Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

Supporting Information

The first transition metal phthalocyanines: sensitizing rubrene emission based on triplet-triplet annihilation

Jianlei Han,[a,b] Fei Zhang [a,b] , Jing You,* [a,b] Yonemura Hiroaki,* [c,d] Sunao Yamada,[c,d] Toru Morifuji,[e] Shirong Wang, [a,b] and Xianggao Li [a,b]

S1. Absorption and Emission spectra of Oxazine 725 and IR-820

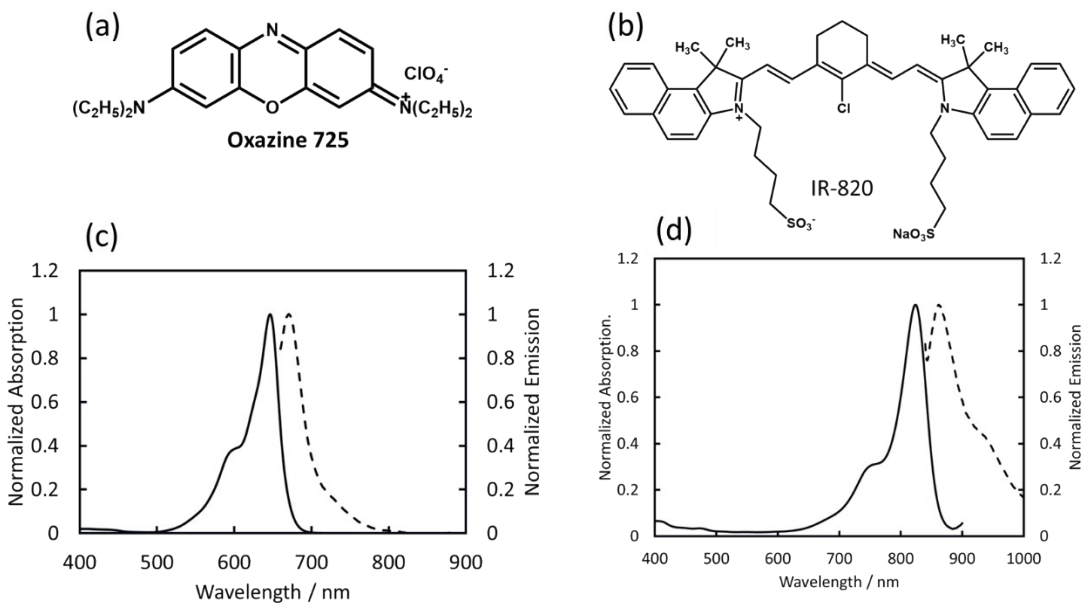

Fig.S1 Molecular structures of Oxazine 725 (a) and IR-820 (b); Normalized absorption (Left) and emission (Right) spectra for Oxazine 725 (c) and IR-820 (d).

S2. Measurement of PUC efficiency

The upconversion quantum yield (Φ_{PUC}) was determined with Oxazine 725 ($^{\Phi_F}$ =11%, in MeOH with concentration of 10^{-5} M)[1] as quantum yield standard with Eq.S1. The equation is multiplied by factor 2 in order to made the maximum quantum yield to be unit.[2]

$$\Phi_{PUC} = 2\Phi_S\left(\frac{A_s}{A_u}\right)\left(\frac{I_u}{I_s}\right)\left(\frac{\eta_u}{\eta_s}\right)^2 \qquad \text{Eq.S1}$$

Where $^{\Phi_S}$ A_s, I_s, and η_s represent quantum yield the absorbance, integrated photoluminescence, and refractive index of solvent for standard, respectively. Similarly, A_u, I_u, and η_u represent those of unknown samples. In this work, the integrated region of photoluminescence for standard (Oxazine 725) was from 650 to 800 nm, for MPc-o-Cou:Rub was from 470 to 620 nm.

S3. Decay profiles of TT absorption of MPc-o-Cou (Co, Cu, Pt, Pd)

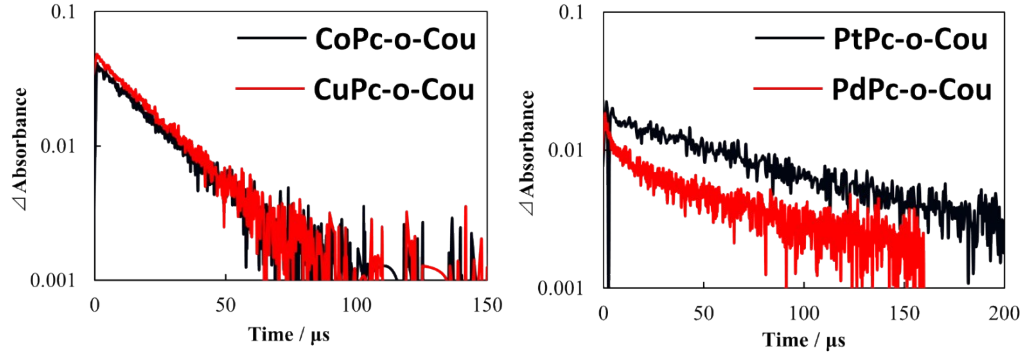

Fig.S2 Decay profiles of time-resolved transient absorption due to the triplet state of MPc-o-Cou with central metal (Cu, Co, Pt, Pd) at 298 K.

The decay profiles of T_0-T_n transition of CoPc-o-Cou and CuPc-o-Cou were recorded at the maximum transition absorption in the wavelength region of 500-600 nm.[3, 4]

S4. Absorption and emission spectra of rubrene

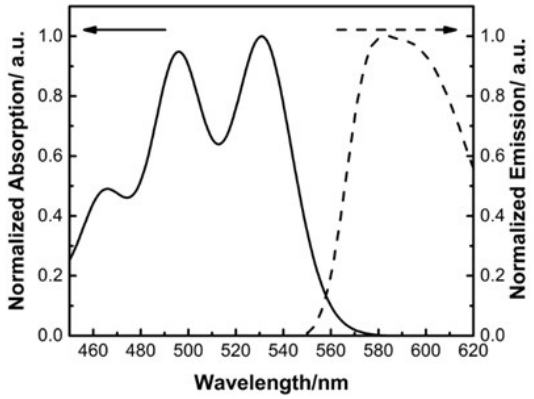

Fig.S3 Normalized absorption and fluorescence emission spectra of Rub.

S5. Upconversion emission spectra of MPc-o-Cou:Rub(Co, Cu, Fe, Ni)

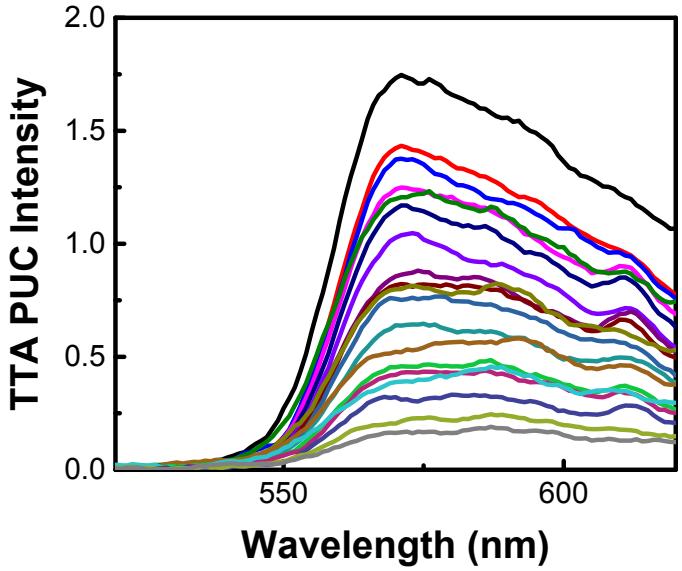

Fig.S4 TTA-PUC emission spectra of FePc-o-Co:Rub system. The concentration of Rub and FePc-o-Cou are 5.86×10^{-4} M and 1.61×10^{-5} M, respectively (λ_{ex}=632.8 nm).

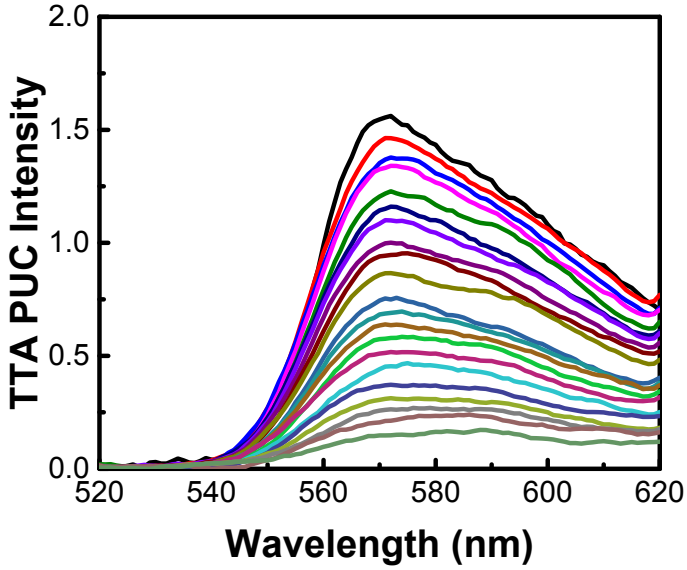

Fig.S5 TTA-PUC emission spectra of CoPc-o-Co:Rub system. The concentration of Rub and CoPc-o-Cou are 5.86×10^{-4} M and 1.61×10^{-5} M, respectively (λ_{ex}=632.8 nm).

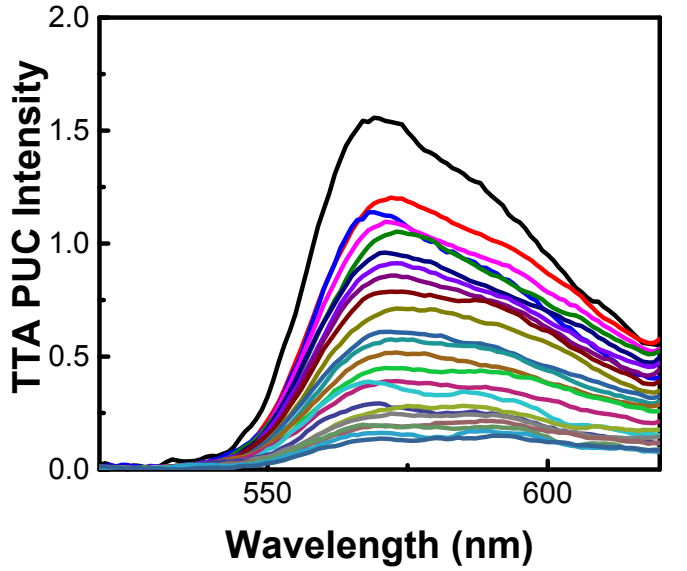

Fig.S6 TTA-PUC emission spectra of NiPc-o-Co:Rub system. The concentration of Rub and NiPc-o-Cou are 5.86×10^{-4} M and 1.61×10^{-5} M, respectively (λ_{ex}=632.8 nm).

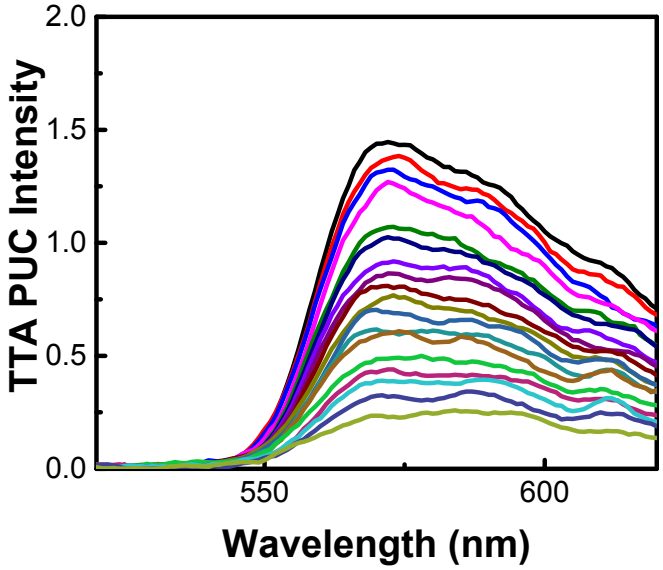

Fig.S7 TTA-PUC emission spectra of CuPc-o-Co:Rub system. The concentration of Rub and CuPc-o-Cou are 5.86×10^{-4} M and 1.61×10^{-5} M, respectively (λ_{ex}=632.8 nm).

1 R. Sens and K. H. Drexhage, Fluorescence quantum yield of oxazine and carbazine laser dyes, *J. Lumin.*, 1981, **24**, 709-712.

2 W. Wu, D. Huang, X. Yi and J. Zhao, Tridentate cyclometalated platinum(II) complexes with strong absorption of visible light and long-lived triplet excited states as photosensitizers for triplet–triplet annihilation upconversion, *Dyes Pigm*, 2013, **96**, 220-231.

3 A. V. Nikolaitchik, O. Korth and M. A. J. Rodgers, Crown Ether Substituted Monomeric and Cofacial Dimeric Metallophthalocyanines. 1. Photophysical Studies of the Free Base, Zinc(II), and Copper(II) Variants, *J. Phys. Chem. A*, 1999, **103**, 7587-7596.

4 A. V. Nikolaitchik and M. A. J. Rodgers, Crown Ether Substituted Monomeric and Cofacial Dimeric Metallophthalocyanines. 2. Photophysical Studies of the Cobalt(II) and Nickel(II) Variants, *J. Phys. Chem. A*, 1999, **103**, 7597-7605.