

Electronic Supplementary Information

Influence of lanthanide ion energy levels on luminescence of corresponding metalloporphyrins

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I. Mass spectra of HMME and Gd-HMME

Figure S1 shows the mass spectra of HMME (a) and Gd-HMME (b). The mass spectra were recorded on liquid chromatography/mass spectra (LC/MS) analyzing system (Thermo Finnigan Surveyor LCQ DECA XP plus, USA). The $[M+H]^+$ peak of HMME appears at about 613.49, which corresponds to the signal of HMME. Meanwhile, the $[M+H]^+$ peak of Gd-HMME appears at about 803.27, which corresponds to the signal of Cl-Gd-HMME. These results indicate that the purity of HMME and Gd-HMME is relatively high.

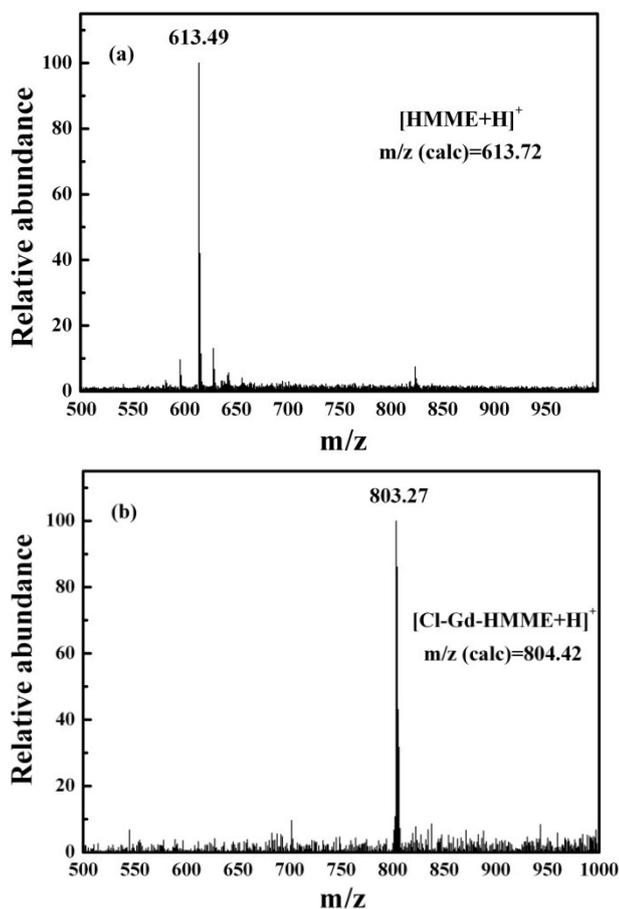


Fig. S1. Mass spectra of HMME and Gd-HMME (positive mode). $[HMME+H]^+$: HMME molecule with proton; $[Cl-Gd-HMME+H]^+$: Gd-HMME molecule with a chloride ion and proton.

II. Fourier transform infrared spectra of HMME and Gd-HMME

Figure S2 shows the Fourier transform infrared (FTIR) spectra of HMME (a) and Gd-

HMME (b). The FTIR spectra (KBr pellets) were recorded on a Varian Excalibur HE 3100 spectrometer. The typical N–H vibration (about 3311 cm^{-1}) for porphyrin free base disappeared in the FTIR spectrum of Gd-HMME.

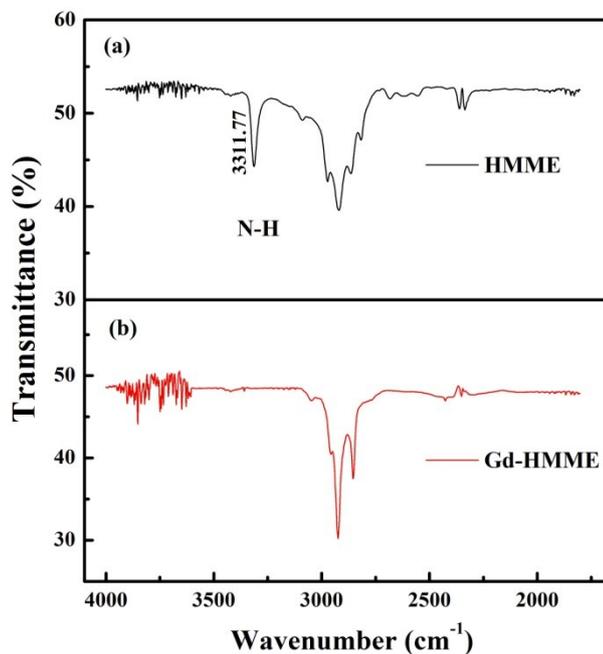


Fig. S2. The FTIR spectra of HMME and Gd-HMME.

III. UV-visible absorption spectra of other lanthanide-HMMEs

Figures S3-S12 present the UV-visible absorption spectra of other lanthanide-HMMEs studied in this work, including La-, Nd-, Sm-, Eu-, Dy-, Ho-, Er-, Tm-, Yb- and Lu-HMME. First of all, the spectrum of La-HMME shows the absorption properties of HMME (four Q bands). The spectrum of Ce-HMME is almost same as that of La-HMME, which also exhibited four Q bands. This indicates that La^{3+} and Ce^{3+} were not coordinated by the tetraazacore of HMME. Secondly, compared to HMME, the difference in the absorption spectra of most lanthanide-HMMEs (except La- and Ce-HMME) is the reduction in the number of Q bands. Lanthanide-HMMEs have only two Q bands peaking at 537 and 571 nm.

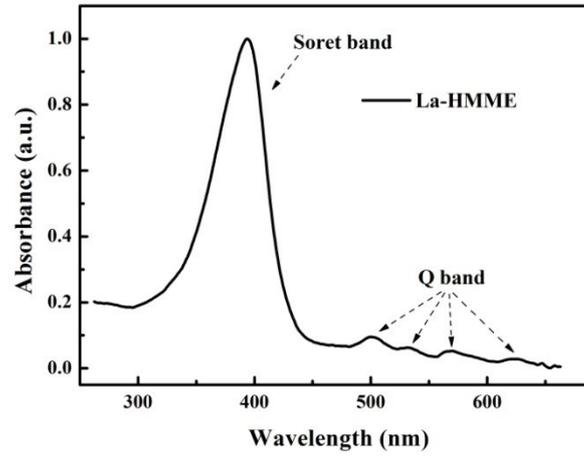


Fig. S3. The UV-visible absorption spectrum of La-HMME.

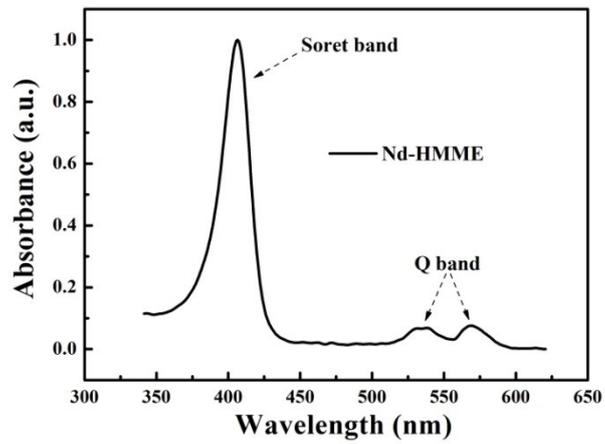


Fig. S4. The UV-visible absorption spectrum of Nd-HMME.

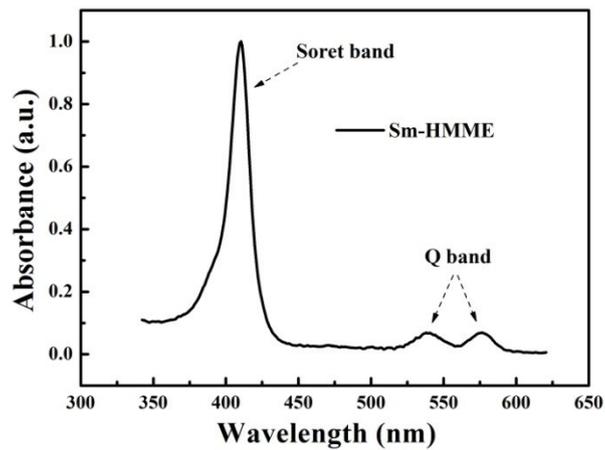


Fig. S5. The UV-visible absorption spectrum of Sm-HMME.

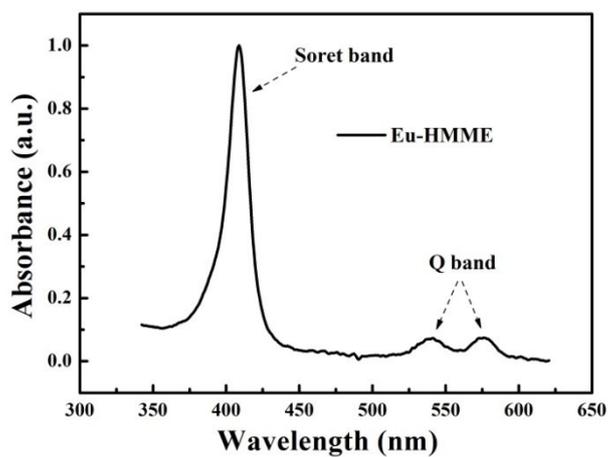


Fig. S6. The UV-visible absorption spectrum of Eu-HMME.

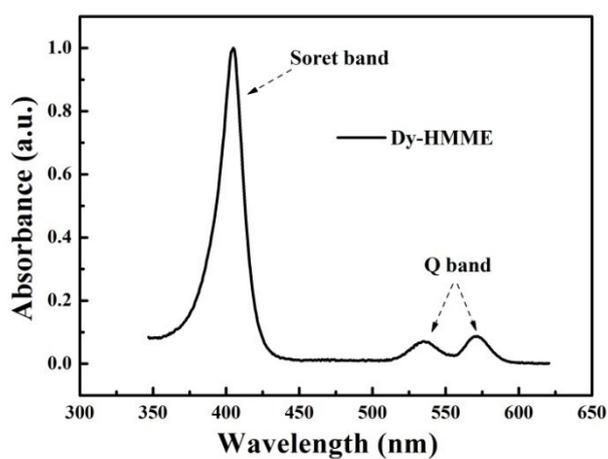


Fig. S7. The UV-visible absorption spectrum of Dy-HMME.

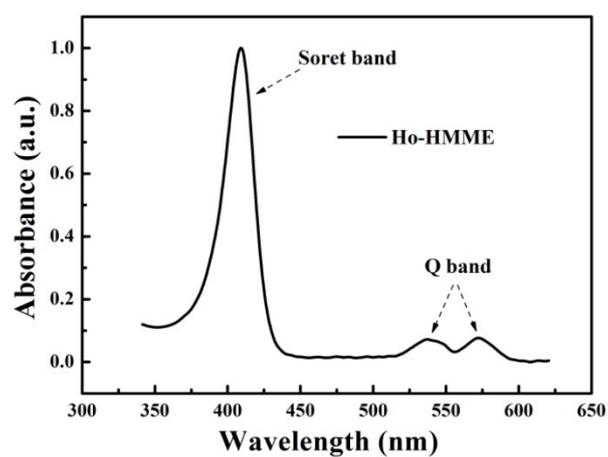


Fig. S8. The UV-visible absorption spectrum of Ho-HMME.

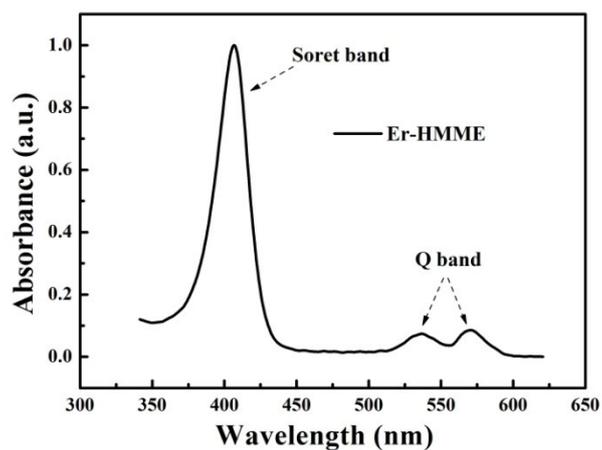


Fig. S9. The UV-visible absorption spectrum of Er-HMME.

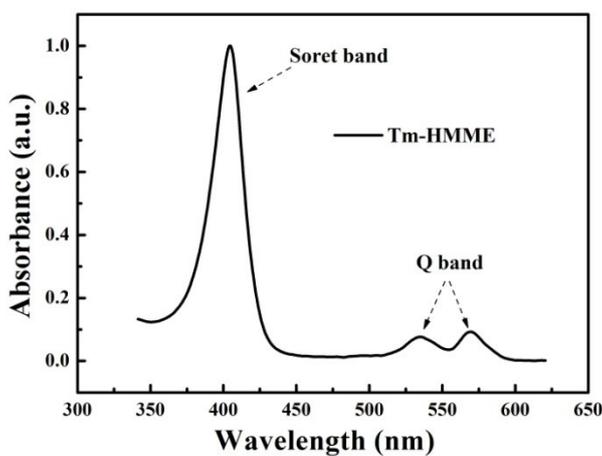


Fig. S10. The UV-visible absorption spectrum of Tm-HMME.

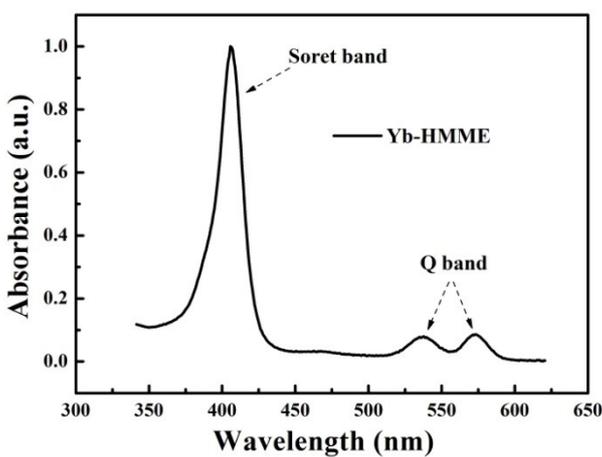


Fig. S11. The UV-visible absorption spectrum of Yb-HMME.

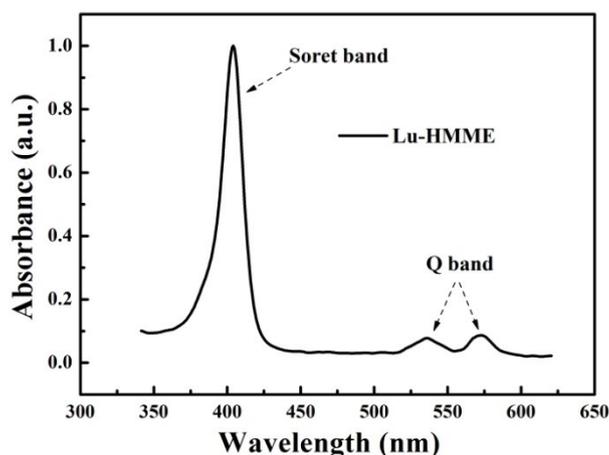


Fig. S12. The UV-visible absorption spectrum of Lu-HMME.

IV. Luminescence spectra of other lanthanide-HMMEs

Figures S13-S17 present the luminescence spectra of other lanthanide-HMMEs studied in this work, including La-, Pr-, Nd-, Eu-, Dy-, Ho-, Er-, Tm- and Yb-HMME. First of all, the luminescence properties of La-HMME (Ce-HMME) are similar to that of HMME (without luminescence peak at about 585 nm). Secondly, compared to HMME, a new luminescence band appears at about 585 nm in the luminescence spectra of most lanthanide-HMMEs (except La- and Ce-HMME). It can be seen there is no red-shifted phosphorescence emission in the luminescence spectra of these lanthanide-HMMEs.

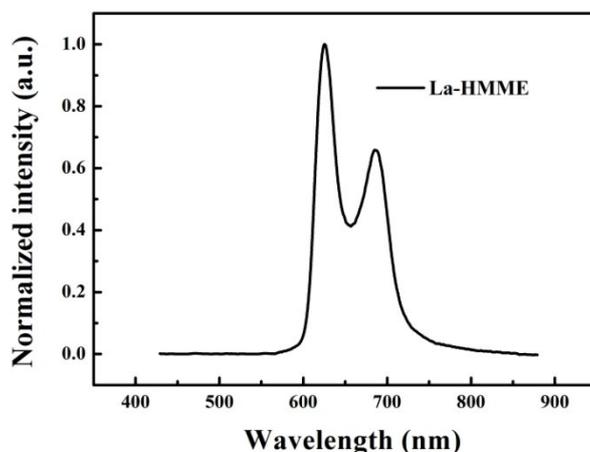


Fig. S13. The luminescence spectrum of La-HMME.

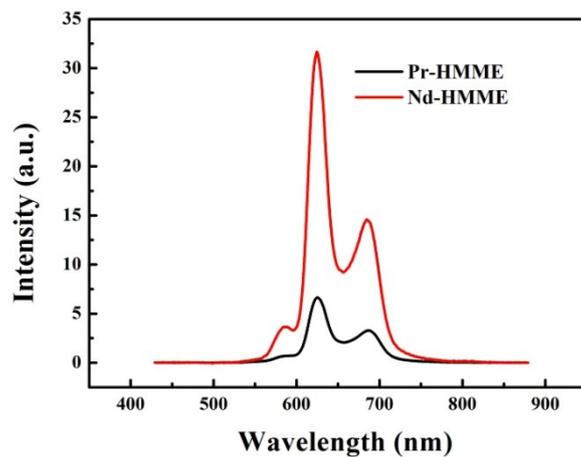


Fig. S14. The luminescence spectra of Pr- and Nd-HMME.

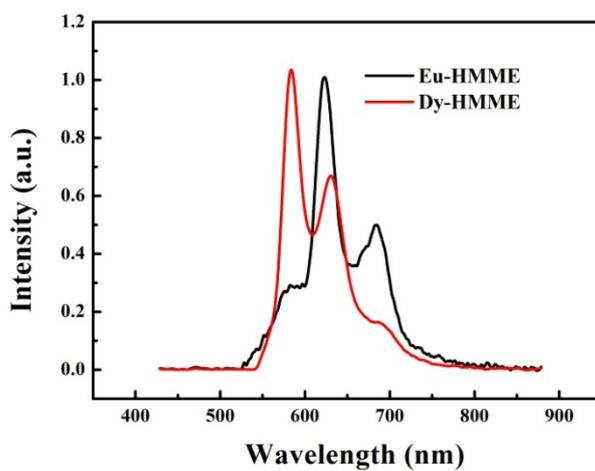


Fig. S15. The luminescence spectra of Eu- and Dy-HMME.

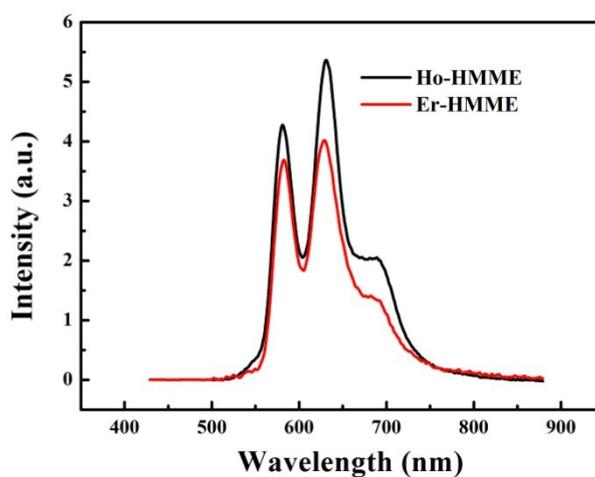


Fig. S16. The luminescence spectra of Ho- and Er-HMME.

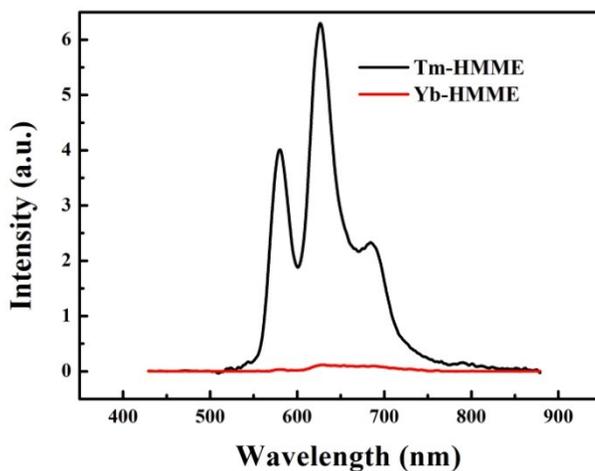


Fig. S17. The luminescence spectra of Tm- and Yb-HMME.

V. Absorption and luminescence of Sc- and Y-HMME

Figure S18 shows the UV-visible absorption (a) and luminescence (b) spectra of yttrium-HMME (Y-HMME). The absorption spectrum of Y-HMME has one Soret band and two Q bands while the luminescence spectrum of Y-HMME has three fluorescence emission bands (without phosphorescence emission), which is similar to other normal lanthanide-HMMEs. Figure S19 shows the UV-visible absorption (a) and luminescence (b) spectra of scandium-HMME (Sc-HMME). It can be seen that Sc-HMME still has four Q bands. To compare the absorption of HMME and Sc-HMME in detail, the absorption spectra of HMME and Sc-HMME were obtained at the same conditions (shown in Fig. S19(a)). One can see that there is obvious difference between the two absorption spectra. Compared with HMME, the absorption of Sc-HMME has a red shift, which is similar to other normal lanthanide-HMMEs. More importantly, the intensity of the first and the last Q bands of Sc-HMME decrease while those of the middle two (corresponding to the absorption of metalloporphyrins) increase as compared to HMME. This indicates that Sc-HMME

formed in our synthesis. The exhibited four Q bands in the absorption spectrum of Sc-HMME indicate that the influence of Sc^{3+} on the molecular structure and absorption of HMME is slight. This resulted from the relatively small atomic number and low heavy atom effect of Sc^{3+} . Sc-TPP was also reported to exhibit more than two Q absorption bands¹. Besides, from Fig. S19(b), the luminescence spectrum of Sc-HMME was in accordance with the luminescence spectra of normal lanthanide-HMMEs (three fluorescence emission bands).

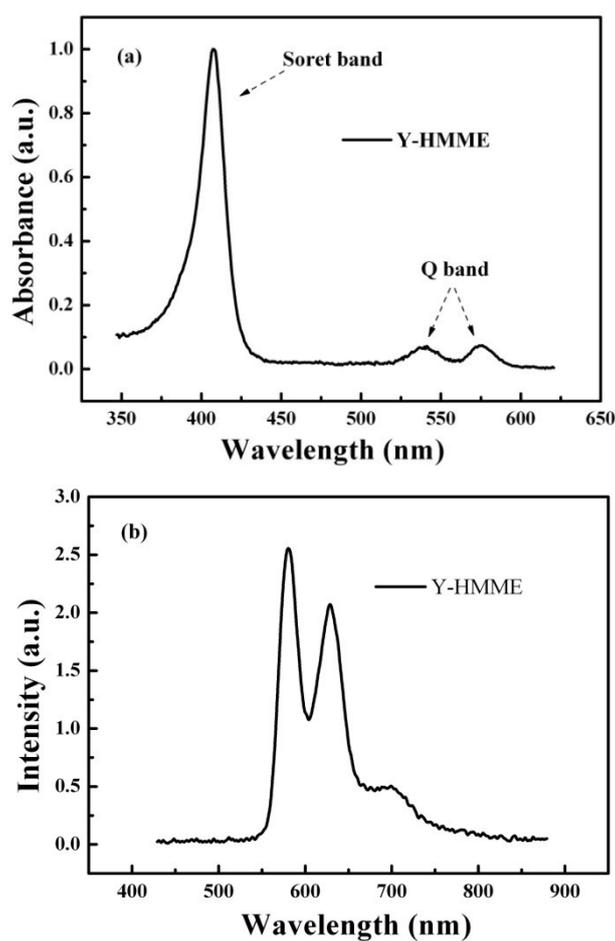


Fig. S18. The UV-visible absorption (a) and luminescence (b) spectra of Y-HMME.

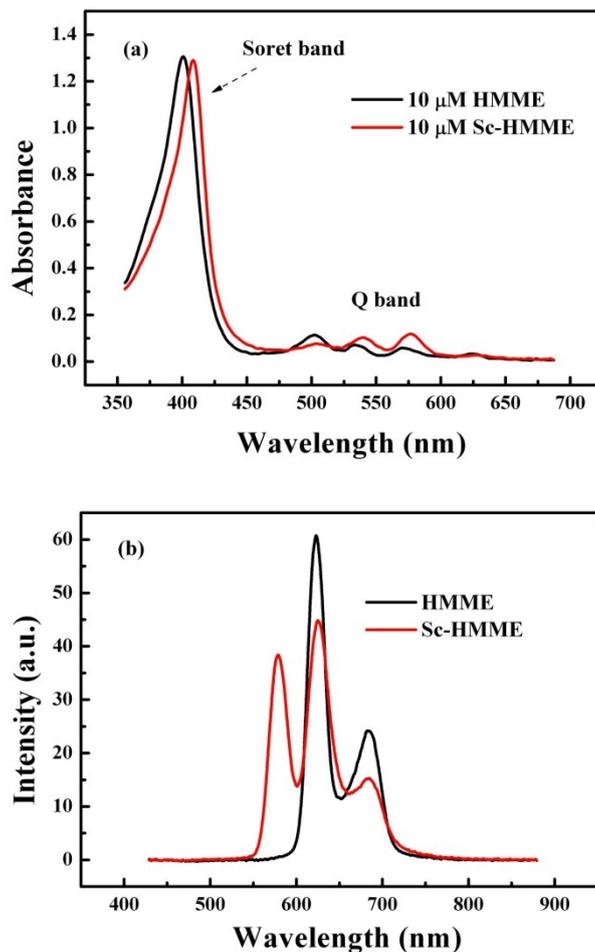


Fig. S19. The UV-visible absorption (a) and luminescence (b) spectra of HMME and Sc-HMME.

VI. Measurement of fluorescence quantum yield of HMME

The fluorescence quantum yield of HMME was measured based on a relative method².

In the measurement, R6G was used as the reference with quantum yield of 0.93 in methanol³. The relationship between Φ of HMME phosphorescence and that of R6G

luminescence was described by the following equation:

$$\Phi = \Phi_r \left(\frac{I}{A} \right) \left(\frac{A_r}{I_r} \right), \quad (1)$$

where Φ_r and Φ are the luminescence quantum yields of R6G and HMME in methanol. A_r and A are the absorbance of R6G and HMME at 532 nm, respectively. I_r and I are the integrated emission intensities of R6G and HMME under the

illumination of 532 nm laser, respectively. The experimental conditions and calculated quantum yields of HMME in methanol are shown in Table S1.

Table S1. Experimental conditions and calculated quantum yields of HMME in methanol.

Photosensitizers	Concentration [μM]	I	A	Φ
R6G	5	7710000	0.71	0.93
HMME	50	136000	0.35	0.03

VII. Method for the measurement for the fluorescence lifetime

To determine the lifetime of fluorescence, a pulse laser centered at 392 nm with 1 MHz was used as light source. Fluorescence signals were recorded by a spectrofluorometer (HORIBA, Fluoromax-4). The fluorescence lifetime evaluation was performed by fitting the decay curve to an exponential function using adjustable parameters.

VIII. Method for the measurement of phosphorescence lifetime

To determine the lifetime of phosphorescence, decay profile was measured. A square wave was given to a diode laser controller (Thorlabs ITC510) to control a diode laser centered at 405 nm (Thorlabs TCLDM9). Photoluminescence signals were recorded by a grating spectrometer (Zolix Omni- λ 300) and amplified by a photomultiplier tube (Zolix PMTH-S1-R212) with a high voltage power supply (Zolix HVC1800). The time-resolved signal was averaged with a digital phosphor oscilloscope (Tektronix DPO5054) and the decay curve was sent to a personal computer for lifetime determination. The lifetime evaluation was performed by fitting the decay curve to an exponential function using adjustable parameters.

IX. Oxygen quenching properties of the luminescence of Gd- and Lu-HMME

Figure S20 shows the luminescence spectra of Gd-HMME (a) and Lu-HMME (b)

with different concentrations of dissolved oxygen in methanol. It can be seen that the exhibited luminescence of Gd-HMME and Lu-HMME at about 710 nm was effectively quenched by oxygen. This indicates that there is energy transfer from the gadolinium and lutetium porphyrins to oxygen. Meanwhile, the luminescence at 585 nm and 626 nm kept unchanged. This further demonstrates that the luminescence of Gd- and Lu-HMME at about 710 nm was phosphorescence.

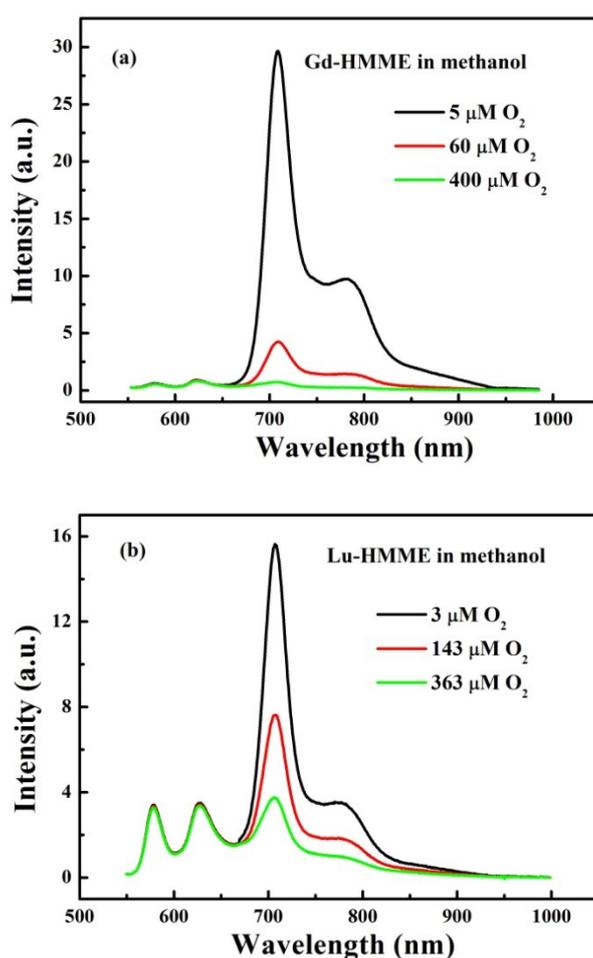


Fig. S20. The luminescence spectra of Gd-HMME (a) and Lu-HMME (b) with different concentrations of dissolved oxygen in methanol.

References

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- 2 F. Su, R. Alam, Q. Mei, Y. Tian, C. Youngbull, R. H. Johnson and D. R. Meldrum, *PLoS ONE*, 2012, **7**, e33390.
- 3 D. Magde, R. Wong and P. G. Seybold, *Photochem. Photobiol.*, 2002, **75**, 327-334.