Electronic Supplementary Material (ESI) for RSC Advances.

Nonlinear absorption in tetrathia[22]porphyrin(2.1.2.1)s: Visualizing strong reverse saturable absorption at non resonant excitation

Kamaljit Singh,*[,a] Shafali Arora,[a] Krishnandu Makhal,[b] Paramjit Kaur[a] and Debabrata Goswami*[,b]

[a]Department of Chemistry, Centre of Advance Study-II (UGC), Guru Nanak Dev University, Amritsar – 143 005, India
[b]Department of Chemistry, Indian Institute of Technology, Kanpur – 208616, India
E-mail: Kamaljit.chem@gndu.ac.in

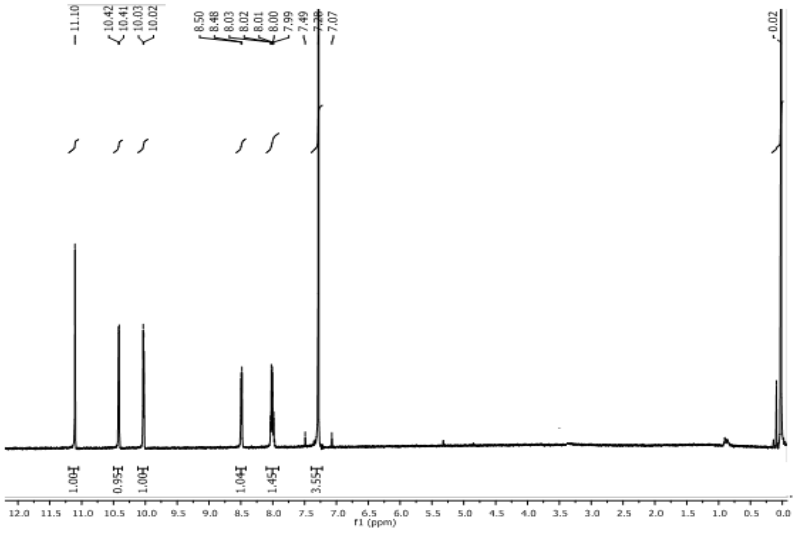
Sr. No.	Content	Page number
1.	**General**	2-3
2.	**Figure S1:** ^{1}H NMR spectra of **1**-**3**.	4
3.	**Figure S2:** TCSPC traces of **1**-**3**.	5
4.	**Figure S3:** UV-visible and fluorescence spectra and fitted spectra of **1**-**3**.	6

General:

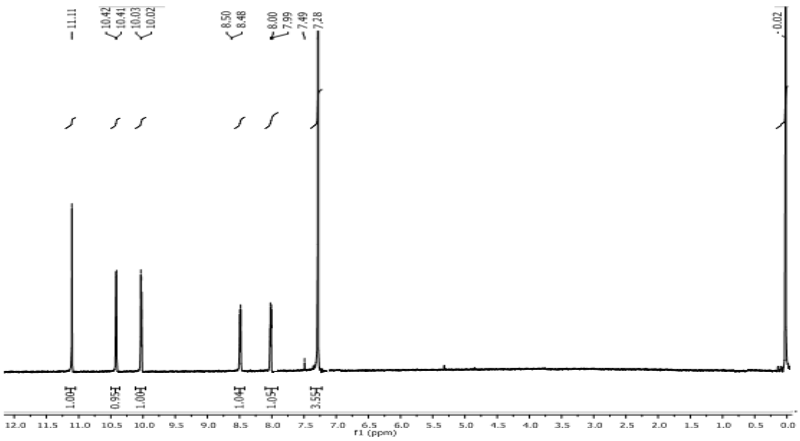
Time resolved fluorescence anisotropy and intensity decays were collected using a commercial time-correlated single-photon counting (TCSPC) setup (LifeSpec-II, Edinburgh Instruments, UK).
All samples (10^{-4} M) were excited at 376 nm and the full width at half maxima (FWHM) of the instrument response function was about 100 ps. For lifetime measurements, peak counts of 5000 were collected with the emission polarizer oriented at magic angle polarization and decays were collected at 455 nm.
A pulse diode laser at 430 nm is used as excitation source. Time resolved Fluorescence traces were fitted with "FAST Software" of Edinburg Instruments. Quality of fit judged by $\chi^2 < 1$. Measurement of TPACS (two-photon absorption cross section) of the synthesized chromophores in chloroform solvent was performed with 527 nm laser pulses of width 120 ns at repetition rate of 250 Hz. The open aperture Z scan study was performed by in home built experimental set up.
The system was calibrated using trans-stilbene in chloroform at concentration of ~1 mM as the standard sample. The sample solutions (1.0 mM) were taken in a 1 mm quartz cuvette and scanned along the direction of the propagation of the laser on a motorized stage that was computer controlled through GPIB using Lab View programming. The Z scan traces were fitted by Matlab 2012b programme. Model used is based on the two equations as already mentioned in paper. UV-visible absorption studies were recorded in chloroform using UV-1800 SHIMADZU UV-spectrophotometer with a quartz cuvette (path length, 1 cm). The cell holder of the spectrophotometer was maintained at 25^{o} C for consistency in the recordings. Fluorescence studies were also carried out in chloroform using PerkinElmer LS 55 fluorescence spectrometer at emission slit width = 5 nm and excitation slit width = 5 nm. As a quantitative probe of aromaticity, we have calculated Nucleus-Independent Chemical Shift, NICS(1), values using *ab initio* quantum mechanical DFT calculations at the B3LYP/6-311G(d) level using the Gauge Independent Atomic Orbitals (GIAO) method. Electrochemical studies were carried out on CHI 660D Electrochemical Workstation with a conventional three-electrode configuration consisting of

platinum working electrode (2 mm diameter), counter electrode and Ag/AgCl as reference electrode. The experiments were carried out on 10^{-4} M solutions of samples in dichloromethane containing 0.1M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte at room temperature. Deoxygenation of the solutions was achieved by bubbling nitrogen for 30 min and the working electrode was cleaned after each run. The voltammograms were recorded with a scan rate of 100 mV s^{-1}. ^1H NMR spectra were recorded on Bruker Biospin Avance III HD at 500 MHz, in $CDCl_3$ containing TMS as internal standard.

^{1}H NMR ($CDCl_3$) spectra of **1**.



^{1}H NMR ($CDCl_3$) spectra of **2**.



^{1}H NMR ($CDCl_3$) spectra of **3**.

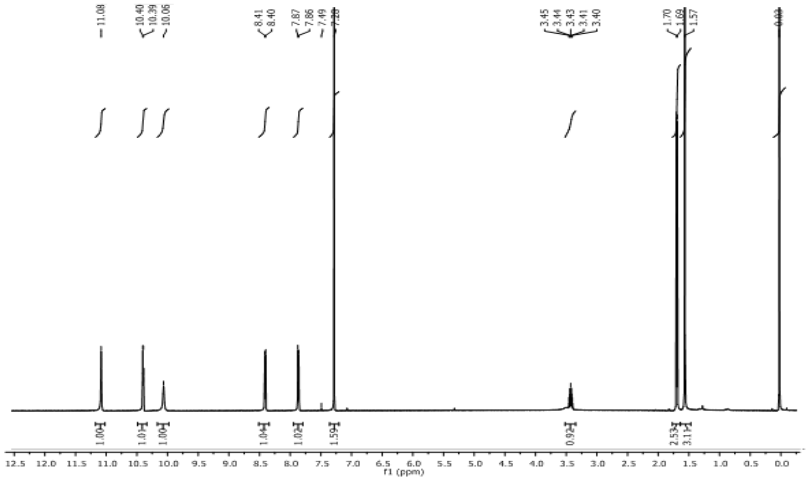


Figure S1: ^{1}H NMR spectra of **1**-**3** (in $CDCl_3$).

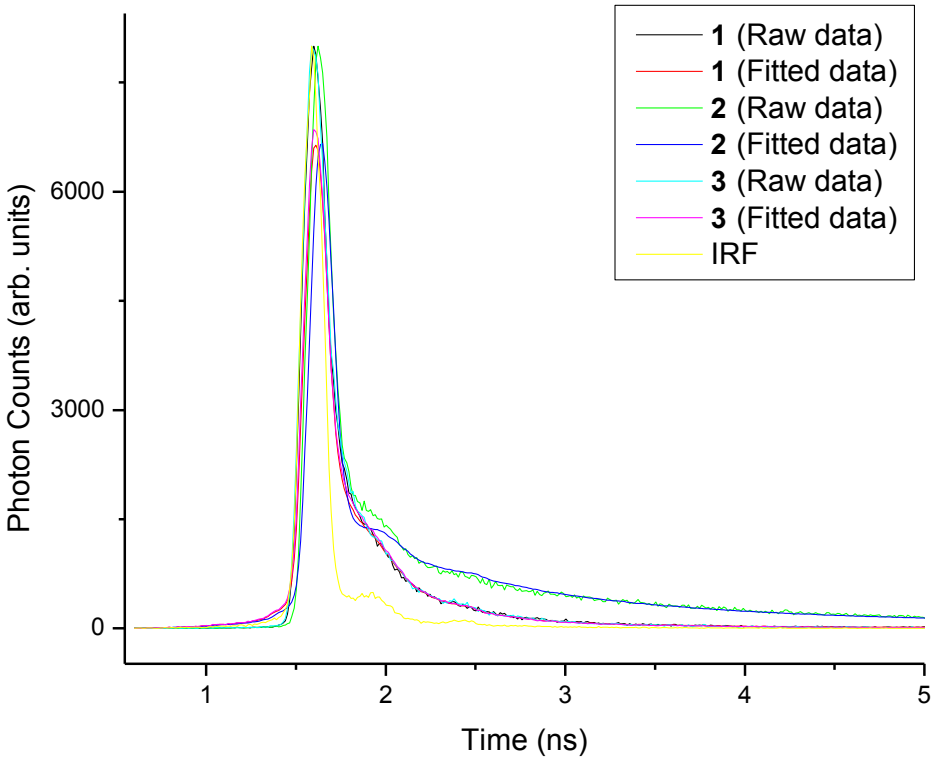
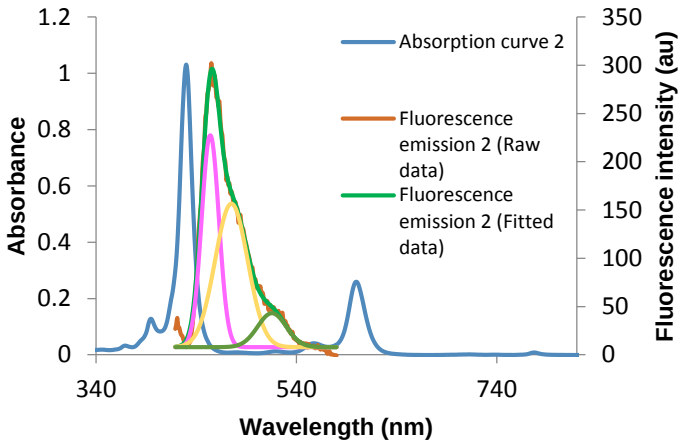
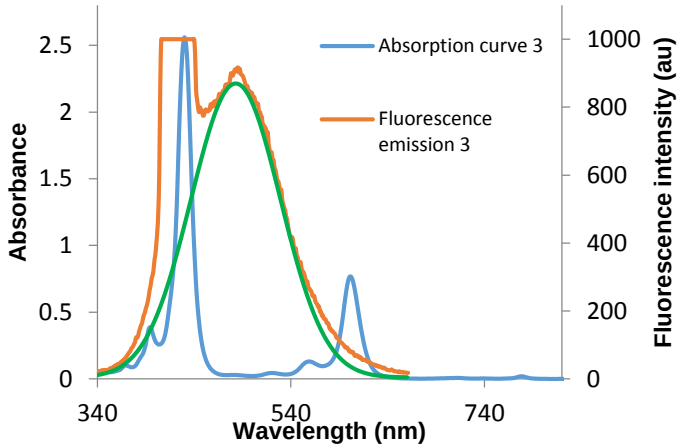


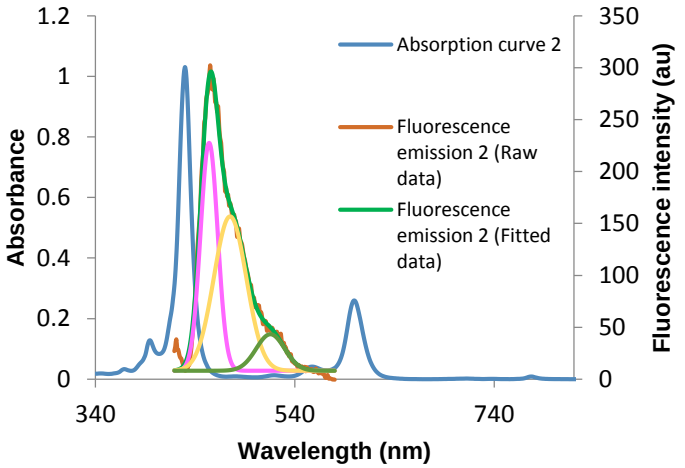
Figure S2: TCSPC traces of **1**-**3** (10^{-4} M in $CHCl_3$).



1



2



3

Figure S3: UV-visible (**1**: 2 x 10^{-5} M; **2**: 5 x 10^{-5} M; **3**: 1 x 10^{-5} M in $CHCl_3$) and fluorescence spectra (**1**: 1.64 x 10^{-5} M; **2**: 2.14 x 10^{-5} M; **3**: 2.01 x 10^{-5} M in $CHCl_3$) and fitted spectra of **1**-**3**.