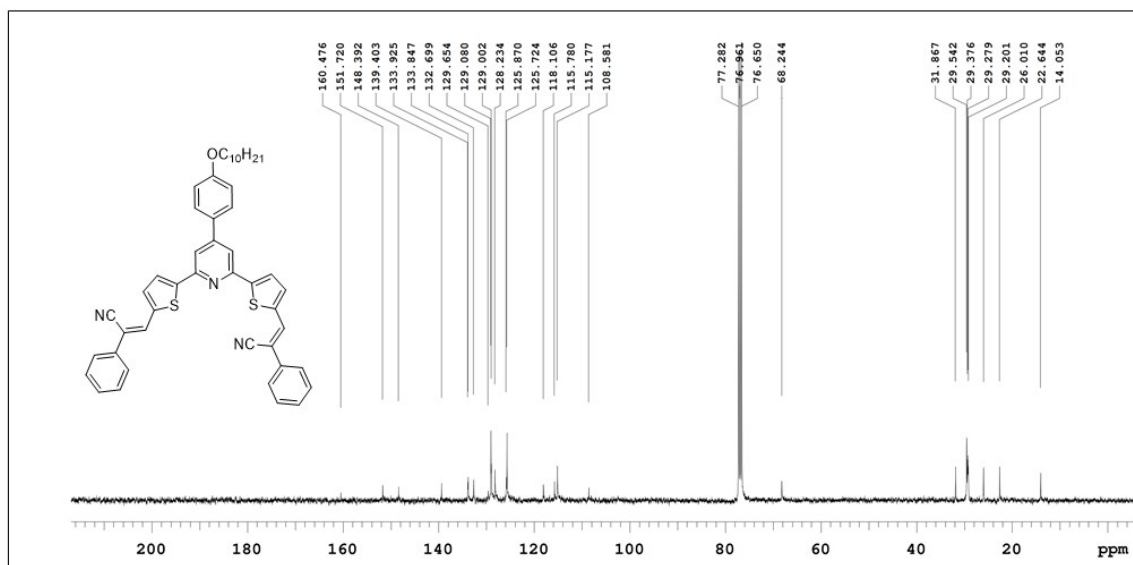
Fig. S14. ^{13}C NMR spectrum of **TPyP**
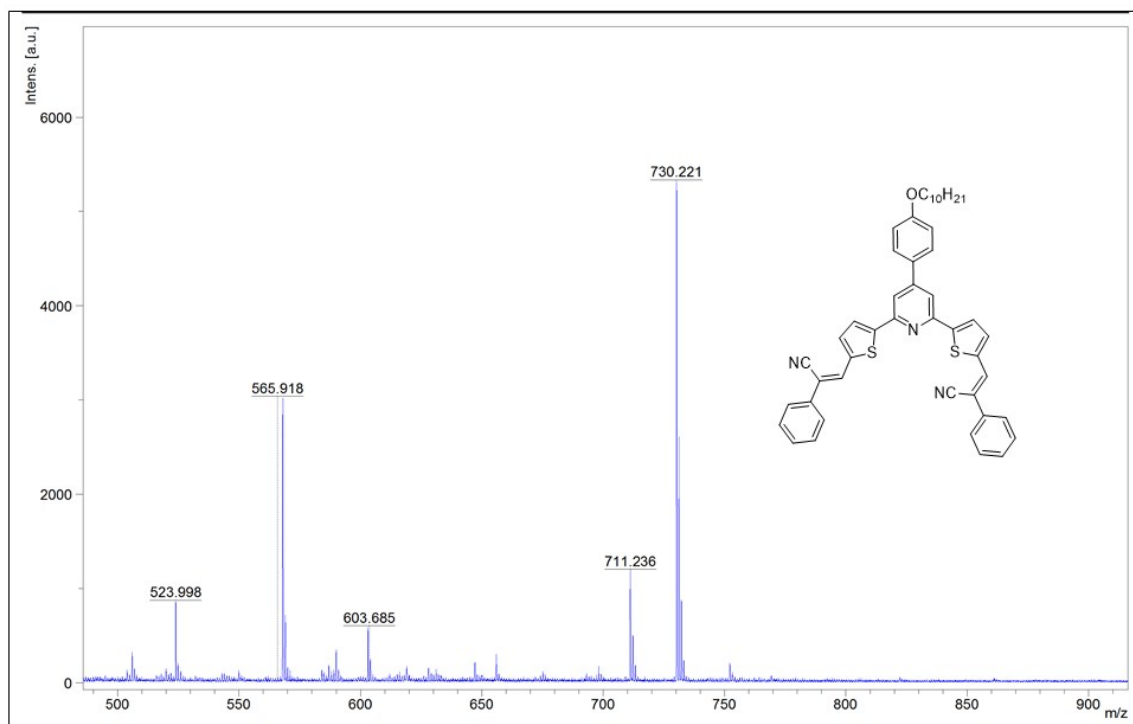
Fig. S15. MALDI-TOF Mass spectrum of **TPyP**
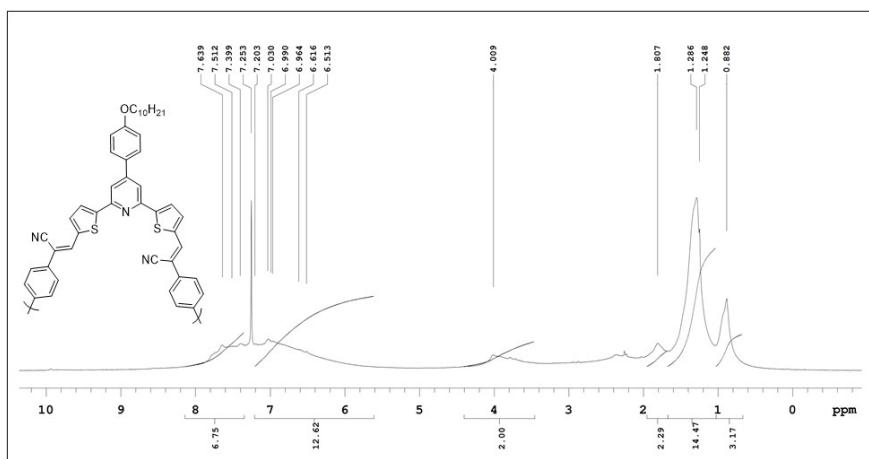
Fig. S16. ^{1}H NMR spectrum of **P2TPy**
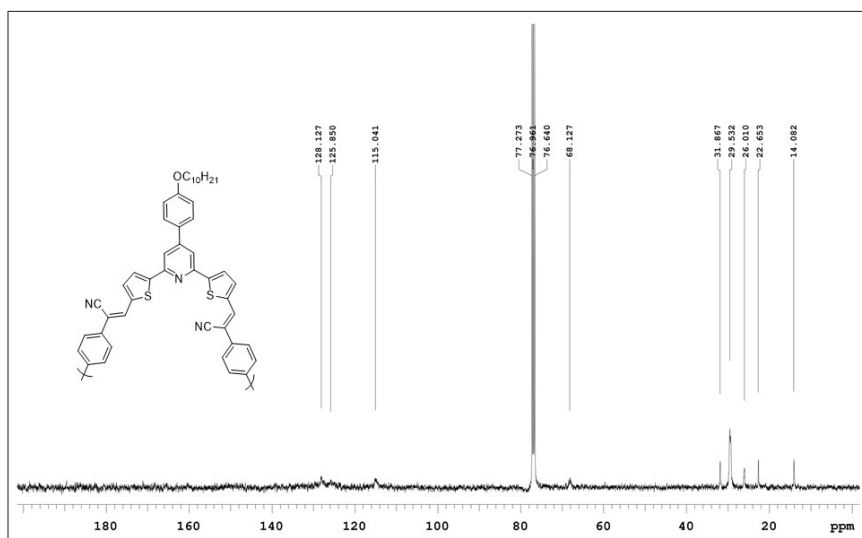
Fig. S17. ¹³C NMR spectrum of **P2TPy**

(n - 1) Average	:	672			Z Average (Mz)		:	30461		
Number Average (Mn)	:	2400			(Z + 1) Average		:	51252		
Weight Average (Mw)	:	10426			PolyDispersity (Mw/Mn) :			4.344		
Total Area	:	8.7680410e+004 (microvolt seconds)								

Peak Molecular Weight Report

Peak	Component	RT	Area	%Area	PMwt	Mw	Mn	Mw/Mn	StartMw	EndMw
1		8.380	87680.4	100.000	6499.4	10426.2	2399.9	4.3444	114983.0	140.0

Fig. S18. GPC spectrum of **P2TPy**

Fig. S19. Cyclic voltammogram of ferrocene recorded in CH_3CN solution containing 0.1 M $Bu_4N(ClO_4)$ as supporting electrolyte at a scan rate of 100 mV s^{-1} using SCE as reference electrode, Pt wire as counter electrode and material coated glassy carbon as working electrode.

Z–scan analysis

The nonlinear optical (NLO) studies were performed by Z–scan technique under nano second excitation [1]. Using this technique nonlinear absorption parameters were measured which provided imaginary part of χ^3 value. The nonlinear absorption (NLA) and optical 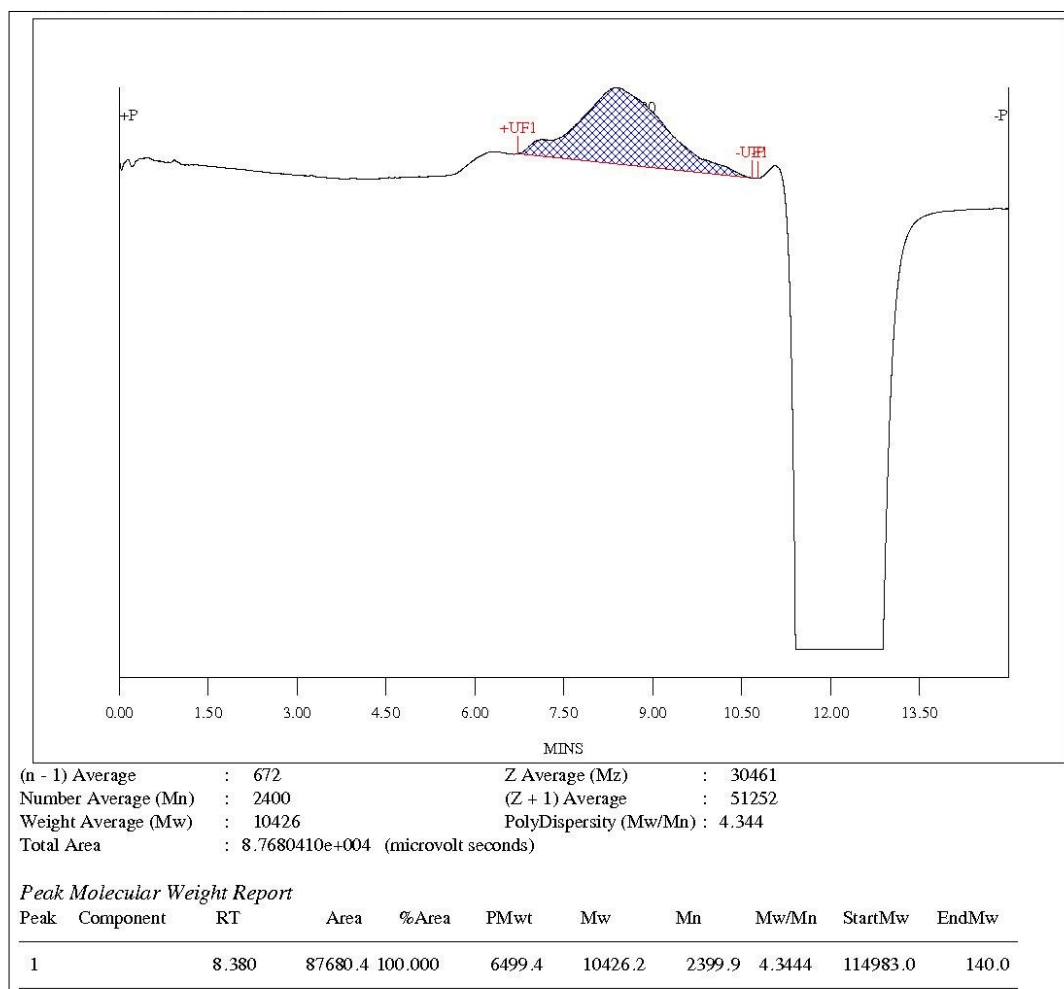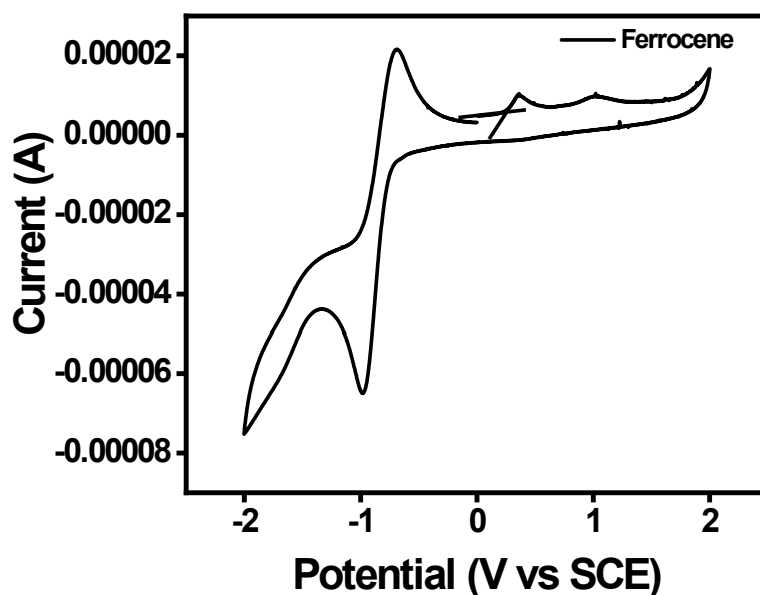limiting (OL) parameters were obtained from open aperture (OA) Z–scan analysis. In OA Z–scan analysis the optical transmittance of the sample was recorded as a function of input intensity. The schematic representation of the Z–scan set up is shown in the Fig. S20. The sample solutions were made to translate across the focus of a convex lens (focal length 150 mm) in the direction of laser beam (z axis from -z to +z) in predetermined steps using a translational stage which was controlled by a computer program.

The maximum intensity of the samples was observed at the focus which decreases equally on either side of the focus. The output transmittance from the sample at each position was collected by a detector which was then plotted against position of the samples. The NLA properties of the samples were measured by numerically fitting the recorded data to the theoretical model. All the experiments were carried out in the "single shot" mode. Sufficient time intervals were provided between successive pulses to avoid accumulative thermal effects in the sample. The NLO studies were performed using a Q– switched Nd–YAG laser Quanta Ray INDI–40 (Austin, USA) (7 ns pulse width) working at a wavelength of 532 nm with a frequency of 10

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Hz. The linear transmittance of all the compounds was fixed between 60–65% at the excitation wavelength when taken in a 1 mm cuvette.

Z–scan experimental set up

A frequency doubled Q switched Nd:YAG laser (Quanta–Ray INDI–40) operating at 532 nm wavelength, 7 ns pulse width and 10 Hz repeating rate excitation source was used for the Z–scan experiment. Using a beam splitter, the laser beam was split into reference beam and the sample beam, which was passed through the sample taken in a 1 mm thick quartz cuvette through a convex lens of focal length 150 mm. The sample cuvette was placed on a computer controlled translational stage and was moved along the direction of laser beam in z–direction from +z to –z about 20 mm on either side of the focus of the lens in predetermined steps (1000 microns). The convex lens was adjusted in such a way that the laser beam provides maximum energy to the sample at the focus which then equally decreases on either side of the focus. Both the reference beam and the transmitted beam from the sample were detected using two pyroelectric detectors (RjP–735, laser Probe Inc, USA) and were collected in the energy meter (Rj–7620, Laser Probe, Inc, USA).
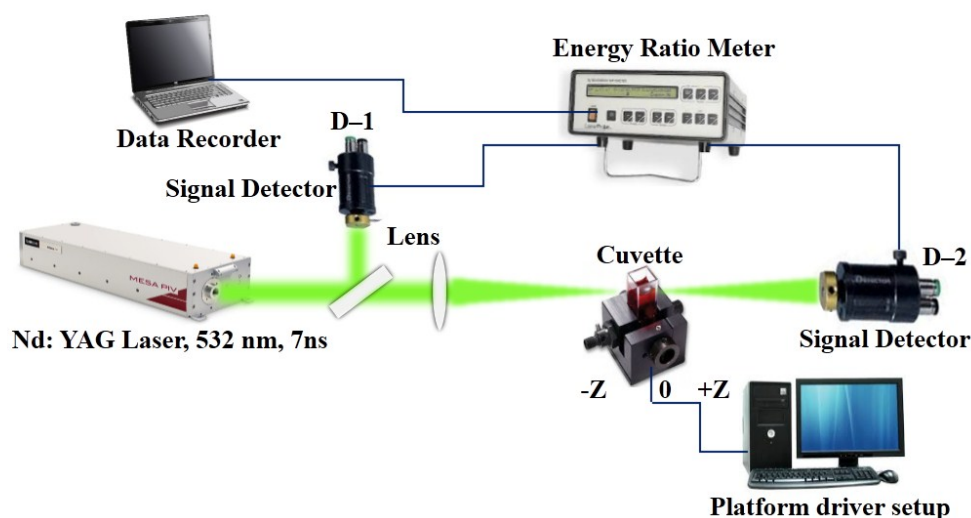
Fig. S20. Schematic representation of Z–scan experimental setup.

Equations used for the theoretical fitting of the experimental results

The intensity dependent effective nonlinear absorption coefficient $\alpha(I)$ for a system where the net NLA is due to both TPA and ESA (RSA) (associated with saturable absorption (SA)), can be expressed as

$$\alpha(I) = \frac{\alpha_o}{1 + I/I_s} + \beta_{eff} I \quad\text{...}(S1)$$

where, α_0 is the unsaturated linear absorption coefficient at the excitation wavelength, I is the incident laser intensity, I_s is the saturation intensity (intensity at which linear absorption drops to half of its original value), β_{eff} is the effective TPA coefficient which includes both TPA and ESA [2].

Also, the nonlinear propagation equation is written as

$$\frac{dI}{dz} = -\left(\frac{\alpha_o}{1+\dfrac{I}{I_s}}\right)I - \beta_{eff}I^2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (S2)$$

where, z is the propagation distance within the sample. The first term in equation S2 expresses the SA and the next term indicates effective TPA part.

The normalized transmittance derived from equations S1 and S2 is given by

$$T(z) = \sum_{m=0}^{\infty} \frac{\left[\dfrac{\alpha I_o L_{eff}}{1 + z^2/z_o^2}\right]^m}{[m+1]} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (S3)$$

where α is the nonlinear absorption coefficient, I_0 is the on–axis peak intensity, L_{eff} is the effective sample length given by $L_{eff} = \left(1 - e^{-\alpha_o L}\right)/\alpha_o$, L the sample length, α_0 is the unsaturated linear absorption coefficient, z is the position of the sample, $z_o = \pi\omega_o^2/\lambda$ is the Raleigh range, ω_0 is the beam waist radius at the focal point and λ is the wavelength of laser beam.

The imaginary part of third order nonlinear susceptibility (χ^3) is given by the equation S4,

$$\mathrm{Im}\,\chi^{(3)} = \frac{n_o^2 \varepsilon_o c \lambda \beta_{eff}}{2\pi} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (S4)$$

where, n_0 is the linear refractive index, c is the speed of light and ε_0 is the permittivity of free space.

References

1 M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan and E. W. Van Stryland, Sensitive measurement of optical nonlinearities using a single beam, *IEEE J. Quantum Electron.*, 1990, **26**, 760–769.

2 M. C. Divyasree, K. Vasudevan, K. A. Basith, P. Jayakrishnan, M. T. Ramesan and K. Chandrasekharan, Third-Order Nonlinear Optical Properties of Phenothiazine-Iodine Charge Transfer Complexes in Different Proportions, *Opt. Laser Technol.*, 2018, **105**, 94–101.

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