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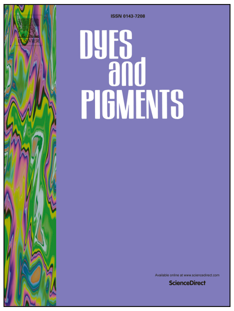

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Donor-π-acceptor type porphyrins with large two-photon absorption cross section

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Abstract: The third-order nonlinear optical properties of 5-(4-pyrenylalkynylphenyl)-10,15,20-tris(4-octyloxyphenyl)porphyrin (**1**) and 5-(4-iodophenyl)-10,15,20-tris(4-octyloxyphenyl)porphyrin (**2**) have been comparatively investigated with symmetrical 5,10,15,20-tetra(4-octyloxyphenyl)porphyrin (**3**) and pyrene (**4**) as reference using femtosecond-pulsed *Z*-scan technique. Due to the D-π-A structure, both A_3B type asymmetric porphyrins **1** and **2** were revealed to exhibit larger two-photon absorption (2PA) cross sections over the symmetrical analogue **3** with the largest value of 6.1×10^5 GM revealed for **1** because of the intramolecular energy transfer from the excited pyrene moiety to the porphyrin moiety as indicated by the fluorescence spectroscopic result. The good 2PA properties of these A_3B type porphyrins with ultrafast response indicate their good application potential in nonlinear photonic devices.

Keywords: Porphyrin; Pyrene; Two-photon absorption; Donor-π-acceptor; Fluorescence resonance energy transfer; Femtosecond-pulsed Z-scan technique

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1. Introduction

Porphyrins are versatile functional pigments with a wide range of applications not only because of their two-dimensional conjugated electronic molecular structure but also associated with their versatile functionalization at the peripheral positions and the central metal ions. Recently, porphyrins have attracted considerable attention due to their potential applications in 3-D microfabrication, optical power limiting, two-photon photodynamic therapy, and fluorescence microscopy [1-5]. However, most of porphyrins have relatively low two-photon absorption (2PA) cross sections (<100 GM) [6-8], therefore limiting their usefulness in 2PA applications. In order to improve the 2PA cross section, considerable efforts have been continuously devoted to the exploration of novel porphyrin derivates [9,10] including porphyrin arrays [11], dimers [12,13], self-assembled porphyrins [14,15], and expanded porphyrins [16,17]. Despite great efforts paid in this direction, most of the newly developed porpphyrin derivatives still exhibit the 2PA cross sections in the range of 10^3~10^6 GM as revealed by the Z-scan measurements under the excitation of femtosecond laser pulses. However, a number of factors have been found to influence the 2PA magnitudes, among which π-electronic delocalization plays important role [18,19]. As a consequence, special attention nowadays is given to the molecule with donor and acceptor sets intervened by a π-conjugation system. Such systems carry an electron donating group on one side of the porphyrin macrocycle and an electron withdrawing group on the other side. The effect of varying the electron-donating or electron-accepting intensity of the end groups as well as introducing additional

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groups to perturb the charge redistribution has been considered in designing new molecular structures [20], resulting in a series of the donor-π-acceptor (D-π-A) type systems such as A_2B_2 and A_2BC porphyrins showing excellent nonlinear optical (NLO) properties with large 2PA cross section. For example, Osuka reported 5,15-A_2BC-bis(azulenylethynyl) zinc(II) porphyrins with the maximum 2PA cross section value of 8030 GM at 1400 nm [20]. Porphyrins with 2,4-bis(dimethylamino)phenylethynyl donor and various acceptor groups were calculated using density functional theory (B3LYP) to evaluate the 2PA cross sections between 400 and 3600 GM at 1300-1500 nm [21]. A similar study on 5,15-A_2B_2 porphyrins with various donor or acceptor groups gave the values of 2PA cross sections between 300 and 3300 GM [22]. However, little research is focused on the 2PA properties of A_3B type asymmetric porphyrins with donor and acceptor groups.

In the present paper, the third-order nonlinear optical properties of 5-(4-pyrenylalkynylphenyl)-10,15,20-tris(4-octyloxyphenyl)porphyrin (**1**) and 5-(4-iodophenyl)-10,15,20-tris(4-octyloxyphenyl)porphyrin (**2**) have been comparatively investigated with symmetrical 5,10,15,20-tetra(4-octyloxyphenyl)porphyrin (**3**) and pyrene (**4**) as reference using femtosecond-pulsed *Z*-scan technique, Fig. 1. Due to the D-π-A structure, both A_3B type asymmetric porphyrins **1** and **2** were revealed to exhibit larger 2PA cross sections over the symmetrical analogue **3** with the largest value of 6.1×10^5 GM revealed for **1** because of the intramolecular energy transfer from the excited pyrene

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moiety to the porphyrin moiety as indicated by the fluorescence spectroscopic result. The good 2PA properties of these A_3B type porphyrins with ultrafast response indicate their good application potential in nonlinear photonic devices.

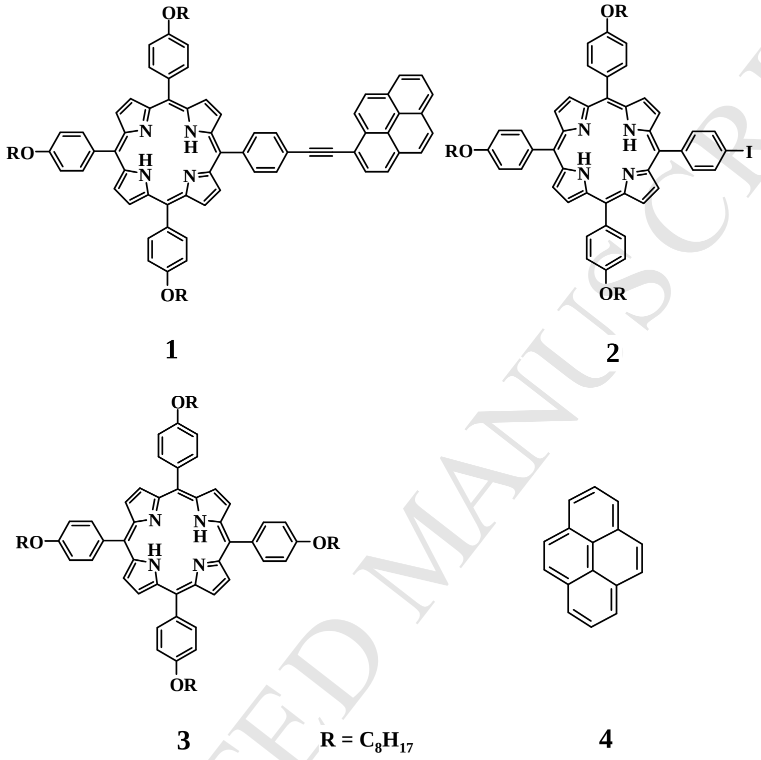

Fig. 1. Schematic molecular structures of A_3B type 5-(1-pyrenylalkynylphenyl)-10,15,20-tris (4-octyloxyphenyl)porphyrin (**1**) and 5-(4-iodophenyl)-10,15,20-tris (4-octyloxyphenyl)porphyrin (**2**) with 5,10,15,20-tetra (4-octyloxyphenyl)porphyrin (**3**) and pyrene (**4**) as references.

2. Results and discussion

2.1 Synthesis

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In order to obtain suitable D-π-A structure with expanded π-electronic delocalization and good solubility in most organic solvent, a A_3B type 5-(4-pyrenylalkynylphenyl)-10,15,20-tris(4-octyloxyphenyl)porphyrin (**1**) was designed and synthesized. The asymmetric 5-(4-iodophenyl)-10,15,20-tris(4-octyloxyphenyl)porphyrin (**2**) substituted with three 4-octyloxyphenyl groups and one 4-iodophenyl group in the meso-positions was synthesized according to the method reported previously [25]. Subsequently, as shown in Fig. 2, porphyrin **1** was prepared from the Pd(0)-catalyzed cross-coupling reaction of porphyrin **2** with 1-ethynylpyrene [23] under mild basic condition without using any copper for the purpose of avoiding the oxidative dimerization of the alkyne component and metalation of the porphyrin unit [24]. In addition, the symmetric porphyrin **3** substituted with four 4-octyloxyphenyl groups in the meso-positions was also synthesized according to the established Adler-Longo method as the reference compound [26,27]. All these porphyrin compounds were purified and isolated by silica-gel column chromatography. The newly prepared porphyrins were unambiguously confirmed by various spectroscopic methods in addition to elemental analysis.

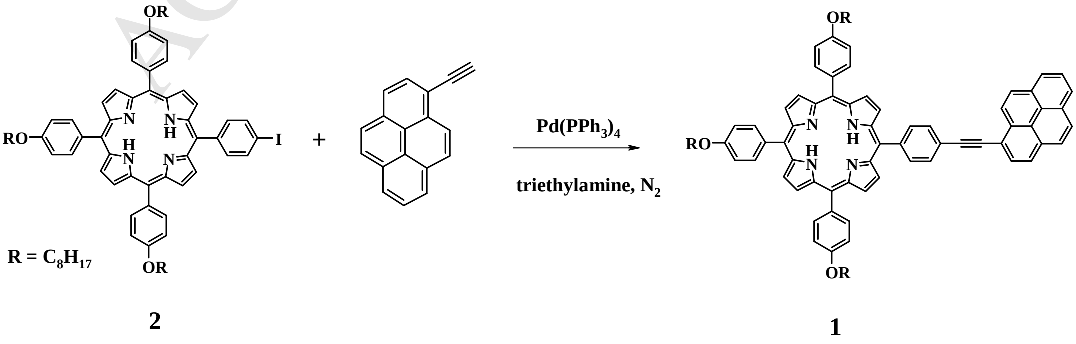

Fig. 2. Synthesis of 5-(1-pyrenylalkynylphenyl)-10,15,20-tris (4-octyloxyphenyl) porphyrin (**1**).

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2.2. Electronic absorption spectra

The electronic absorption spectra of A_3B type asymmetric porphyrin **1** and **2** in $CHCl_3$ are shown in Fig. 3. For comparative purpose, the electronic absorption spectra of the reference compounds **3** and **4** are also shown in the same figure. It is worth noting that because of the poor solubility in $CHCl_3$, the spectrum of **4** was recorded in methanol. Compared with the symmetrical porphyrin **3**, the absorption spectra of the asymmetric porphyrins **1** and **2** show similar Soret band at 423-425 nm and Q bands between 500 and 660 nm, in line with the results reported previously [28,29]. In addition, the common bands at 280 and 370 nm for porphyrin **1** can be ascribed to the absorption of pyrenyl group. The absorption spectrum of **1** is identical with the sum of the spectra of porphyrin **3** and pyrene **4**, indicating that there is no appreciable interaction between porphyrin moiety and pyrenly group in compound **1** in the ground-state [30]. In comparison with porphyrin **3**, little red-shift takes place on the Soret band of porphyrin **1**, by 2 nm, which demonstrates that the pyrene substituent is a stronger electron donor than that of OC_8H_{17} substituent.

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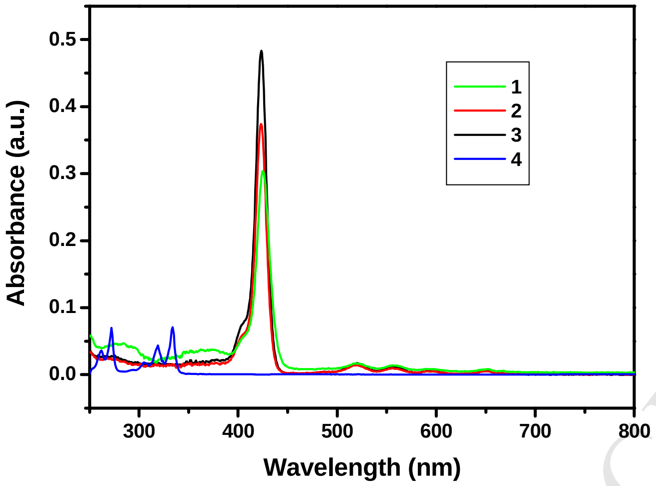

Fig. 3. The electronic absorption spectra of A_3B type porphyrin **1** and **2** with reference porphyrin **3** and pyrene **4** recorded at room temperature. The concentrations were held at 10^{-6} mol/L.

2.3 Fluorescence spectra

Figs. 4 and 5 show the fluorescence emission spectra of A_3B type asymmetric porphyrin **1** and **2** as well as **3** and **4** excited at 410 and 270 nm, respectively, with their concentrations being kept constant at 10^{-6} mol/L. As shown in Fig. 4, the fluorescence spectra of asymmetric porphyrin **1** and **2** showed similar emission bands at about 660 nm compared with the symmetrical porphyrin **3** when porphyrin was selectively excited at 410 nm, which suggest the porphyrin origin of these emission bands [28,31-33].

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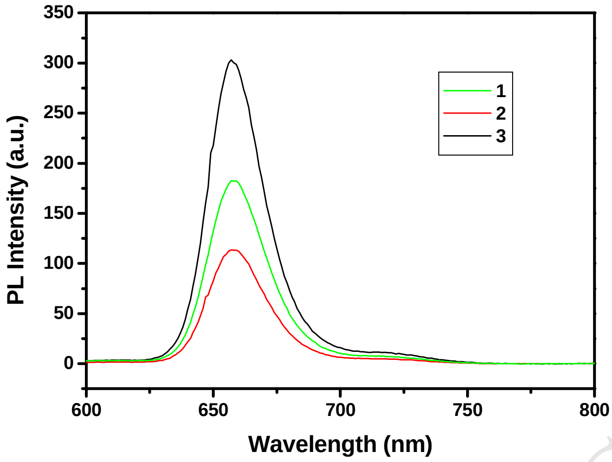

Fig. 4. Fluorescence emission spectra of A_3B type porphyrin **1** and **2** with reference porphyrin **3** recorded at room temperature. The concentrations were held constant to 10^{-6} mol/L for all of the species. λ_{ex} = 410 nm.

As shown in Fig. 5(a), excitation of **4** at 270 nm results in the expected emission from the pyrene with intense peaks at 380 and 392 nm [31]. However, when the pyrene unit in porphyrin **1** was selectively excited at 270 nm, the intense fluorescence peak of pyrene was significantly quenched. Simultaneously, the characteristic emission peak of porphyrin at 660 nm is observed in porphyrin **1**, Fig. 5(b). This is, however, not true for porphyrins **2** and **3** since no fluorescence signals were detected in both cases. These results indicate the efficient fluorescence resonance energy transfer (FRET) from the pyrene donor to the porphyrin acceptor due to the rigid molecular structure as well as the good overlap between emission of the pyrene group and absorption of the porphyrin unit in **1**. The fluorescence excitation spectroscopic result gives further confirmation for the presence of FRET in porphyrin **1**. As shown in Fig. 6, an obvious band at 280 nm attributed to pyrenyl group and a series of bands

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between 400-600 nm attributed to porphyrin are observed for **1**. However, only characteristic porphyrin bands are observed for porphyrins **2** and **3**.

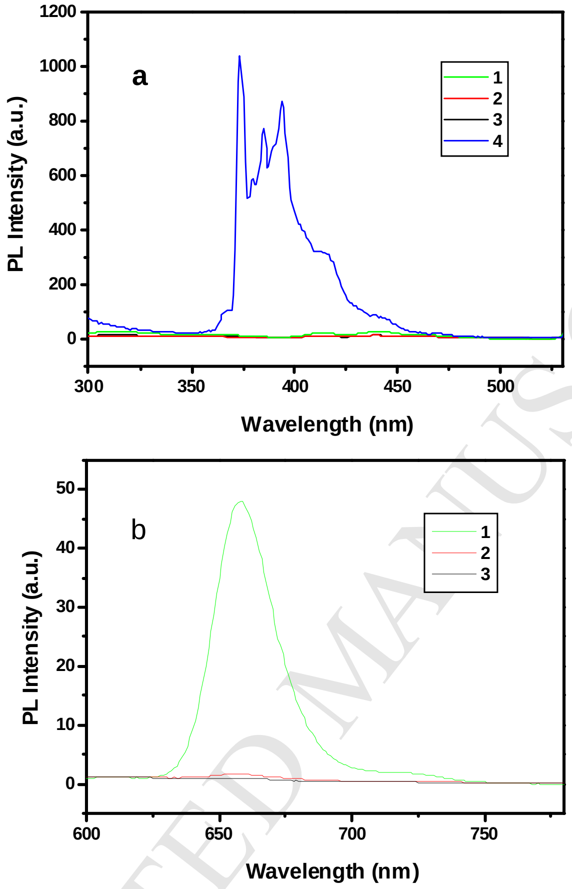

Fig. 5. Fluorescence emission spectra of A_3B type porphyrin **1** and **2** with reference porphyrin **3** and pyrene **4** recorded at room temperature. The concentrations were held constant to 10^{-6} mol/L for all of the species. λ_{ex} = 270 nm.

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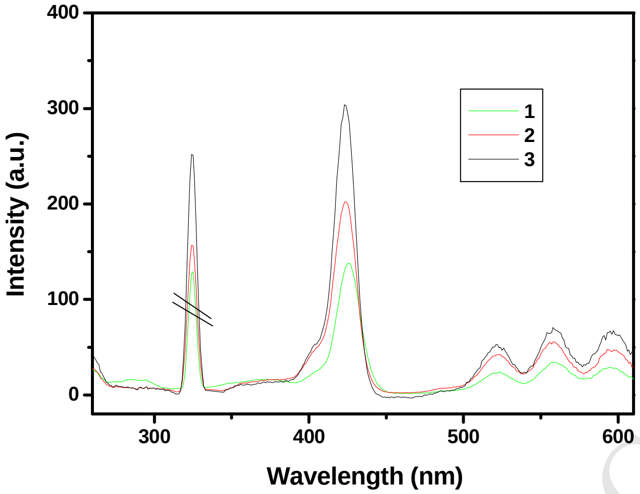

Fig. 6. Excitation spectra of A_3B type asymmetric porphyrin **1** and **2** with reference symmetric porphyrin **3** recorded at room temperature. λ_{em} = 650 nm.

*2.4 Molecular structure of A_3B type porphyrin **1***

To obtain the information about the molecular structure for A_3B type porphyrin **1**, PM3 method [35,36] in Gaussian 98W [37] was carried out on the basis of simplified molecular models in which the octyloxy groups are replaced with methyloxy groups on the porphyrin unit. The optimized structure for **1** obtained is shown in Fig. 7. It appears that the meso-phenyl moiety and the pyrenyl moiety are apparently coplanar through the alkynyl bridge. The porphyrin ring is approximately vertical to the meso-phenyl moiety and the pyrenyl group. Obviously the D-π-A system gets expanded in porphyrin **1**, resulting in the elongation of the π-conjugation length by introducing a pyrene group to porphyrin linked by ethynyl bond.

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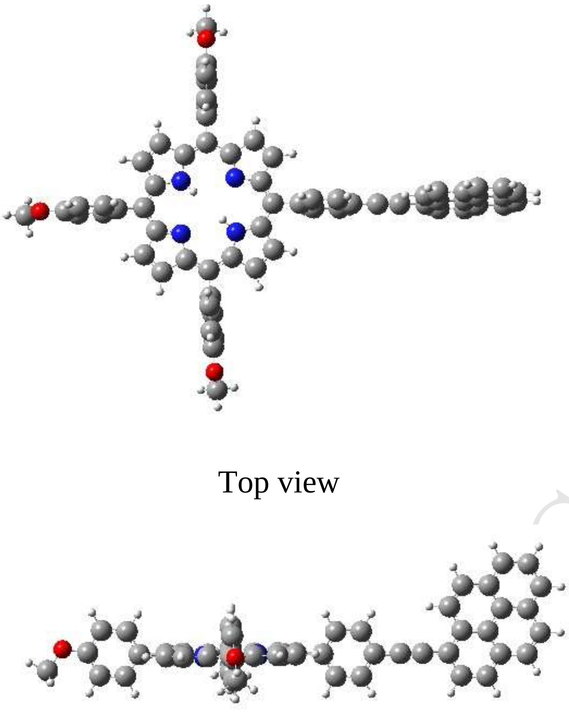

Fig. 7. PM3 method optimized structure of A_3B type porphyrin **1** in the top and side view. The three OC_8H_{17} groups attached on the meso-phenyls of porphyrin are replaced by OCH_3 groups for clarity.

2.5 2PA properties

Open-aperture Z-scan measurements were carried out for the solution of asymmetric porphyrins **1** and **2** as well as symmetrical porphyrin **3** in $CHCl_3$ and pyrene (**4**) in methanol with the concentrations of 10^{-3} mol/L contained in 1 mm thick quartz cell. As shown in Fig. 8, all Z-scan traces display a symmetrical valley with respect to the focus, suggesting that all these compounds in respective solution exhibit the positive nonlinear absorption in nature. Interestingly, the experimental data are in good agreement with the theoretical fitting using Z-scan theory as described in literature [38], Fig. 8. At the end of this section, it is noteworthy that for pure chloroform or methanol in quartz cell, the nonlinear absorption effect can be safely ignored because no peak or valley was observed according to the open-aperture Z-scan experiments.

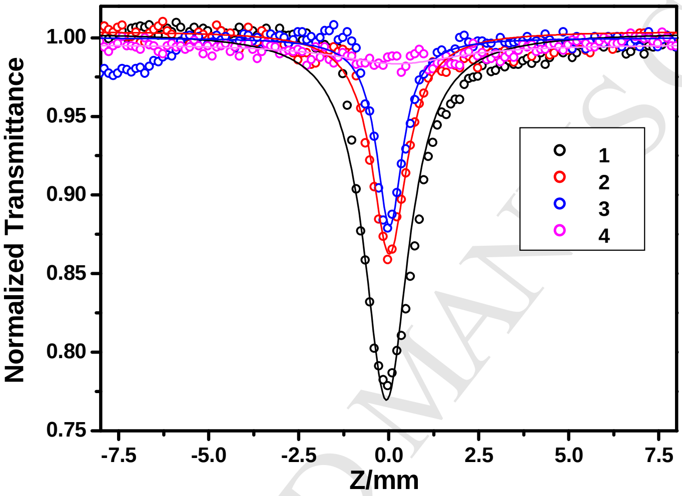

Fig. 8. Z-scan data for A_3B type porphyrin **1** and **2** with reference porphyrin **3** and pyrene **4** obtained under an open-aperture configuration. The concentration of them is 10^{-3} mol/L. The dots are the experimental data while the solid curves are the theoretical fit.

As shown in Fig. 3, all porphyrins exhibit strong absorption band centered at 423-425 nm, resulting in the highly transparent nature for their $CHCl_3$ solution in the near infrared range. As a consequence, the nonlinear absorption effect measured at the wavelength of 800 nm is only able to originate from 2PA. By best fittings between the measured Z-scan traces and the Z-scan theory for characterizing two-photon absorber

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[39], the 2PA coefficients were extracted with β = 0.148 and 0.076 for the asymmetric A_3B type porphyrin **1** and **2** and 0.062 cm/GW for the symmetrical porphyrin **3**, respectively. Furthermore, according to the formula $\sigma_{2PA} = \hbar\omega\beta/N$, where $\hbar\omega$ is the incident photon energy, and N is the number density of sample in solution the 2PA coefficient was converted into the 2PA cross section with the value of σ_{2PA} at 800 nm, 6.1×10^{-45} cm^4•s•$photon^{-1}$ and 3.1×10^{-45} cm^4•s•$photon^{-1}$ for porphyrin **1** and **2** and 2.5×10^{-45} cm^4•s•$photon^{-1}$ for **3,** respectively. According to 1 GM = 10^{-50} cm^4•s•$photon^{-1}$, the values of σ_{2PA} at 800 nm are estimated to be 6.1×10^5 GM for **1**, 3.1×10^5 GM for **2**, and 2.5×10^5 GM for **3**. In spite of the obvious NLO absorptive effect of the porphyrin, no obvious NLO absorption was observed for pyrene (**4**).

For comparative reason, some of corresponding results for porphyrin and porphyrin derivatives including monomer porphyrins [40], porphyrin arrays, self-assembled porphyrins and expanded porphyrins reported previously have been listed in Table 1. As shown in Table 1, both A_3B type asymmetric porphyrins **1** and **2** exhibit large 2PA cross sections. Their σ_{2PA} values are even on the same order of magnitude with porphyrin arrays [11,15], self-assembled porphyrins [14,16], expanded porphyrins [17], and trisporphyrins [41] reported previously, indicating that they are excellent candidates for 2PA materials.

Table 1 Optical parameters of selected 2PA compounds.

Compounds	σ_{2PA} *(GM)*	*Technique*	*λ (nm)*	*Solvent*	*Reference*
H_2TPP	16	Z-scan fs	810	$CHCl_3$	42

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CuTPP	101	Z-scan fs	810	$CHCl_3$	42
Conjugated bis-(imidazolylporphyrin)	4.4×10^5	Z-scan fs	873	$CHCl_3$	16
Expanded porphyrins	0.8×10^5	Z-scan fs	780	CH_2Cl_2	17
Porphyrin arrays	0.9×10^4	Z-scan fs	800	toluene	11
Self-assembled porphyrins	7.6×10^3	Z-scan fs	887	$CHCl_3$	14
tris-ZnPor	1.18×10^5	Z-scan fs	800	THF	41
A_3B type porphyrin **1**	6.1×10^5	Z-scan fs	800	$CHCl_3$	This work
A_3B type oorphyrin **2**	3.1×10^5	Z-scan fs	800	$CHCl_3$	This work
Symmetric porphyrin **3**	2.5×10^5	Z-scan fs	800	$CHCl_3$	This work

Previous theoretical and experimental results have demonstrated that organic molecules with strong electron donor and electron acceptor groups that are connected by a large conjugated π-electron system should have high nonlinear effects [41,42]. As shown in Fig. 1, the pyrene unit serves as donor and the three octyloxy groups of porphyrin serve as accepter to form a D-π-A system in porphyrin **1**. Similarly, iodine substituent serves as acceptor and the three octyloxy groups of porphyrin serve as donors in porphyrin **2**. These two A_3B type porphyrins provide the structure with highly delocalized π-electron system, which induces the enhancement of 2PA response. It is worth noting that both A_3B type asymmetric porphyrins **1** and **2** exhibit larger 2PA cross sections over the symmetrical analogue **3**.

Pyrenyl group-substituted A_3B type porphyrin **1** shows more excellent 2PA property than porphyrin **2**. Several factors are considered to be responsible for the enhancement of 2PA cross section. The expansion of the D-π-A system by

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introducing a pyrenyl group to porphyrin linked by ethynyl group is believed to play an important role in contributing to increasing the σ_{2PA} value of porphyrin **1**. In addition, due to the good overlap between the emission of pyrenyl group and the absorption of porphyrin, the pyrenyl group transfers energy with high efficiency to the porphyrin unit in porphyrin **1**, which is another factor for leading to the large σ_{2PA} value of porphyrin **1**. In addition, previous research has proved that elongating the effective π-conjugation length is effective to improve 2PA behavior [20,41,42]. Since the alkynyl bond increases the conjugated path of porphyrin **1**, the σ_{2PA} value of porphyrin **1** is larger than that of porphyrin **2**.

3. Experimental Section

3.1 Materials and measurements

Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200-300 mesh) with the indicated eluents. CH_2Cl_2 and triethylamine were purified by distillation over CaH_2. All other reagents and solvents were used as received. The compound 1-ethynylpyrene was prepared according to the published procedures [23]. 5-(4-iodophenyl)-10,15,20-tris(4-octyloxyphenyl) porphyrin (**2**) was prepared according to the method we have reported previously [25].

^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$. Spectra were referenced internally by using the residual solvent resonance (δ

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= 7.26 for $CDCl_3$) relative to $SiMe_4$. Electronic absorption spectra were recorded with a Shimadzu UV-3600 spectrophotometer. Fluorescence experiments were performed with a RF-5301 PC spectrofluorophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses for C, H and N were performed with a Vario EL III elemental analyzer.

3.2 2PA measurements

The 2PA properties of asymmetric porphyrin **1** and **2** with symmetrical porphyrin **3** and pyrene (**4**) were measured by using an open-aperture Z-scan method [38]. The laser source for the experiments was a Ti: sappire regenerative amplifier (Coherent Inc.), operating at 800 nm wavelength with a pulse duration of 170 fs and a repetition rate of 1 kHz. The laser pulses had near-Gaussian spatial and temporal profiles. In the Z-scan measurements, the laser beam was focused by a lens with a 150 mm focal length, producing the beam waist at the focus $w_0 = 15$ μm ± 2 and the corresponding Rayleigh length is 0.88 μm. To carry out Z-scan measurements, we perform the Z-scan measurements at the intensity of $I_0 = 132.96$ GW/cm^2, the sample was scanned across the focus along the optical axis using a computer-controlled stage, while the transmitted pulse energies were probed by a detector, producing the open-aperture Z-scan trace. The Z-scan system was calibrated with a piece of cadmium sulfide bulk crystal and the experimental uncertainty should be within ±20%.

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*3.3 Preparation of 5-(1-pyrenylalkynylphenyl)-10,15,20-tris (4-octyloxyphenyl) porphyrin (**1**)*

A deaerated solution of pophyrin **2** (0.05 mmol, 56 mg) in 5 mL of triethylamine and CH_2Cl_2 (1:1) was stirred with 5 mg (0.005 mmol) of $Pd(PPh_3)_4$ at room temperature for 15 min under nitrogen atmosphere, then 1-ethynylpyrene (0.05 mmol, 11 mg) was added. The resulting mixture was heated to reflux with stirring under nitrogen atmosphere for 2 h. After being cooled to room temperature, the volatiles were removed under the reduced pressure and the residue was purified by chromatography on a silica-gel column with $CHCl_3$ as the eluent to give a fraction containing the desired compound. Repeated chromatography followed by recrystallisation from $CHCl_3$ and CH_3OH gave pure **1** as purple powder (23 mg, 38%). ^{1}H NMR (300 Hz, 25°C, TMS): δ -2.79 (s, 2H, NH), 0.96 (t, 9H, CH_3), 1.40 (m, 24H, $CH_2CH_2CH_2CH_2$), 1.69 (m, 6H, CH_2), 2.01 (m, 6H, CH_2), 4.28 (t, 6H, OCH_2), 7.29 (AA'BB', 6H, ArH), 8.15 (AA'BB', 6H, ArH), 8.09 (AA'BB', 2H, ArH), 8.89 (AA'BB', 2H, ArH), 8.18-8.40 (9H, pyrene), 8.94 (m, 8H, β-pyrrole); MS (MALDI-TOF): m/z = 1223.7 [calcd. for $C_{86}H_{86}N_4O_3$ (M^+) 1223.6]. Anal. calcd. (%) for $C_{86}H_{86}N_4O_3$: C 84.41, H 7.08, N 4.58. Found: C 84.76, H 7.27, N 4.70.

*3.4 Preparation of 5,10,15,20-tetra(4-octyloxyphenyl)porphyrin (**3**)*

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5,10,15,20-tetra(4-octyloxyphenyl)porphyrin (**3**) was synthesized by the Adler-Longo method [26,27]. A mixture of 4-octyloxybenzaldehyde (4.68 g, 20 mmol), and pyrrole (1.34 g, 20 mmol) in propyl acid (150 mL) was refluxed for 2 h, and CH_3OH (400 mL) was added into the reaction mixture after being cooled to room temperature. The precipitate was filtered and washed with CH_3OH, then subjected to chromatography on a silica gel column with $CHCl_3$ and petroleum ether (7:3) as eluent. After removing the solvent in vacuo, the residue was re-chromatographed under similar condition followed by recrystallisation from $CHCl_3/CH_3OH$ to give the target compound **3** (1.65g, 30%). ^{1}H NMR (300 Hz, 25°C, TMS): δ -2.73 (s, 2H, NH), 0.95 (t, 12H, CH_3), 1.46 (m, 32H, $CH_2CH_2CH_2CH_2$), 1.67 (m, 8H, CH_2), 2.01 (m, 8H, CH_2), 4.27 (t, 8H, OCH_2), 7.30 (AA'BB', 8H, ArH), 8.15 (AA'BB', 8H, ArH), 8.89 (m, 8H, β-pyrrole); MS (MALDI-TOF): *m*/*z* = 1127 [calcd. for $C_{76}H_{94}N_4O_4$ (M^+) 1127.6] Anal. calcd. (%) for $C_{76}H_{94}N_4O_4$: C 80.95, H 8.40, N 4.97. Found: C 80.67, H 8.38, N 4.60.

4. Conclusion

In summary, the 2PA properties of two A_3B type porphyrins **1** and **2** have been comparatively investigated with symmetrical porphyrin **3** as reference using femtosecond-pulsed *Z*-scan technique. Due to the D-π-A structure, both A_3B type asymmetric porphyrins **1** and **2** were revealed to exhibit larger 2PA cross sections over the symmetrical analogue **3** with the largest value of 6.1×10^5 GM revealed for **1** because of the intramolecular energy transfer from the excited pyrene moiety to the porphyrin moiety as indicated by the fluorescence spectroscopic result. The experimental results confirm that construction of high polarizable π-electronic systems is one of the useful strategies to improve the 2PA properties of porphyrins and FRET from suitable substituent to porphyrin is considered to be another effective method to enhance the 2PA cross section of porphyrins.

Acknowledgements

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Table 1 Optical parameters of selected 2PA compounds.

Compounds	σ_{2PA} *(GM)*	*Technique*	*λ (nm)*	*Solvent*	*Reference*
H_2TPP	16	Z-scan fs	810	$CHCl_3$	42
CuTPP	101	Z-scan fs	810	$CHCl_3$	42
Conjugated bis-(imidazolylporphyrin)	4.4×10^5	Z-scan fs	873	$CHCl_3$	16
Expanded porphyrins	0.8×10^5	Z-scan fs	780	CH_2Cl_2	17
Porphyrin arrays	0.9×10^4	Z-scan fs	800	toluene	11
Self-assembled porphyrins	7.6×10^3	Z-scan fs	887	$CHCl_3$	14
tris-ZnPor	1.18×10^5	Z-scan fs	800	THF	41
A_3B type porphyrin **1**	6.1×10^5	Z-scan fs	800	$CHCl_3$	This work
A_3B type oorphyrin **2**	3.1×10^5	Z-scan fs	800	$CHCl_3$	This work
Symmetric porphyrin **3**	2.5×10^5	Z-scan fs	800	$CHCl_3$	This work

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Figure Captions

Fig. 1. Schematic molecular structures of A_3B type 5-(1-pyrenylalkynylphenyl)-10,15,20-tris (4-octyloxyphenyl)porphyrin (**1**) and 5-(4-iodophenyl)-10,15,20-tris (4-octyloxyphenyl)porphyrin (**2**) with 5,10,15,20-tetra (4-octyloxyphenyl)porphyrin (**3**) and pyrene (**4**) as references.

Fig. 2. Synthesis of 5-(1-pyrenylalkynylphenyl)-10,15,20-tris (4-octyloxyphenyl) porphyrin (**1**).

Fig. 3. The electronic absorption spectra of A_3B type porphyrin **1** and **2** with reference porphyrin **3** and pyrene **4** recorded at room temperature. The concentrations were held at 10^{-6} mol/L.

Fig. 4. Fluorescence emission spectra of A_3B type porphyrin **1** and **2** with reference porphyrin **3** recorded at room temperature. The concentrations were held constant to 10^{-6} mol/L for all of the species. $\lambda_{ex} = 410$ nm.

Fig. 5. Fluorescence emission spectra of A_3B type porphyrin **1** and **2** with reference porphyrin **3** and pyrene **4** recorded at room temperature. The concentrations were held constant to 10^{-6} mol/L for all of the species. $\lambda_{ex} = 270$ nm.

Fig. 6. Excitation spectra of A_3B type asymmetric porphyrin **1** and **2** with reference symmetric porphyrin **3** recorded at room temperature. $\lambda_{em} = 650$ nm.

Fig. 7. PM3 method optimized structure of A_3B type porphyrin **1** in the top and side view. The three OC_8H_{17} groups attached on the meso-phenyls of porphyrin are replaced by OCH_3 groups for clarity.

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Fig. 8. Z-scan data for A_3B type porphyrin **1** and **2** with reference porphyrin **3** and pyrene **4** obtained under an open-aperture configuration. The concentration of them is 10^{-3} mol/L. The dots are the experimental data while the solid curves are the theoretical fit.

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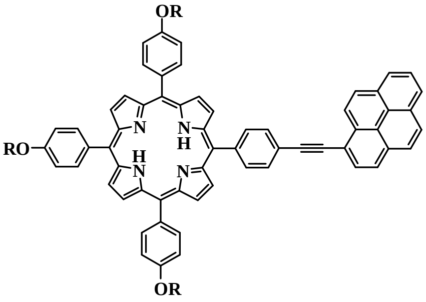

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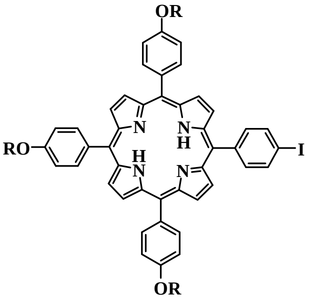

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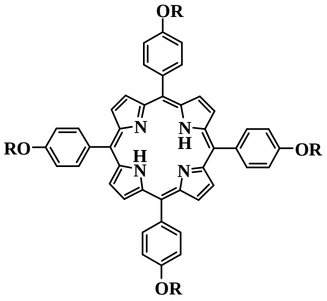

3

R = C_8H_{17}

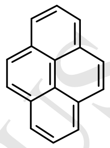

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Fig. 1. Schematic molecular structures of A_3B type 5-(1-pyrenylalkynylphenyl)-10,15,20-tris (4-octyloxyphenyl)porphyrin (**1**) and 5-(4-iodophenyl)-10,15,20-tris (4-octyloxyphenyl)porphyrin (**2**) with 5,10,15,20-tetra (4-octyloxyphenyl)porphyrin (**3**) and pyrene (**4**) as references.

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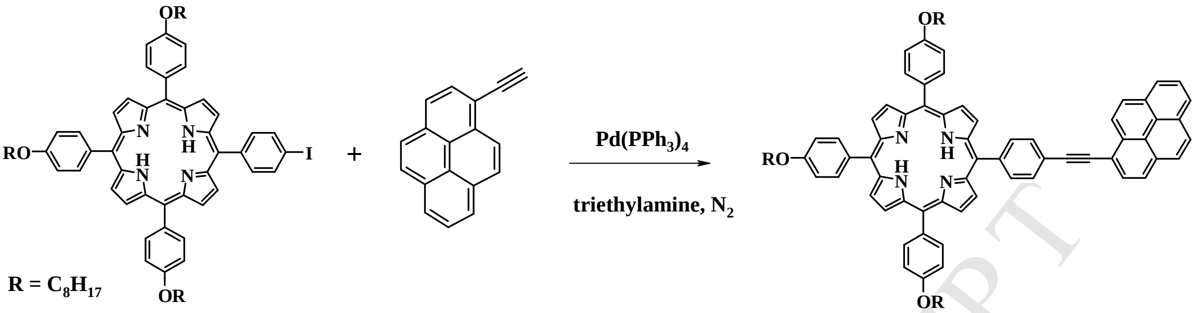

2 **1**

Fig. 2. Synthesis of 5-(1-pyrenylalkynylphenyl)-10,15,20-tris (4-octyloxyphenyl) porphyrin (**1**).

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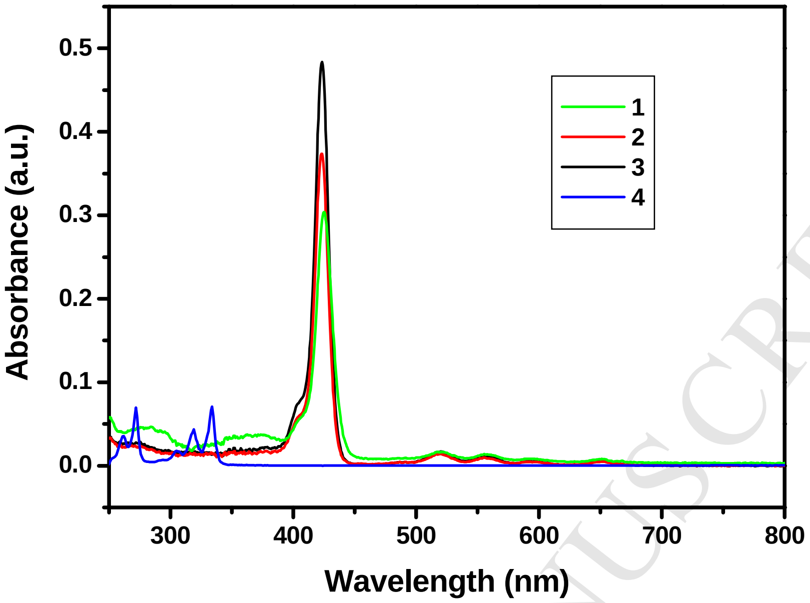

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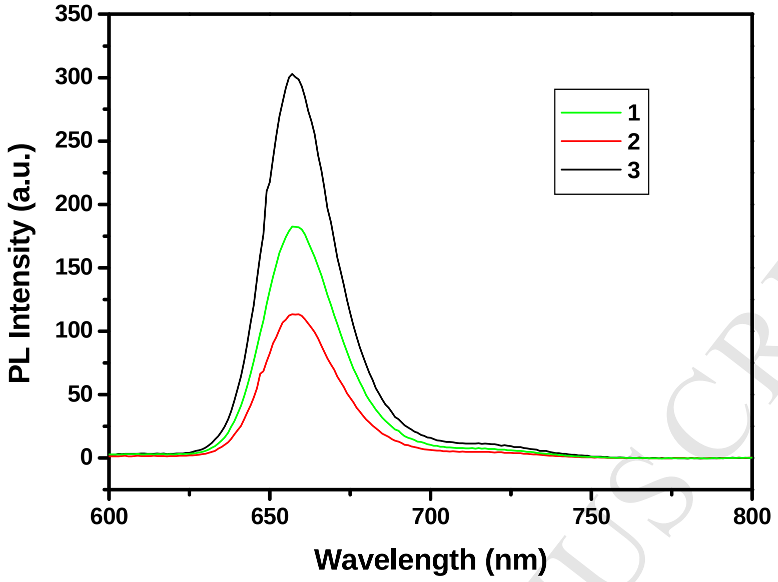

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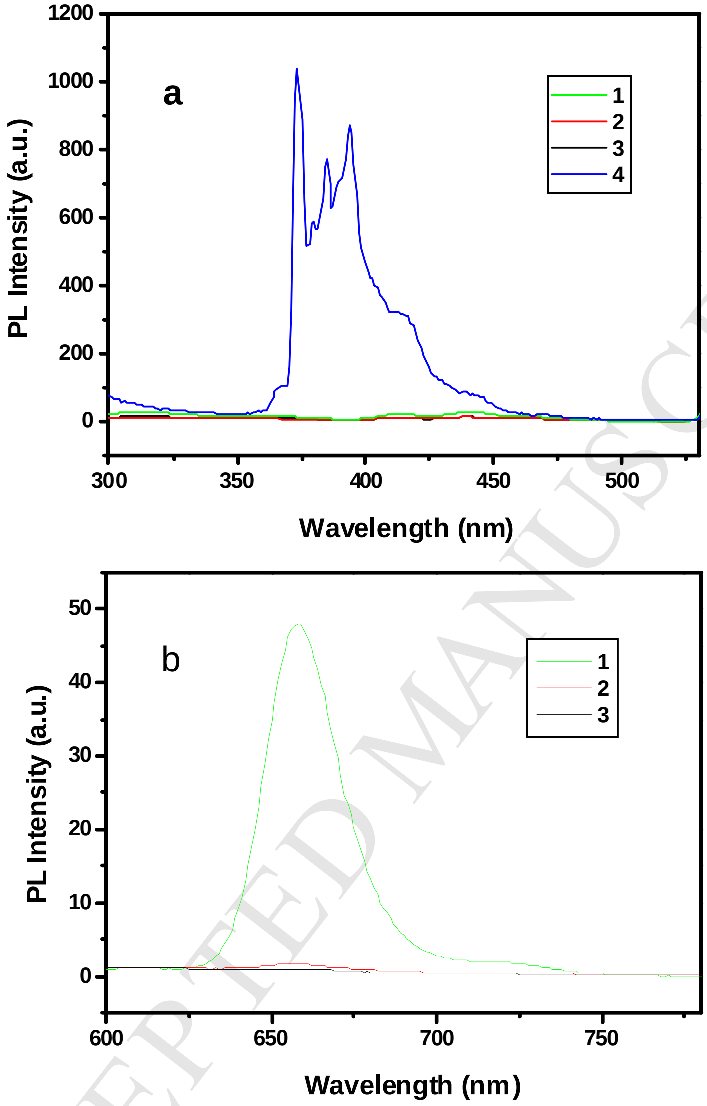

Fig. 5. Fluorescence emission spectra of A_3B type porphyrin **1** and **2** with reference porphyrin **3** and pyrene **4** recorded at room temperature. The concentrations were held constant to 10^{-6} mol/L for all of the species. λ_{ex} = 270 nm.

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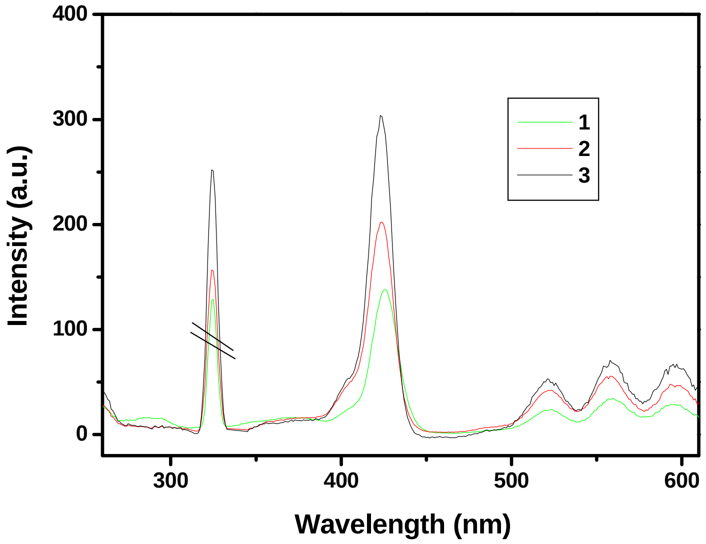

Fig. 6. Excitation spectra of A_3B type asymmetric porphyrin **1** and **2** with reference symmetric porphyrin **3** recorded at room temperature. λ_{em} = 650 nm.

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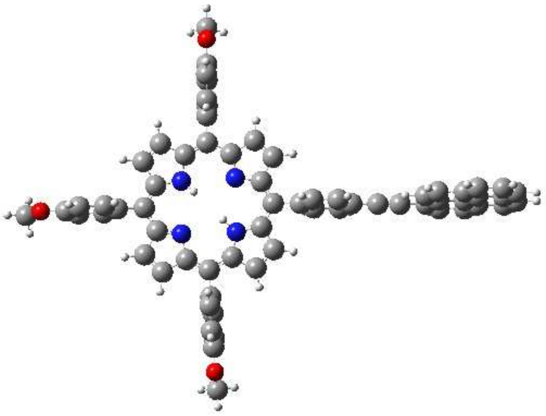
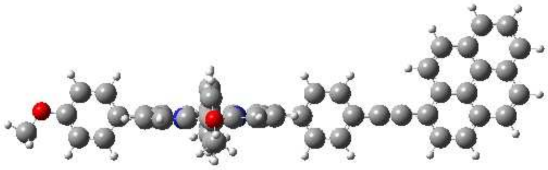


Top view



Side view

Fig. 7. PM3 method optimized structure of A_3B type porphyrin **1** in the top and side view. The three OC_8H_{17} groups attached on the meso-phenyls of porphyrin are replaced by OCH_3 groups for clarity.

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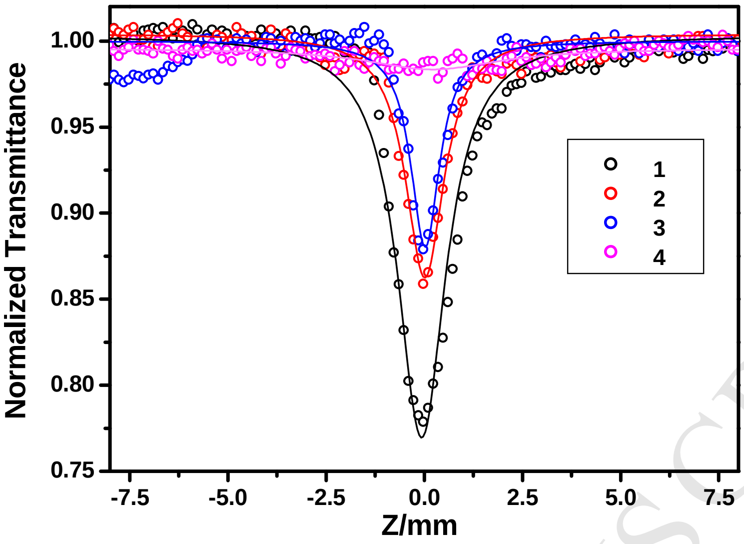

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- Both D-π-A type porphyrins exhibit large 2PA cross sections.
- The 2PA properties of them were investigated using femtosecond-pulsed *Z*-scan technique.
- Intramolecular energy transfer takes place in the newly prepared asymmetric porphyrin.

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