

# Supporting Information

## Highly-efficient red-to-yellow/green upconversion sensitized by phthalocyanine palladium with high triplet energy-level

Kai Wang,<sup>#</sup> Suqin Huang,<sup>#</sup> Ping Ding, Zuoqin Liang, Shuoran Chen, Lin Li, Changqing Ye,<sup>\*</sup> Xiaomei Wang<sup>\*</sup>

---

Suzhou Key Laboratory of Flexible & Printing Optoelectronic Materials, School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou, 215009, China.

E-mail: yechangqing@mail.usts.edu.cn, wangxiaomei@mail.usts.edu.cn

<sup>#</sup>These authors contributed equally to this work.

### 1. Measurements

<sup>1</sup>H NMR and <sup>13</sup>C NMR were performed on an INOVA-400 spectrometer. Mass spectra were obtained on Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS) produced by Bruker Company (bruker solarix X). IR spectra were obtained on Thermo Fisher Nicolet iS5.

### 2. Synthesis and characterization of palladiumphthalocyanines.

**2.1 Palladiumphthalocyanine (PdPc).** Under nitrogen and stirring condition, 1,2-dicyanobenzene (0.51 g, 4 mmol) was added to the three-necked flask in the presence of 40 mL of n-pentanol. The mixture solution becomes colorless transparent solution after heated at 50 °C for 1 hour. To this solution was added 0.3 g (1 mmol) of palladium acetylacetonate (Pd(acac)<sub>2</sub>) and 0.4 mL of 1.8-diazabicyclo[5, 4, 0] undec-7-ene (DBU). The mixture solution becomes bright orange at once and black after refluxing for 0.5 hour. Continuing refluxing for 24 hours under the nitrogen atmosphere until 1,2-dicyanobenzene and Pd(acac)<sub>2</sub> were completely disappeared by TLC detection, the mixture was evaporated under reduced pressure to get black powders. The crude powders were washed with ethanol, DMF, chloroform and n-hexane, respectively; and then dried to get 0.32 g of black powders (yield 52%) with decomposition temperature (T<sub>d</sub>) at 435 °C. IR (KBr, cm<sup>-1</sup>): 3426s, 3288w (C=N), 2934w (C-H), 1718w, 1649w, 1506w, 1417w, 1339m (C=C, C-N), 1132s, 1003s (C-H), 873w, 730s (C-H out-of-plane).

**2.2 3,7,11,15-tetra(tertbutyl)phthalocyanine palladium (TBPcPd):** Under argon atmosphere

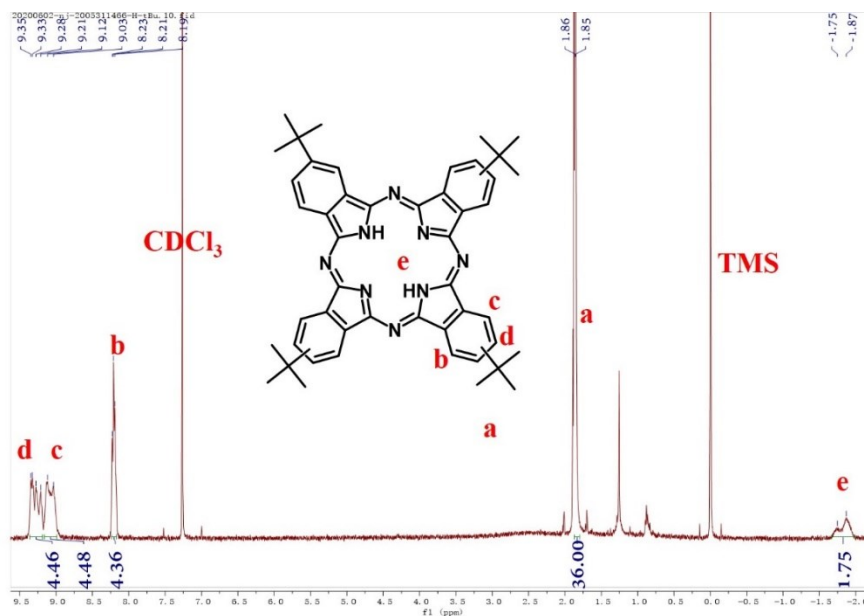
and stirring condition, 4-*tert*-butylphthalonitrile (0.83 g, 4.5 mmol) was dissolved in 20 mL *n*-pentanol in the presence of 5 mL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The mixed solution was refluxed in argon atmosphere overnight until 4-*tert*-butylphthalonitrile was disappeared. The reaction solution was cooled to room temperature and 30 mL of methanol was added into. Then, the reaction mixtures were stirred for a while and put aside overnight for the precipitation. The blue powders were obtained by filtration. Then, ligand 3,7,11,15-tetra(*tert*butyl)phthalocyanine (**Pc 1**) was obtained (0.55 g, yield 66.3%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 9.36 - 9.19 (m, 4H), 9.08 (d, 4H), 8.21 (t, 4H), 1.87 - 1.80 (m, 36H), -1.81 (d, 2H). (**Fig. S1**, ESI). MS (MALDI-TOF): Calcd. for C<sub>48</sub>H<sub>50</sub>N<sub>8</sub> [M<sup>+</sup>] 738.42; Found 738.42 (Mz) (**Fig. S2**, ESI).

**Pc 1** (0.1 g, 0.14 mmol) and PdCl<sub>2</sub> (0.03 g, 0.17 mmol) were dissolved in 20 mL of *n*-pentanol. The mixed solution was bubbled in argon for 15 minutes, and then 5 mL of deoxygenated DBU was added in argon atmosphere. The above mixed solution was refluxed in argon atmosphere for 24 hours. Then, 30 mL of methanol was added into the reaction solution and stirred to get blue crude powders. The blue powder of *tert*butylphthalocyanine palladium (**TBPcPd**) was purified through filtration. Yield 17.0% (0.02 g). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*): δ 9.02 (s, 2H), 8.59 (s, 4H), 8.03 (d, 6H), 1.87 (s, 36H). (**Fig. S3**, ESI). MS (MALDI-TOF): Calcd. for C<sub>48</sub>H<sub>48</sub>N<sub>8</sub>Pd [M<sup>+</sup>] 842.31; Found 842.31 (Mz) (**Fig. S4**, ESI).

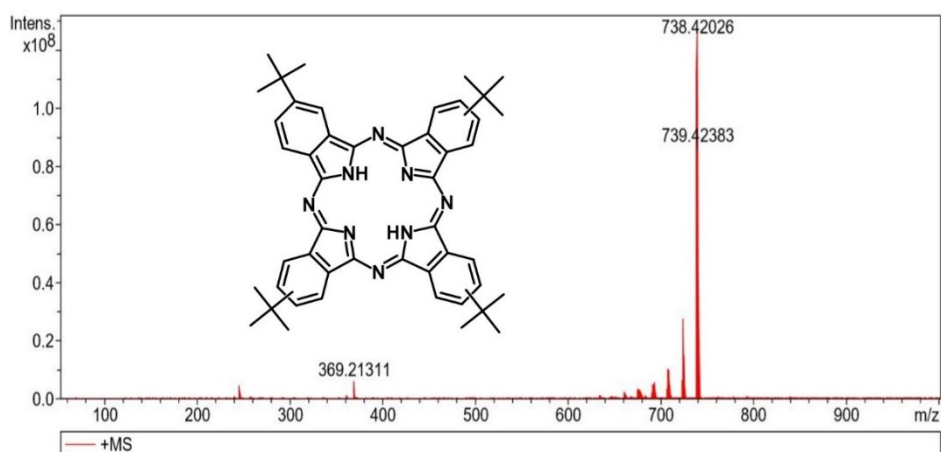
**2.3 3,7,11,15-tetra(pentyloxy)phthalocyanine palladium (POPcPd)**: Under argon atmosphere and stirring condition, 4-*n*-pentyloxyphthalonitrile (2.6 g, 12 mmol) was dissolved in 20 mL *n*-pentanol in the presence of 5 mL 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Using the similar procedures mentioned above, the ligand 3,7,11,15-tetra(pentyloxy)phthalocyanine (**Pc 2**) was obtained (1.56 g, yield 60.6%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*): δ 7.76 (d, 2H), 7.50 (d, 3H), 7.08 (d, 2H), 6.99 - 6.76 (m, 4H), 6.63 (d, 3H), 4.12 - 3.86 (m, 8H), 1.99 (s, 8H), 1.64 (s, 16H), 1.16 (t, 12H). (**Fig. S5**, ESI). MS (MALDI-TOF): Calcd. for C<sub>52</sub>H<sub>58</sub>N<sub>8</sub>O<sub>4</sub> [M<sup>+</sup>] 858.46; Found 858.46 (Mz) (**Fig. S6**, ESI).

**Pc 2** (0.5 g, 0.58 mmol) and PdCl<sub>2</sub> (0.11 g, 0.62 mmol) were dissolved in 20 mL of *n*-pentanol. The mixed solution was bubbled in argon for 15 minutes, and then 5 mL of deoxygenated DBU was added in argon atmosphere. Using the similar procedures mentioned above, **POPcPd** was synthesized. Bottle green powders **POPcPd** was purified through stirred for a while and put aside overnight for the precipitation. The bottle green powders were obtained by filtration. Yield 18.0 %

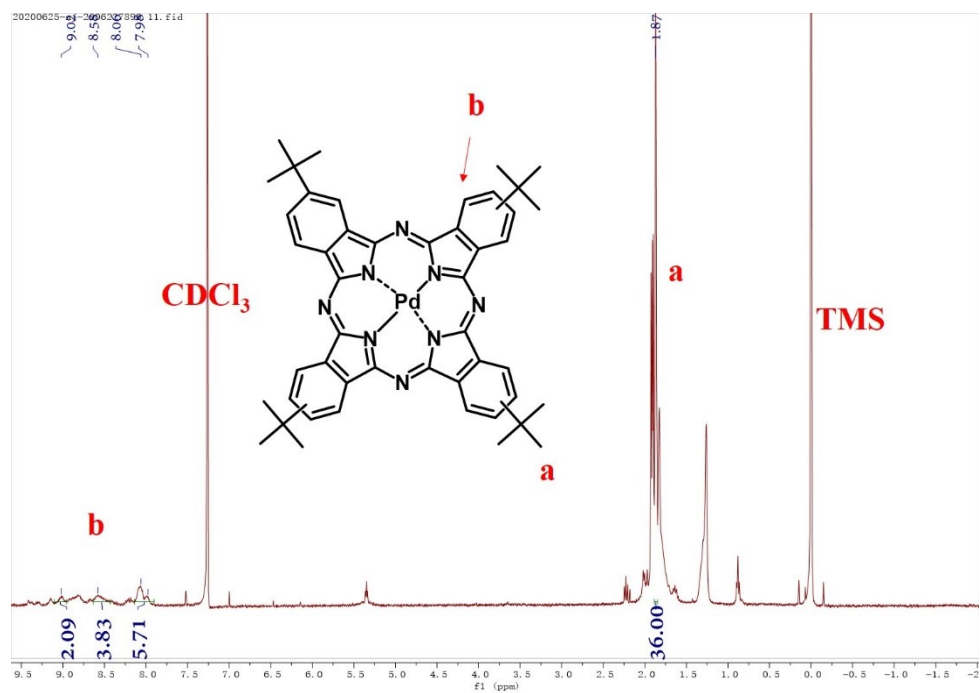
(0.10 g).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*):  $\delta$  7.59 (s, 1H), 7.07 (s, 2H), 6.62 (s, 4H), 6.47 - 5.98 (m, 5H), 3.83 - 3.41 (m, 8H), 1.82 (s, 8H), 1.53 (s, 16H), 1.12 - 1.05 (m, 12H). (**Fig. S7**, ESI).MS (MALDI-TOF): Calcd. for  $\text{C}_{52}\text{H}_{56}\text{N}_8\text{O}_4\text{Pd}$  [ $\text{M}^+$ ] 962.35; Found 962.35 (Mz) (**Fig. S8**, ESI).



**Fig. S1**  $^1\text{H}$  NMR for 3,7,11,15-tetra(tertbutyl)phthalocyanine (**Pc 1**) (solvent: chloroform-*d*).

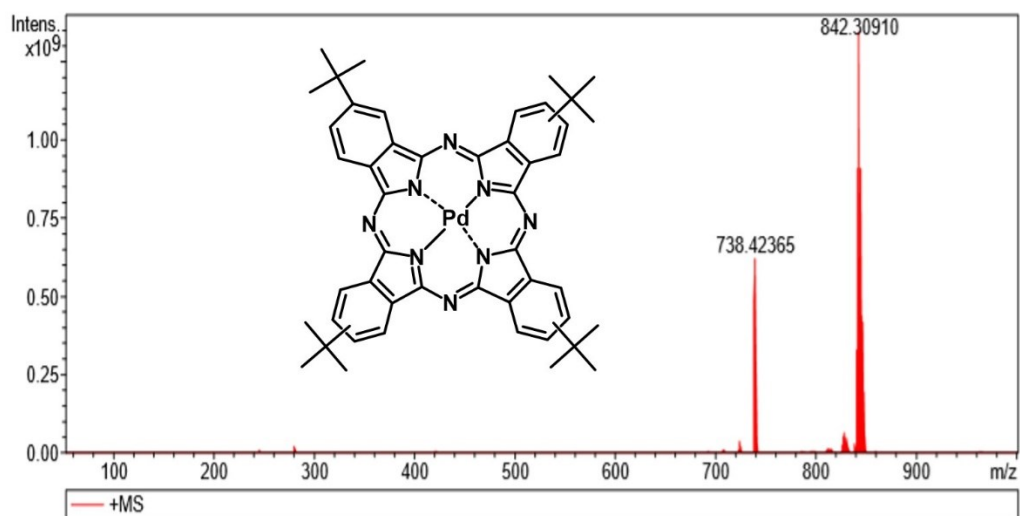


**Fig. S2** Mass spectrum of 3,7,11,15-tetra(tertbutyl)phthalocyanine (**Pc 1**).



**Fig. S3** <sup>1</sup>H NMR for 3,7,11,15-tetra(tertbutyl)phthalocyanine palladium (TBPcPd) in chloroform-

*d.*



**Fig. S4** Mass spectrum of 3,7,11,15-tetra(tertbutyl)phthalocyanine palladium (TBPcPd).

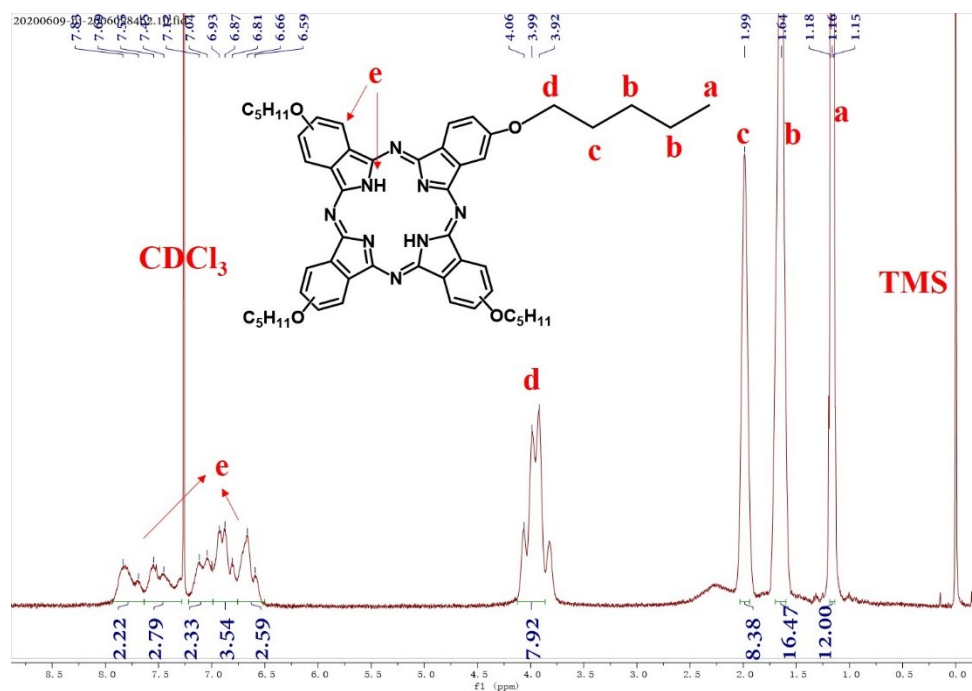


Fig. S5 <sup>1</sup>H NMR for 3,7,11,15-tetra(pentyloxy)phthalocyanine (**Pc 2**) (solvent: chloroform-*d*).

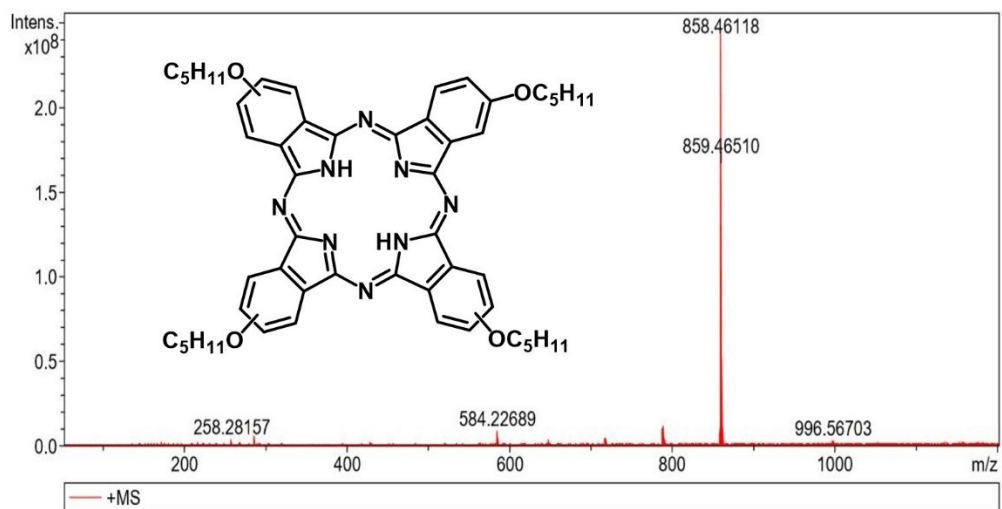
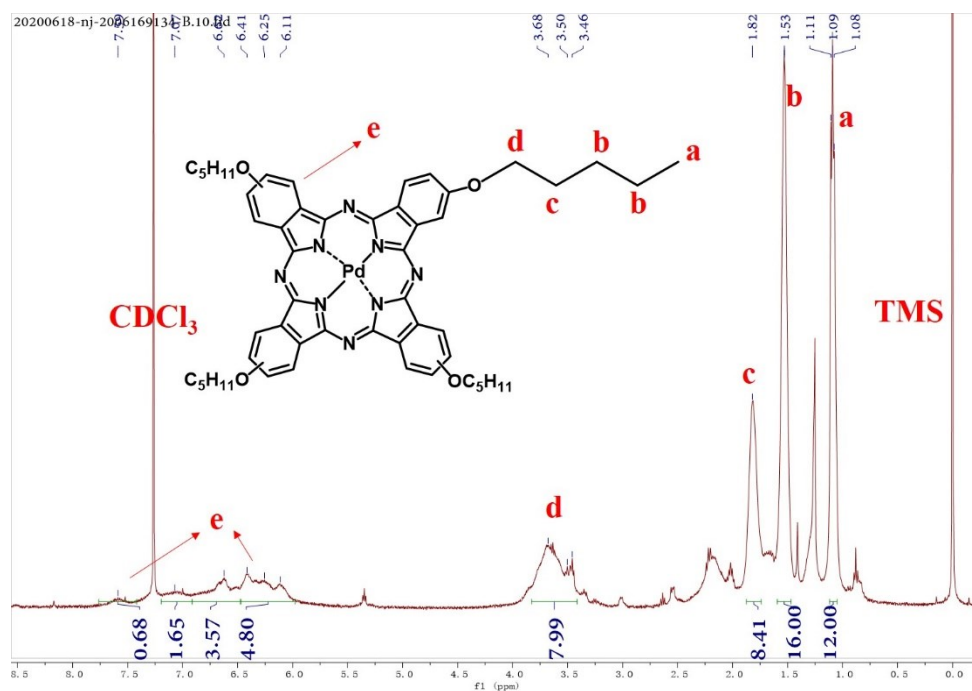
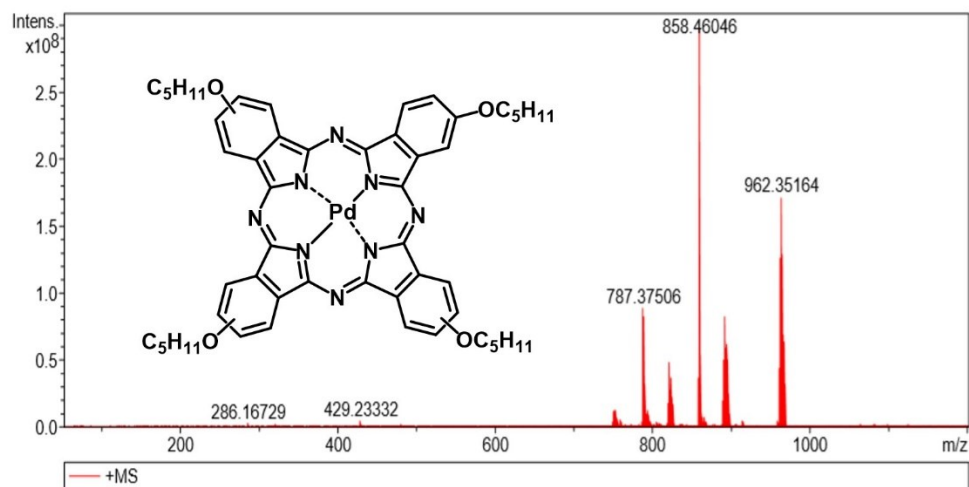


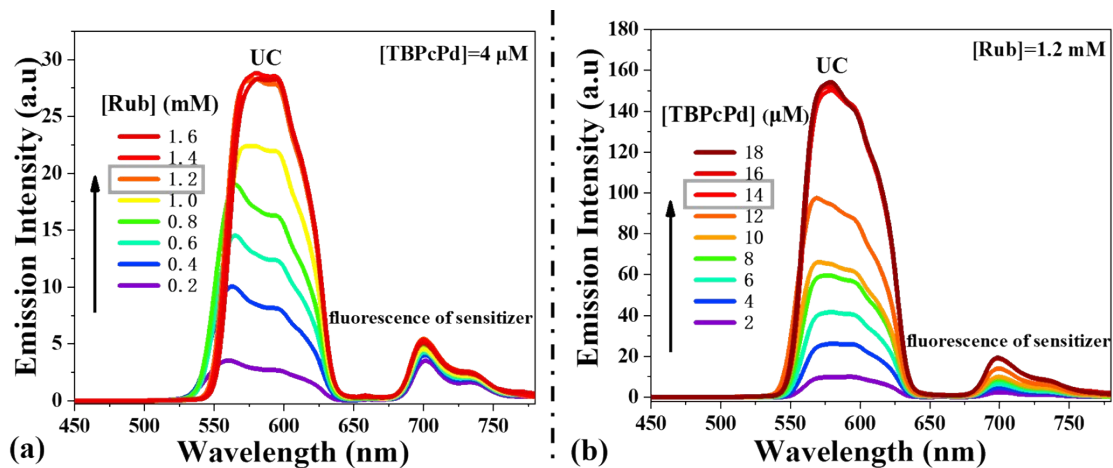
Fig. S6 Mass spectrum of 3,7,11,15-tetra(pentyloxy)phthalocyanine (**Pc 2**).



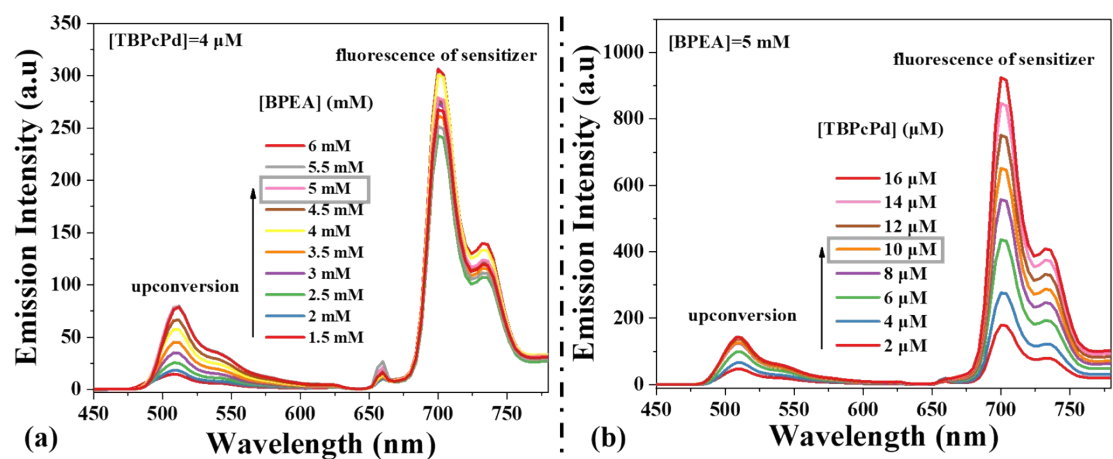
**Fig. S7** <sup>1</sup>H NMR for 3,7,11,15-tetra(pentyloxy)phthalocyanine palladium (POPcPd) in chloroform-*d*.



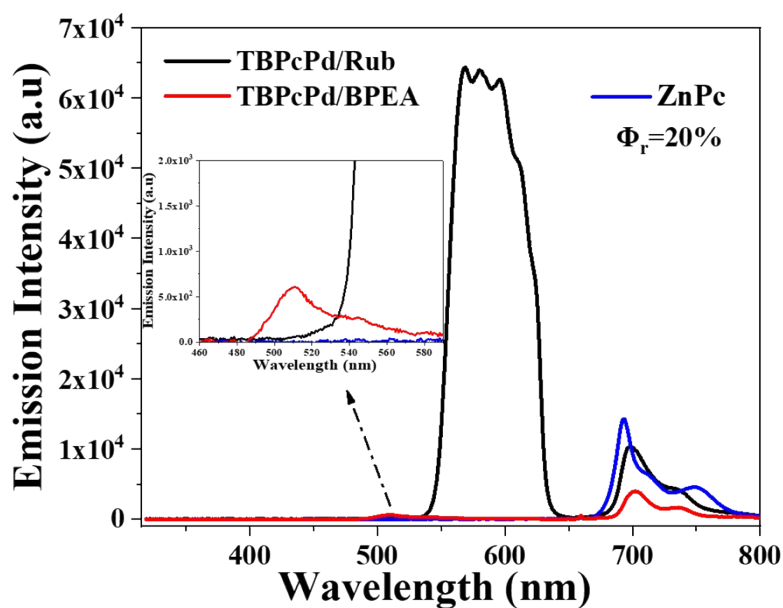
**Fig. S8** Mass spectrum of 3,7,11,15-tetra(pentyloxy)phthalocyanine palladium (POPcPd).



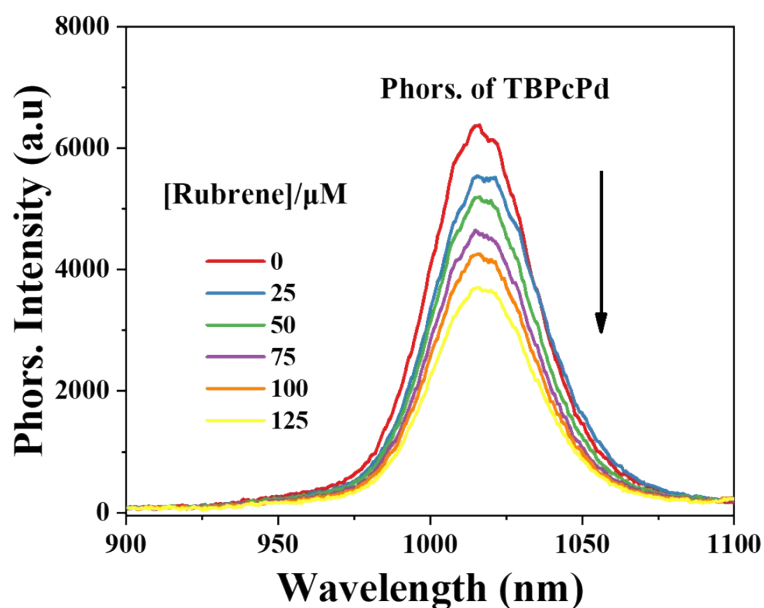
**Fig. S9** The concentration-dependent upconversion spectra of TBPcPd/Rub in degassing toluene at 655 nm excitation.



**Fig. S10** The concentration-dependent upconversion spectra of TBPcPd/BPEA in degassing toluene at 655 nm excitation.

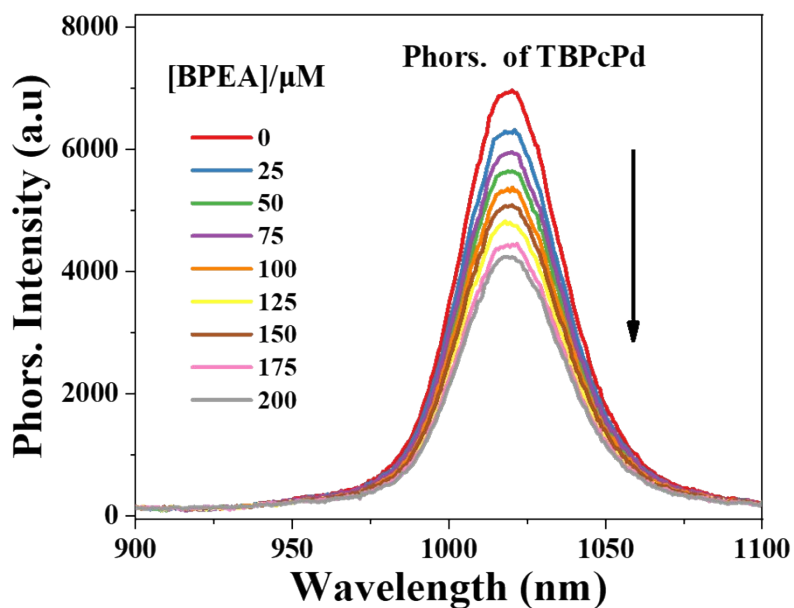


**Fig. S11** UC spectra of **TBPcPd/Rub** (14  $\mu\text{M}$ /1.2 mM) and **TBPcPd/BPEA** (10  $\mu\text{M}$ /5 mM) as well as the fluorescence spectrum of **ZnPc** (0.5  $\mu\text{M}$ ) under the excitation of 655 nm ( $\sim 1.5 \text{ W}\cdot\text{cm}^{-2}$ ) laser (**ZnPc** as reference with  $\Phi_r=20\%$ ).

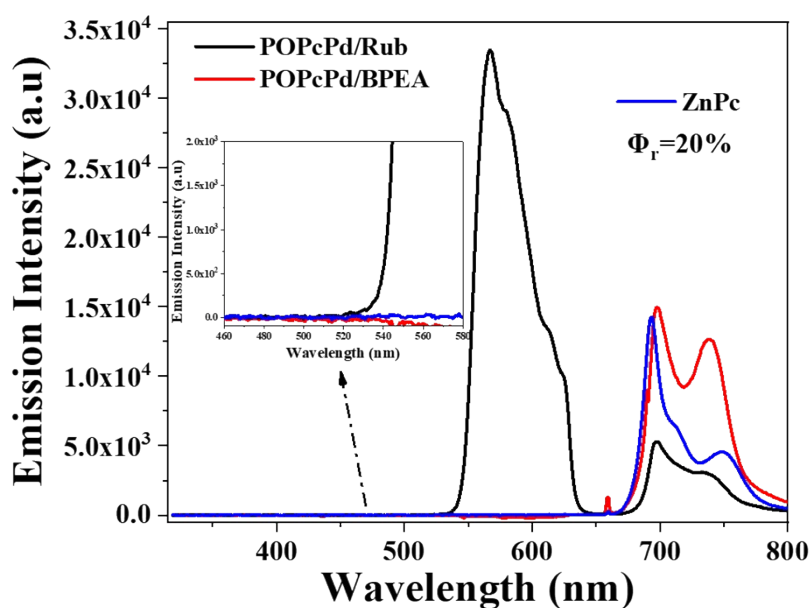


**Fig. S12** The phosphorescence intensity of **TBPcPd** (14  $\mu\text{M}$ ) quenched by **Rub** with different concentration (0–125 $\mu\text{M}$ ) in toluene under the excitation of 655 nm at  $\sim 1.5 \text{ W}\cdot\text{cm}^{-2}$ . ( $\text{N}_2$  atmosphere and room temperature)

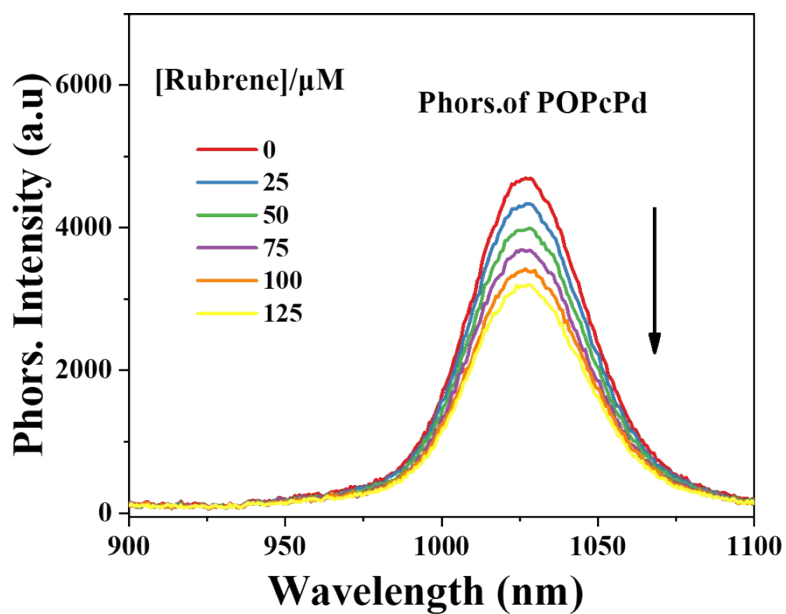




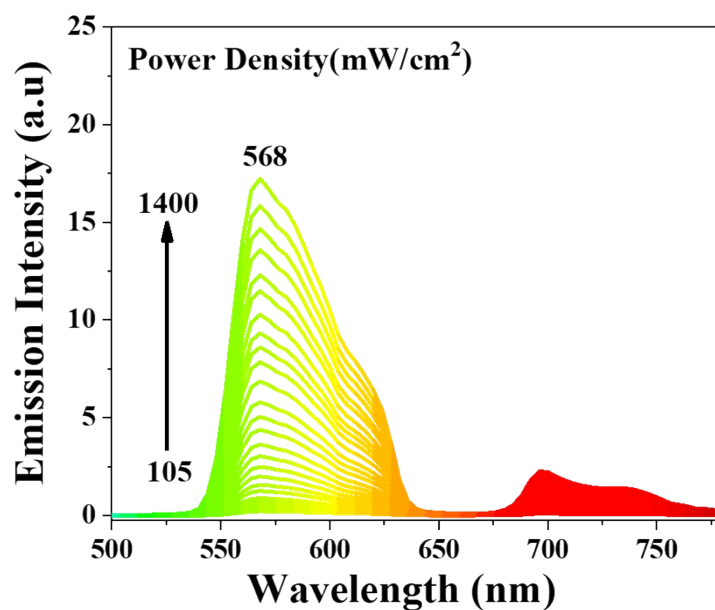
**Fig. S13** The phosphorescence intensity of TBPCPd (10 μM) quenched by BPEA with different concentration (0~200 μM) in toluene under the excitation of 655 nm at  $\sim 1.5 \text{ W}\cdot\text{cm}^{-2}$ . ( $\text{N}_2$  atmosphere and room temperature)



**Fig. S14** UC spectra of POPcPd/Rub (14 μM/1.2 mM) and POPcPd/BPEA (10 μM/5 mM) as well as the fluorescence spectrum of ZnPc (0.5 μM) under the excitation of 655 nm at  $\sim 1.5 \text{ W}\cdot\text{cm}^{-2}$  (ZnPc as reference with  $\Phi_r = 20\%$ ).



**Fig. S15** The phosphorescence intensity of **POPcPd** (14 μM) quenched by **Rub** with different concentration in toluene under the excitation of 655 nm at  $\sim 1.5 \text{ W}\cdot\text{cm}^{-2}$ . ( $\text{N}_2$  atmosphere and room temperature)



**Fig. S16** Power-dependent upconversion of **POPcPd/Rub** in deaerated toluene at 655 nm excitation, ( $[\text{POPcPd}]/[\text{Rub}]$ : 14 μM/1.2 mM)

**Table S1** The parameters based on the *Eqn. (1)* for different upconversion systems in degassing toluene and ZnPc (in DMSO).

	$A_{655 \text{ nm}}^*$	$F$	$\eta$	$\Phi_{UC}(\%)$
ZnPc (reference)	0.008	576612	1.478	20
<b>TBPcPd/Rub</b>	0.295	4162050	1.4967	8.03
<b>POPcPd/Rub</b>	0.773	1706230	1.4967	1.83
<b>TBPcPd/BPEA</b>	0.215	26919	1.4967	0.07
<b>POPcPd/BPEA</b>	0.628	/	1.4967	/

\* The absorbance of sensitizer within bicomponent system at the respective optimised concentration.