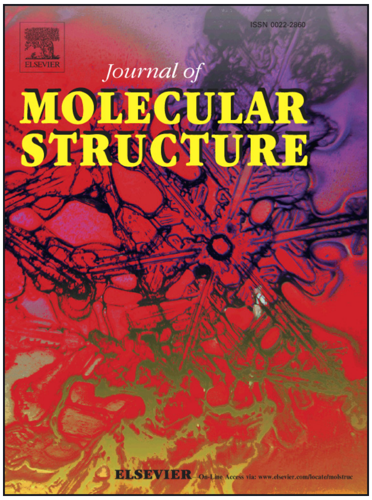

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Synthesis, characterization and properties of covalently linked porphyrin-naphthalimide pentamer and its metal complexes

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Abstract:

A novel porphyrin-naphthalimide pentamer **5** was synthesized by linking four light-harvesting naphthalimide units to a central porphyrin, via ether bridges. The corresponding metal (Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}) complexes **6a-6e** were obtained under different reaction conditions. The structures of these compounds were characterized by ^1H and ^{13}C NMR spectra, FT-IR, MALDI-TOF-MS and elemental analysis. The photophysical properties have been investigated by UV-Vis absorption and steady-state fluorescence spectroscopy. It is found that the excitation energy transfer occurs from the naphthalimide units to the porphyrin core, and that the free base porphyrin **5** and Zn porphyrin **6a** can emit intense red light. Additionally, the electrochemical properties of compounds **5** and **6a-6e** were also investigated by cyclic voltammetry.

Key words: Porphyrin; Naphthalimide; Metal complex; Light harvesting

Introduction

Porphyrins, a class of macrocycle compounds with interesting spectroscopic and chemical properties, have attracted considerable attention for many decades due to their comprehensive applications in a number of rapidly growing research fields, such as organic light emitting diodes (OLEDs) [1], organic photovoltaic (OPV) [2, 3], and photocatalytic degradation [4, 5].

Porphyrins are versatile molecules whose physicochemical properties can be readily adjusted by modification of the electronic distribution on the aromatic ring via peripheral substitution [6]. Furthermore, the porphyrin skeleton permits to be functionalized by attaching four photo-harvesting units at the porphyrin macrocycle periphery, to form light-harvesting system. This kind of molecular system, in which a porphyrin acceptor is covalently linked to four donor chromophores, forms a suitable choice for the antenna function. In recent years, a wide variety of substituents [7-12] have been introduced to the porphyrin core to form the peripherally functionalized porphyrin molecules, which are good candidates for light-harvesting systems and fluorescence emitting materials.

On the other hand, the 1,8-naphthalimide derivatives are a special class of environmentally sensitive chromophores [13]. Because of their strong fluorescence and good photostability, 1,8-naphthalimide derivatives have found extensive application in the field of organic photo-electronics[13,14,16]. In recent years, a series of light-harvesting molecules based on a core as an energy acceptor and peripherally functionalized with naphthalimide as a donor surface have attracted much attention in biomedical applications [13-23]. In those molecules, naphthalimide moiety exhibits a good energy pumping antenna function. If naphthalimide is introduced to the porphyrin skeleton, its excitation energy may transfer to porphyrin fragment, showing interesting photophysical properties. Moreover, the naphthalimide structure with strong absorption in the UV region will also help improve the light harvesting ability of the functionalized porphyrin molecules. To the best of our knowledge, there is no report on the synthesis of the naphthalimide functionalized porphyrin. Herein, we report the design and synthesis of a novel porphyrin-naphthalimide light-harvesting system **5** (**TNPPH$_2$**) where the four naphthalimide units are linked via ether bridges to the meso-phenyl groups of the porphyrin (**Scheme 1**). Moreover, the metal complexation reactions of **5** and metal ions (Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}) were also performed on different reaction conditions to finally obtain metal complexes **6a-6e**. Additionally, the structure characterization, photophysical, photo-induced energy transfer and electrochemical results are also reported. These studies provide wider ground for choice and application of the materials in the field of organic photo-electronics.

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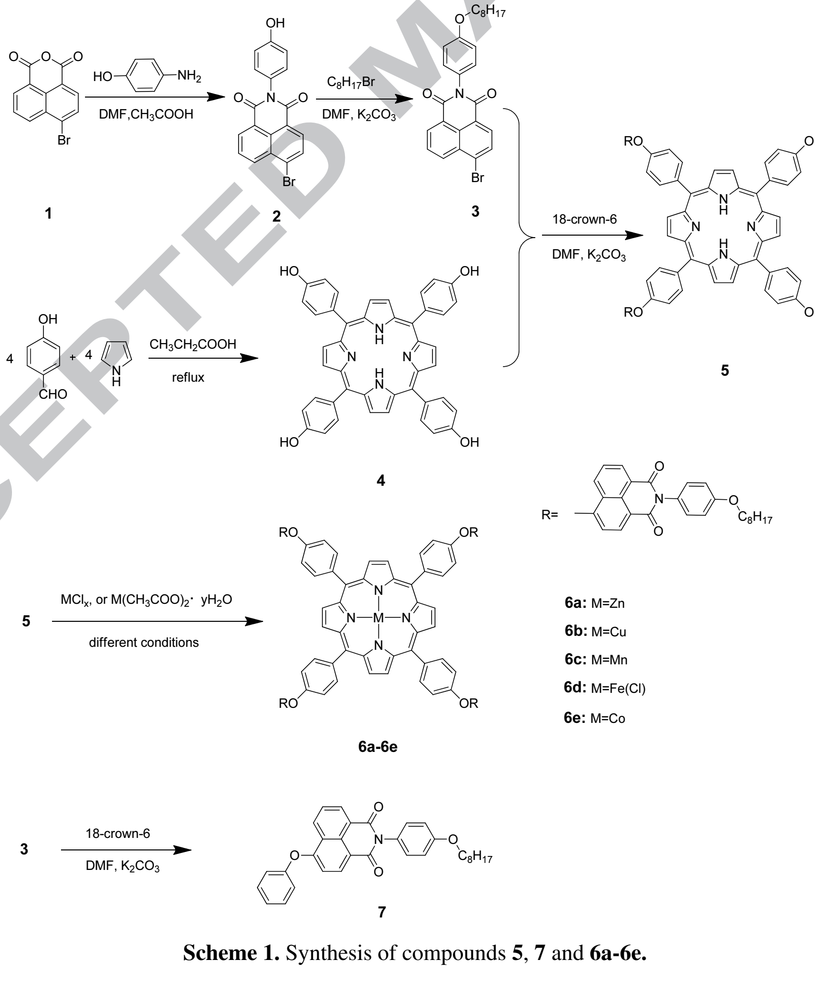
Results and discussion

2.1. Synthesis

The synthetic routes for compounds **5**, **7** and **6a-6e** are shown in **Scheme 1**. 4-Bromo-1,8-naphthalic anhydride **1** as the starting material was reacted with 4-aminophenol in a mixture of N,N-dimethylformamide (DMF) and acetic acid (volume ratio, 20/3) to afford **2**. Because of its poor solubility in common solvents, such as dichloromethane (CH_2Cl_2), petroleum ether and ethyl acetate, we use the crude product **2** for the next reaction without further purification. Then, the crude product **2** was reacted with n-octylbromide in the presence of anhydrous potassium carbonate (K_2CO_3), affording **3** as a white solid in high yield (76%).

The target compound **5** was synthesized in a moderate yield (61%) by the reaction of **3** with **4** in DMF, using finely ground anhydrous K_2CO_3 as a base in the presence of 18-crown-6. Next, the complex **6a** was prepared by the reaction of **5** with $Zn(CH_3COO)_2{\cdot}2H_2O$ in a mixture of trichloromethane ($CHCl_3$) and methanol (volume ratio, 3/1) at 70 ^oC. During the reaction, the UV-Vis absorption spectra of the reaction mixture were monitored by a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer. The reaction mixture was refluxed until no change in the Q bands was observed, which confirmed the formation of Zn complex. The preparation of **6b** was similar to the procedure for **6a** except for the addition of a suitable amount of KOH to the reaction mixture. However, when **5** was reacted with other metal salts ($FeCl_3$, $MnCl_2$ and $CoCl_2$) under the similar reaction conditions reported above, although using even a larger excess of metal salts and a longer reaction time, no corresponding metal complex could be obtained. The difficulty in the complexation of the transition metal irons and free base porphyrin **5** may come from the nonplanar distortions of the porphyrin ring caused by the peripheral substitution of electron withdrawing naphthalimide units, as well as the comparatively larger ionic radius of Fe^{3+}, Mn^{2+} and Co^{2+}. Finally, with the optimum solvent ratio of $CHCl_3$/DMF/methanol (volume ratio, 3/2/1) and proper feeding sequence, the preparation of **6c**, **6d** and **6e** can be easily achieved by heating the final reaction mixture under reflux for 15-30 h.



Scheme 1. Synthesis of compounds **5**, **7** and **6a-6e.**

2.2. Structure characterization

2.2.1. MALDI-TOF-MS and NMR characterization

Matrix-assisted laser desorption/ionization time-of-flight mass spectra (MALDI-TOF-MS) were performed to quantitatively analyze the molecular weights of **5** and its complexes **6a-6e**. The analysis of date worked well for compounds **5**, **6a**, **6b**, **6c** and **6e**, giving a single peak in good agreement with the theoretical value, respectively. But the MALDI-TOF mass spectrum of **6d** shows only one mass ionic peak at 2330.3, not the theoretical value of 2365.9. The similar phenomenon was also reported in the previous literatures [7, 11]. In fact, the peak at 2330.3 can be assigned to a mass ionic state without axial chloride, which can be expressed as the form of $[M\text{-}Cl]^+$.

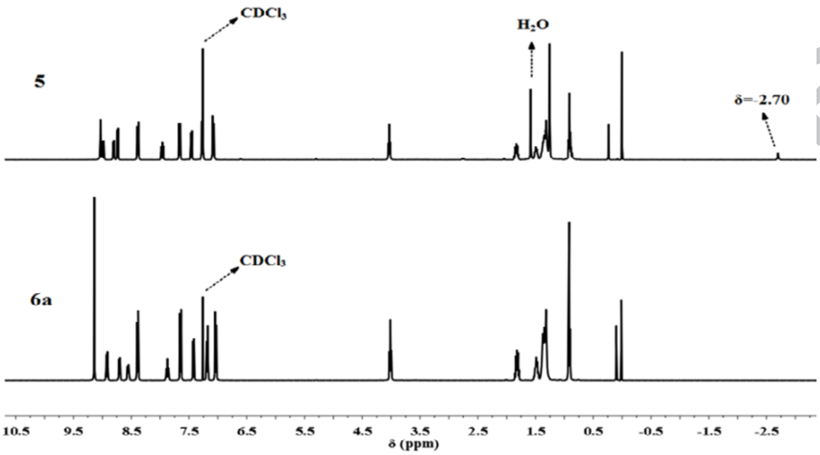


Fig. 1. ^{1}H NMR study (in $CDCl_3$) of free base porphyrin **5** in comparison to Zn porphyrin **6a**

The ^{1}H NMR signals obtained in $CDCl_3$ for **5** and **6a** are fine and well resolved (**Fig. 1**). For free base porphyrin **5**, the characteristic chemical shift of pyrrole NH in the porphyrin inner is located at -2.70 ppm. For the Zn complex **6a**, the signal peak at -2.70 ppm disappears, since the hydrogen atom in the N-H bond is replaced by zinc ion. In addition, the other proton signals are quite similar to that of **5**. Moreover, the ^{13}C spectra of compounds **5** and **6a** show a similar pattern. The two peaks at around 164.79 and 164.19 ppm are assigned to the two carbonyl carbon atoms of the naphthalimide structure.

Table 1
FT-IR spectral data of **5** and **6a-6e** in cm^{-1}

compounds	Assignment											
	$\nu_{N\text{-}H}$	$\delta_{N\text{-}H}$	$\nu_{C\text{-}H}$	$\nu_{C\text{-}H}$	$\delta_{C\text{-}H}$	$\nu_{C=C}$	$\nu_{C=C}$	$\nu^{s}_{C=O}$	$\nu^{as}_{C=O}$	$\nu_{C\text{-}N}$	$\nu_{C\text{-}O}$	^{a}N-M	$\delta_{C\text{-}H}^{arom}$
5	3313	966	2922	2852	1465	1581	1510	1708	1670	1355	1242		781
6a			2924	2852	1466	1582	1508	1708	1668	1355	1242	997	779
6b			2922	2852	1465	1583	1510	1707	1666	1357	1246	999	779
6c			2922	2850	1465	1581	1508	1708	1670	1355	1242	1004	779
6d			2924	2852	1465	1582	1508	1708	1670	1357	1246	999	781
6e			2924	2852	1465	1583	1509	1708	1669	1355	1244	1001	781

^{a}N-metal coordination bonds in the porphyrin-metal complexes.

Table 2
UV-Vis absorption and fluorescence data of **4**, **5** and **6a-6e**.

Compounds	Absorption λ_{max}/nm(ε/M^{-1}cm^{-1})						PL λ_{max}/nm	$^d\Phi_F$
	$^c\pi$-π*	B(0—0)	Q_x(1—0)	Q_x(0—0)	Q_y(1—0)	Q_y(0—0)		
^{b}**4**		419	517	554	592	649		
5	363(6.85×10^4)	420(4.25×10^5)	515(2.05×10^4)	550(1.15×10^4)	591(7.50×10^3)	646(6.50×10^3)	654, 711	0.14
6a	358(7.60×10^4)	421(5.90×10^5)		548(2.90×10^4)	587(8.50×10^3)		599, 643	0.08
6b	360(5.95×10^4)	417(4.29×10^5)		539(2.05×10^4)				
6c	374(1.19×10^5)	477(1.25×10^5)			583(1.15×10^4)	619(1.40×10^4)		
6d	364(4.85×10^4)	414(8.7×10^4)			575(5.50×10^3)	611(3.50×10^3)		
6e	362(7.05×10^4)	412(3.3×10^5)		529(1.75×10^4)				

^{b}Absorption data of **4** were recorded in a CH_2Cl_2 /ethanol mixture at room temperature.
$^c\pi$-π^* transitions of the naphthalimide groups.
^{d}Fluorescence qantum yield recorded in CH_2Cl_2 solution.

2.2.2. FT-IR spectra characterization

The structural information was further confirmed using Fourier transform infrared spectrometer. A comparison of FT-IR spectra of free base porphyrin **5** and its metal complexes **6a-6e** is shown in **Table 1**. For compound **5**, the absorption bands at 3313 and 966 cm^{-1} are assigned to the N–H stretching and in plane bending vibration of the pyrrole group, respectively [24, 25]. These absorption bands disappear in metal complexes **6a-6e**, since the hydrogen atom of the N–H bond is replaced by metal ion to form metal–N bond. It is well known that the band at around 1000 cm^{-1} is metal-sensitive in the porphyrin-metal complex [25, 26]. In the FT-IR spectra of metal complexes **6a-6e** (**Fig. 2**, **Fig. S12, S14, S16,**), a new strong absorption band appears at 997 cm^{-1} (**6a**)、999 cm^{-1} (**6b**)、1004 cm^{-1} (**6c**)、999 cm^{-1} (**6d**) and 1001 cm^{-1} (**6e**), respectively, which further confirm the formation of metal complexes. The FT-IR spectra of all compounds **5** and **6a-6e** show intense absorption bands at around 1708 cm^{-1} and 1670 cm^{-1}, respectively, which are characteristic of symmetrical and asymmetrical vibrations of the carboyl groups from the 1,8-naphthalimide structure [27, 28]. Additionally, the absorption bands at about 1355 cm^{-1} are also characteristic for the imide (C–N–C) bonds in the naphthalimide structure [28]. Bands at around 1582 and 1509 cm^{-1} originate from the C=C vibrations of the aromatic system, and bands peaking at around 780 cm^{-1} are related to the deformation vibrations of aromatic rings. The intensive bands at 2852-2922 cm^{-1} are characteristic of the vibration of methylene groups. In addition, bands at 1465 cm^{-1} are assigned to the bending vibration of methylene or methyl groups.

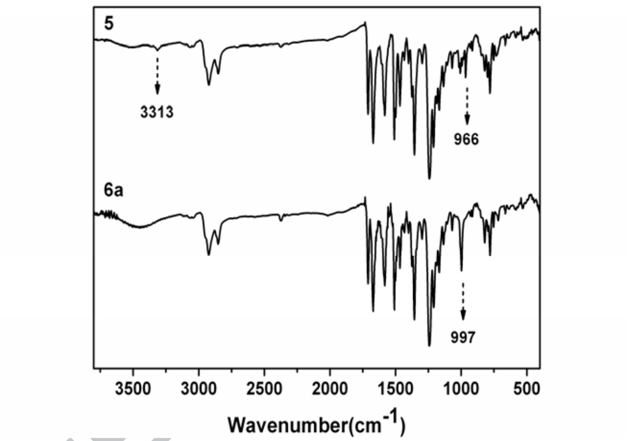


Fig. 2. FT-IR study of free base porphyrin **5** in comparison to Zn porphyrin **6a**

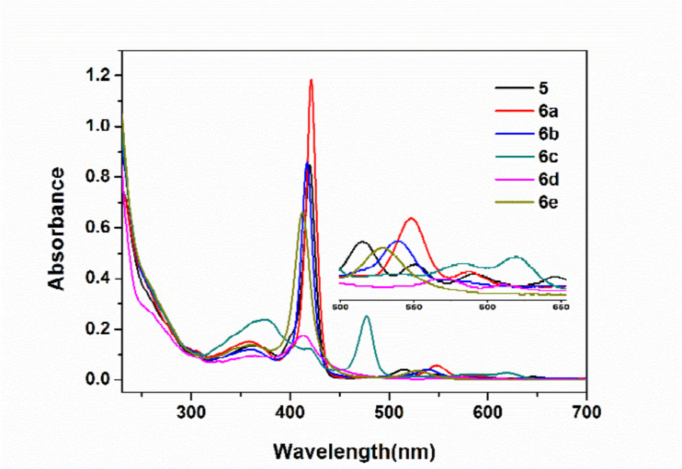


Fig. 3. UV-Vis absorption spectra for compounds **5** and **6a-6e**, in CH_2Cl_2 at room temperature (2.0×10^{-6}M).

2.3. Photophysical properties

2.3.1. Steady-state absorption spectra

The UV-Vis absorption spectra of compound **5** and its metal complexes **6a-6e** are shown in **Fig. 3**. All the compounds show a characteristic absorption band peaking at around 360 nm, which can be assigned to π-π^* transition associated specifically with the naphthalimide group [29]. It is known that the absorption bands of the porphyrins are due to the electronic transitions from the ground state S_0 to the lowest singlet excited states S_1 (Q state) and S_2 (B state). The absorption spectrum of **5** in CH_2Cl_2 displays a strong Soret-absorption band (420 nm) corresponding to the transition from S_0 to S_2, and four minor Q-absorption bands at 515, 550, 591 and 646 nm corresponding to the transition from S_0 to S_1. After the metal ions entered the porphyrin ring, the number of Q bands decreased to one or two in the visible light region, because of the increasing of the symmetry of the molecular structure [30]. The absorption spectrum of **4** in a mixture of CH_2Cl_2/ethanol displays a Soret-absorption band at 419 nm and Q-absorption bands at 517, 554, 592 and 649 nm (**Table 2**). However, the Soret band and Q-bands of **5** remained almost unaltered compared to **4**. The similarity between the absorption spectra of **4** and **5** indicates that the electronic coupling between the peripheral naphthalimide groups and porphyrin ring in the ground state is negligibly small.

2.3.2. Luminescence spectra and photo-induced energy transfer.

Fig. 4 presents the fluorescence spectra of free base porphyrin **5** and its metal complexes **6a-6e** in CH_2Cl_2 excited at 540 nm. The emission for the free base porphyrin **5** shows two peaks, one strong peak at 654 nm and a weaker shoulder at 711 nm. However, for **6a**, the spectrum shows a different behavior. The fluorescence spectrum shows a strong peak maximum at 599 nm and a smaller one at 643 nm. In addition, the fluorescence intensities of the other transitional metal complexes **6b-6e** are much weaker than that of **5** and **6a**, which confirms that the transitional metal located in the porphyrin core quench the fluorescence of the porphyrin.

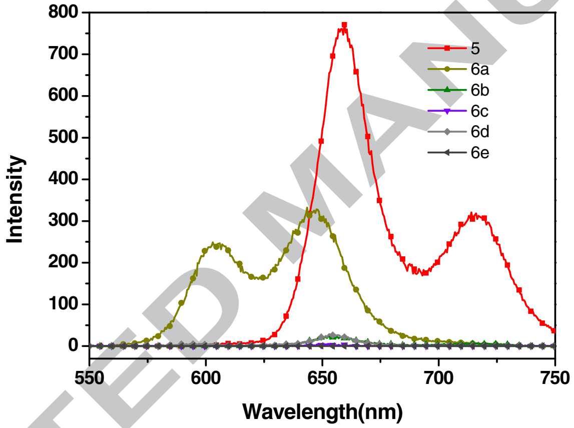


Fig. 4. Emission spectra of **5** and **6a-6e** in CH_2Cl_2 (1.0×10^{-4}M) excited at 540 nm.

The fluorescence quantum yields (Φ_F) of **5** and **6a** were next determined by comparing with a standard compound 5,10,15,20-tetraphenyl porphyrin (**TPP**) in degassed toluene solution presenting a fluorescence quantum of 0.12 [10]. The quantum yields of fluorescence were calculated according to **Eq. (1)**, A_{ref}, S_{ref}, n_{ref}, *and* A_{sample}, S_{sample}, n_{sample} represent the absorbance at the excited wavelength, the integrated emission band area and the solvent refractive index of the standard and the sample [17]. The Φ_F values of compounds **5** and **6a** are 0.14 and 0.08 respectively, which were higher than the reference compound **TPP**. The improved Φ_F may come from the energy transfer from the naphthalimide units to the porphyrin core.

$$\Phi_F = \Phi_{ref}\left(\frac{S_{sample}}{S_{ref}}\right)\left(\frac{A_{ref}}{A_{sample}}\right)\left(\frac{n_{sample}}{n_{ref}}\right)^2 \qquad (1)$$

In order to further investigate the energy transfer in the light-harvesting molecules **5** and **6a**, we synthesized a peripheral “donor” fluorophore 4-phenyloxy-N-(4-(octyloxy)phenyl)-1,8-naphthalimide **7** as a reference compound. The normalized absorption of **TPP** and emission of reference 1,8-naphthalimide **7** are shown in **Fig. 5**. It is clear that there is a good spectral overlap between the donor dye and the absorbance of the acceptor chromophore, which is a requirement for efficient energy transfer in the donor-acceptor light-harvesting molecules.

The fluorescence spectra of the reference compound **7** and light-harvesting molecules **5** and **6a** in CH_2Cl_2 solution, obtained after excitation within the spectral region of maximal absorption (360 nm) of the peripheral 4-phenyloxy-1,8-naphthalimides are illustrated in **Fig. 6**. As a result of energy transfer, the emission intensity of the periphery (4-phenyloxy-1,8-naphthalimides) in compounds **5** and **6a** are strongly decreased with respect to the reference compound **7**. The efficiency of the energy transfer in the light-harvesting molecules **5** and **6a** were calculated to be 94% and 89% recpectively using **Eq. (2)**, where F_D is the fluorescence intensity of the donor without acceptor (compound **7**) and F_{DA} is the fluorescence intensity of the donor chromophore in the presence of acceptor (compounds **5** and **6a**) [16].

$$E = 1 - F_{DA}/F_D \qquad (2)$$

On the other hand, as can be seen from **Fig. 7**, when selected as a reference compound compared to the core of light-harvesting molecule **5**, under excitation at 360 nm (within the maximal absorption of the peripheral 4-phenyloxy-1,8-naphthalimides), **TPP** shows a red light emission in the spectral region of 680-750 nm, while the core fluorescence intensity of light-harvesting molecule **5**, due to the energy transfer from the periphery, is considerably higher. All these results indicate that the novel compounds **5** and **6a** would be able to act as efficient light harvesting antennae.

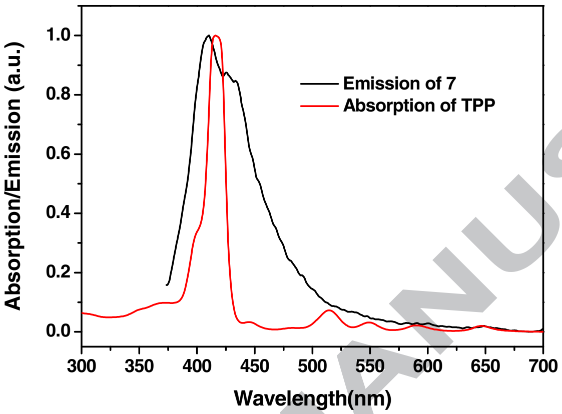


Fig. 5. Normalized absorption of **TPP** and emission of reference 1,8-naphthalimide **7**.

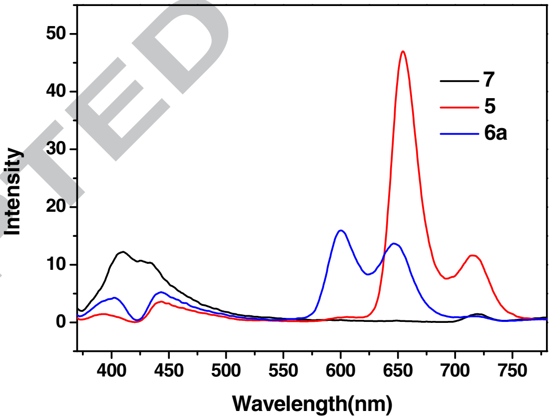


Fig. 6. Emission spectra of **5, 7** and **6a** in CH_2Cl_2 (1.0×10^{-5}M) excited at 360 nm, recorded at the same optical density.

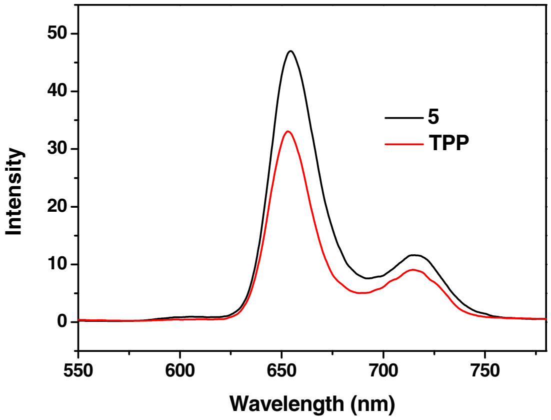


Fig. 7. Emission spectra of **5, TPP** in CH_2Cl_2 (1.0×10^{-5}M) excited at 360 nm, recorded at the same optical density.

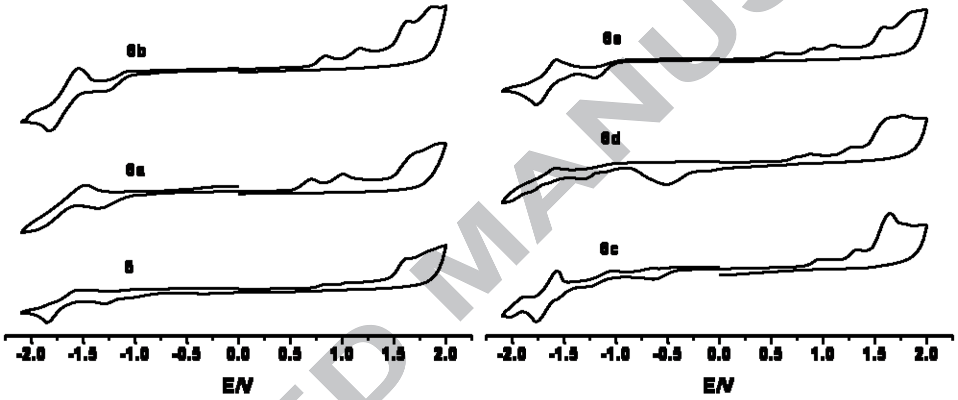


Fig. 8. Cyclic voltammograms of compounds **5** and **6a-6e** in CH_2Cl_2.

2.4. Electrochemistry

Table 3

Summary of ring redox potentials of compound **5** and **6a-6e**.

Compounds	E_{ox2}/V	E_{ox1}/V	E_{red1}/V	E_{red2}/V	$^{d}\Delta E/V$
5	1.06	0.84	-1.31	-1.83	2.15
6a	1.02	0.73	-1.37		2.10
6b	1.17	0.83	-1.27	-1.82	2.10
6c	1.31	0.96	-1.21	-1.76	2.17
6d	1.27	0.86	-1.33	-1.78	2.19
6e	1.10	0.92	-1.19	-1.77	2.11

$^{d}\Delta E = E_{ox1} - E_{red1}$

The oxidation and reduction properties of **5** and its metal complexes **6a-6e** have been studied by cyclic voltammetry. The cyclic voltammograms are illustrated in **Fig. 8**, and the redox potentials of ring are summarized in **Table 3**. The six porphyrin compounds **5** and **6a-6e** exhibit a similar ring oxidation and reduction behavior, showing one irreversible oxidation and one or two reversible reduction within the potential window of the solvent, respectively. The difference between the first ring oxidation potential and the first ring reduction potential lies in the range of 2.10 to 2.19 V, which are in agreement with the values of 2.25±0.15 V reported by K.M. Kadish [31]. As for **5** (**$TNPPH_2$**), the redox potentials are located at 0.84, 1.06, -1.31, and -1.83 V, and the corresponding reaction can be illustrated as follows:

Reduction (ring)

$$[\mathrm{TNPPH_2}]^{0} + e^{-} \rightleftharpoons [\mathrm{TNPPH_2}]^{-}$$

$$[\mathrm{TNPPH_2}]^{-} + e^{-} \rightleftharpoons [\mathrm{TNPPH_2}]^{2-}$$

Oxidation (ring)

$$[\mathrm{TNPPH_2}]^{0} - e^{-} \rightleftharpoons [\mathrm{TNPPH_2}]^{+}$$

$$[\mathrm{TNPPH_2}]^{+} - e^{-} \rightleftharpoons [\mathrm{TNPPH_2}]^{2+}$$

As shown in **Fig. 8**, the cyclic voltammograms of **5**, **6a** and **6b** are similar in shape. But **6c** and **6d** show an unusual reduction wave, located at -0.61 and -0.53V, respectively. The reduction potential of -0.53V corresponds to the reduction reaction Fe(III)/Fe(II). The unique reduction potential of -0.61V can be explained as follows: Mn(II) is unstable in the air and it is easy to be oxidized to Mn(III) by oxygen from the surroundings. Therefore, after being kept in natural conditions for several days, portion of Mn(II) turned to Mn(III), and **6c** finally shows a similar redox behavior to that of **6d**. Additionally, the first oxidation wave of **6e** located at 0.56 V is corresponding to the oxidation reaction Co(II)/Co(III).

Conclusions

In summary, a novel porphyrin-naphthalimide pentamer **5** was synthesized by linking four light-harvesting naphthalimide units to a central porphyrin, via ether bridges. And the corresponding metal complexes **6a-6e** were obtained under different reaction conditions. All the new compounds **5** and **6a-6e** show broad absorption covering UV to visible light region. The compounds **5** and **6a** have been shown to behave as efficient light-harvesting antennae. After being excited at 540 nm, the free base porphyrin **5** and porphyrin complex **6a** show intense red fluorescence emission, but fluorescence of complexes **6b-6d** were quenched in different degrees. Electrochemical study indicates that all compounds **5** and **6a-6d** show a similar ring oxidation and reduction behavior. All these studies provide wider ground for choice and application of the materials in the field of organic photo-electronics such as OLEDs, OPV and photocatalytic degradation. Further work is ongoing to use these materials in the study of photocatalytic degradation of organic pollutants.

Experimental section

4.1. General

Silica gel (200-300 mesh, Qingdao Haiyang) and aluminum oxide (100-200 mesh, Shanghai Ludu Chemical Reagent) was used for column chromatography. CH_2Cl_2 suitable for electrochemical and photospectral experiments was obtained by distillation over calcium hydride, and all other chemicals used for synthesis were reagent grade unless otherwise stated.

The ^1H and ^{13}C NMR (δ in ppm) spectra were recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer with TMS as the internal standard and $CDCl_3$ and DMSO-d_6 as solvent. MALDI-TOF mass spectra were acquired by a Bruker Autoflex mass spectrometer (Bruker Daltonics, Bremen, Germany). UV–vis absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR Spectrophotometer. Steady state fluorescence spectra were obtained with a Shimadzu RF-5301PC Fluorescence Spectrophotometer. IR spectra were obtained on a Shimadzu IRPrestige-21 Fourier transform infrared spectrometer as KBr pellets. Cyclic voltammetric (CV) measurements were carried out with a CHI660C electrochemical workstation (Shanghai Chenhua, China) utilizing the three electrode configuration consisting of a glassy carbon (working electrode), platinum wire (auxiliary electrode) and Ag/$AgNO_3$ (reference electrode) electrodes. The experiments were done in dry CH_2Cl_2 using 0.1M tetrabutylammoniumhexafluorophosphate as supporting electrolyte. Melting points were determined using a SGW X-4 micro melting point apparatus (Shanghai Precision & Scientific Instrument Co., LTD) and uncorrected. Elemental analyses were performed with a German Elementary Varil EL III instrument.

4.2. General procedure for the Synthesis of 2, 3 and 7

*4.2.1. Synthesis of 4-Bromo-N-(4-hydroxyphenyl)-1,8-naphthalimide(**2**).* 4-Bromo-1,8-naphthalic anhydride (1.94 g, 7 mmol) and 4-aminophenol (0.82 g, 7.5 mmol) were dissolved in a mixture solvent composed of DMF (20 mL) and acetic acid (3 mL). The resulting mixture was heated at 100 °C under N_2 atmosphere for 10 h. After cooling to room temperature, the mixture was poured to cold water. The precipitated product was collected by filtration, washed with water for several times and dried in a vacuum oven to afford crude product **2**, which was used for the next step without any further purification.

*4.2.2. Synthesis of 4-Bromo-N-(4-(octyloxy)phenyl)-1,8-naphthalimide(**3**).* The crude product **2** (1.48 g) was dissolved in 20 mL of DMF, and 1.38 g (10 mmol) of anhydrous K_2CO_3 was added. After the mixture was vigorously stirred at room temperature for 20 min, n-octylbromide (1.1 g, 5.7 mmol) was slowly added via syringe. The resulting reaction mixture was stirred at 80 °C under N_2 atmosphere for 10 h. After cooling to room temperature, the reaction mixture was poured into cold water, The precipitated product was collected by filtration, washed with ethanol for several times, and purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (volume ratio, 1/1) as the eluent. Further purification was performed by recrystallization from CH_2Cl_2/ethanol to obtain **3** as a white solid (1.47 g, 3.1 mmol, 76%). Melting points: 183–185 °C. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.70 (dd, J = 7.3, 1.1 Hz, 1H), 8.63 (dd, J = 8.5, 1.1 Hz, 1H), 8.46 (d, J = 7.9 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.88 (dd, J = 8.5, 7.3 Hz, 1H), 7.24–7.16 (m, 2H), 7.10–6.99 (m, 2H), 4.02 (t, J = 6.5 Hz, 2H), 1.89–1.72 (m, 2H), 1.53–1.44 (m, 2H), 1.41–1.27 (m, 8H), 0.90 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.00, 163.97, 159.29, 133.53, 132.42, 131.57, 131.19, 130.76, 130.56, 129.41, 129.32,128.17, 127.27, 123.32, 122.45, 115.27, 68.24, 31.85, 29.38, 29.28, 29.26, 26.08, 22.69, 14.14. IR (KBr, cm^{-1}): 2922, 2852, 1707, 1666, 1587, 1512, 1473, 1363, 1236, 786. MS: (MALDI-TOF) m/z: 480.306 $[M+H]^+$; LC/MS: m/z: 480.10 $[M+H]^+$ (calcd for $C_{26}H_{26}BrNO_3$, 480.394). Anal. Calcd for $C_{26}H_{26}BrNO_3$: C, 65.00%, H, 5.46%, N, 2.92%. Found: C, 65.11%, H, 5.44%, N, 3.01%.

*4.2.3. Synthesis of 4-phenyloxy-N-(4-(octyloxy)phenyl)-1,8-naphthalimide (**7**).*

4-Bromo-N-(4-(octyloxy)phenyl)-1,8-naphthalimide (480 mg, 1 mmol) was added to a mixture of phenol (141 mg, 1.5 mmol), finely ground potassium hydroxide (690 mg, 5 eq), 18-crown-6 (catalytic amount), and 10 mL of DMF at room temperature. The resulting mixture was stirred at 90 °C under N_2 for 12 h. After cooled to room temperature, the mixture was then poured into cold water. The precipitated product was collected by filtration, washed with ethanol for several times, and purified by silica gel column chromatograph by using CH_2Cl_2 as the eluent to obtain **7** as a white solid (463 mg, 94%). Melting points: 174–175 °C. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 8.76 (d, J = 8.4 Hz, 1H), 8.70 (d, J = 7.3 Hz, 1H), 8.50 (d, J = 8.3 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.50 (t, J = 7.9 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.9 Hz, 4H), 7.04 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.3 Hz, 1H), 4.01 (t, J = 6.6 Hz, 2H), 2.00 – 1.71 (m, 2H), 1.47 (d, J = 7.1 Hz, 2H), 1.40 – 1.26 (m, 8H), 0.90 (t, J = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.75, 164.10, 160.09, 159.13, 154.78, 133.19, 132.26, 130.46, 130.04, 129.53, 128.83, 127.77, 126.58, 125.69, 124.05, 122.82, 120.84, 116.70, 115.22, 110.61, 68.22, 31.87, 29.40, 29.29, 26.11, 22.71, 14.16. IR (KBr, cm^{-1}): 2924, 2854, 1713, 1669, 1588, 1513, 1467, 1366, 1240, 777. MS: (MALDI-TOF) m/z: 495.346 $[M+H]^+$.

4.3.General procedure for the Synthesis of free base porphyrins 4 and 5

*4.3.1. Synthesis of 5,10,15,20-tetrakis(4-hydroxyphenyl)-porphyrin (**4**).*The porphyrin **4** was prepared according to Adler-Longo method after some modifications [32]. 4-hydroxy-benzaldehyde (14.7 g, 120 mmol) was dissolved in 300 mL of propionic acid, and the resulting solution was heated to reflux under N_2 atmosphere. Then, fresh distilled pyrrole (8.1 g, 120 mmol) was added dropwise via syringe. After addition was complete, the reaction mixture was stirred for further 40 min. After cooed to room temperature, the reaction mixture was allowed for one night stay at room temperature. Propionic acid was transferred to a beaker and solid was dissolved in 300 mL of CH_3CH_2OH. The resulting solution and the above reacted propionic acid were combined, and stored at –18 °C overnight. After filtration, the solid product was washed repeatedly with a mixture of EtOH and propionic acid (volume ratio, 1/1), followed by CH_2Cl_2. The crude product was purified by silica gel column chromatography (CH_2Cl_2/CH_3CH_2OH, 1/1) to give **4** as a purple solid with a yield of 15%. ^1H NMR (400 MHz, DMSO): δ ppm: 9.98 (s, 4H, -OH), 8.87 (s, 8H, β-pyrrole), 8.00 (d, J = 8.1 Hz, 8H, 2,6-phenyl), 7.20 (d, J = 8.2 Hz, 8H, 3,5-phenyl), -2.88 (s, 2H, NH-pyrrole). UV-Vis (EtOH/CH_2Cl_2), λ_{max}: 419 nm (Soret), 517, 554, 592, 649 nm. IR (KBr, cm^{-1}): 3313, ν(N–H); 966, ν(N–H); 1604 and 1508, ν(C=C); 1469, (C-H); 1348, ν(C-N); 1232, ν(C-O). MS: (MALDI-TOF) m/z: 678.961 $[M+H]^+$; LC/MS: m/z: 679.20 $[M+H]^+$ (calcd for $C_{44}H_{30}N_4O_4$, 678.733). Anal. Calcd for $C_{44}H_{30}N_4O_4$: C, 77.86%, H, 4.46%, N, 8.25%. Found: C, 77.83%, H, 4.31%, N, 8.14%.

4.3.2. *Synthesis of free base porphyrin **TNPPH$_2$** (**5**).*

A mixture of **4** (2.04 g, 3 mmol), 4-bromo-N-(4-(octyloxy)phenyl)-1,8-naphthalimide **3** (7.22 g, 15 mmol, 5 eq), finely ground anhydrous K_2CO_3 (3.38 g, 8 eq), and 18-crown-6 (catalytic amount) in DMF (120 mL) was heated at 90 °C for 12 h. After cooled to room temperature, the mixture was poured into ethanol. The precipitated product was collected by filtration, washed with ethanol for several times, and purified by neutral alumina column chromatography (100-200 mesh) using CH_2Cl_2 as the eluent to obtain **TNPPH$_2$ 5** (4.15 g, 1.82 mmol, 61%) as a purplish red solid. Melting points > 300 °C. ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 9.09–8.95 (m, 12H), 8.84–8.70 (m, 8H), 8.38 (d, J = 8.4 Hz, 8H), 8.01–7.92 (m, 4H), 7.66 (d, J = 8.5 Hz, 8H), 7.46 (d, J = 8.2 Hz, 4H), 7.31–7.28 (m, 8H), 7.15–7.03 (m, 8H), 4.03 (t, J = 6.5 Hz, 8H), 1.91–1.75 (m, 8H), 1.54–1.41 (m, 8H), 1.39–1.32 (m, 32H), 0.98–0.62 (m, 12H), -2.70 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 164.79, 164.19, 159.88, 159.21, 155.10, 139.31, 136.39, 133.27, 132.53 , 130.28, 129.55 , 128.91, 127.72, 126.91, 124.41, 123.04, 119.28, 119.01 , 117.34, 115.28, 111.35, 68.26, 31.86, 29.39, 29.28, 26.10, 22.70, 14.15. IR (KBr,

cm^{-1}): 3313, 2922, 2582, 1708, 1670, 1581, 1510, 1465, 1355, 1242, 966, 781. MS: (MALDI-TOF) m/z: 2277.161 $[M+H]^+$ (calcd for $C_{148}H_{130}N_8O_{16}$, 2276.660). Anal. Calcd for $C_{148}H_{130}N_8O_{16}$: C, 78.08%, H, 5.76%, N, 4.92%. Found: C, 78.11%, H, 5.71%, N, 4.97%.

4.4. General procedure for the Synthesis of metal complexes 6a-6e

*4.4.1. Synthesis of Zn porphyrin **TNPPZn (6a)**.* To a mixture solvent composed of $CHCl_3$ (30 mL) and methanol (10 mL), **$TNPPH_2$ 5** (455 mg, 0.2 mmol) and $Zn(CH_3COO)_2·2H_2O$ (440 mg, 2 mmol, 10 eq) were added. The resulting mixture was stirred at 70 °C for 1 h. After cooling to room temperature, the mixture was washed with deionized water, dried over Mg_2SO_4 and concentrated under reduced pressure. The residue was purified by neutral alumina column chromatograph using $CHCl_3$ as the eluent, to obtain **6a** as a purplish red solid (440 mg, 94% yield). ^1H NMR (400 MHz, $CDCl_3$) δ ppm: 9.14 (s, 8H), 8.92 (d, J = 8.3 Hz, 4H), 8.70 (d, J = 7.2 Hz, 4H), 8.55 (dd, J = 8.2, 2.3 Hz, 4H), 8.39 (d, J = 8.4 Hz, 8H), 7.87 (t, J = 7.7 Hz, 4H), 7.65 (d, J = 8.5 Hz, 8H), 7.42 (d, J = 8.2 Hz, 4H), 7.19 (d, J = 8.0 Hz, 8H), 7.04 (d, J = 8.8 Hz, 8H), 4.01 (t, J = 6.5 Hz, 8H), 1.88–1.75 (m, 8H), 1.52–1.28 (m, 40H), 0.92 (dd, J = 8.9, 12H). ^{13}C NMR (100 MHz, CDCl3) δ ppm: 164.68, 164.07, 159.93, 159.14, 154.81, 150.33, 140.14, 136.24, 133.22 , 132.43, 132.19 , 130.16, 129.47 , 128.84, 127.62, 126.80, 124.30, 122.92, 120.13, 118.87, 117.11, 115.22, 111.19, 68.25, 31.86, 29.39, 29.28, 26.10, 22.70, 14.15. IR (KBr, cm^{-1}): 2924, 2852, 1708, 1668, 1582, 1508, 1466, 1355, 1242, 997, 779. MS: (MALDI-TOF) m/z: 2340.014 $[M+H]^+$ (calcd for $C_{148}H_{128}N_8O_{16}Zn$, 2340.054). Anal. Calcd for $C_{148}H_{128}N_8O_{16}Zn$: C, 75.96%, H, 5.51%, N, 4.79%. Found: C, 76.02%, H, 5.44%, N, 4.75%.

*4.4.2 Synthesis of Cu porphyrin **TNPPCu (6b)**.* To a mixture solvent composed of $CHCl_3$ (30 mL)and methanol (10 mL), **$TNPPH_2$ 5** (455 mg, 0.2 mmol), $Cu(CH_3COO)_2$ (364 mg, 2 mmol, 10 eq) and KOH (110 mg, 2 mmol) were added. The following procedure is similar to that for **6a**, to obtain **6b** as a purplish red solid (0.44 g, 94% yield). IR (KBr, cm^{-1}): 2922, 2852, 1707, 1666, 1583, 1510, 1465, 1357, 1246, 999, 779. MS: (MALDI-TOF) m/z: 2338.228 $[M+H]^+$ (calcd for $C_{148}H_{128}N_8O_{16}Cu$, 2338.190). Anal. Calcd for $C_{148}H_{128}N_8O_{16}Cu$: C, 76.02%, H, 5.52%, N, 4.79%. Found: C, 76.10%, H, 5.46%, N, 4.78%.

*4.4.3 Synthesis of Mn porphyrin **TNPPMn (6c)**.*A reaction flask charged with **$TNPPH_2$ 5** (455 mg, 0.2 mmol) was degassed by several vacuum-nitrogen cycles. $CHCl_3$ (30 mL) was added to the reaction flask and the mixture was stirred for 10 min at room temperature. A solution of $MnCl_2$ (252 mg, 2 mmol, 10 eq) in DMF (20 mL) was added via syringe. After the addition was completed, the reaction mixture was heated to 70 °C and stirred for 10 min, and then a solution of KOH in methanol (10 mL) was added to the reaction mixture. After completion, the final mixture was heated to reflux for 20 h. After cooling to room temperature, the mixture was filtrated and the solvent was removed under reduced pressure. The residue resulting from evaporation was dissolved in CH_2Cl_2, and the resulting solution was washed with deionized water, dried over Mg_2SO_4 and concentrated under reduced pressure. The crude product was purified by neutral alumina column chromatography using $CHCl_3$ as the eluent, to obtain **6c** as a blue black solid (363 mg, 78% yield). IR (KBr, cm^{-1}): 2922, 2850, 1708, 1670, 1581, 1508, 1465, 1355, 1242, 1004, 779. MS: (MALDI-TOF) m/z: 2329.392 $[M+H]^+$ (calcd for $C_{148}H_{128}N_8O_{16}Mn$, 2329.582). Anal. Calcd for $C_{148}H_{128}N_8O_{16}Mn$: C, 76.30%, H, 5.54%, N, 4.81%. Found: C, 76.21%, H, 5.52%, N, 4.88%.

*4.4.4 Synthesis of Fe porphyrin **TNPPFeCl (6d)**.* The synthetic precedure for **TNPPFeCl 6d** is similar to that for **6c** by using $FeCl_3$ (325 mg, 2 mmol, 10 eq) as the starting material to obtain **6d** as a greenish black solid (355 mg, 75% yield). IR (KBr, cm^{-1}): 2924, 2852, 1708, 1670, 1582, 1508, 1465, 1357, 1246, 999, 781. MS: (MALDI-TOF) m/z: 2330.323 $[M-Cl]^+$ (calcd for $C_{148}H_{128}N_8O_{16}FeCl$, 2365.942; $C_{148}H_{128}N_8O_{16}Fe$, 2330.489). Anal. Calcd for $C_{148}H_{128}N_8O_{16}FeCl$: C, 75.13%, H, 5.45%, N, 4.74%. Found: C, 75.08%, H, 5.44%, N, 4.72%.

*4.4.5 Synthesis of Co porphyrin **TNPPCo (6e).*** The synthetic precedure for **TNPPCo 6e** is similar to that for **6c** by using $CoCl_2$ (260 mg, 2 mmol, 10 eq) as the starting material to obtain **6e** as a red solid (373 mg, 80% yield). IR (KBr, cm^{-1}): 2924, 2852, 1708, 1669, 1583, 1509, 1465, 1355, 1244, 1001, 781. MS: (MALDI-TOF) m/z: 2333.404 $[M+H]^+$(calcd for $C_{148}H_{128}N_8O_{16}Co$, 2333.577). Anal. Calcd for $C_{148}H_{128}N_8O_{16}Co$: C, 76.17%, H, 5.53%, N, 4.80%. Found: C, 76.12%, H, 5.50%, N, 4.81%.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version at

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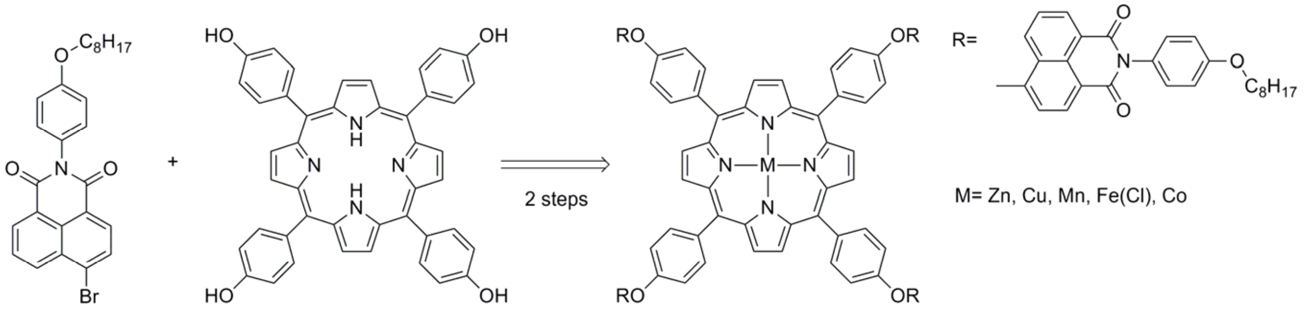
Graphical abstract



1) DMF, K_2CO_3, 18-crown-6

2) metallation on different conditons

Synthesis, characterization and properties of covalently linked porphyrin-naphthalimidepentamer and its metal complexes

High lights:

1. A novel porphyrin-naphthalimide pentamer was synthesized and the corresponding metal (Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}) complexes were obtained under different reaction conditions.

2. The porphyrin-naphthalimide pentamer **5** and its Zn complexes **6a** emit intense red light. The fluorescence quantum yields were 0.14 and 0.08 respectively.

3. Due to the efficient energy transfer, the compound 5 and **6a** can act as efficient light-harvesting antennae.