

Synthesis, characterization and near-infrared photoluminescent studies of diethyl malonate appended mono-porphyrinate lanthanide complexes

Hong-Shan He,^{a,c} Zhi-Xin Zhao,^a Wai-Kwok Wong,^{*a} King-Fai Li,^b Jian-Xin Meng^d and Kok-Wai Cheah^{a,b}

^a Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong

^b Department of Physics, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong

^c Department of Applied Chemistry, National Huaqiao University, Quanzhou 362011, P. R. China

^d Department of Chemistry, Jinan University, Guangzhou, 510275, P. R. China

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A new unsymmetrical diethyl malonate appended porphyrin and its Yb³⁺, Er³⁺ and Nd³⁺ complexes were prepared and characterized by elemental analysis, NMR, IR, UV-visible and mass spectral methods. The results revealed that the porphyrinate behaved as a tri-deprotonated hexadentate ligand with the appended diethyl malonate group coordinated to the lanthanide ion as an anion. Photoluminescent studies showed that the porphyrin ring transferred the absorbed visible light to the metal ions, which led to emission characteristic of the lanthanide ions in the near-infrared region. The factors affecting the emission intensity were also investigated.

Introduction

Trivalent rare earth ions are known for their unique optical properties such as line-like emission bands and relatively long luminescence lifetimes.¹ These unique properties have drawn considerable interest for their potential application as fluorescence imaging agents.² Direct excitation of lanthanide ions, however, is difficult because of the forbidden nature of their electronic transitions.³ To overcome this problem, the luminescent lanthanide ions are usually encapsulated by an organic chromophore (often referred to as an "antenna chromophore"), the excitation of which, followed by energy transfer, causes the sensitized luminescence of the metal ion.^{4,5} Most of the investigations in the field of luminescent lanthanide complexes have been devoted to the Eu³⁺, Tb³⁺, Dy³⁺ and Sm³⁺ compounds,^{6–13} which emit in the visible spectral region and are used as sensors⁸ and as luminescent labels in fluoroimmuno-assays.⁶ Recently, there has been increasing interest in complexes of Yb³⁺, Nd³⁺, and Er³⁺,^{12–20} which have emission bands ranging from 880 to 1550 nm. These lanthanide(III) complexes, which emit in the near-infrared (NIR) region, a region where biological tissues and fluids are relatively transparent, are promising probes for fluoroimmuno-assays.^{17a} Furthermore they also have potential applications in optical amplification^{18a,21} and in laser system.^{19c}

Porphyrin, a highly conjugated system that absorbs strongly in the UV-visible region, can act as an antenna for photoluminescence. Their transition metal complexes as photo-sensitizers have been widely investigated.^{22–25} However, there are relatively few studies on lanthanide porphyrinate complexes, especially on monoporphyrylate lanthanide complexes, even though the monoporphyrylate lanthanide complexes were reported early in 1974.²⁶ The first report on porphyrins as sensitizers for Yb³⁺ ion appeared in 1990,²⁷ and their properties were only briefly studied. Eleven years later, Korovin *et al.*²⁸ reported the photo-physical properties of Yb³⁺ complexes of crown ether linked porphyrin and found that the luminescence of the complex was completely quenched in the presence of alkali metal ions. Recently we reported the synthesis and near-infrared luminescent properties of bimetallic monoporphyrylate lanthanide

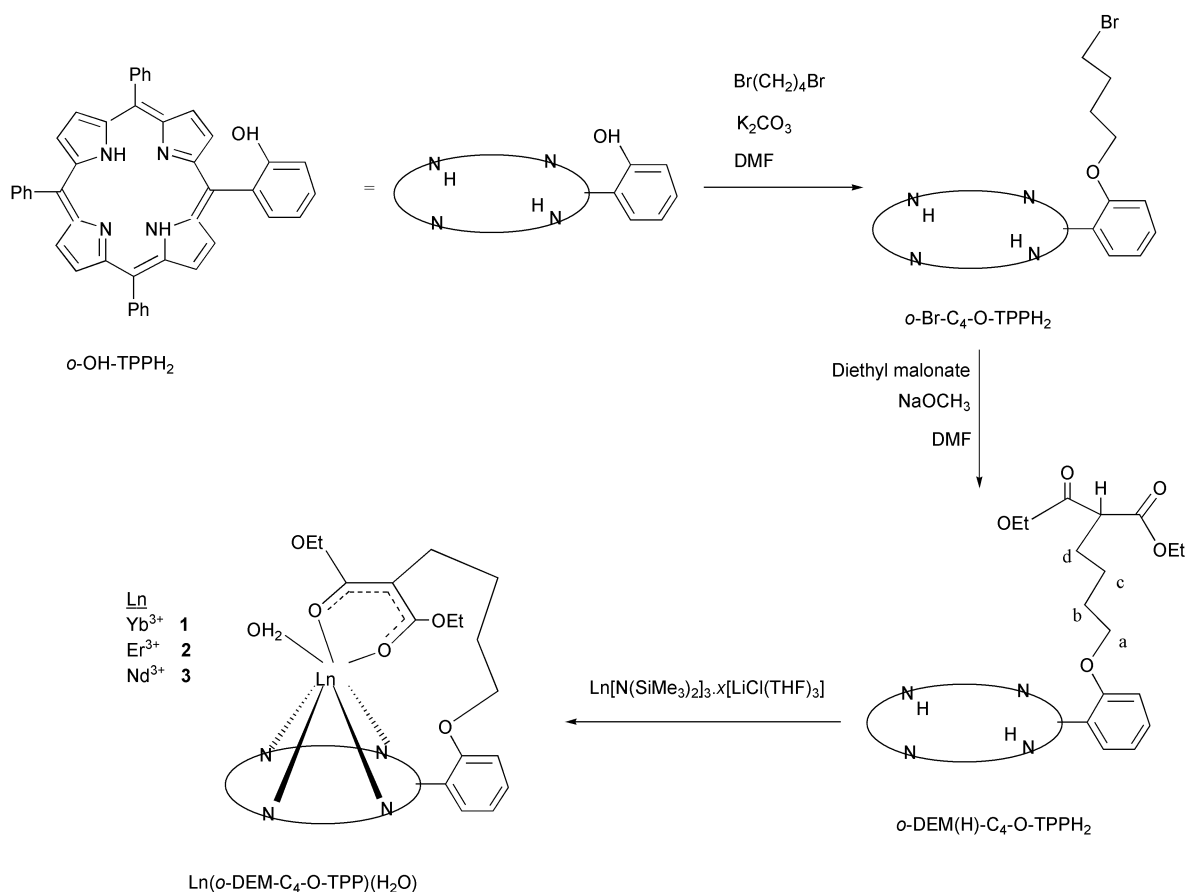
complexes, [Ln(TMPP)(L_{OEt})] (Ln = Yb or Er; L_{OEt} = (η⁵-C₅H₅)-Co[P(=O)(OEt)₂]₃⁻ anion), and demonstrated that porphyrin could absorb and transfer the visible light to lanthanide ions, which led to NIR emission.²⁹

Tailed metalloporphyrins have attracted considerable attention for the various kinds of functions the tailed group exhibited. The pendant group that is linked to the porphyrin ring *via* amide or ether linkage can act as an axial ligand in biochemical mimicking of cytochrome P-450 or as an interaction site in molecular recognition.^{30–33} However, no β-diketonato appended porphyrin and its lanthanide complex have been reported due to the limitations of the traditional method for the preparation of porphyrinate complexes. Recently we reported a new synthetic method for the preparation of cationic monoporphyrylate lanthanide complex [Ln(Por)(H₂O)₃]Cl *via* the interaction of Ln[N(SiMe₃)₂]₃·x[LiCl(THF)₃] with porphyrin free base (H₂Por).³⁴ However for lanthanide ions with large ionic radii, we were unable to isolate stable cationic lanthanide porphyrinate complexes. As most β-diketonates can coordinate to lanthanide ions and form stable lanthanide complexes with the porphyrinate dianion,^{26,35} we propose that stable complexes should be obtained if β-diketonate was appended to the appropriate position of the porphyrin ring through an alkyl chain. In this paper, we report the synthesis and characterization of diethyl malonate (DEM) appended porphyrin and its Yb³⁺, Er³⁺ and Nd³⁺ complexes. The results revealed that the lanthanide complexes were quite stable due to the coordination of the diethyl malonate group. Photoluminescence studies showed that the porphyrin ring could act as an efficient photosensitizer.

Results and discussion

Synthesis and characterization of appended porphyrin

The diethyl malonate appended porphyrin free base, 5-[2-(5,5'-ethoxycarbonyl)pentoxy]phenyl-10,15,20-triphenylporphyrin [*o*-DEM(H)-C₄-O-TPPH₂], was prepared as shown in Scheme 1. 5-(2-Hydroxyphenyl)-10,15,20-triphenylporphyrin (*o*-OH-TPPH₂) was prepared conveniently from the condensation of



o-hydroxybenzaldehyde, benzaldehyde and pyrrole in a molar ratio of 3 : 1 : 4 in propionic acid.³¹ Interaction of *o*-OH-TPPH₂ with an excess amount of 1,4-dibromobutane in dry DMF in the presence of anhydrous K₂CO₃ gave 5-(2-(4-bromobutyl)-phenyl)-10,15,20-triphenylporphyrin (*o*-Br-C₄-O-TPPH₂), which then reacted with diethyl malonate in the presence of a slight excess of sodium methoxide in dry DMF to give *o*-DEM(H)-C₄-O-TPPH₂ in high yield.

The purple porphyrin free base, *o*-DEM(H)-C₄-O-TPPH₂, is stable in the air and soluble in most organic solvents except in methanol and hexane. The UV-visible absorption spectrum of the compound (Fig. 1) is almost identical to that of 5,10,15,20-tetraphenylporphyrin (H₂TPP).³⁶ The Soret and Q bands were observed at 418 and 516, 550, 589, 645 respectively in

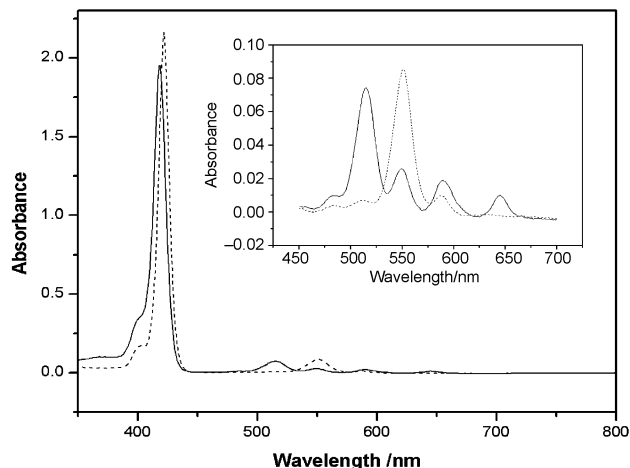


Fig. 1 UV-VIS spectra of DEM-C₄-TPP (solid line) and its Er³⁺ complex (dashed line) in CHCl₃. Inset shows the corresponding plots for an etio-type porphyrin free base.

chloroform solution. The relative intensities of the four Q bands are typical of an etio-type porphyrin free base (inset of Fig. 1).³⁷ In its FAB (positive) mass spectrum, peaks corresponding to [M + H]⁺, [M - CO₂Et]⁺ and [M - (CH₂)₄-CH(CO₂Et)₂]⁺ were observed at 845, 771 and 629 respectively. Furthermore, the electrospray ionization high-resolution mass spectrum (ESI-HRMS) in methanol (positive mode) shows the [M + H]⁺ peak at *m/z* 845.3672 (C₅₅H₄₉N₄O₅ requires 845.3702) confirming that the diethyl malonate group has appended to the porphyrin free base. Its ¹H NMR spectrum (Fig. 2) confirmed that the diethyl malonate has connected to the porphyrin *via* the -(CH₂)₄- chain at its methylene position. The chemical shift of the NH protons of the porphyrin ring was observed at δ -2.77, which is identical to that of H₂TPP. Peaks at δ 3.88, 1.04, 0.51 and 1.53 are attributed to the protons in a, b, c and d positions (Scheme 1) of the four -CH₂- groups, respectively. The chemical shifts of the protons of the diethyl malonate moiety have changed greatly. The chemical shifts of the protons in the two -CH₃ groups, two -OCH₂ groups and one -CH are at δ 0.89, 3.70 and 2.55, respectively. These are more up-field than those of free diethyl malonate (δ 1.28, 4.21 and 3.36 for -CH₃, -OCH₂ and -CH₂ groups, respectively). It is known that the porphyrin ring can produce a ring current, which can make the chemical shifts of the protons closer to the ring center more up-field.³⁸

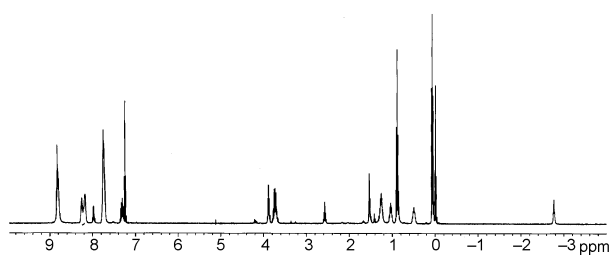


Fig. 2 ¹H NMR spectrum of *o*-DEM-C₄-O-TPPH₂ in CDCl₃.

Our previous investigations^{31,32} on various kinds of heterocyclic base appended porphyrins and their transition metal complexes also confirmed that the chemical shifts of protons in heterocyclic bases appended in the *ortho* position of the phenyl group were more up-field than those in *meta* or *para* positions due to their closer location to the porphyrin ring center. So the large changes of chemical shifts of the protons in diethyl malonate to high field indicate that the group is close to the ring center. In fact, this conformation is quite favorable for the coordination of the diethyl malonate to lanthanide ions.

Synthesis and characterization of lanthanide porphyrinate complexes

Recently, we established a new synthetic method for the preparation of cationic lanthanide porphyrinate complexes [Ln(Por)(H₂O)₃]Cl via the interaction of Ln[N(SiMe₃)₂]₃·x[LiCl(THF)₃] (Ln = Yb³⁺, Er³⁺ and Y³⁺) with porphyrin free base.³⁴ Furthermore, we demonstrated that these cationic porphyrinate complexes were good precursors for the preparation of other lanthanide porphyrinate complexes. For instance, [Ln(Por)(H₂O)₃]Cl reacted with anionic tripodal ligands to form novel neutral seven coordinated porphyrinate complexes.²⁹ However, with lighter lanthanide ions, such as Nd³⁺ which has a larger ionic radius, the [Nd(Por)(H₂O)₃]Cl complex which was only observed spectroscopically, was rather unstable and decomposed rapidly via de-metallation to regenerate the porphyrin free base upon exposure to air and moisture. However, when the diethyl malonate appended porphyrin was used, we were able to obtain complexes 1–3.

Interaction of the porphyrin free base *o*-DEM(H)-C₄-O-TPPH₂ with an excess amount of Ln[N(SiMe₃)₂]₃·x[LiCl(THF)₃] (Ln = Yb, Er or Nd) in refluxing bis(2-methoxyethyl) ether gave purple air stable lanthanide porphyrinate complexes (1 Yb, 2 Er or 3 Nd) (Scheme 1). Complexes 1–3 were quite stable toward moisture and could be purified by column chromatography on silica gel. The complexes were soluble in chloroform, dichloromethane, THF and methanol but insoluble in hexane. The electronic absorption spectra of complexes 1–3 were characteristic of regular-normal metalloporphyrins³⁶ (Fig. 1) and similar to that of [Ln(TPP)(acac)].²⁶ After complexation the number of Q bands of the porphyrin ring (four for porphyrin free base) reduced to two bands at 552 and 589 nm (see inset of Fig. 1). This is in agreement with Gouterman's four-orbital model,³⁹ which predicts that due to an increase in symmetry, the four Q bands of the porphyrin free base will be reduced to two upon the formation of a metalloporphyrin. In the absorption spectra of regular metalloporphyrins, there are two Q bands between 500 and 600 nm. The lower-energy band (α band) is the electronic origin Q(0,0) of the lowest singlet excited state S₁. The second band (β band) is its vibrational overtone and is labeled as Q(1,0). The relative intensities of these bands can be a qualitative yardstick of just how stable is the metal complexed to the four porphyrinic nitrogen atoms. Thus, when the intensity of the α band is greater than that of the β band, the metal forms a stable complex with the porphyrin; whereas when $\alpha < \beta$, the metal is easily displaced by protons.³⁷ The α/β relative intensity ratios for complexes 1–3 are 0.26, 0.19 and 0.17, respectively. In the IR spectra, the $\nu_{C=O}$, which appeared at 1735 cm⁻¹ for the appended porphyrin free base, was shifted to 1698 cm⁻¹ indicating that the C=O group had coordinated to the lanthanide ions. This is in accordance with the literature reported [Ln(TPP)(acac)] compound.²⁶ Conductivity measurements showed that the complexes were non-conducting in chloroform and methanol indicating that the complexes were neutral. Treatment of a methanol solution of the complexes with an aqueous solution of AgNO₃ did not give any AgCl precipitation indicating that there was no chloride (whether as a coordinated ligand or as an anion) present in the complexes. The above observations indicate that the

porphyrinate behaved as a tri-deprotonated hexadentate ligand with the appended diethyl malonate group coordinated to the lanthanide ion as an anion. Complexes 1–3 show similar fragmentation patterns in their mass spectra. The electrospray ionization high-resolution mass spectra (positive mode) of the complexes in methanol shows mass peaks at *m/z* corresponding to [Ln(*o*-DEM-C₄-O-TPP) + H]⁺ and its fragment ion [Ln(*o*-DEM-C₄-O-TPP) – C₂H₄ + H]⁺. For instance, the Er³⁺ complex exhibited mass peaks at *m/z* 1010.2809 and 982.2499 which deviate by less than 5 ppm from the theoretical peak match values of 1010.2805 for the elemental composition of [Er(*o*-DEM-C₄-O-TPP) + H]⁺ and 982.2493 for [Er(*o*-DEM-C₄-O-TPP) – C₂H₄ + H]⁺. The observed isotope distribution patterns of these peaks also match the expected theoretical signals. Elemental analyses suggested that the complexes should be formulated as [Ln(*o*-DEM-C₄-O-TPP)(H₂O)]. The presence of a water molecule is indicated by the IR spectra of the complexes, which show ν_{O-H} at around 3444 cm⁻¹. It is not uncommon for lanthanide complexes with coordination number 6 or lower to have solvent molecules coordinated to the metal centres raising their coordination number to 7, 8 or 9.⁴⁰ Thus, for compounds 1–3, it is very likely that the water molecule is coordinated to the metal centre. This is further supported by luminescent studies (*vide infra*), which show that the luminescent intensity of the complexes varies with the solvents. Attempts to grow single crystals of compounds 1–3 suitable for X-ray diffraction studies were unsuccessful. However, based on the above spectroscopic evidence, the structure of compounds 1–3 (shown in Scheme 1) can be considered as a 7 coordinated species with four N of the porphyrinate and three O (two from the appended diethyl malonate anion and one from water) coordinated to the metal centre.

Complexes 1–3 are quite stable in air, which, we believe, can only be attributed to the coordination of the appended diethyl malonate anion. This makes us believe that the second ligand is crucial for the preparation of stable monoporphyrinate lanthanide complexes, particularly those metals with large ionic radii. In fact our recent results show that anionic tripodal ligands such as (η^5 -C₅H₅)Co[P(=O)(OEt)₂]₃⁻ anion and hydrotris(1-pyrazolyl)borate, could be used to stabilize monoporphyrinate complexes of lanthanide ions (*e.g.* Nd³⁺ and Sm³⁺) with large ionic radii.⁴¹

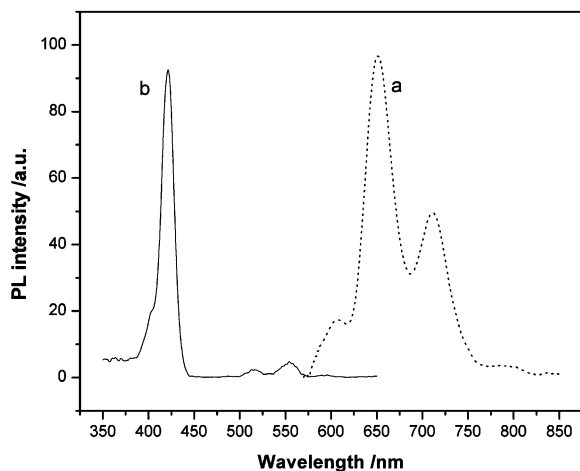
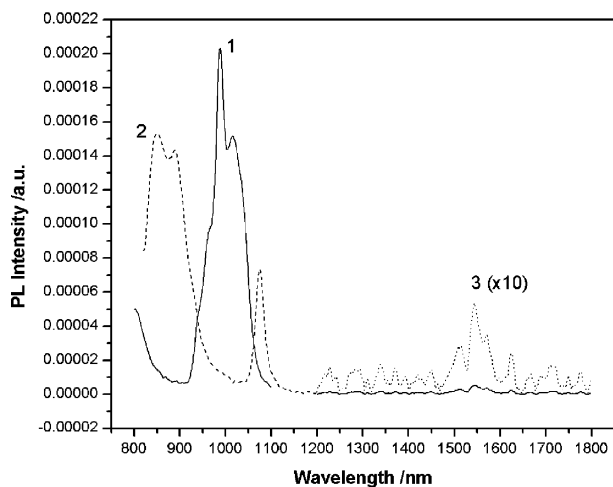
Photophysical studies of complexes

The photophysical properties of compounds 1–3 have been examined and are summarized in Table 1. The room temperature solution electronic absorption and emission spectra of compounds 1–3 in the UV-VIS region are almost identical and characteristic of intra-ligand transitions of normal porphyrinate complexes.³⁶ Fig. 1 shows the absorption spectrum of 1, and Fig. 3 shows the emission (excited at 422 nm) and excitation (monitored at 650 nm) spectra of 1. The excitation spectrum closely resembles the absorption spectrum. The absorption bands at 422, 552 and 589 nm and emission peak at 650 nm ($\tau = 5.1$ ns and $\Phi_{em} = 0.15 \times 10^{-3}$ for 1; $\tau = 3.3$ ns and $\Phi_{em} = 0.98 \times 10^{-4}$ for 2; $\tau = 8.9$ ns and $\Phi_{em} = 5.02 \times 10^{-3}$ for 3) can be assigned to the intra-ligand $\pi \rightarrow \pi^*$ transitions of the porphyrinate ligand. The quantum efficiency of the metalloporphyrin is much lower than that of the appended porphyrin free base ($\Phi_{em} = 3.56 \times 10^{-2}$). Other than the visible emission, compounds 1–3 also exhibit emissions corresponding to the lanthanide(III) ion in the near-infrared (NIR) region (Fig. 4). These NIR emissions are very similar to those reported for Yb³⁺, Er³⁺ and Nd³⁺.^{17a,20} For 1 and 2, the emission peaks centred at 980 and 1544 nm can be assigned to the ²F_{5/2} \rightarrow ²F_{7/2} transition of Yb³⁺ and ⁴I_{13/2} \rightarrow ⁴I_{15/2} transition of Er³⁺, respectively. For 3, the emission peaks centred at 853 and 890 nm can be assigned to ⁴F_{3/2} \rightarrow ⁴I_{9/2} and 1074 nm to ⁴F_{3/2} \rightarrow ⁴I_{11/2} transitions of Nd³⁺. The excitation spectra for the NIR emission of 1

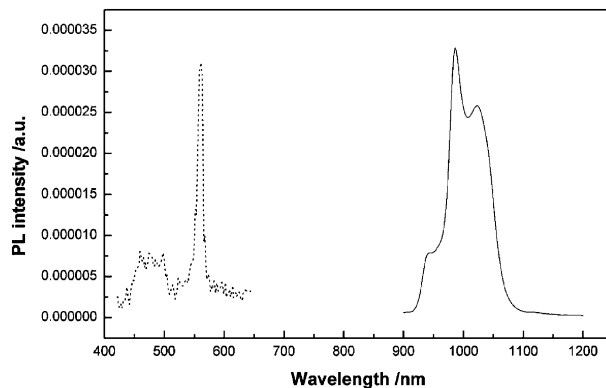
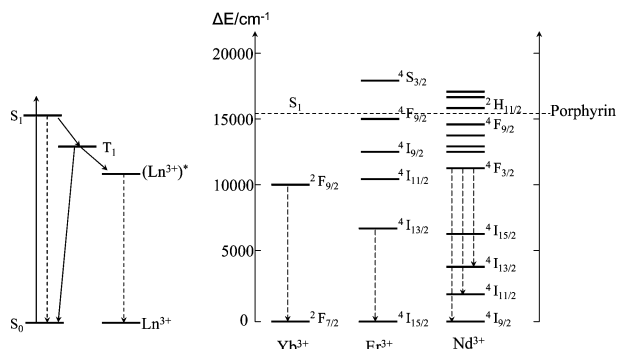
Table 1 Photophysical data of compounds **1**, **2** and **3**^a

Compound	Absorption: λ_{\max}/nm [$\log(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$]	Excitation: $\lambda_{\text{exc}}/\text{nm}$	Emission: $\lambda_{\text{em}}/\text{nm}$ (τ , $\Phi_{\text{em}} \times 10^3$) ^{b,c}
1	422 (5.88), 552 (4.55) 589 (3.96)	422	650 (5.1 ns, 0.15) 980 (2.43 μs)
2	422 (5.71), 551 (4.31) 589 (3.58)	422	650 (3.3 ns, 0.098) 1544 ^d
3	422 (5.68), 551(4.28) 594 (3.52)	422	650 (8.9 ns, 5.02) 853 ^e

^a Photophysical measurements were made in CHCl_3 solution at room temperature. ^b Quantum yields were determined relative to $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ in air-equilibrated water ($\Phi = 0.028$). ^c Due to the limitations of the instrument, we were unable to determine the quantum yields of the NIR luminescence of compounds **1**, **2** and **3**. ^d Due to the limitations of the instrument, we were unable to measure the lifetime of the NIR luminescence of compound **2**. ^e Compound **3** decomposes upon irradiation with N_2 laser at 337 nm. Thus, its NIR luminescence lifetime could not be measured.

**Fig. 3** Emission spectrum (a) and excitation spectrum (b), monitored at 650 nm, of **1** in CHCl_3 .**Fig. 4** NIR luminescence spectra of complexes **1–3** in CHCl_3 .

and **3** are very similar. Fig. 5 shows the NIR emission and excitation spectra of **1**. The excitation band of **1** in chloroform solution at 298 K (monitored at 980 nm) is observed at 560 nm, which almost coincides with its visible absorption band at 552 nm. This clearly shows that the excitation of the Yb^{3+} ion originates from the $\pi \rightarrow \pi^*$ transitions of the porphyrinate antenna and excitation of the porphyrin is the photophysical pathway leading to the observable NIR luminescence. The NIR luminescence lifetime of **1** is 2.43 μs and is much longer than the lifetime of the porphyrinate emission. Due to the limitations of our equipment, we were unable to measure the excitation (monitored at 1544 nm) spectrum and the NIR luminescence lifetime of **2**. **3** decomposed upon irradiation with an N_2 laser at 337 nm, and therefore its NIR luminescence lifetime could not be measured. A simple photophysical model for the description

**Fig. 5** NIR luminescence spectrum (solid line) and excitation spectrum (dashed line), monitored at 980 nm, of **1** in CHCl_3 .**Fig. 6** Schematic energy diagram of diethyl malonate appended lanthanide complexes. The arrows indicate the excitation mechanism of lanthanide ions by the porphyrin sensitizer ($S_0 \rightarrow S_1$ transition followed by intersystem crossing and energy transfer).

of the sensitization process is depicted in Fig. 6. Generally the energy transfer from an antenna to lanthanide ions is considered to take place through the triplet state of the antenna and its singlet state has little contribution to the sensitization process. Excitation of the $\pi \rightarrow \pi^*$ transitions of the porphyrinate produced the singlet S_1 state, which *via* intersystem crossing transferred part of its energy to the triplet T_1 state. The T_1 state then transferred its energy to the lanthanide metal ions, which led to NIR emission.^{17a,42}

The photoluminescence intensity of the complexes is quite different under the same conditions (Fig. 4). The NIR emission intensities of the Yb^{3+} and Nd^{3+} complexes are an order of magnitude stronger than that of the Er^{3+} complex. As the lanthanide ions are in the same environment, we can conclude that this difference stems from the different energy transfer efficiency of porphyrin to the lanthanide ions. The luminescence of lanthanide ions was heavily affected by the kinds of solvent used. Research showed that OH oscillators, *e.g.* in bound water molecules, OH-containing solvents, could quench the luminescence.⁴³ Fig. 7 shows the luminescence of complex **1** in different

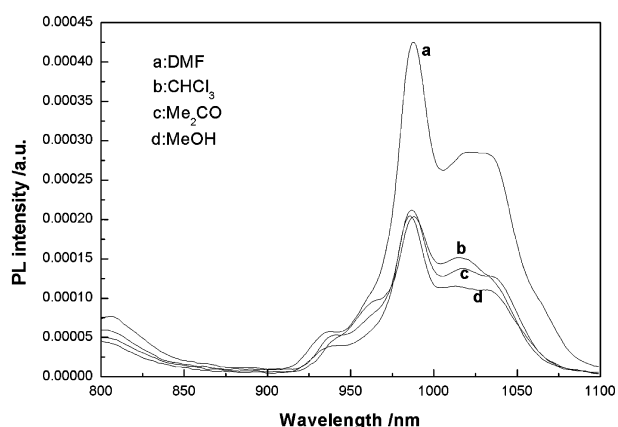


Fig. 7 Photoluminescence of **1** in different solvents at room temperature.

solvents. The results revealed that an OH-rich solvent, for example MeOH, had a slight effect on their emission. However, we found that DMF could enhance the emission intensity, which, we believe, could only be attributed to the substitution of coordinated H₂O by DMF. This is supported by the electrospray ionization high-resolution mass spectrum of a DMF solution of **1** in MeOH, which exhibits a peak at m/z 1162.4081 corresponding to $(M - H_2O + 2DMF + H)^+$ (C₆₁H₆₀N₆O₇Yb requires 1162.3923). Furthermore, in the IR spectrum of the resultant porphyrinate complex obtained by removing the solvent of a DMF solution of **1**, the ν_{O-H} at 3446 cm⁻¹ had disappeared and a new peak at 1664 cm⁻¹, which probably corresponded to the $\nu_{C=O}$ of coordinated DMF, was observed. Thus, the above spectroscopic data support the conclusion that the coordinated H₂O molecule of **1** has been substituted by DMF when dissolved in DMF.

Conclusion

In this paper, we have described the detailed synthesis and characterization of a novel diethyl malonate appended porphyrin and its lanthanide(III) complexes [Ln(*o*-DEM-C₄-O-TPP)-(H₂O)] (Ln³⁺ = Yb³⁺, Er³⁺ and Nd³⁺). Spectroscopic evidence suggests that the structures of these complexes can be considered as 7 coordinated species with four N of the porphyrinate and three O (two from the appended diethyl malonate anion and one from water) coordinated to the metal centre. We further show that the diethyl malonate appended porphyrin can behave as a tri-deprotonated hexadentate ligand to encapsulate and stabilize lanthanide metal ions with large ionic radii. Photoluminescence studies showed that the porphyrin ring could act as an antenna for the near-infrared emission of lanthanide ions. Better donating solvents could enhance the luminescence efficiency by replacing the coordinated water molecule.

Experimental

Procedures

All reactions were carried out in an atmosphere of dry nitrogen. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from Aldrich Chemical Company and, where appropriate, degassed before use. The IR spectra (KBr pellets) were recorded on a Nicolet Magna-IR 550 spectrometer and NMR spectra on a Varian INOVA 400 spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Low-resolution mass spectra were obtained on a Finnigan MAT SSQ-710 in FAB (positive) mode. Electrospray ionization high-resolution mass spectra (ESI-HRMS) were recorded on a QSTAR mass spectrometer.

Electronic absorption spectra in the UV-VIS region were recorded on a Hewlett Packard 8453 UV-Visible spectrophotometer, steady-state visible fluorescence and PL excitation spectra on a Photon Technology International (PTI) Alphascan spectrofluorimeter and visible decay spectra on a pico-N₂ laser system (PTI Time Master) with $\lambda_{exc} = 337$ nm. NIR emission was detected by a liquid nitrogen cooled InSb IR detector (EG & G) with a preamplifier and recorded by a lock-in amplifier system as the third harmonic, the 355 nm line of a Nd:YAG laser (Quantel Brilliant B) was used as the excitation source and also to pump the OPO (Opotek MagicPrism VIR) to provide a continuously tunable laser source from 410–670 nm with a pulse-width of 4 ns. NIR decay spectra were detected by an Oriel 77343 photomultiplier and monitored by a HP54522A 500 MHz oscilloscope. Quantum yields were computed according to the literature method⁴⁴ using [Ru(bipy)₃]Cl₂ as the reference standard ($\Phi = 0.028$ in air-equilibrated water).⁴⁵ To avoid any second-order light reaching the detector, 710 and 830 nm cutoff filters were used where applicable. The complexes in different solutions were analyzed in quartz cells with concentration 2×10^{-5} M. The power on the cell was 1 W and all spectra were corrected for the detector response.

Preparation of porphyrin free bases

5-(2-Hydroxyphenyl)-10,15,20-triphenylporphyrin (*o*-OH-TPPH₂). This compound was prepared by a modification of the literature method.²³ A solution of benzaldehyde (5.5 cm³, 54 mmol) and *o*-hydroxybenzaldehyde (3.7 cm³, 35 mmol) in propionic acid (250 cm³) was heated to reflux with mechanical stirring. Then freshly distilled pyrrole (5.0 cm³, 72 mmol) in propionic acid (50 cm³) was added slowly to the solution in half an hour. Upon cooling to room temperature, methanol (300 cm³) was added to the reaction mixture. The resultant solution was kept in a refrigerator overnight. Filtration gave about 1.3 g of crude product, which was redissolved in a minimum amount of chloroform and chromatographed on a silica gel column with dichloromethane as eluent. The second band gives the desired *o*-OH-TPPH₂. Yield: 1.10 g, 5%. UV-VIS data in CHCl₃, 20 °C, λ_{max}/nm : 418, 516, 550, 589 and 645. FAB-MS (+ve mode) m/z : 631 (M + H)⁺.

5-(2-(4-Bromobutyl)phenyl)-10,15,20-triphenylporphyrin (*o*-Br-C₄-O-TPPH₂). To a suspension of *o*-OH-TPPH₂ (0.50 g, 0.8 mmol) and anhydrous K₂CO₃ in dry DMF was added 2 cm³ of 1,4-dibromobutane, the mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After 24 h, chloroform (100 cm³) was added to the reaction mixture, which was then washed with water (6 × 50 cm³) until all of the DMF and potassium carbonate were removed. The organic phase was evaporated to dryness *in vacuo* and the residue was re-dissolved in chloroform/hexane (v/v, 1 : 1) and chromatographed on a silica gel column using chloroform/hexane (v/v, 5 : 1) as eluent. The first band gave the product *o*-Br-C₄-O-TPPH₂. Yield: 0.58 g, 95%. ¹H NMR (in CDCl₃): δ -2.76 (s, 2H), 8.83–8.78 (m, 8H), 8.24–8.19 (m, 6H), 8.04–8.02 (m, 2H), 7.38–7.21 (m, 11H), 3.92 (s, 2H), 2.39 (s, 2H), 1.13 (s, 2H), 0.82 (s, 2H). UV-VIS data in CHCl₃, 20 °C, λ_{max}/nm : 419, 515, 550, 589 and 645. FAB-MS (+ve mode) m/z : 765 (M + H)⁺ for ⁷⁹Br.

5-[2-(5,5'-Ethoxycarbonyl)pentoxy]phenyl-10,15,20-triphenylporphyrin [*o*-DEM(H)-C₄-O-TPPH₂]. Sodium methoxide (1.0 g, 18.5 mmol) was added to a solution of diethyl malonate (2.8 cm³, 18.5 mmol) in DMF (50 cm³) and the resulting suspension was stirred under nitrogen at 60°C until the solution was clear. Then a solution of *o*-Br-C₄-O-TPPH₂ (0.3 g, 0.4 mmol) in DMF (5.0 cm³) was added slowly to the solution in 30 min. The mixture was stirred further for about 2 h. Upon cooling to room temperature, the reaction mixture was diluted

with chloroform (100 cm³) and washed with water (6 × 50 cm³). The organic layer was dried over anhydrous Na₂SO₄ and filtered. The solvent of the filtrate was removed *in vacuo* and the residue was redissolved in 5 cm³ of chloroform/hexane (v/v, 5 : 1) and chromatographed on silica gel using chloroform/hexane (v/v, 5 : 1) as eluent. The second band gives the desired compound *o*-DEM(H)-C₄-O-TPPH₂ after re-crystallization in a chloroform/methanol solution. Yield: 0.30 g, 89%. M.p. 108–110 °C. IR (cm⁻¹, in KBr): 3462 w, 3312w, 2962m, 1746m, 1728s, 1600m, 1471m, 1441m, 1356m, 1261s, 1094s, 1024s, 964s, 800vs, 749m, 729m, 701s. ¹H NMR (CDCl₃): δ -2.77 (s, 2H), 8.83–8.78 (m, 8H), 8.26–8.18 (m, 6H), 7.98–7.96 (m, 2H), 7.78–7.71 (m, 9H), 7.34–7.28 (m, 2H), 3.87 (t, 2H), 3.69 (m, 4H), 2.55 (s, 1H), 1.26 (t, 2H), 1.01 (s, 2H), 0.87 (m, 6H), 0.48 (s, 2H). UV-VIS in CHCl₃, 20 °C, λ_{max}/nm [log(ε/dm³ mol⁻¹ cm⁻¹) in parentheses]: 419 (5.63), 514 (4.26), 548 (3.87), 590 (3.71), 649 (3.78). Fluorescence data in CHCl₃, 20 °C, λ_{exc}/nm: 425, 514, 544, 594; λ_{em}/nm: 652, 715; Φ_{em} = 3.56 × 10⁻²; τ = 9.4 ns (652 nm). FAB-MS (+ve mode) *m/z*: 845 (M + H)⁺, 771 (M - CO₂Et)⁺ and 629 [M - (CH₂)₄CH(CO₂Et)₂]⁺. ESI-HRMS (+ve mode, in CH₃OH) *m/z*: 845.3672 [(M + H)⁺, C₅₅H₄₉N₄O₅ requires 845.3702]. Anal. found (calc.) for C₅₅H₄₈N₄O₅·1.5H₂O: C, 75.92 (75.75); H, 5.91 (5.90); N, 6.26 (6.43%).

Preparation of lanthanide complexes

Compounds 1–3 were prepared with the same procedure. A typical procedure is given for 1.

[Yb^{III}(*o*-DEM-C₄-O-TPP)(H₂O)] 1. A solution of *n*-BuLi (1.6 M, 3.0 cm³, 4.8 mmol) in hexane was added dropwise over a period of 10 min to a solution of (Me₃Si)₂NH (0.78 g, 4.8 mmol) in THF (15 cm³), the reaction mixture was allowed to stirred at room temperature for 2 h, then transferred slowly to a suspension of anhydrous YbCl₃ (0.44 g, 1.6 mmol) in THF (10 cm³). After stirring at room temperature for 24 h, the mixture was concentrated to ca. 5 cm³ and filtered. The filtrate was added to a solution of *o*-DEM(H)-C₄-O-TPPH₂ (0.25 g, 0.30 mmol) in bis(2-methoxyethyl) ether (5 cm³). The resultant solution was refluxed for 24 h. Upon cooling to room temperature, chloroform (50 cm³) was added to the solution and filtered. The filtrate was washed with water (5 × 30 cm³), dried over anhydrous Na₂SO₄ and filtered. The organic layer was evaporated to dryness *in vacuo* and the residue was redissolved in chloroform and chromatographed on silica gel using chloroform/methanol (v/v, 5 : 1) as eluent. The second band gave the desired complex 1. Yield: 0.29 g, 95%. M.p. > 300 °C. IR (cm⁻¹, in KBr): 3446m, 2955m, 2918m, 2867m, 1739m, 1698m, 1615m, 1594s, 1439s, 1263s, 1196s, 1113m, 1072m, 989s, 798vs, 756s, 710s, 658m. UV-VIS in CHCl₃, 20 °C, λ_{max}/nm [log(ε/dm³ mol⁻¹ cm⁻¹) in parentheses]: 422 (5.88), 552 (4.55), 589 (3.96). Fluorescence data in CHCl₃, 20 °C, λ_{exc}/nm: 422; λ_{em}/nm: 650, 715, 980; Φ_{em} = 0.15 × 10⁻³; τ = 5.1 ns (650 nm), 2.43 μs (980 nm). FAB-MS (+ve mode) *m/z*: 1016 (M - H₂O + H)⁺ for ¹⁷⁴Yb. ESI-HRMS (+ve mode, in CH₃OH) *m/z*: 1016.2826 [(M - H₂O + H)⁺, C₅₅H₄₆N₄O₅Yb requires 1016.2867], 988.2494 [(M - H₂O - C₂H₄ + H)⁺, C₅₃H₄₂N₄O₅Yb requires 988.2553]. Anal. found (calc.) for C₅₅H₄₇N₄O₅Yb: C, 63.94 (63.95); H, 4.47 (4.59); N, 5.63 (5.42%).

[Er^{III}(*o*-DEM-C₄-O-TPP)(H₂O)] 2. Anhydrous ErCl₃ (0.44 g, 1.6 mmol) was used. Yield: 0.30 g, 92%. M.p. > 300 °C. IR (cm⁻¹, in KBr): 3441m, 2975m, 2924m, 2851m, 1698m, 1620m, 1600m, 1574m, 1445m, 1331m, 1264s, 1103s, 1015s, 798vs, 700m. UV-VIS in CHCl₃, 20 °C, λ_{max}/nm [log(ε/dm³ mol⁻¹ cm⁻¹) in parentheses]: 422 (5.71), 551 (4.31), 589 (3.58). Fluorescence data in CHCl₃, 20 °C, λ_{exc}/nm: 422; λ_{em}/nm: 650, 715, 1544; Φ_{em} = 0.98 × 10⁻⁴; τ = 3.3 ns (650 nm). FAB-MS (+ve mode) *m/z*: 1008 (M - H₂O + H)⁺ for ¹⁶⁶Er. ESI-HRMS (+ve mode, in CH₃OH) *m/z*: 1010.2809 [(M - H₂O + H)⁺,

C₅₅H₄₆N₄O₅Er requires 1010.2805), 982.2499 [(M - H₂O - C₂H₄ + H)⁺, C₅₃H₄₂N₄O₅Er requires 982.2493]. Anal. found (calc.) for C₅₅H₄₇N₄O₅Er·CH₃OH·H₂O: C, 62.55 (62.43); H, 5.09 (4.96); N, 5.00 (5.20%).

[Nd^{III}(*o*-DEM-C₄-O-TPP)(H₂O)] 3. Anhydrous NdCl₃ (0.40 g, 1.6 mmol) was used. Yield: 0.27 g, 90%. M.p. > 300 °C. IR (cm⁻¹, in KBr): 3451s, 2960w, 2924m, 2862w, 1703m, 1625m, 1594s, 1574s, 1481s, 1450s, 1268m, 1207m, 989vs, 803s, 757s, 710s. UV-VIS in CHCl₃, 20 °C, λ_{max}/nm [log(ε/dm³ mol⁻¹ cm⁻¹) in parentheses]: 419 (5.68), 550 (4.28), 594 (3.52). Fluorescence data in CHCl₃, 20 °C, λ_{exc}/nm: 422; λ_{em}/nm: 650, 715, 853, 890, 1074; Φ_{em} = 5.02 × 10⁻³; τ = 8.9 ns (650 nm). FAB-MS (+ve mode) *m/z*: 984 (M - H₂O + H)⁺ for ¹⁴²Nd. ESI-HRMS (+ve mode, in CH₃OH) *m/z*: 986.2526 [(M - H₂O + H)⁺, C₅₅H₄₆N₄O₅Nd requires 986.2581] and 958.2322 [(M - H₂O - C₂H₄ + H)⁺, C₅₃H₄₂N₄O₅Nd requires 958.2267]. Anal. found (calc.) for C₅₅H₄₇N₄O₅Nd: C, 66.02 (65.78); H, 4.84 (4.72); N, 5.65 (5.58%).

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