

Electronic Supporting Information (ESI) for

# Third-order Nonlinear Optical Properties of Highly Electron Deficient, Nonplanar Push-Pull Porphyrins: $\beta$ -Nitro-Hexa- Substituted Porphyrins Bearing Bromo, Phenyl, and Phenylethynyl groups

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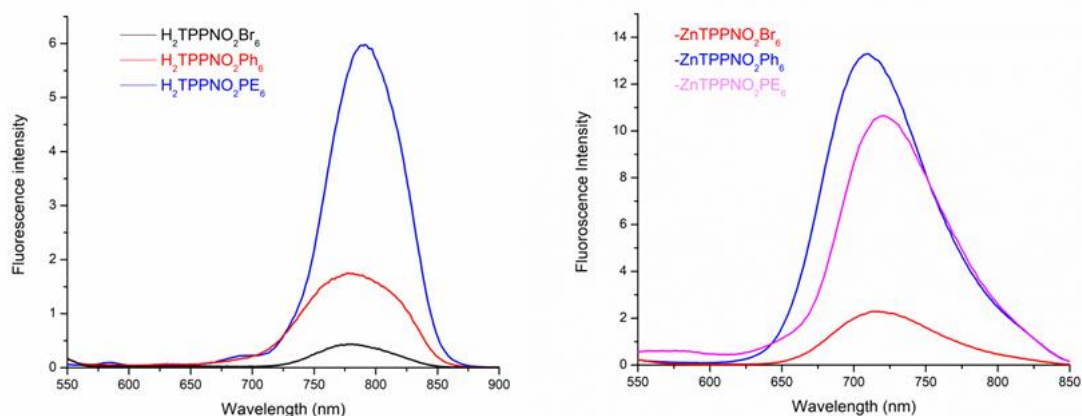
## Table of contents

**Figure S1.** The emission profile of H<sub>2</sub>TPP(NO<sub>2</sub>)X<sub>6</sub> [X = Br, Ph, PE] (right) and ZnTPP(NO<sub>2</sub>)X<sub>6</sub> [X = Br, Ph, PE] (left) in toluene at 298 K.

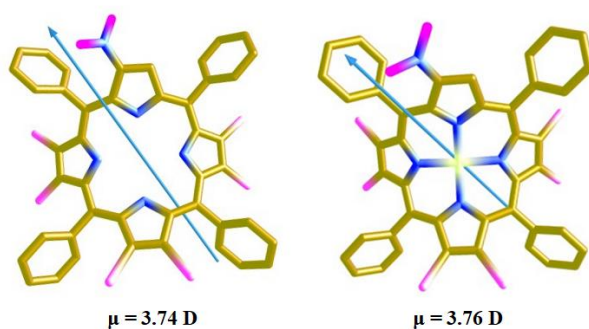
**Figure S2.** The dipole moment of H<sub>2</sub>TPP(NO<sub>2</sub>)Br<sub>6</sub> (right) and CuTPP(NO<sub>2</sub>)Br<sub>6</sub> (left) procured from DFT calculations.

**Figure S3.** The dipole moment of H<sub>2</sub>TPP(NO<sub>2</sub>)Ph<sub>6</sub> (right) and H<sub>2</sub>TPP(NO<sub>2</sub>)PE<sub>6</sub> (left) procured from DFT calculations.

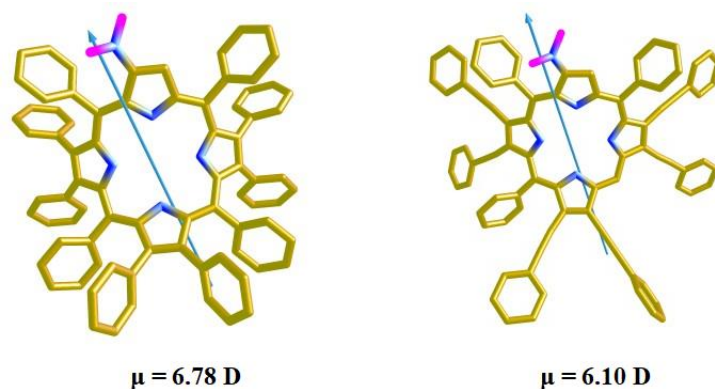
**Figure S4.** Schematic of the fs Z-scan experimental setup.



**Figure S1.** The emission profile of  $\text{H}_2\text{TPP}(\text{NO}_2)\text{X}_6$  [ $\text{X} = \text{Br}, \text{Ph}, \text{PE}$ ] (right) and  $\text{ZnTPP}(\text{NO}_2)\text{X}_6$  [ $\text{X} = \text{Br}, \text{Ph}, \text{PE}$ ] (left) in toluene at 298 K.



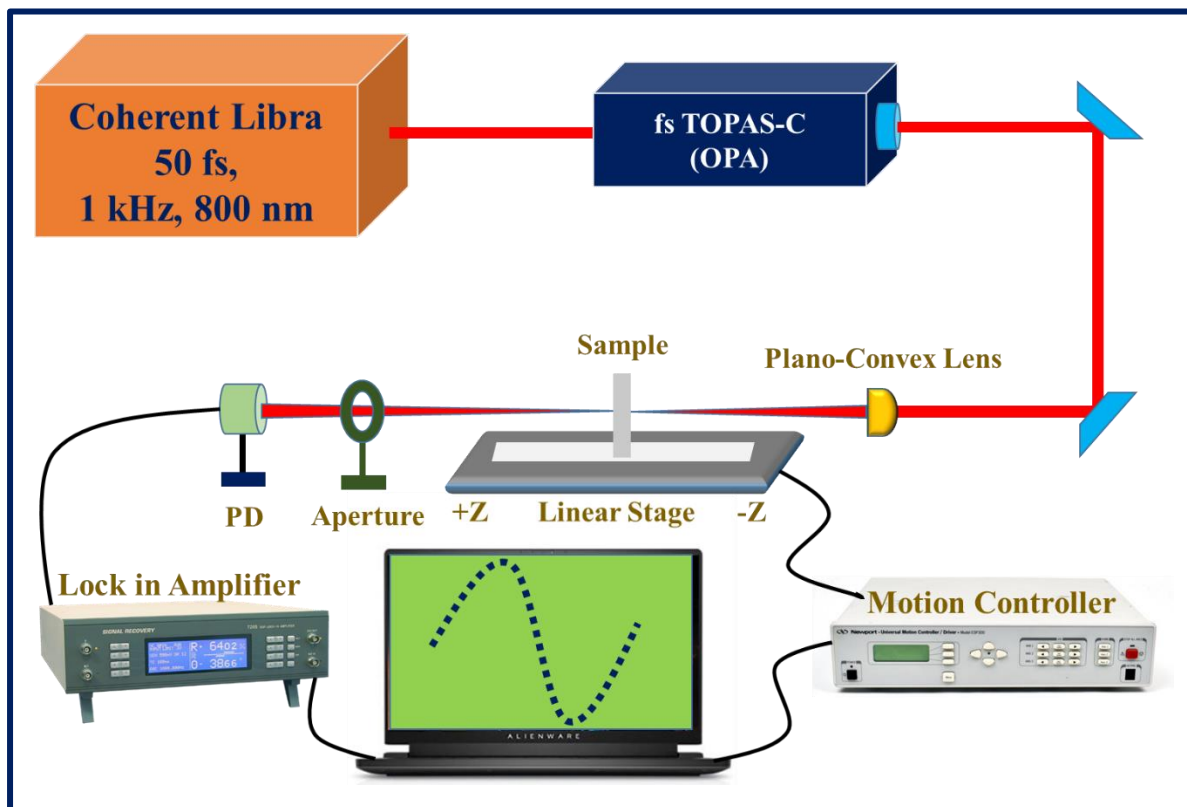
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### Femtosecond Z-scan experimental details:

A Ti: sapphire amplifier (Libra, M/s Coherent) with a repetition rate of 1 kHz was used by us to produce ~50 fs pulses at a wavelength of 800 nm, which was used for Z-scan measurements. The amplifier uses a nanosecond Nd: YAG laser operating at 532 nm as the pump. The output from the laser system was ~50 fs pulses delivered with ~4 mJ energy, centered at 800 nm and a bandwidth of ~28 nm with a repetition rate of 1 kHz. A broadband oscillator (a repetition rate of 80 MHz, ~30 fs at 800 nm with a bandwidth of ~35 nm) is placed to seed for the amplifier. The samples were put on a linear translation stage, and a photodiode (Silicon PD) was used to capture the transmission. A lock-in amplifier received the photodiode's output. One LabVIEW programme that was particularly built was used to control every instrument. Figure 4 below shows the experimental design for the Z-scan.



**Figure S4.** Schematic of the fs Z-scan experimental setup.