Supporting Information

Photophysical Properties of N-confused Hexaphyrins: Effects of Confusion of Pyrrole Rings and Molecular Shape on Electronic Structures

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Experimental Section

Sample Preparation. Regular hexaphyrin **1**[S1], doubly N-confused hexaphyrin **2**[S2], and triply N-confused hexaphyrin **3**[S3] were synthesized according to the previously reported papers. Toluene was used as solvents (Sigma-Aldrich, spectrophotometric grade) without further purification. Commercial trifluoroacetic acid, TFA (Sigma-Aldrich, spectrophorometric grade, 99+ %) was used for protonation.

Steady-state Absorption and Fluorescence. Steady-state absorption spectra were obtained using an UV-VIS-NIR spectrometer (Varian, Cary5000) and steady-state fluorescence were measured by a Hitachi model F-2500 fluorometer at room temperature. For the observation of steady-state fluorescence spectra in NIR region, a photomultiplier tube (Hamamatsu, R5108 and H9170-75), a lock-in amplifier (EG&G, 5210) combined with a mechanical chopper and a CW He-Cd laser (Melles Griot, Omnichrome 74) for photo-excitation at 442 nm were used.

UV-vis-NIR Spectrophotometric Titration. Two milliliters solution of samples in toluene solvent were titrated carefully in a 1 cm absorption cell by addition of 0.1 M-TFA standard solution which was made by mixing TFA and toluene with exact ratio of volume. Using microliter syringe, TFA standard solution was added in 10 μL aliquots. After addition of each aliquot, UV-vis-NIR absorption spectra were measured. The total volume change during the titration was corrected by each absorption spectrum multiplied by correction factor, f = (original volume) volume of aliquots)/(original volume).

Femtosecond Transient Absorption Measurements. The femtosecond time-resolved transient absorption (TA) spectrometer consisted of a homemade noncollinear optical parametric amplifier (NOPA) pumped by a Ti:sapphire regenerative amplifier system (Quantronix, Integra-C) operating at 1 kHz repetition rate and an optical detection system. The generated visible NOPA pulses had a pulse width of ~ 100 fs and an average power of 1 mW in the range 500-700 nm which were used as pump pulses. White light continuum (WLC) probe pulses were

generated using a sapphire window (2 mm of thickness) by focusing of small portion of the fundamental 800 nm pulses which was picked off by a quartz plate before entering to the NOPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (Newport, ILS250). Intensities of the spectrally dispersed WLC probe pulses are monitored by miniature spectrograph (OceanOptics, USB2000+). To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 25 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 6000 pulses excite samples to obtain the TA spectra at a particular delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) in order to prevent polarization-dependent signals. Cross-correlation fwhm in pump-probe experiments was less than 200 fs and chirp of WLC probe pulses was measured to be 800 fs in the 400-800 nm region. To minimize chirp, all reflection optics in probe beam path and 2 mm path length of quartz cell were used.

Two-photon Absorption Cross-Section ($\sigma^{(2)}$). The TPA measurements were performed using the open-aperture Z-scan method with 130 fs pulses from an optical parametric amplifier (Light Conversion, TOPAS) operating at a 2 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane X). After passing through a $f = 10$ cm lens, the laser beam was focused to 1 mm-quartz cell. As the position of the sample cell was varied along the laser-beam direction (z-axis), the transmitted laser beam from the sample cell was then probed using a Ge/PN photodiode (New Focus, 2033) as used for reference monitoring. Assuming a Gaussian beam profile, the nonlinear absorption coefficient β can be obtained by curve fitting to the observed open aperture traces with the following equation:[S4]

$$T(z) = 1 - \frac{\beta I_0 (1 - e^{-\alpha_0 l})}{2\alpha_0 (1 + (z/z_0)^2)},$$

where α_0 is a linear absorption coefficient, I_0 is the on-axis peak intensity of the incident pulses at the focal point, l is a sample length, and z_0 is the diffraction length of the incident beam. After obtaining the nonlinear absorption coefficient β, the TPA cross-section $\sigma^{(2)}$ (in unit of 1 GM = 10^{-50} cm^4 ·s·photon^{-1}molecule^{-1}) of a single solute molecule can be determined by using the following relationship:

$$\beta = \frac{\sigma^{(2)} N_A d \times 10^{-3}}{hv}$$

where N_A is the Avogadro constant, d is the concentration of the TPA compound in solution, h is Planck's constant, and v is the frequency of the incident laser beam. The TPA cross-section value of AF-50 was measured as a reference compound, which was found to exhibit a TPA value of 50 GM at 800 nm.[55]

Cyclo Voltammetry Measurement. Cyclic voltammetry (CV) measurements were performed at 298K on CHI electrochemical analyzer model 660B in deaerated dichloromethane (CH2Cl2) solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF6) as a supporting electrolyte. A three-electrode system was utilized and consisted of a platinum working electrode, a platinum wire counter electrode, and a Ag/Ag+ reference electrode. Due to the instability, the oxidation potentials of **1** can not be measured.[56]

Computational Method. Quantum mechanical calculation were performed with the Gaussian 03 program suite.[57] All calculations were carried out by the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP),[58,59] employing the 6-31G* basis set. The X-ray crystal structures of normal hexaphyrin **1**, doubly N-confused hexaphyrin **2**, and triply N-confused hexaphyrin **3** were used as initial geometry for geometry optimization without any modification.
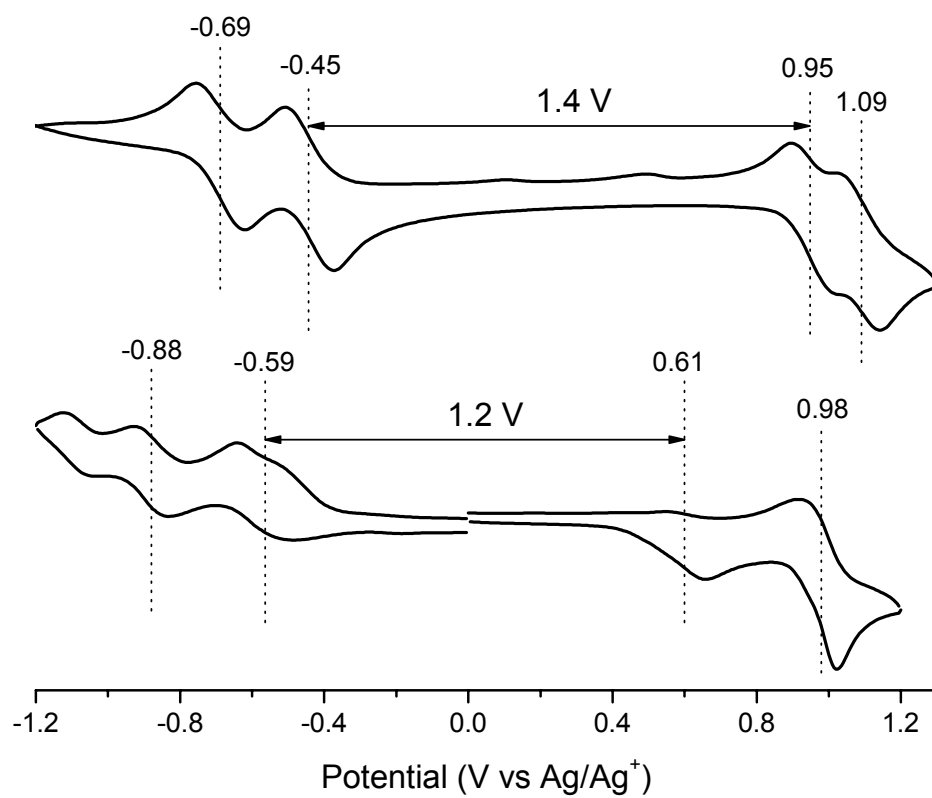
Fig S1. Cyclic voltammograms of doubly N-confused hexaphyrin **2** (up) and triply N-confused hexaphyrin **3** (bottom) in dichloromethane.
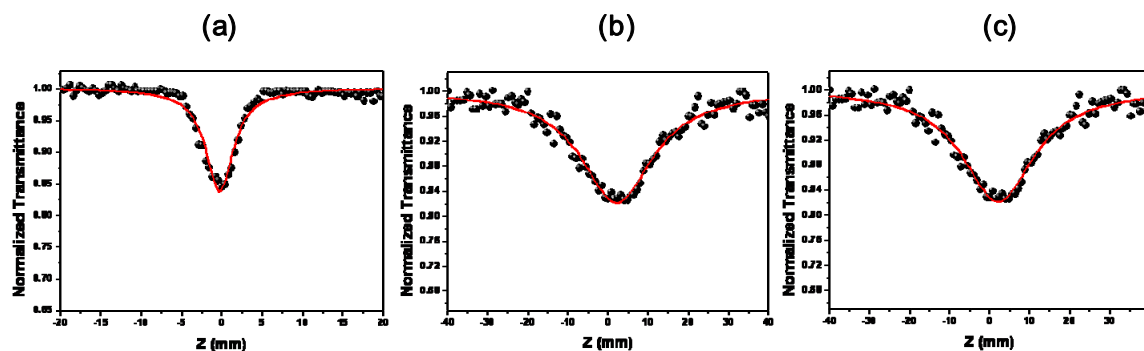
Fig. S2 Z-scan trace at 1200 nm of (a) regular hexaphyrin **1**, (b) doubly N-confused hexaphyrin **2** and (c) triply N-confused hexaphyrin **3** in toluene, respectively. The solid line is the best curve fit line of experimental data.
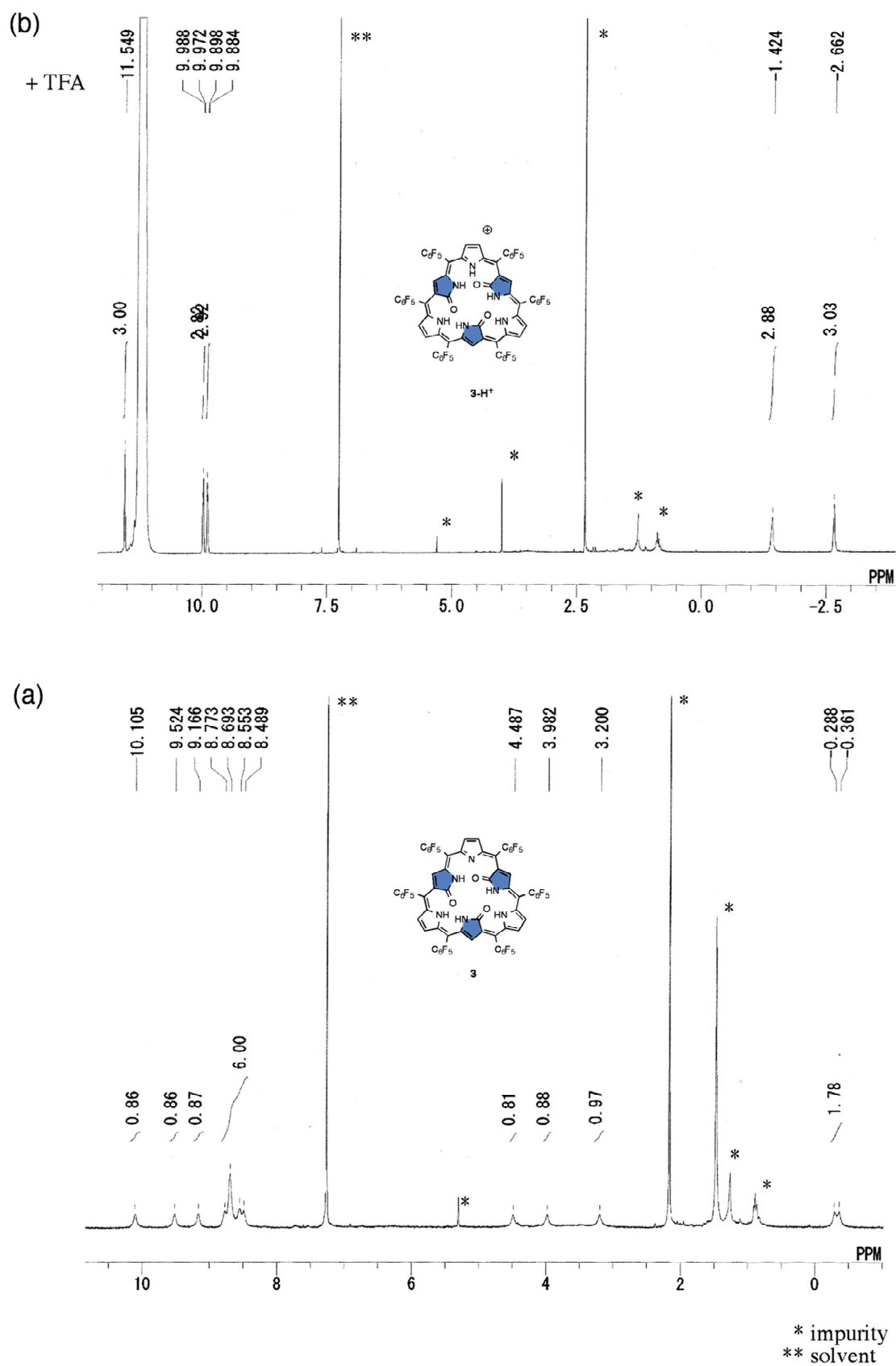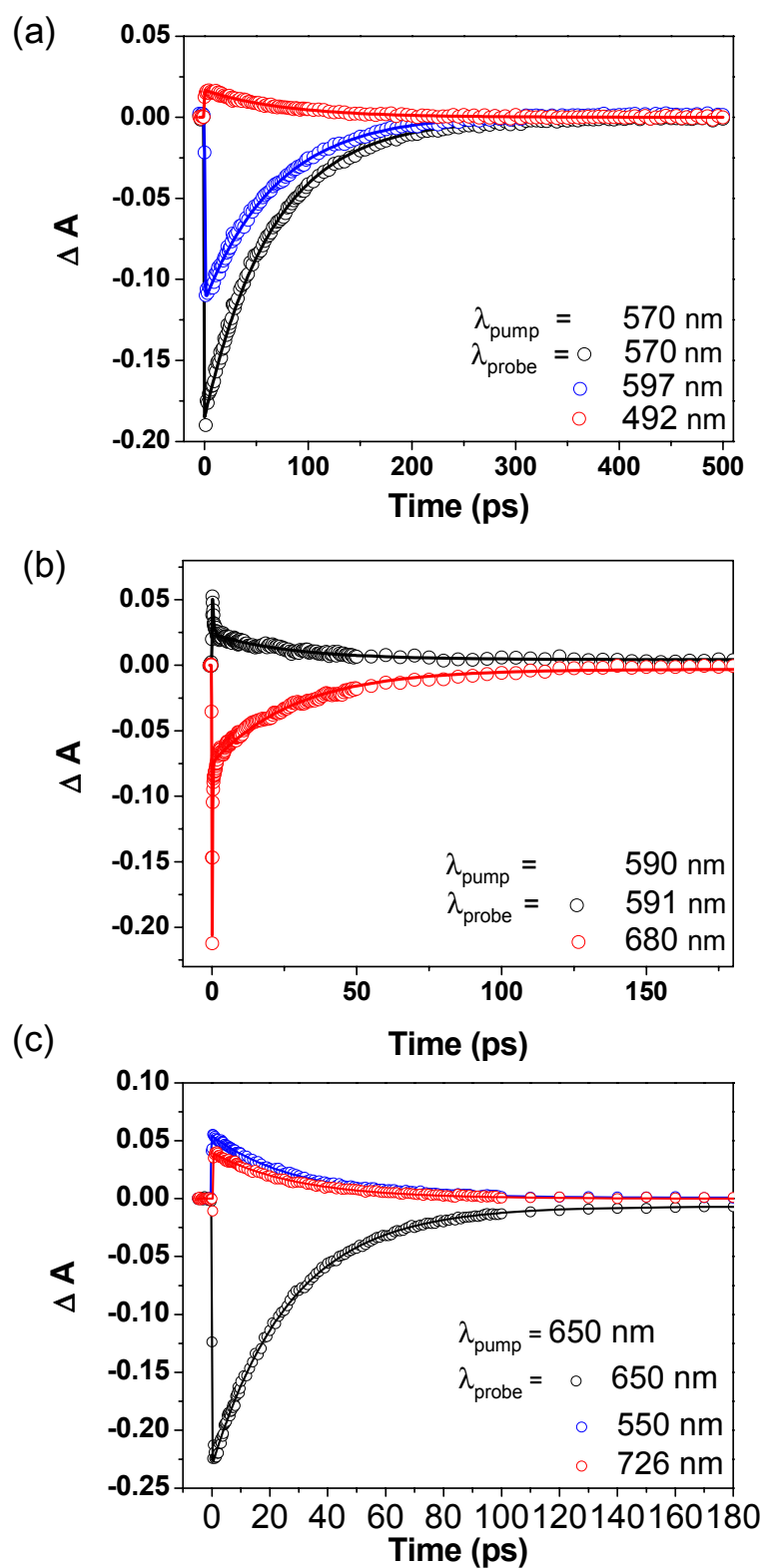
Fig. S3 ^{1}H NMR spectra of (a) **3** and (b) protonated **3** with TFA, in CDCl$_3$ at ambient temperature.

Fig. S4 Femtosecond transient absorption decay profiles of (a) doubly N-confused hexaphyrin **2**, (b) triply N-confused hexaphyrin **3**, and (c) protonated triply N-confused hexaphyrin.

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