Electronic Supplementary Information

Effect of imidazole on the enhancement of gadolinium-porphyrin phosphorescence at room temperature

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I. Characterizations of Gd-HMME by mass spectroscopy and Fourier-transform infrared spectroscopy

Figures S1 and S2 present the basic characterizations of Gd-HMME by mass spectroscopy and Fourier-transform infrared spectroscopy. From Fig. S1, the ESI mass spectrum of Gd-HMME has an intense peak at m/z=803.05 (calc m/z=803.17) corresponding to [Cl-Gd-HMME+H^+]. From Fig. S2, HMME has the absorption peak at 3315 cm^{-1} for N-H. Meanwhile, Gd-HMME does not have this absorption peak because of the coordination of Gd^{3+} in the center of HMME.

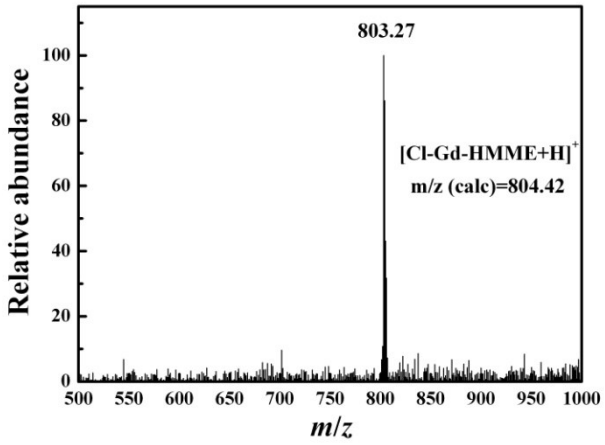

Figure S1. Basic characterization for Gd-HMME by mass spectroscopy.

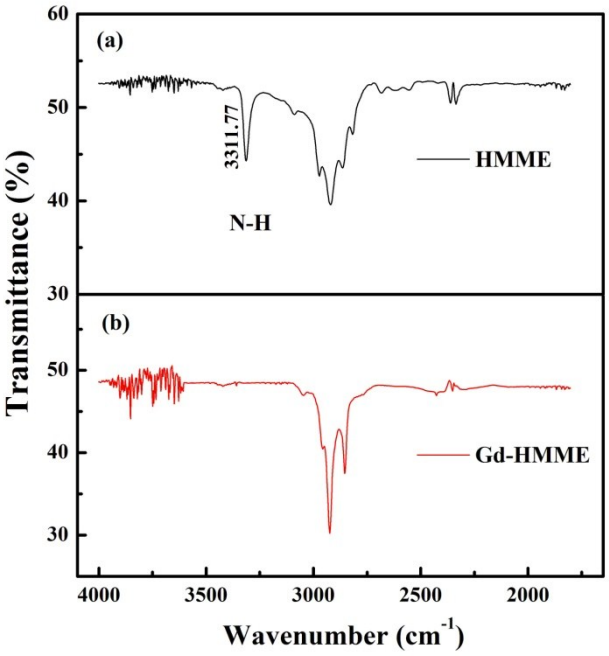

Figure S2. Basic characterization of Gd-HMME by Fourier-transform infrared spectroscopy.

II. Phosphorescence decay curve measurements

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). The parameters we used in the method are listed as follows: the power density of the diode laser was about 2.1 mW/cm^2; the cycle time for the square wave was 1 ms and the duty cycle was 50%. Photoluminescence signals were recorded by a grating spectrometer (Zolix Omni-λ300) 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.

III. Assessment of the standing time of Gd-HMME RTP emission upon the addition of imidazole

In order to investigate the dynamic interaction between imidazole and phosphor, phosphorescence intensity of Gd-HMME was monitored in a certain time. The results shown in Fig. S3 indicate that the intensity increases dramatically at the very beginning. When standing time was over 8 s, the interaction between Gd-HMME and imidzole reached saturation. The results mean that a quite fast interaction between Gd-HMME and imidazole happened. Eventually, Gd-HMME would dwell in the rigid microenvironment provided by imidazole. Effect of standing time of the addition of free Gd^{3+} on the phosphorescence emission is similar to that of imidazole.

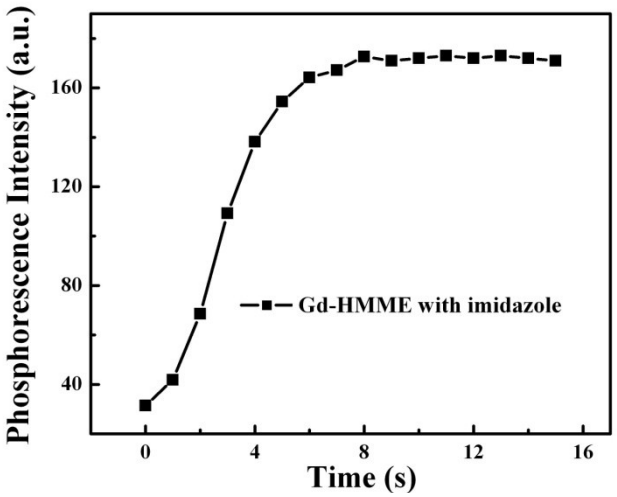

Figure S3. Standing time of Gd-HMME RTP intensity upon addition of imidazole.

IV. The influence of oxygen on the phosphorescence emission

Oxygen plays an important role in phosphorescence intensity and lifetime values in solution.[S1] For the sample involved in this study, the phosphorescence intensity and lifetime in the presence of different oxygen concentrations were measured.

To measure the oxygen dependence of the luminescence spectra of Gd-HMME in solution, solutions of Gd-HMME (500 μM) were put into a quartz cuvette (1 × 1 ×

4 cm). The cuvette was placed in a homemade gas chamber (150 × 30 × 30 cm). Different concentrations of oxygen were introduced into the chamber on the surface of the methanol solutions. The oxygen concentration in solution was monitored using a Clark electrode.

Figures S4(a) and (b) show the luminescence spectra and decay profiles of Gd-HMME in the presence of different oxygen concentrations. It can be seen that the phosphorescence intensity and lifetime of Gd-HMME decrease with the concentration of oxygen.

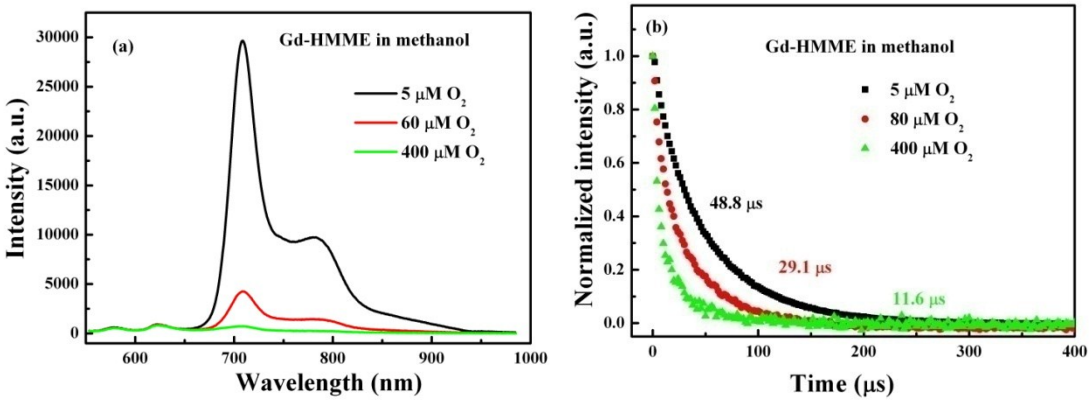

Figure S4. Luminescence spectra and phosphorescence decay profiles for Gd-HMME in the presence of various concentrations of oxygen.

V. The dependence of standing time on the excitation intensity

There are some effects where oxygen is consumed with irradiation time of excitation light.[S2] To check whether there is oxygen consumption effect in this work, we measured the standing time (the time required for the intensity to reach saturation) for Gd-HMME upon the addition of imidazole at different excitation intensities. Figure S5 shows the time dependence of the Gd-HMME phosphorescence intensity upon the addition of imidazole at various excitation power densities from 5 to 30 mW/cm^2. From Fig. S5, the standing times under these power densities were evaluated to be 8.3,

8.0, 8.2, 7.8, 8.4, and 8.3 s. The standing time is independent of the excitation intensity.

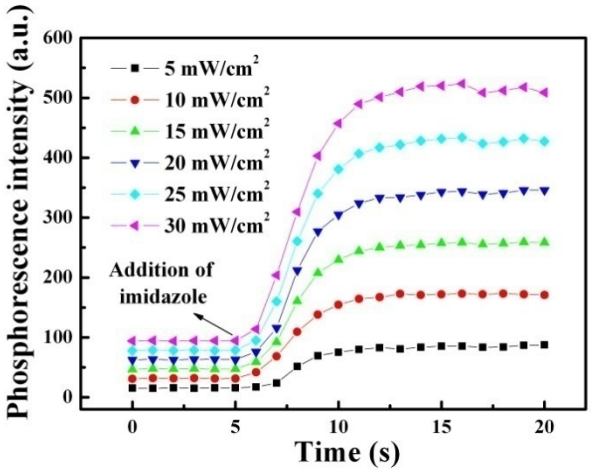

Figure S5. The time dependences of the phosphorescence intensity of Gd-HMME upon addition of imidazole under various excitation power density from 5 to 30 mW/cm^2.

Reference

S1. F. Marsico, A. Turshatov, R. Peköz, Y. Avlasevich, M. Wagner, K. Weber, D. Donadio, K. Landfester, S. Baluschev and F. R. Wurm, *J. Am. Chem. Soc.*, 2014, 136, 11057.

S2. A. Jana, B. J. Crowston, J. R. Shewring, L. K. McKenzie, H. E. Bryant, S. W. Botchway, A. D. Ward, A. J. Amoroso, E. Baggaley and M. D. Ward, *Inorg. Chem.*, 2016, 55, 5623.