

Supplementary Information

Novel Non-Peripheral Mercaptopyridine Substituted Mono and Double- Decker Lutetium (III) Phthalocyanines: Synthesis, photophysicochemical, and electrochemical properties

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1. Materials and equipment

3-(2-mercaptopyridine)phthalonitrile¹ and 1(4), 8(11), 15(18), 22 (25)-tetrakis-(2-mercaptopyridine)phthalocyanine (**H₂Pc**)² were synthesized by the according to the literature. Also, all chemicals and reagents were purchased from commercial suppliers. FT-IR spectra were recorded on a Perkin Elmer Spectrum spectrometer. The mass spectra were obtained on a Bruker Microflex LT by MALDI-TOF technique by using dithranol (DIT) as a MALDI matrix. Absorption spectra were recorded with a Shimadzu 1800 UV-Vis spectrophotometer and a Shimadzu 3600 Plus UV-Vis-NIR spectrophotometer. Fluorescence emission spectra were obtained by a Varian Eclipse spectrofluorometer. Fluorescence lifetimes were measured by a time-correlated single photon counting (TCSPC) method using a Fluorolog-3 spectrofluorometer (Horiba JobinYvon, Edison, NJ) equipped with a NanoLED and a standard air-cooled R928 PMT detector. ¹H-NMR spectrum was recorded on a Bruker 500 MHz spectrometer in DMSO-d₆ and a chemical shift (δ) is shown in ppm. The electron spin resonance (ESR) spectrum was recorded at room temperature with a microwave frequency of 9.86 Hz with a JEOL ESR spectrometer (JESFA300).

2. Photophysical and photochemical measurements

2.1. Fluorescence quantum yields (Φ_F) and lifetimes (τ_F)

Fluorescence quantum yield (Φ_F) is determined by the comparative method according to the equation 1^{3,4}

$$\Phi_F = \Phi_{F(Std)} \frac{F \times A_{Std} \times n^2}{F_{Std} \times A \times n_{Std}^2}$$

(1)

where F and F_{Std} are the areas under the fluorescence emission curves of the novel non-peripheral tetra mercaptopyridine substituted lutetium (III) phthalocyanines (**LuPc** and **LuPc₂**) and the standard, respectively. A and A_{Std} are the respective absorbance of the compounds (**LuPc** and **LuPc₂**) and standard at the excitation wavelengths, respectively. n^2 and n_{Std}^2 are the refractive indices of solvents used for the sample and standard, respectively. Unsubstituted ZnPc was employed as a standard compound ($\Phi_F = 0.20$ in DMSO).⁵ The absorbances of the studied lutetium (III) phthalocyanine compounds (**LuPc** and **LuPc₂**) and the standard unsubstituted ZnPc were kept ~ 0.05 at the excitation wavelength.

Fluorescence lifetimes were measured using a time-correlated single photon counting setup (TCSPc). The average fluorescence lifetime of the charge carriers is estimated by using equation 2.⁶

$$\tau_a = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i}$$

(2)

2.2. Singlet oxygen quantum yields (Φ_Δ)

Singlet oxygen quantum yields (Φ_Δ) of the non-peripheral tetra mercaptopyridine substituted phthalocyanines (**H₂Pc**, **LuPc**, and **LuPc₂**) were carried out using the experimental set-up described in the literature.^{7, 8} Typically, a 3 mL portion of phthalocyanine solutions ($C = 1 \times 10^{-5}$ M) containing the singlet oxygen quenchers were irradiated in the Q band region with the photo-irradiation set-up described in references.^{7.}

⁸ Singlet oxygen quantum yields (Φ_Δ) were determined in air using the relative method

using unsubstituted ZnPc in DMSO as a reference. 1,3-Diphenylisobenzofuran (DPBF) was used as a chemical quencher for singlet oxygen in DMSO. Equation 3 was employed for the determination of Φ_{Δ} value:

$$\Phi_{\Delta} = \Phi_{\Delta}^{Std} \frac{R \times I_{abs}^{Std}}{R^{Std} \times I_{abs}}$$

(3)

where is the singlet oxygen quantum yield for the standard ZnPc ($\Phi_{\Delta} = 0.67$ in DMSO)⁹ R and R_{Std} are the DPBF photobleaching rates in the presence of the respective phthalocyanines (**H₂Pc**, **LuPc**, and **LuPc₂**) in DMSO and standard, respectively. I_{abs} and I_{abs}^{Std} are the rates of light absorption by compounds (**H₂Pc**, **LuPc**, and **LuPc₂**) and standard, respectively. To avoid chain reactions induced by quenchers (DPBF) in the presence of singlet oxygen, the concentration of quencher (DPBF) was lowered to $\sim 3 \times 10^{-5}$ M.¹⁰ Solution of a sensitizer ($C = 1 \times 10^{-5}$ M) containing a quencher (DPBF) was prepared in the dark and irradiated by the light at around the Q band of the studied phthalocyanines. The DPBF photooxidation was monitored at 417 nm. The light intensity 6.21×10^{15} photons $s^{-1} cm^{-2}$ was used for Φ_{Δ} determination.

3. Electrochemical measurements

Electrochemical measurements were performed by CHI Instruments/CHI842B using the three-electrode system with a glassy carbon working electrode (GCE, 3 mm), Ag/AgCl reference electrode, and platinum wire as a counter electrode. The electrochemical properties of phthalocyanine compounds (**LuPc** and **LuPc₂**) were studied by cyclic voltammetry (CV) and square wave voltammetry (SWV). These measurements were carried out with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as a

supporting electrolyte in dichloromethane (DCM) at 25 °C under a high purity argon atmosphere.

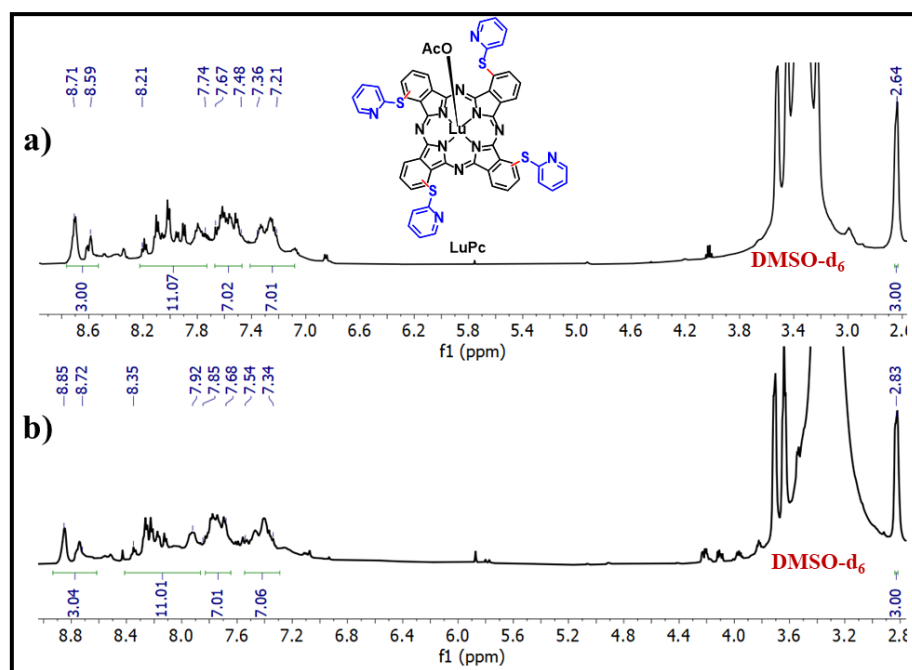


Fig. S1: ¹H-NMR spectra of LuPc in DMSO-d₆ a) room temperature and b) 65 °C.

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