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Octupolar trisporphyrin conjugates exhibiting strong two-photon absorption

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Abstract

We report octupolar trisporphyrin conjugates, derived from the symmetrical functionalization of a triphenylamine core with three ethynylporphyrin wings, exhibiting largely enhanced two-photon absorption (TPA) compared to the porphyrin monomers. Octupolar trisporphyrin conjugate **tris-H_2P** was synthesized by the Pd(0)-catalyzed Sonogashira cross-coupling reaction of tris(4-iodophenyl)amine with 5,10,15-tri-(*p*-tolyl)-20-ethynylporphyrin, and fully characterized by various spectroscopic methods and elemental analysis. The optimized geometry of **tris-H_2P** obtained by semi-empirical AM1 calculations reveals that **tris-H_2P** adopts a propeller-shaped structure. Our photophysical studies strongly manifest that the trisporphyrin conjugates are promising octupolar fluorophores with effective π-conjugation over the porphyrin wings through the octupolar core. The trisporphyrin conjugates exhibit much larger TPA cross-section values in comparison with the monomers; the TPA cross-section $\sigma^{(2)}$ value of **tris-ZnP** (11,800 GM) exceeds that of **mono-ZnP** (630 GM) by about 20 times.

1. Introduction

Molecular materials for nonlinear optics (NLO) have been extensively investigated due to their potential applications in the area of optoelectronics.[1] Among many interesting phenomena derived from the NLO-active molecules, two-photon absorption (TPA) has attracted growing interest over recent years for a variety of applications such as microfabrication,[2] three-dimensional optical data storage,[3] optical power limitation,[4] localized photodynamic therapy,[5] and two-photon laser scanning fluorescence imaging.[6] Porphyrins deserve a particular attention in the development of molecular TPA materials due to their favorable features of large π-conjugation, various coordination properties by accommodated metal ions, and photophysical properties easily tuned by changing the accomodated metal ion as well as peripheral substitutions.[7] Tetrapyrrolic chromophores such as porphyrins have been also regarded inherently suitable for medical and biological applications.[8] The enhancement of TPA cross-section values for porphyrinic TPA materials has been mainly achieved in conjugated porphyrin oligomers[9] and polymers[7c,10] with one-dimensional dipolar structures, or intermolecular porphyrin assemblies.[11] So far little attention has been devoted to the porphyrinic TPA materials with octupolar structures,[12] although it has been realized that increased dimensionality and branched structures could lead to highly effective TPA.[13] In this perspective, we have designed and synthesized octupolar trisporphyrin conjugates derived from the alkyne cross-coupling reaction with a functionalized triphenylamine core and three ethynylporphyrin wings. We here report synthesis, spectroscopic and TPA properties of the octupolar trisporphyrin conjugates.

2. Experiments

2.1. Materials and measurements

All chemicals were purchased of reagent grade or better. Merck silica gel 60 was used for column chromatography.

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Tris(4-iodophenyl)amine was prepared by the reported procedure.[14] CH_2Cl_2, $CHCl_3$, tetrahydrofuran, and triethylamine were purified by distillation over CaH_2. UV–vis spectra were recorded on a Hewlett-Packard 8453 diode array. ^1H and ^{13}C NMR spectra were obtained on a Bruker DRX-500 spectrometer. APCI and MALDI-TOF mass spectra were recorded on a Waters ZQ 2000 LC/MS spectrometer and a Bruker Daltonics Reflex III spectrometer, respectively. Elemental analyses were performed on a ThermoQuest EA 1110 analyzer.

2.2. Syntheses

2.2.1. 5,10,15-Tri-(p-tolyl)-20-trimethylsilylethynylporphyrin

To a mixture of pyrrole (0.69 mL, 11 mmol), *p*-tolualdehyde (0.71 mL, 5.8 mmol), and 3-trimethylsilylpro-2-pynal (0.59 mL, 5.4 mmol) in $CHCl_3$ (1 L), trifluoroboron etherate (0.13 mL, 0.79 mmol) was added. The reaction mixture was stirred for 6 h at room temperature in the dark. DDQ (1.7 g, 7.5 mmol) was added in one portion, and the resulting mixture was further stirred for 1 h. The solvent was evaporated to dryness under reduced pressure. The desired porphyrin was separated from the crude residue by column chromatography (silica gel, eluting with 1:1 CH_2Cl_2/*n*-hexane, $R_f \sim 0.5$). After recrystallization from CH_2Cl_2 and *n*-hexane, the product was yielded in 13% (0.23 g). ^1H NMR (500 MHz, $CDCl_3$): δ 9.64 (d, J=4.25 Hz, 2H, β-pyrrolic H), 8.90 (d, J=4.13 Hz, 2H, β-pyrrolic H), 8.77 (s, 4H, β-pyrrolic H), 8.08 (d, J=7.27 Hz, 4H, *o*-Ph), 8.05 (d, J=7.72 Hz, 2H, *o*-Ph), 7.57 (d, J=7.34 Hz, 4H, *m*-Ph), 7.54 (d, J=7.77 Hz, 2H, *m*-Ph), 2.71 (s, 6H, *p*-CH_3), 2.69 (s, 3H, *p*-CH_3), 0.60 (s, 9H, $Si(CH_3)_3$), −2.41 (s, 2H, NH). ^{13}C NMR (500 MHz, $CDCl_3$): δ 139.3, 139.0, 137.6, 134.6, 134.5, 127.7, 127.6, 122.3, 121.2, 107.4, 101.8, 98.8, 29.9, 21.7, 0.51. UV–vis (THF, nm): λ_{max} (log ε) 427 (5.46), 527 (3.90), 565 (4.11), 605 (3.16), 663 (3.46). MS (APCI): *m*/*z* 676.8 [M^+ requires 676.30]. Anal. Calcd for $C_{46}H_{40}N_4Si$: C, 81.62; H, 5.96; N, 8.28. Found: C, 81.46; H, 6.21; N, 8.56%.

2.2.2. 5,10,15-Tri-(p-tolyl)-20-phenylethynylporphyrin, **mono-H₂P**

To a solution of 5,10,15-tri-(*p*-tolyl)-20-trimethylsilylethynylporphyrin (51 mg, 0.08 mmol) in THF/CH_2Cl_2 (5:1, 25 mL) was slowly added a solution of tetrabutylammonium fluoride (0.10 mL, 1.0 M in THF) for removing the trimethylsilyl group. A spatula of $CaCl_2$ was added to quench the reaction after 30 min. The reaction mixture was washed with water, the organic layer dried over anhydrous magnesium sulfate, the solvent removed under reduced pressure. The generated 5,10,15-tri-(*p*-tolyl)-20-ethynylporphyrin was combined with 4-iodobenzene (17 mg, 0.08 mmol), tris(dibenzylideneacetone)dipalladium (11 mg, 0.01 mmol) and triphenylarsine (19 mg, 0.06 mmol) in anhydrous THF/triethylamine (1:1, 10 mL) under argon. The reaction mixture was heated at reflux for 14 h under argon. The solvent was evaporated to dryness under reduced pressure. The crude residue was chromatographed on silica gel with CH_2Cl_2/*n*-hexane (1:1) as eluent. After recrystallization from CH_2Cl_2 and methanol, **mono-H_2P** was yielded in 55% (26 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 9.72 (d, J=4.6 Hz, 2H, β-pyrrolic H), 8.92 (d, J=4.71 Hz, 2H, β-pyrrolic H), 8.76 (s, 4H, β-pyrrolic H), 8.08 (d, J=7.81 Hz, 4H, *o*-Ph), 8.03 (m, 4H, (*o*-Ph+*o*-ethynyl Ph)), 7.56 (d, J=7.82 Hz, 4H, *m*-Ph), 7.53 (m, 5H, (*m*-Ph+*m*,*p*-ethynyl Ph)), 2.70 (s, 6H, *p*-CH_3), 2.68 (s, 3H, *p*-CH_3), −2.30 (s, 2H, NH). UV–vis (THF, nm): λ_{max} (log ε) 432 (5.49), 532 (4.00), 573 (4.38), 610 (3.67), 669 (3.96). MS (APCI): *m*/*z* 680.1 [M^+ requires 680.29].

2.2.3. [5,10,15-Tri-(p-tolyl)-20-phenylethynylporphyrin]-zinc(II), **mono-ZnP**

A mixture of **mono-H_2P** (12 mg, 0.018 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (6 mg, 0.035 mmol) in THF (10 mL) was heated at reflux. After 1 h, the solvent was evaporated to dryness under reduced pressure. The residue was extracted with $CHCl_3$ and passed through a silica pad. The solvent of the filtrate was evaporated under reduced pressure. After recrystallization from $CHCl_3$ and methanol, **mono-ZnP** was yielded in 92% (12 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 9.82 (d, J=4.40 Hz, 2H, β-pyrrolic H), 9.01 (d, J=4.40 Hz, 2H, β-pyrrolic H), 8.87 (s, 4H, β-pyrrolic H), 8.08 (d, J=7.98 Hz, 4H, *o*-Ph), 8.03 (m, 4H, (*o*-Ph+*o*-ethynyl Ph)), 7.56 (d, J=7.58 Hz, 4H, *m*-Ph), 7.54 (m, 5H, (*m*-Ph+*m*,*p*-ethynyl Ph)), 2.71 (s, 6H, *p*-CH_3), 2.68 (s, 3H, *p*-CH_3). UV–vis (THF, nm): λ_{max} (log ε) 439 (5.71), 573 (4.25), 621 (4.50). MS (APCI): *m*/*z* 742.5 [$(MH)^+$ requires 742.21].

2.2.4. Tris(free base-porphyrinyl)amine, **tris-H₂P**

To a solution of 5,10,15-tri-(*p*-tolyl)-20-trimethylsilylethynylporphyrin (95 mg, 0.14 mmol) in THF/CH_2Cl_2 (5:1, 25 mL) was slowly added a solution of tetrabutylammonium fluoride (0.17 mL, 1.0 M in THF) for removing the trimethylsilyl group. A spatula of $CaCl_2$ was added to quench the reaction after 30 min. The reaction mixture was washed with water, the organic layer dried over anhydrous magnesium sulfate, the solvent removed under reduced pressure. The generated 5,10,15-tri-(*p*-tolyl)-20-ethynylporphyrin was combined with tris(4-iodophenyl)amine (26 mg, 0.04 mmol), tris(dibenzylideneacetone)dipalladium (35 mg, 0.04 mmol), and triphenylarsine (64 mg, 0.21 mmol) in anhydrous THF/triethylamine (1:1, 20 mL) under argon. The reaction mixture was heated at reflux for 14 h under argon. The solvent was evaporated to dryness under reduced pressure. The crude residue was chromatographed on silica gel with THF/*n*-hexane (2:1) as eluent. After recrystallization from THF and methanol, **tris-H_2P** was yielded in 83% (71 mg). ^1H NMR (500 MHz, $CDCl_3$): δ 9.78 (d, J=4.62 Hz, 6H, β-pyrrolic H), 8.96 (d, J=3.60 Hz, 6H, β-pyrrolic H), 8.78 (s, 12H, β-pyrrolic H), 8.11 (d, J=7.25 Hz, 12H, *o*-Ph), 8.07 (m, 12H, (*o*-Ph+N−Ph)), 7.59 (d, J=7.40 Hz, 12H, *m*-Ph), 7.54 (m, 12H, (*m*-Ph+*N*−Ph)), 2.72 (s, 18H, *p*-CH_3), 2.70 (s, 9H, *p*-CH_3), −2.25 (s, 6H, NH). UV–vis (THF, nm): λ_{max} (log ε) 430 (5.66), 590 (4.90), 677 (4.62). MS (MALDI-TOF): *m*/*z* 2051.3 [M^+ requires 2051.86]. Anal. Calcd for $C_{147}H_{105}N_{13}$: C, 85.98; H, 5.15; N, 8.87. Found: C, 85.65; H, 5.37; N, 8.54%.

2.2.5. Tris(Zn-porphyrinyl)amine, **tris-ZnP**

A mixture of **tris-H_2P** (30 mg, 14.6 μmol) and $Zn(OAc)_2\cdot 2H_2O$ (13 mg, 73 μmol) in THF (20 mL) was heated at reflux. After 1 h, the solvent was evaporated to dryness under reduced pressure. The residue was extracted with $CHCl_3$ and passed through a silica pad. The solvent of the filtrate was evaporated under reduced pressure. After recrystallization from $CHCl_3$ and methanol, **tris-ZnP** was yielded in 92% (30 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.87 (d, J=3.76 Hz, 6H, β-pyrrolic H), 9.05 (d, J=3.93 Hz, 6H, β-pyrrolic H), 8.89 (s, 12H, β-pyrrolic H), 8.11 (d, J=6.86 Hz, 12H, *o*-Ph), 8.07 (m, 12H, (*o*-Ph+N−Ph)), 7.58 (d, J=6.97 Hz, 12H, *m*-Ph), 7.53 (m, 12H, (*m*-Ph+N−Ph)), 2.72 (s, 18H, *p*-CH_3), 2.70 (s, 9H, *p*-CH_3). UV−vis (THF, nm): λ_{max} (log ε) 439 (5.70), 575 (4.48), 635 (4.97). MS (MALDI-TOF): *m/z* 2237.2 [M^+ requires 2237.60]. Anal. Calcd for $C_{147}H_{99}N_{13}Zn_3$: C, 78.69; H, 4.45; N, 8.12. Found: C, 78.34; H, 4.79; N, 8.48%.

2.3. Photophysical measurements

2.3.1. Time-resolved fluorescence lifetime

Time-resolved fluorescence was detected using a time-correlated single photon counting (TCSPC) technique. A home-made cavity-dumped Ti:Sapphire oscillator pumped by a CW Nd:YVO_4 laser (Coherent, Verdi) was used as the excitation light source; this provided ultrashort pulses (100 fs at full-width at half-maximum (fwhm)) and allowed for a high repetition rate (200−400 kHz). The output pulse of the oscillator was frequency-doubled with a second harmonic crystal. The TCSPC detection system consisted of a multichannel plate photomultiplier (Hamamatsu, R3809U-51) with a cooler (Hamamatsu, C4878), a TAC (time-to-amplitude converter) (EG&G Ortec, 457), two discriminators (EG&G Ortec, 584 (signal) and Canberra, 2126 (trigger)), and two wideband amplifiers (Philip Scientific (signal) and a Mini Circuit (trigger)). A personal computer with a multichannel analyzer (Canberra, PCA3) was used for data storage and processing. The overall instrumental response function was about 60 ps (fwhm). The decay fittings were made by using a least-squares deconvolution fitting process (LIFETIME program with an iterative nonlinear least-squares deconvolution procedure developed at the University of Pennsylvania).[15]

2.3.2. Two-photon absorption cross-section ($\sigma^{(2)}$)

Two-photon absorption coefficient were measured by using an open-aperture *Z*-scan method with ∼130 fs pulses at 5 kHz repetition rate generated from a Ti:sapphire regenerative amplifier system (Spectra-Physics, Hurricane). The laser beam was divided into two parts. One was monitored by a Ge photo-diode as intensity reference and the other was used for transmittance measurement. After passing through an f=10 cm lens, the laser beam was focused and passed through a quartz cell. The position of the sample cell could be varied along the laser-beam direction (*z*-axis), so the local power density within the sample cell could be changed under a constant laser power level. The thickness of the cell is 1 mm. The transmitted laser beam from the sample cell was then detected by the same photo-diode as used for reference monitoring. The on-axis peak intensity of the incident pulses at the focal point I_0 was 80 GW/cm^2. 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:

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

where, α_0 is the linear absorption coefficient, l the sample length, and z_0 the diffraction length of the incident beam.

After obtaining the nonlinear absorption coefficient β, the TPA cross-section $\sigma^{(2)}$ of one solute molecule (in units of 1 GM=10^{-50} cm^4 s/photon·molecule) can be determined by using the following relationship:

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

where N_A is the Avogadro constant, d is the concentration of the TPA compound in solution, h is the Planck constant, and ν is the frequency of the incident laser beam.[16]

3. Results and discussion

Octupolar trisporphyrin conjugate **tris-H_2P** (Fig. 1) was synthesized by the Pd(0)-catalyzed Sonogashira cross-coupling reaction of tris(4-iodophenyl)amine[13] with 5,10,15-tri-(*p*-tolyl)-20-ethynylporphyrin generated by the treatment of 5,10,15-tri-(*p*-tolyl)-20-trimethylsilylethynylporphyrin with tetrabutylammonium fluoride. The monomeric porphyrin 5,10,15-tri-(*p*-tolyl)-20-phenylethynylporphyrin (**mono-H_2P**) for the reference was also synthesized from the similar reaction using 4-iodobenzene. The zinc(II) porphyrin derivatives, **mono-ZnP** and **tris-ZnP** were prepared by the standard method using zinc(II) acetate and free base porphyrin derivatives, **mono-H_2P** and **tris-H_2P**, respectively. Reagents and conditions for the syntheses of all porphyrin compounds are summarized in Scheme 1.

All porphyrin compounds were fully characterized by various spectroscopic methods and elemental analysis. In the ^{1}H NMR spectrum of **tris-H_2P**, a set of three resonances with relative intensities of 1:1:2 attributed to the β-pyrrolic protons and the large downfield shifts of the resonances for the triphenylamine core strongly imply **tris-H_2P** having the desired symmetry with a three-fold axis. The ^{1}H NMR spectrum of **tris-ZnP** shows similar resonating patterns except disappearance of a resonance due to the internal N−H protons in the porphyrin moiety upon metalation. Data of mass spectra and elemental analyses for all the porphyrin compounds are also consistent with their molecular formulations.

To explore geometrical features of trisporphyrin conjugates, we have performed semi-empirical AM1 calculations on **tris-H_2P** using a suite of Gaussian 03 program.[17] The optimized geometry of **tris-H_2P** reveals that **tris-H_2P** adopts a propeller-shaped structure as shown in Figure 2. The nitrogen of triphenylamine core is trigonal planar and the phenyl rings are twisted by about 45°. The porphyrin planes and the phenyl rings

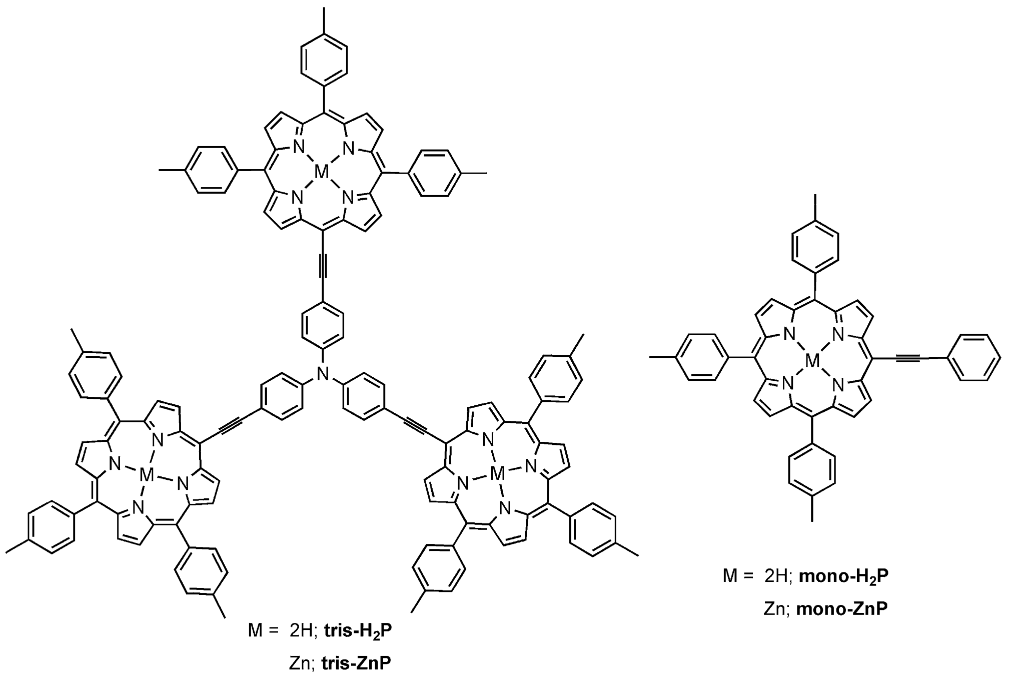
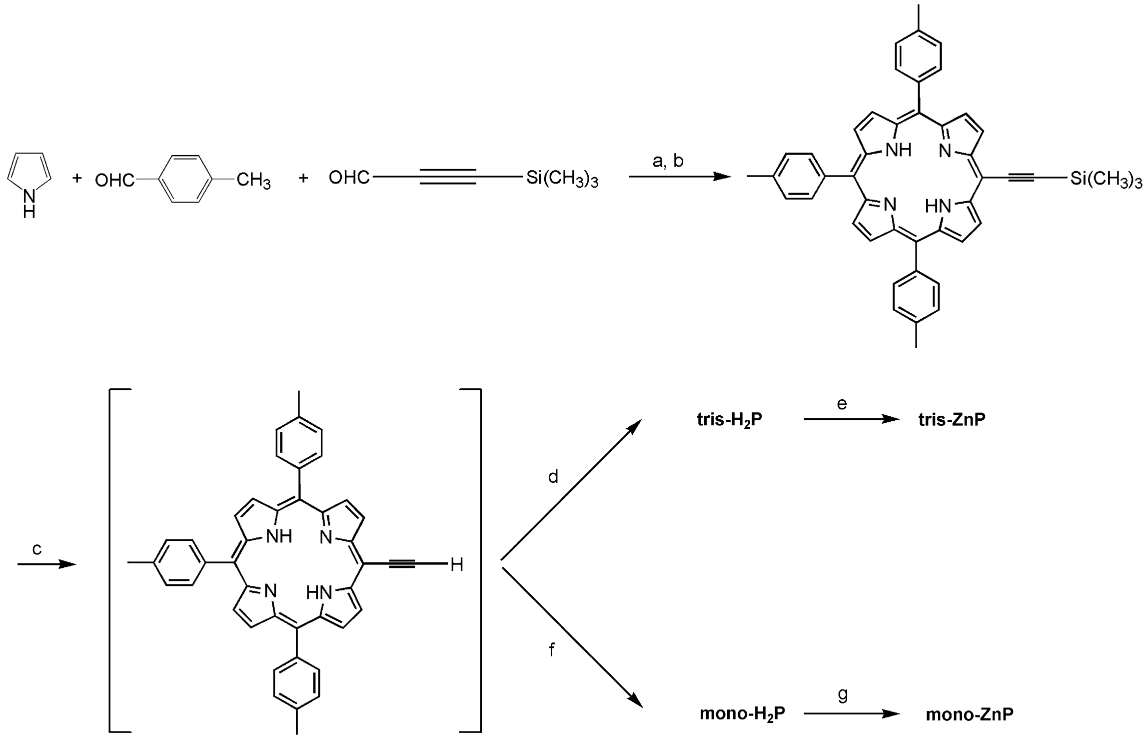


Figure 1. Chemical structures of trisporphyrin conjugates (**tris-H_2P** and **tris-ZnP**) and the monomeric porphyrins (**mono-H_2P** and **mono-ZnP**).

of triphenylamine core are apparently coplanar through the alkynyl bridges. The dihedral angles between the two planes are small estimating about 17°. The porphyrin wing planes in the propeller-shaped **tris-H_2P** are slightly tilted by ~28° with respect to a plane composed of the core nitrogen and the three carbons at *p*-position in the triphenylamine. The center-to-edge distance, that is, the distance between the nitrogen of triphenylamine core and the farthest *meso* carbon of the porphyrin moiety, is also estimated to be about 1.5 nm. Based on the optimized geometry, **tris-H_2P** can be thus regarded as a nano-



Scheme 1. Syntheses of trisporphyrin conjugates (**tris-H_2P** and **tris-ZnP**) and the monomeric porphyrins (**mono-H_2P** and **mono-ZnP**). Reagents and conditions: (a) $BF_3\cdot OEt_2$, $CHCl_3$, rt; (b) DDQ, rt (13%); (c) $(Bu_4N)F$, THF/CH_2Cl_2 (5:1) (quantitative generation); (d) tris(4-iodophenyl)amine, tris(dibenzylideneacetone)dipalladium, $AsPh_3$, THF/Et_3N (1:1), reflux (83%); (e) $Zn(OAc)_2\cdot 2H_2O$, THF, reflux (92%); (f) 4-iodobenzene, tris(dibenzylideneacetone)dipalladium, $AsPh_3$, THF/Et_3N (1:1), reflux (55%); (g) $Zn(OAc)_2\cdot 2H_2O$, THF, reflux (92%).

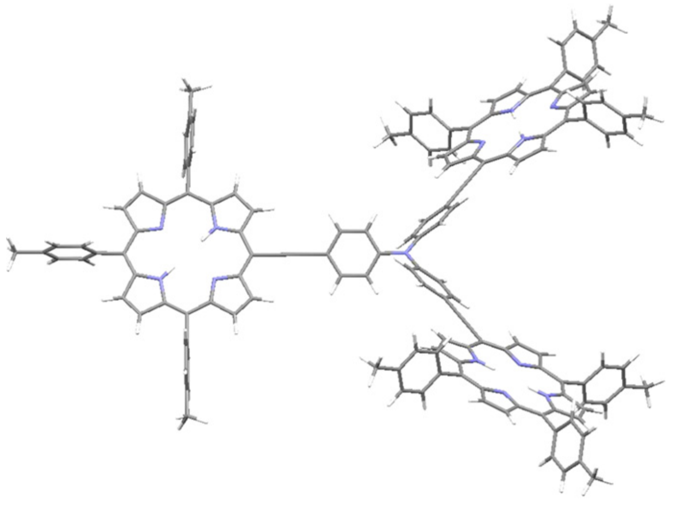


Figure 2. The optimized geometry of **tris-H_2P** by semi-empirical AM1 calculations using a suite of Gaussian 03 program.

sized octupolar fluorophore with extended π-conjugation over the three porphyin wings through the triphenylamine core.

Figure 3 shows the UV–vis absorption spectra of trisporphyrin conjugates in comparison with those of corresponding monomers. In the UV–vis spectra of free base porphyrin derivatives, the Soret band of **tris-H_2P** is remarkably broadened with a absorption maximum (full-width at half-maximum, fwhm=41 nm; λ_{max}=430 nm) relative to that of **mono-H_2P** (fwhm=15 nm; λ_{max}=432 nm). Interestingly, the typical porphyrin four-band spectrum in the Q-region observed in **mono-H_2P** transforms into a two-band spectrum in **tris-H_2P**. The absorbance of Q-bands in **tris-H_2P** is much stronger and the lowest-energy Q-band shifts to the red (663→677 nm) compared to the Q-bands in **mono-H_2P**. The Soret band in the UV–vis absorption spectrum of **tris-ZnP** (fwhm=38 nm; λ_{max}=439 nm) is similarly broadened comparing that of **mono-ZnP** (fwhm=13 nm; λ_{max}=439 nm). The absorption of the lowest-energy Q-band is stronger than that of the higher-energy Q-band in **tris-ZnP**, contrasting those in **mono-ZnP**. As described above, the ground-state absorption of trisporphyrin conjugate **tris-H_2P** or **tris-ZnP** remarkably differs from that of the corresponding monomer **mono-H_2P** or **mono-ZnP**. This is in sharp contrast with the case of the phenylene ethynylene linked C_3-symmetric tetraarylporphyrin trimers.[12] The ground-state absorption of phenylene ethynylene linked tetraarylporphyrin trimers is nearly the same as that of the porphyrin monomer, suggesting electronic communication between the porphyrin chromophores is very weak. It is thus manifested that the three porphyrin wings electronically communicate to each other through the C_3-triphenylamine core in **tris-H_2P** or **tris-ZnP**. The ground-state absorption showing strong electronic coupling between the porphyrin chromophores of **tris-H_2P** or **tris-ZnP** is also consistent with the predicted geometrical features of **tris-H_2P**.

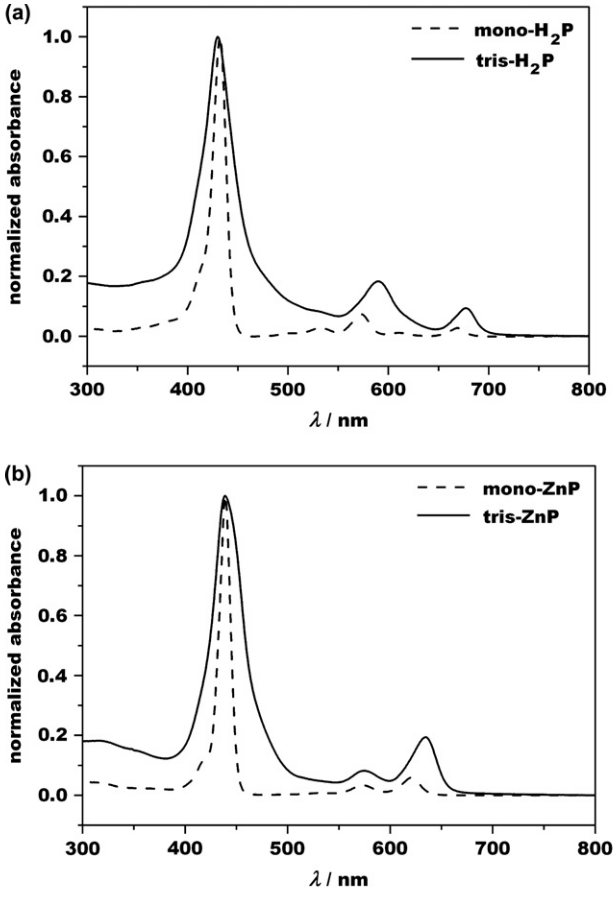


Figure 3. Absorption spectra obtained in THF of (a) **mono-H_2P** (dashed line) and **tris-H_2P** (solid line), and (b) **mono-ZnP** (dashed line) and **tris-ZnP** (solid line).

We also carried out fluorescence spectroscopy to further investigate photophysical properties of octupolar trisporphryin conjugates. The steady-state Q-band emissions by the excitation at 420 nm in **tris-H_2P** exhibit two bands at 685 and 757 nm, which are shifted to lower energy than those of **mono-H_2P** at 673 and 745 nm (Fig. 4a and b). In the emission spectra of Zn porphyrin derivatives, similar red-shifts were observed; at 645 and 712 nm in **tris-ZnP**, and at 629 and 684 nm in **mono-ZnP** (Fig. 4c and d). Photophysical characteristics for monomers and trisporphyrin conjugates are summarized in Table 1. Trisporphyrin conjugates exhibit the greater Stokes shifts and the higher fluorescence quantum yields than the corresponding monomers. The fluorescence decay profiles (λ_{exc}=420 nm, Fig. 5) of monomers and trisporphyrin conjugates in THF measured by time-correlated single photon counting (TCSPC) technique also revealed that the fluorescence lifetimes for both trisporphyrin conjugates (6.9 ns for **tris-H_2P** and 1.5 ns for **tris-ZnP**) are shorter than those for corresponding monomers (9.3 ns for **mono-H_2P** and 1.9 ns for **mono-ZnP**). The greater Stokes shift in trisporphyrin conjugates together with their higher fluorescence quantum yields and shorter fluorescence lifetimes relative to those in the monomers imply that conformational variations of the propeller-shaped trisporphyrin conjugates in solution would be noticeably significant. Conformations for the propeller-shaped trisporphyrin conjugates can be varied in a range of torsional twist angles between the porphyrin wing planes and the triphenylamine core, leading to a distribution in the efficiency of overall π-conjugations in the propeller-shaped trisporphyrin conjugates.[18]

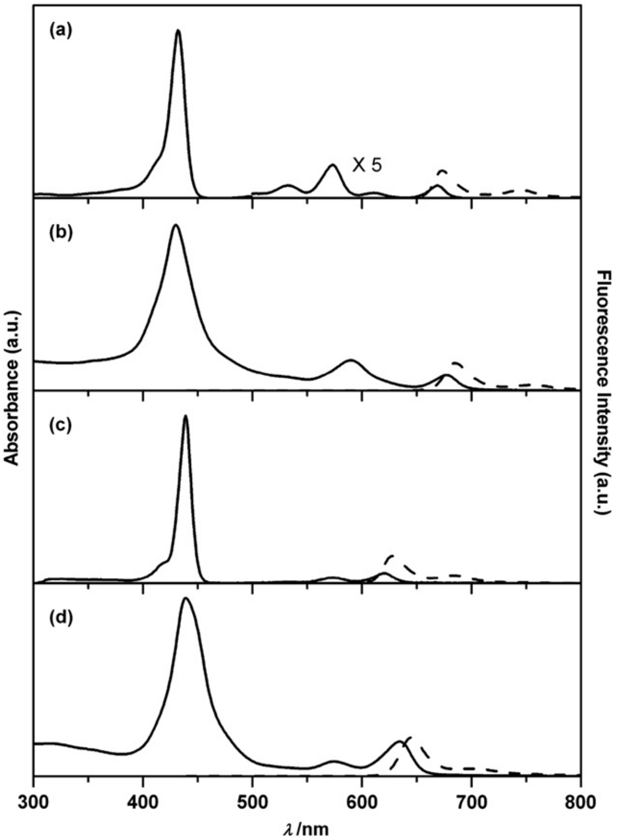


Figure 4. Absorption (solid line) and fluorescence (λ_{exc}=430 nm, dashed line) spectra obtained in THF of (a) **mono-H_2P**, (b) **tris-H_2P**, (c) **mono-ZnP**, and (d) **tris-ZnP**.

Table 1
Photophysical characteristics and TPA cross-section values of **mono-H_2P**, **tris-H_2P**, **mono-ZnP**, and **tris-ZnP**

	Stokes shift (cm^{-1})	Φ_F (λ_{max}/nm)[a]	τ_s[b] (ns)	$\sigma^{(2)c}$ (GM)
mono-H_2P	90	0.117 (673)	9.3	540 (±200)
tris-H_2P	194	0.133 (685)	6.9	8100 (±500)
mono-ZnP	204	0.063 (629)	1.9	630 (±200)
tris-ZnP	245	0.095 (645)	1.5	11,800 (±500)

[a] Fluorescence quantum yield; numbers in parentheses indicates a peak position.

[b] Excited singlet-state lifetime.

[c] TPA cross-section; 1 GM=10^{-50} cm^4 s/photon·molecule; excitation at 800 nm.

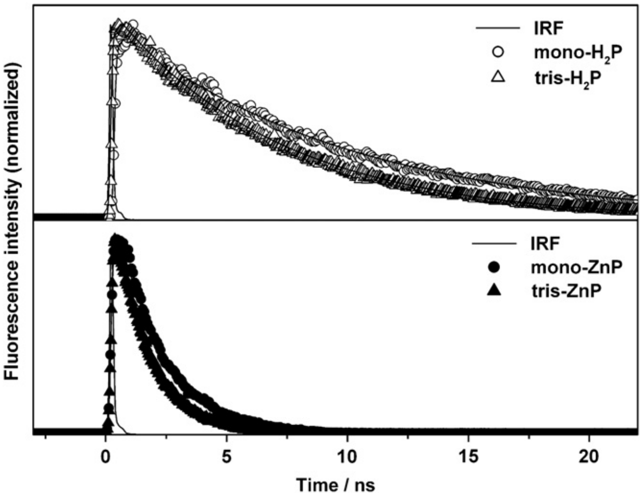


Figure 5. Time-resolved fluorescence decay profiles of **mono-H_2P**, **tris-H_2P**, **mono-ZnP**, and **tris-ZnP** measured by using the excitation wavelength 420 nm in THF. IRF represents the instrument response function of our TCSPC system.

Finally, the TPA cross-section $\sigma^{(2)}$ values of the monomers and the trisporphyrin conjugates were measured in THF by using an open-aperture *Z*-scan method with ~130 fs pulses and excitation at 800 nm, where no ground-state absorption was observed. Figure 6 shows the *Z*-scan curves for the monomers and the trisporphyrin conjugates. The nonlinear absorption properties of the trisporphyrin conjugates are strongly enhanced comparing with those of the monomers as can be noticed immediately. Thus the trisporphyrin conjugates exhibit much larger TPA cross-section values in comparison with the monomers (Table 1). For example, the TPA cross-section $\sigma^{(2)}$ value of **tris-ZnP** (11,800 GM) exceeds that of **mono-ZnP** (630 GM) by about 20 times. The TPA cross-section values of **tris-ZnP** and **tris-H_2P** are also comparable or larger than those of conjugated porphyrin oligomers with one-dimensional dipolar structures.[9] Therefore, our overall studies lead to the conclusion that remarkably large TPA cross-section values for trisporphyrin conjugates are evidently attributed to the intrinsic nature of the octupolar π-conjugations over the three porphyin wings through the triphenylamine core in the propeller-shaped trisporphyrin conjugates.

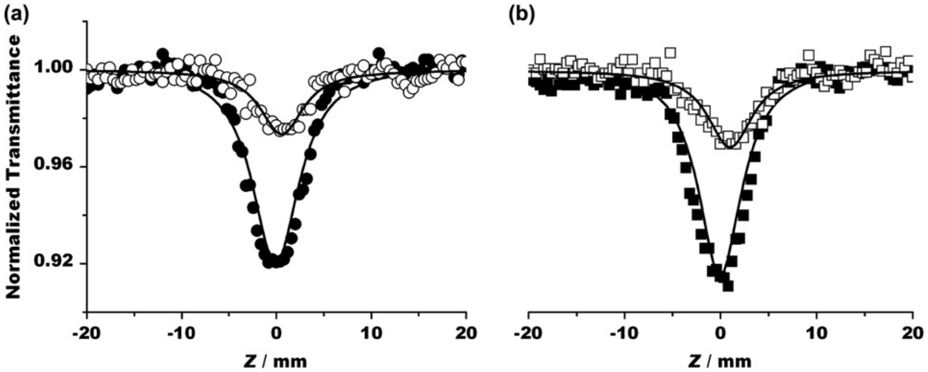


Figure 6. Open-aperture femtosecond *Z*-scan traces of (a) **mono-H_2P** (open circle) and **tris-H_2P** (filled circle), and (b) **mono-ZnP** (open square) and **tris-ZnP** (filled square) in THF. The peak irradiance at the focal point is 80 GW/cm^2 at 800 nm. The solid lines are the best fitted curves of experimental data.

4. Conclusion

In this report, we have successfully synthesized the octupolar trisporphyrin conjugates using a functionalized triphenylamine core and three *meso*-ethynylporphyrin wings. Our photophysical and TPA studies strongly manifest that the trisporphyrin conjugates are promising octupolar fluorophores with effective π-conjugation over the porphyrin wings through the octupolar core. Such octupolar porphyrin conjugates can afford valuable advantages in applications of TPA materials such as in photodynamic therapy and imaging of biological processes.

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