A series of polycyclic aromatic hydrocarbon-substituted metal-free porphyrins: substituent effect on two-photon absorption property

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Abstract: The third-order nonlinear optical properties of a series of naphthyl, phenanthrenyl, and pyrenyl substituted porphyrins have been comparatively investigated by performing the femtosecond-pulsed Z-scan measurements. Due to the expanded π system, both pyrenyl substituted porphyrin (**1**) and phenanthrenyl substituted porphyrin (**2**) exhibit large two-photon absorption cross sections up to 4.26×10^4 GM for **1** and 1.36×10^4 GM for **2** at the wavelength of 800 nm. The pyrenyl substituted porphyrin (**1**) has the most excellent two-photon absorption property because of the intramolecular energy transfer from the excited pyrene moiety to the porphyrin moiety in porphyrin **1**. The results confirm that porphyrins conjugated with external π electronic systems can lead to the significant enhancement in the two-photon absorption cross-section values. This research provides a useful guideline to the design of efficient two-photon absorbing materials.

Keywords: Porphyrin; Two-photon absorption; Polycyclic aromatic hydrocarbon; Femtosecond-pulsed Z-scan technique; Substituent effect; Intramolecular energy transfer

1. Introduction

Many efforts have been devoted to develop π -conjugated organic compounds exhibiting large two-photon absorption (2PA) cross sections (σ) due to their potential applications in fluorescence microscopy, optical power limiting and two-photon photodynamic therapy [1-5]. Among a variety of π -conjugated organic compounds, porphyrins and their derivatives have emerged as promising candidates for nonlinear optical materials because of their rigid two-dimensional and highly π -conjugated structures [6-8]. However, the majority of regular porphyrin show small two-photon absorption (2PA) cross sections (<100 GM) ($1 \text{ GM} = 10^{-50} \text{ cm}^4 \cdot \text{s} \cdot \text{photon}^{-1}$) [9-11], therefore limiting their usefulness in 2PA applications. So far, various novel porphyrin and porphyrin derivatives owing to large two-photon absorption (2PA) cross sections have been explored, including porphyrin arrays [12], dimmers [13,14], self-assembled porphyrins [15,16], and expanded porphyrins [17,18]. In the same time, many factors have been found to influence the 2PA magnitudes, among which π -electron delocalization throughout a molecular framework plays important role. Considerable efforts have been devoted to the exploration of extensively π -conjugated porphyrins. It is an effective approach to combine porphyrin monomer with π -conjugated molecular such as perylene diimide, tris(4-iodophenyl)amine [19] and azulene. Osuka reported several 5,15-bis(azulenylethynyl) substituted zinc(II) porphyrins with the maximum 2PA cross section value of 8030 GM at 1400 nm [20]. Several azulene-fused porphyrins with large 2PA cross section were also reported due to the effective π -electron conjugation pathway throughout the porphyrin moiety [21]. In addition, perylene substituted porphyrin exhibits 2PA cross sections over 7000 GM at telecommunication wavelengths due to the strong donor-acceptor intramolecular

charge transfer [22]. Although it has been realized that the increment of π -electron delocalization could lead to highly effective 2PA, so far little attention has been devoted to the influence of the conjugation of the substituent on the 2PA of porphyrin. In this work, the third-order nonlinear optical properties of a series of naphthyl, phenanthrenyl, and pyrenyl substituted porphyrins (Fig.1) have been comparatively investigated by performing the femtosecond-pulsed Z-scan measurements. Due to the expanded π system, both pyrenyl substituted porphyrin (**1**) and phenanthrenyl substituted porphyrin (**2**) exhibit large two-photon absorption cross sections up to 4.26×10^4 GM for **1** and 1.36×10^4 GM for **2** at the wavelength of 800 nm. The pyrenyl substituted porphyrin (**1**) has the most excellent two-photon absorption property because of the intramolecular energy transfer from the excited pyrene moiety to the porphyrin moiety in porphyrin **1**. The results confirm that porphyrins conjugated with external π electronic systems can lead to the significant enhancement in the two-photon absorption cross-section values. This research provides a useful guideline to the design of efficient two-photon absorption materials.

2. Results and discussion

2.1. Electronic absorption spectra

The electronic absorption spectra of H₂TPYRP (**1**), H₂TPHEP (**2**), H₂TN β HP (**3**) and H₂TN α HP (**4**) in CHCl₃ are shown in Fig. 2. All the electronic absorption spectra of them show similar intense Soret band with maxima around 423-434 nm and four Q-band in the lower energy region between 514 nm and 657 nm, which is in agreement with those reported porphyrins previously [23,24]. In addition, the

common bands at 280 nm and 370 nm for porphyrin **1** can be ascribed to the absorption of pyrenyl group, indicating that there is no appreciable interaction between porphyrin moiety and pyrenyl group in compound **1** in the ground-state [25]. It is obvious that a gradual bathochromic shift in the Soret band is clearly observed in the order **1** > **2** > **3** $\approx$ **4**, demonstrating that the electron-donating ability of the substituent increases in the order pyrenyl group > phenanthrenyl group > naphthyl group.

2.2 Fluorescence spectra

The fluorescence spectra of **1-4** with excitation of 410 nm are shown in Fig. 3. All the porphyrins have the characteristic emission band at 654-656 nm. Previous reports have shown that an efficient fluorescence resonance energy transfer (FRET) from the pyrenyl group to the porphyrin ring exist in porphyrin **1** due to the rigid molecular structure and the good overlap between emission of the pyrenyl group and absorption of the porphyrin units [26-28]. As shown in Fig. S1 for porphyrin **2**, when the phenanthrenyl units in porphyrin **2** were selectively excited at 380 nm, the emission spectrum of porphyrin **2** showed not only the emission band of porphyrin but also the band of phenanthrenyl units. Similarly, when the porphyrin unit in porphyrin **2** was selectively excited at 410 nm, the emission spectrum of compound **2** still showed the emission band of both porphyrin unit and phenanthrenyl units. It is clear that there are no FRET from the phenanthrenyl group to the porphyrin ring exists in porphyrin **2** because of no overlap between emission of the phenanthrenyl group and absorption of the porphyrin unit [29]. In addition, the fluorescence intensity of the porphyrin **1** and **2** is larger than that of porphyrin **3** and **4**, because the pyrenyl group substituted

porphyrin **1** and the phenanthrenyl group substituted porphyrin **2** own more expanding π systems.

2.3 Molecular structure of porphyrin 1 and 2

To obtain the information about the molecular structures for polycyclic aromatic hydrocarbon-substituted metal-free porphyrins **1** and **2**, PM3 method [30,31] in Gaussian 98W [32] was carried out. The optimized structures for **1** and **2** are shown in Fig. 4. It appears that the porphyrin ring is approximately vertical to the meso-pyrenyl groups for porphyrin **1** and the phenanthrenyl groups for **2**, due to the steric hindrance. Obviously the π systems get expanded in them.

4. 2PA properties

In order to investigate the nonlinear absorption effect of porphyrins **1-4**, we perform open-aperture Z-scan measurements [33] for the solution of porphyrins **1-4** in CHCl_3 with the concentrations of 10^{-3} mol/L contained in 1 mm thick quartz cell at the intensity of $I_0 = 56.9 \text{ GW/cm}^2$. It is noteworthy that for pure chloroform in quartz cell, nonlinear absorption effect can be safely ignored because no peak or valley was observed in the open-aperture Z-scan. In spite of the porphyrin **1** and **2** exhibiting huge absorptive nonlinearities, the nonlinear absorption was not detected for porphyrin **3** and **4** under our experimental condition. As shown in Fig. 5, the Z-scan traces of porphyrin **1** and **2** display symmetric valleys with respect to the focus, suggesting that chloroform solutions of porphyrin **1** and **2** exhibit the positive nonlinear absorption in nature. By best fittings between the measured Z-scan traces and the Z-scan theory for characterizing two-photon absorber [34], we extracted the

2PA coefficients of 0.107 and 0.034 cm/GW for porphyrin **1** and **2**, respectively. Furthermore, we convert the 2PA coefficient into the 2PA cross section by the conversion formula $\sigma_{2PA} = \hbar\omega\beta/N$, where $\hbar\omega$ is the incident photon energy, and N is the density of sample in solution. The values of σ_{2PA} at 800 nm are estimated to be 4.26×10^{-46} cm⁴•s•photon⁻¹ for porphyrin **1** and 1.36×10^{-46} cm⁴•s•photon⁻¹ for porphyrin **2**, respectively. According to 1 GM = 10^{-50} cm⁴•s•photon⁻¹, the values of σ_{2PA} at 800 nm are estimated to be 4.26×10^4 GM for **1** and 1.36×10^4 GM for **2**.

Previous reports have shown that most of symmetrical porphyrins have low 2PA cross sections (<100 GM) [9-11], actually we did not detected the nonlinear absorption response of porphyrin **3** and **4**, however, porphyrin **1** and **2** were revealed to exhibit larger 2PA cross sections, their σ_{2PA} values are even on the same order of magnitude with other excellent 2PA materials including porphyrin arrays [12,16], self assembled porphyrins [15], expanded porphyrins [18], and donor- π -acceptor type porphyrins [27] reported previously, indicating that porphyrin **1** and **2** are excellent candidates for 2PA materials. Substituent effect was considered to play an important role on the two-photon absorption property of these porphyrins since organic molecules with expanded π -electron system should have high optical nonlinear effects [35,36]. The polycyclic aromatic hydrocarbon naphthyl group, phenanthrenyl group and pyrenyl group are planar conjugated π -electron system. The nonlinear optical properties can be improved when the meso positions of the porphyrins were linked by these planar conjugated π -electron substituents. Compared with naphthyl group, both phenanthrenyl group and pyrenyl group can provide more π -electrons to the porphyrin ring, which enhance the 2PA effects of porphyrin **1** and **2**. Therefore, introducing the planar conjugated π -electron group to porphyrin is believed to play an important role

in the contribution of the increased the σ_{2PA} value of porphyrins.

In addition, pyrenyl substituted porphyrin **1** shows more excellent 2PA property than that of phenanthrenyl substituted porphyrin **2**. Several factors are considered to be responsible for the enhancement of 2PA cross section of porphyrin **1**. Firstly, the porphyrin modified by pyrenyl groups owns larger π -system compared with that of phenanthrenyl groups. Moreover, π -electron density of pyrenyl substituted porphyrin **1** is larger than that of phenanthrenyl substituted porphyrin **2**, which is helpful to improve the nonlinear optical properties. It is worth mentioning that 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 important factor for leading to the large σ_{2PA} value of porphyrin **1**.

3. Experimental Section

3.1 Materials and measurements

9-Phenanthrene and pyrrole were purchased from J&K Scientific. All other reagents and solvents were used as received. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200-300 mesh) with the indicated eluents. The porphyrin meso-tetrakis(β -naphthyl)porphyrin ($H_2T\beta NP$), meso-tetrakis(α -naphthyl)porphyrin ($H_2T\alpha NP$) and meso-tetrakis(1-pyrenyl)porphyrin (H_2TPYRP) were prepared according to the method we have reported previously [37-39].

1H 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 ($\delta = 7.26$ 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.

3.2 2PA measurements

The 2PA properties of porphyrin **1** and **2** with porphyrin **3** and pyrene (**4**) were measured by using an open-aperture Z-scan method [33]. The laser source for the experiments was a Ti: sapphire 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 $\omega_0 = 21 \mu\text{m}$ (the Rayleigh length $z_0 = 0.88 \text{ mm}$). To carry out Z-scan measurements, we perform the Z-scan measurements at the intensity of $I_0 = 56.9 \text{ GW/cm}^2$, 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 $\pm 20\%$.

3.3 Preparation of 5,10,15,20--tetra (phenanthrenly) porphyrin (**2**)

H₂TPHEP (**2**) was synthesized by the Adler-Longo method [40]. A mixture of 9-phenanthrenecarboxaldehyde (618 mg, 3 mmol) and pyrrole (204 mg, 3 mmol) in propyl acid (30 ml) was refluxed for 1 h under a slow stream of nitrogen, the CH₃OH

(100 mL) was added into the reaction solution after it had been cooled to room temperature. The precipitate was filtered and washed with CH₃OH, then subjected to chromatography on a silica gel column with CHCl₃ and petroleum ether (7:3) as eluent. After removing the solvent in *vacuo*, the residue was re-chromatographed under similar conditions followed by recrystallization from CHCl₃/ CH₃OH to give the target compound H₂TPHEP (**2**) (152 mg, 20%). The MS and ¹H NMR spectra of porphyrin **2** were shown in Fig. S2 and Fig. S3. ¹H NMR (300 Hz, 25°C, TMS): δ = 8.98 (8H, β -pyrrole), 8.60 (4H, phenanthrene), 8.58 (4H, phenanthrene), 8.05 (4H, phenanthrene), 7.89 (4H, phenanthrene), 7.62 (4H, phenanthrene), 7.24 (8H, phenanthrene), -2.06 (s, 2H, NH); MS (MALDI-TOF): m/z = 1019.1 [calcd. for C₇₆H₄₆N₄ (M+4)⁺ 1019.2].

4. Conclusions

In summary, the 2PA properties of a series of naphthyl, phenanthrenyl, and pyrenyl substituted porphyrins have been comparatively investigated using femtosecond-pulsed Z-scan technique. Due to the expanded π system, both pyrenyl-substituted porphyrin and phenanthrenyl-substituted porphyrin exhibit large two-photon absorption cross sections at the wavelength of 800 nm. The pyrenyl-substituted porphyrin (**1**) exhibited the most excellent two-photon absorption property due to the intramolecular energy transfer from the excited pyrene moiety to the porphyrin moiety in porphyrin **1**. The results confirm that porphyrins conjugated with external π -electronic systems can lead to the significant enhancement in the two-photon absorption cross-section values. The large 2PA effects with ultrafast response indicate that pyrenyl-substituted porphyrin and phenanthrenyl-substituted porphyrin should be

desirable for potential applications in nonlinear photonic devices. This research provides a useful guideline to the design of efficient two-photon absorption materials.

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References

1. Zhou W, Kuebler SM, Braun KL, Yu T, Cammack JK, Ober CK, Perry JW, Marder SR. An efficient two-photon-generated photoacid applied to positive-tone 3D microfabrication. *Science* 2002; 296: 1106-9.
2. Hone DC, Walker PI, Evans-Gowing R, FitzGerald S, Beeby A, Chambrier I, Cook MJ, Russell DA. Generation of cytotoxic singlet oxygen via phthalocyanine-stabilized gold nanoparticles: a potential delivery vehicle for photodynamic therapy. *Langmuir* 2002; 18: 2985-7.
3. Lin TC, He GS, Zheng QD, Prasad PN. Degenerate two-/three-photon absorption and optical power-limiting properties in femtosecond regime of a multi-branched chromophore. *J Mater Chem* 2006; 16: 2490-8.
4. Cumpston BH, Ananthavel SP, Barlow S, Dyer DL, Ehrlich JE, Erskine LL,

- Heikal AA, Kuebler SM, Lee IYS, McCord-Maughon D, Qin J, Röckel H, Rumi M, Wu XL, Marder SR, Perry JW. Two-photon polymerization initiators for three-dimensional optical data storage and microfabrication. *Nature* 1999; 398: 51-4.
5. Coenjarts C, García O, Llauger L, Palfreyman J, Vinette AL, Scaiano JC. Mapping photogenerated radicals in thin polymer films: fluorescence imaging using a prefluorescent radical probe. *J Am Chem Soc* 2003; 125: 620-1.
 6. Jaquinod L. The porphyrin handbook, ed. Kadish KM, Smith KM, Guillard R. Academic Press, San Diego, 2000, vol. 1, p. 201.
 7. Vicente MGH, Jaquinod L, Smith KM. Oligomeric porphyrin arrays. *Chem Commun* 1999; 1771-82.
 8. Anderson HL. Building molecular wires from the colors of life: conjugated porphyrin oligomers. *Chem Commun* 1999; 2323-30.
 9. Kruk M, Karotki A, Drobizhev M, Kuzmitsky V, Gael V, Rebane A. Two-photon absorption of tetraphenylporphyrin free base. *J Lumin* 2003; 105: 45-55.
 10. Drobizhev M, Karotki A, Kruk M, Rebane A. Resonance enhancement of two-photon absorption in porphyrins. *Chem Phys Lett* 2002; 355: 175-82.
 11. Drobizhev M, Karotki A, Kruk M, Mamardashvili NZ, Rebane A. Drastic enhancement of two-photon absorption in porphyrins associated with symmetrical electron-accepting substitution. *Chem Phys Lett* 2002; 361: 504-12.
 12. Ahn TK, Kim KS, Kim DY, Noh SB, Aratani N, Ikeda C, Osuka A, Kim D. Relationship between two-photon absorption and the π -conjugation pathway in porphyrin arrays through dihedral angle control. *J Am Chem Soc* 2006; 128: 1700-4.

13. Screen TEO, Thorne JRG, Denning RG, Bucknall DG, Anderson HL. Amplified optical nonlinearity in a self-assembled double-strand conjugated porphyrin polymer ladder. *J Am Chem Soc* 2002; 124: 9712-3.
14. Drobizhev M, Stepanenko Y, Rebane A, Wilson CJ, Screen TEO, Anderson HL. Strong cooperative enhancement of two-photon absorption in double-strand conjugated porphyrin ladder arrays. *J Am Chem Soc* 2006; 128: 12432-3.
15. Ogawa K, Ohashi A, Kobuke Y, Kamada K, Oht K. Strong two-photon absorption of self-assembled butadiyne-linked bisporphyrin. *J Am Chem Soc* 2003; 125: 13356-7.
16. Ogawa K, Kobuke Y. Various strategies for highly-efficient two-photon absorption in porphyrin arrays. *J Photochem Photobiol C* 2006; 7: 13-28.
17. Ogawa K, Ohashi A, Kobuke Y, Kamada K, Ohta K. Two-photon absorption properties of self-assemblies of butadiyne-linked bis(imidazolylporphyrin). *J Phys Chem B* 2005; 109: 22003-12.
18. Rath H, Sankar J, Prabhuraja V, Chandrashekar TK, Nag A, Goswami D. Core-modified expanded porphyrins with large third-order nonlinear optical response. *J Am Chem Soc* 2005; 127: 11608-9.
19. Seo JW, Jang SY, Kim D, Kim HJ. Octupolar trisporphyrin conjugates exhibiting strong two-photon absorption. *Tetrahedron* 2008; 64: 2733-9.
20. Kim KS, Noh SB, Katsud T, Ito S, Osuka A, Kim D. Charge transfer induced enhancement of near-IR two-photon absorption of 5,15-bis(azulenylethynyl) zinc(II) porphyrins. *Chem Commun* 2007; 2479-81.
21. Kurotobi K, Kim KS, Noh SB, Kim D, Osuka A. A quadruply azulene-fused porphyrin with intense near-IR absorption and a large two-photon absorption

- cross section. *Angew Chem Int Ed* 2006; 45: 3944-7.
22. Huang X, Shi Q, Chen W, Zhu C, Zhou W, Zhao Z, Duan X, Zhan X. Low-band gap conjugated donor-acceptor copolymers based on porphyrin with strong two-photon absorption. *Macromolecules* 2010; 43: 9620-6.
 23. Fukuzumi S, Endo Y, Kashiwagi Y, Araki Y, Ito O, Imahori H. Novel photocatalytic function of porphyrin-modified gold nanoclusters in comparison with the reference porphyrin compound. *J Phys Chem B* 2003; 107: 11979-86.
 24. Rodriguez J, Kirmaier C, Holten D. Optical properties of metalloporphyrin excited states. *J Am Chem Soc* 1989; 111: 6500-6.
 25. D'Souza F, Smith PM, Zandler ME, McCarty AL, Itou M, Araki Y, Ito O. Energy transfer followed by electron transfer in a supramolecular triad composed of boron dipyrin, zinc porphyrin, and fullerene: a model for the photosynthetic antenna-reaction center complex. *J Am Chem Soc* 2004; 126: 7898-907.
 26. Sheng N, Sun J, Bian Y, Jiang J, Xu D. Synthesis and third-order nonlinear optical properties of novel ethynyl-linked heteropentamer composed of four porphyrins and one pyrene. *J Porphyrins Phthalocyanines* 2009; 13: 275-82.
 27. Sheng N, Liu D, Wu J, Gu B, Wang Z, Cui Y. Donor- π -acceptor type porphyrins with large two-photon absorption cross section. *Dyes and Pigments* 2015; 119: 116-21.
 28. Sheng N, Yuan Z, Wang J, Chen W, Sun J, Bian Y. Third-order nonlinear optical properties of sandwich-type mixed (phthalocyaninato)(porphyrinato) europium double- and triple-decker complexes. *Dyes and Pigments* 2012; 95: 627-31.
 29. Pan X, Liu J, Zhang D. Binding of phenanthrene to extracellular polymeric substances (EPS) from aerobic activated sludge: A fluorescence study. *Colloids*

- and Surfaces B: Biointerfaces 2010; 80: 103-6.
30. Stewart JJP. Optimization of parameters for semiempirical methods I. Method. J Comp Chem 1989; 10: 209-20.
 31. Stewart JJP. Optimization of parameters for semiempirical methods II. Applications. J Comp Chem 1989; 10: 221-64.
 32. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JAJR, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, MalickDK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C and Pople JA. Gaussian 03, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, 1998.
 33. Sheik-Bahae M, Said AA, Van Stryland EW. High-sensitivity, single-beam n_2 measurements. Opt Lett 1989; 14: 955-7.
 34. Gu B, Huang X, Tan S, Wang M, Ji W. Z-scan analytical theories for characterizing multiphoton absorbers. Appl Phys B 2009; 95: 375-81.
 35. Brédas JL, Adant C, Tackx P, Petersoons A and Pierce BM. Third-order nonlinear

- optical response in organic materials: theoretical and experimental aspects. *Chem Rev* 1994; 94: 243-76.
36. Nalwa HS. Organic materials for third-order nonlinear optics. *Adv Mater* 1993; 5: 341-58.
37. George RG, Padmanabhan M. Studies on some new meso-aryl substituted octabromo-porphyrins and their Zn (II) derivatives. *Polyhedron* 2003; 22: 3145-54.
38. Sheng N, Zong S, Cao W, Jiang J, Wang Z, Cui Y. Water dispersible and biocompatible porphyrin-based nanospheres for biophotonics applications: a novel surfactant and polyelectrolyte-based fabrication strategy for modifying hydrophobic porphyrins. *ACS Appl Mater Interfaces* 2015; 7: 19718-25.
39. Sheng N, Zhu P, Ma C, Jiang J. The synthesis, spectroscopy, electrochemistry and photophysical properties of novel, sandwich europium(III) complexes with a porphyrin ligand bearing four pyrenyl groups in meso-positions. *Dyes and Pigments* 2009; 81: 91-6.
40. Adler AD, Longo FR, Finarelli JD, Goldmacher J, Assour J, Korsakoff LA. Simplified synthesis for meso-tetraphenylporphine. *J Org Chem* 1967; 32: 476-80.

Fig. 1. Schematic molecular structures of H₂TPYRP (1), H₂TPHEP (2), H₂TNβHP (3) and H₂TNαHP (4).

Fig. 2. The electronic absorption spectra of H₂TPYRP (**1**), H₂TPHEP (**2**), H₂TNβHP (**3**) and H₂TNαHP (**4**) recorded at room temperature. The concentrations were held at 10⁻⁶ mol/L.

Fig. 3. Fluorescence emission spectra of H₂TPYRP (**1**), H₂TPHEP (**2**), H₂TNβHP (**3**) and H₂TNαHP (**4**) recorded at room temperature. The concentrations were held constant to 10⁻⁶ mol/L for all of the species. $\lambda_{\text{ex}} = 410$ nm.

Fig. 4. PM3 method optimized structure of porphyrin **1** and **2** in the top and side view.

Fig. 5. Z-scan curves for H₂TPYRP (1) and H₂TPHEP (2) 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.