Electronic Supplementary Information (ESI):

Multiwavelength hot-band excitated triplet-triplet annihilation upconversion with Pt(II)porphyrin complexes/ 9,10-diphenylanthracene and multiple encrypted information application

Quanlun Chen, Changqing Ye,* Shigang Wan, Shuoran Chen, Zuoqin Liang, Lin Li, Yizhong Shi, Xiaomei Wang*

Suzhou Key Laboratory of New Energy Materials and Low-carbon Technology, School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou, 215009, China

* *Corresponding authors: yechangqing@mail.usts.edu.cn,* wangxiaomei@mail.usts.edu.cn

1. Measurements.

Absorption and emission spectra were measured with a Hitachi U-3500 spectrophotometer and FLS920 Edinburgh fluorophotometer, respectively. Time-resolved phorsphorescence decay was measured under detection of μF lamp to obtain the lifetime (τ_p) with monoexponential fit give acceptable statistics parameters of $\chi 2 <$ 1.1 ($\chi 2$ is the "reduced chi-square").

Under excitation of the diode solid state laser (635 nm, 655 nm, 671 nm or 785nm), the upconversion spectra were recorded with PR655 Spectra Scan colorimeter. The SEM image was taken on the Hitachi Regulus8100. The particle size distribution plot was measured on the Zetasizer Nano ZS. The XRD patterns was measured on the smartlab. I–V curve of TTA-UC powered Si-photodiode was measured on the Keithley 2400.

2. Materials.

Platinum(II)tetraphenyltetrabenzoporphyrin (**PtTPBP**) was purchased from J&K Scientific and 9,10-bis(phenylethynyl)anthracene (**BPEA**) was purchased from Richjoint. Sodium dodecyl sulfate (SDS) was purchased from Aladdin.

The solution containing annihilator/sensitizer (**BPEA**/**PtTPBP**) pair was prepared in $CHCl_3$ or DMF with degassing for about 15 min with N_2 before UC measurements. The solvent for measurements was commercially available spectral pure.

Slow-rate reprecipitation preperations of **PtTPTBP**-doped **BPEA** crystallites: Under the quick stirring condition, a mixture of solution (20 mL, $CHCl_3$) containing **PtTPTBP/BPEA** (1/1000, mol/mol) was slowly injected into deionized water (100 mL) in the presence of sodium dodecyl sulfate (SDS, 0.288 g) for about 1.5 hours and then stirred vigorously for another 24 hours. The obtained non-transparent solution is subjected to centrifugation, filtration and dry. The yellow crystallites powders were obtained. Then,

the microcrystals were sealed between two coverslips in a glove box for measurements.

Fast-rate reprecipitation preperations of **PtTPTBP**-doped **BPEA** crystallites: Under the quick stirring condition, a mixture of solution (THF, 20 mL) containing **PtTPTBP/BPEA** (1/1000, mol/mol) was quickly injected into water (100 mL) and then continuously stirred vigorously for 10 mins. The obtained non-transparent solution is subjected to filtration and dry. The yellow crystallites powders were obtained.

PtTPTBP-doped **BPEA** crystallites for anti-counterfeiting measurements. Under the quick stirring condition, a mixture of solution (THF, 20 mL) containing **PtTPTBP/BPEA** (1/50000, mol/mol) was quickly injected into water (100 mL) and then continuously stirred vigorously for 10 mins. The obtained non-transparent solution is subjected to filtration and dry. The yellow crystallites powders were obtained.

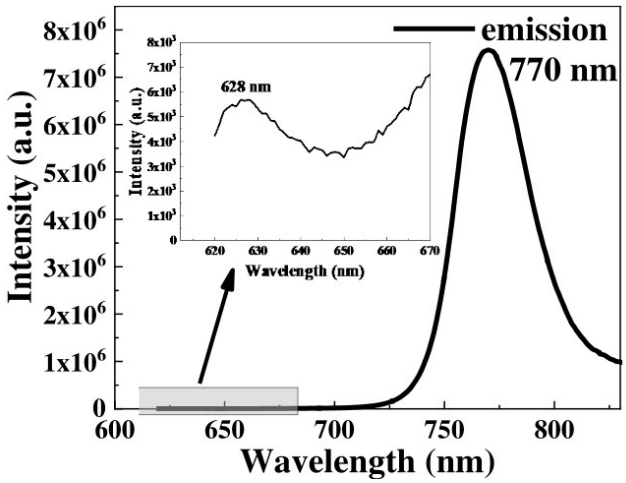

Fig. S1 The emission spectrum of **PtTPBP** ($CHCl_3$, 10 μM), under the excitation of 429 nm in the air (r.t.).

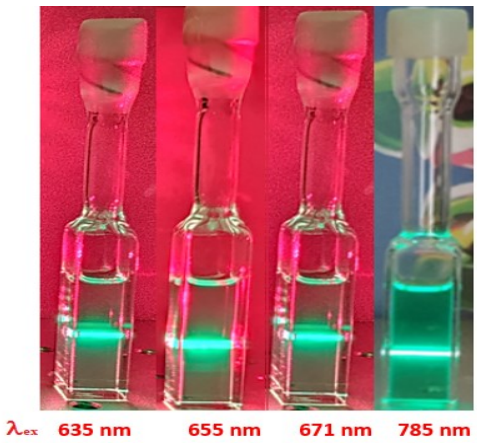

Fig. S2 Photographs of the upconverted fluorescence of **PtTPBP/BPE**A (50 μM/0.6 mM) degassing solution ($CHCl_3$), under excitation of 635 nm (1 $W{\cdot}cm^{-2}$) though a notch filter, 655 nm (1.7 $W{\cdot}cm^{-2}$) though a notch filter, 671 nm (8.5 $W{\cdot}cm^{-2}$) though a 650-short pass filter and 785 nm (8.5 $W{\cdot}cm^{-2}$) though a 650-short pass filter, respectively. The upconversion excited by 635 nm is also shown for comparison.

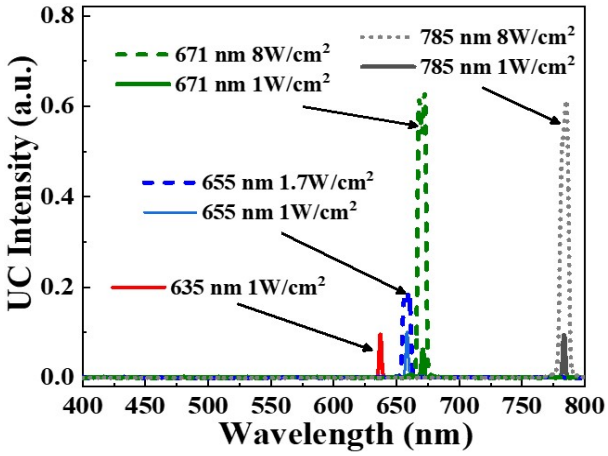

Fig. S3 Upconversion spectra measurements of **BPEA** (0.6 mM, degassing $CHCl_3$) under the excitation of dioder laser with 635 nm (1 W·cm^{-2}), 655 nm (1 W·cm^{-2}, 1.7 W·cm^{-2}), 671 nm (1 W·cm^{-2}, 8 W·cm^{-2}) and 785 nm (1 W·cm^{-2}, 8 W·cm^{-2}), respectively.

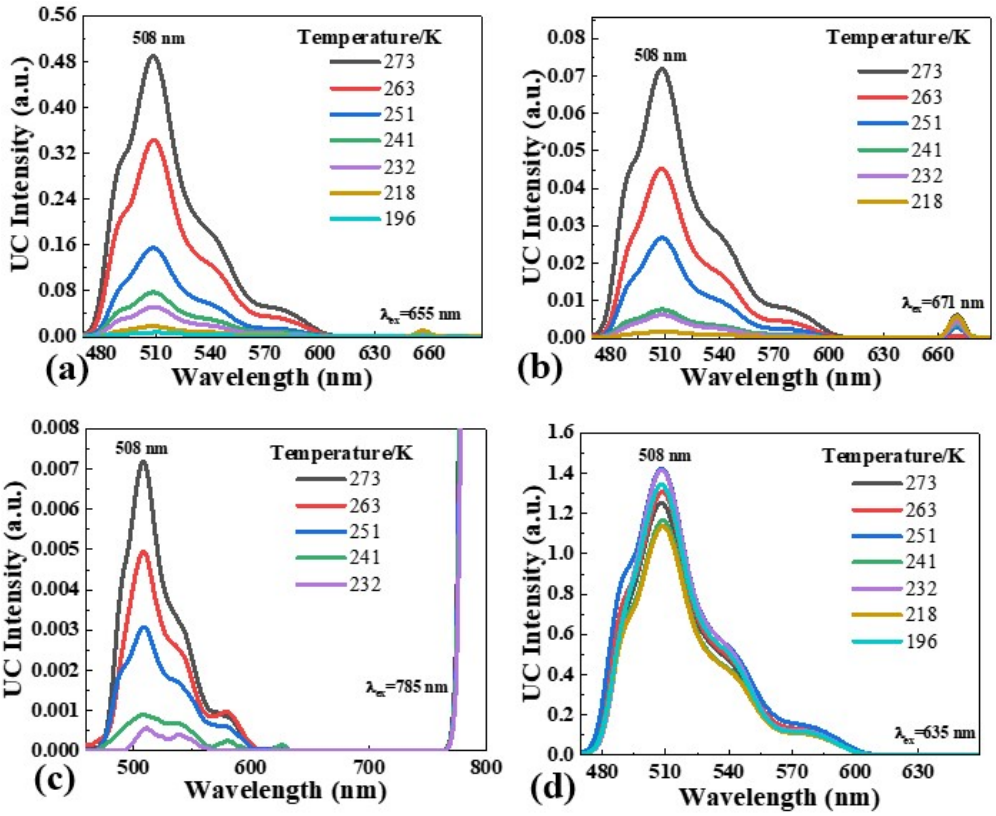

Fig. S4 Temperature-dependent upconversion spectra of **PtTPBP** (50 μM)/ **BPEA** (0.6 mM) (in degassing DMF solution) under the excitation of diode laser (1 W·cm^{-2}) at 635 nm **(a)**, 655 nm **(b)**, 671 nm **(c)** and 785 nm **(c)** with 600-short pass filter.

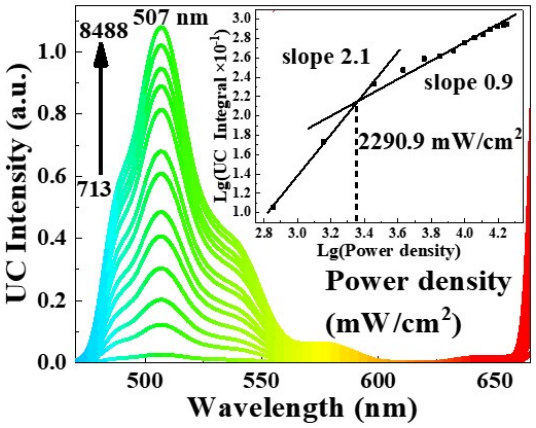

Fig. S5 Power-dependent upconversion spectra of **PtTPBP**/**BPEA** (50 μM /0.6 mM) in degassing $CHCl_3$ under excitation of 671 nm through a 650-short pass filter.

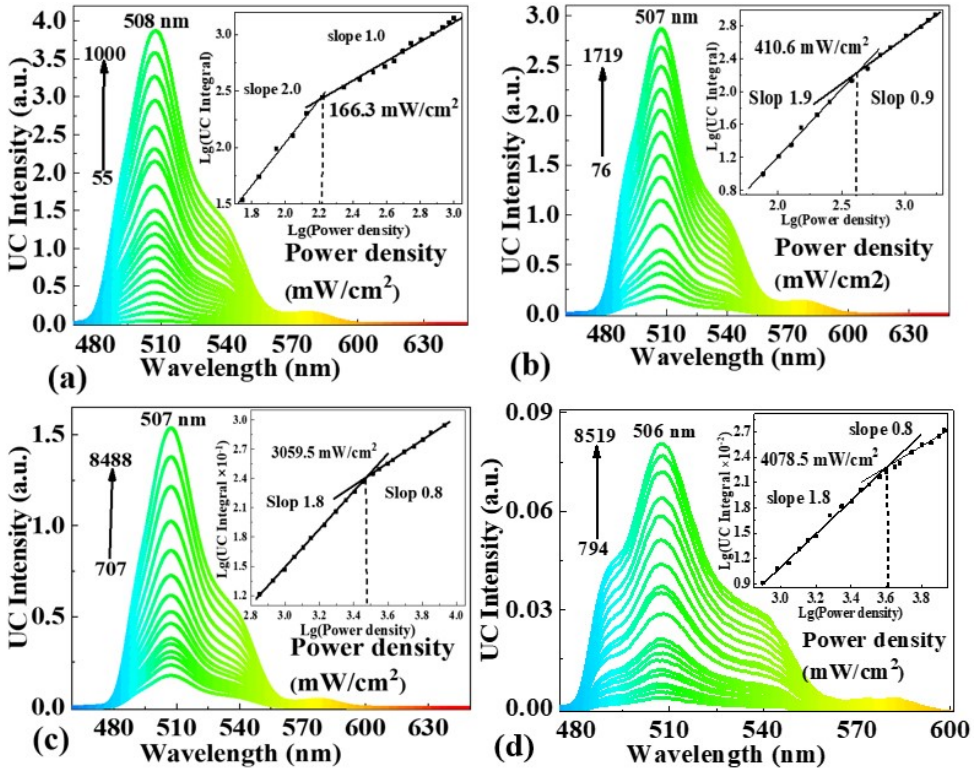

Fig. S6 Power-dependent upconversion spectra of **PtTPBP**/**BPEA** (50μM/0.6 mM) in degassing DMF, under excitation of 635 nm through a notch filter (**a**), 655 nm through a notch filter (**b**) 671 nm through a 650-short pass filter (**c**) and 785 nm through a 650-short pass filter (**d**).

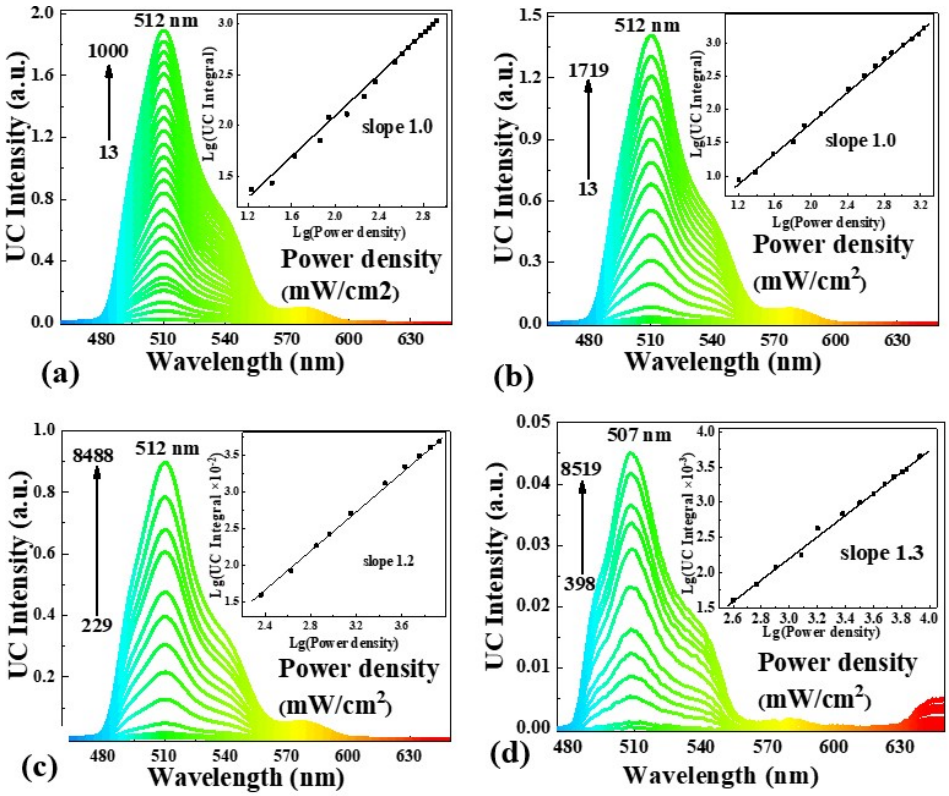

Fig. S7 Power-dependent upconversion spectra of **PtTPBP**/**BPEA** (50 μM/0.6 mM) in degassing DMSO under excitation of 635 nm through a notch filter (**a**), 655 nm through a notch filter (**b**) 671 nm through a 650-short pass filter (**c**) and 785 nm through a 650-short pass filter (**d**). The slope changing from ~2 to ~1 cannot be observed here, due to weak TTA-UC in DMSO solution.

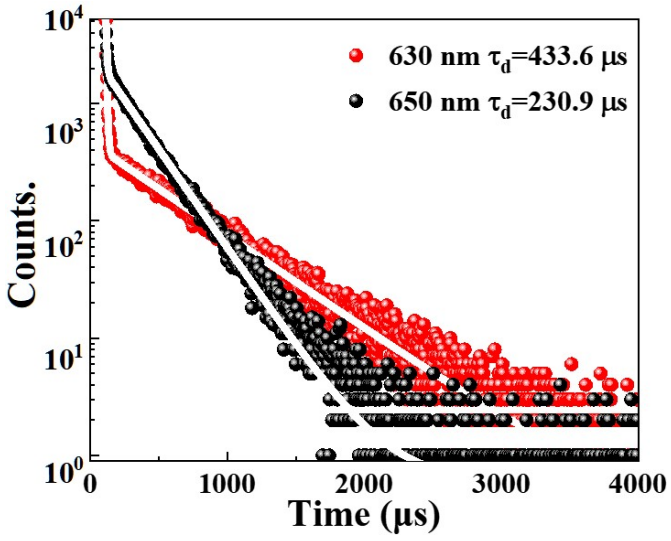

Fig. S8 Delay fluorescence curves of **BPEA** (0.6 mM) combined with **PtTPBP** (50 μM) under a pulsed excitation at 630 nm (red) and 650 nm (black) (detection at 508 nm, degassing DMF). Due to the weak upconversion emission, the delay fluorescence curves of **BPEA** cannot obtained under a pulsed excitation at 676 nm and 785 nm.

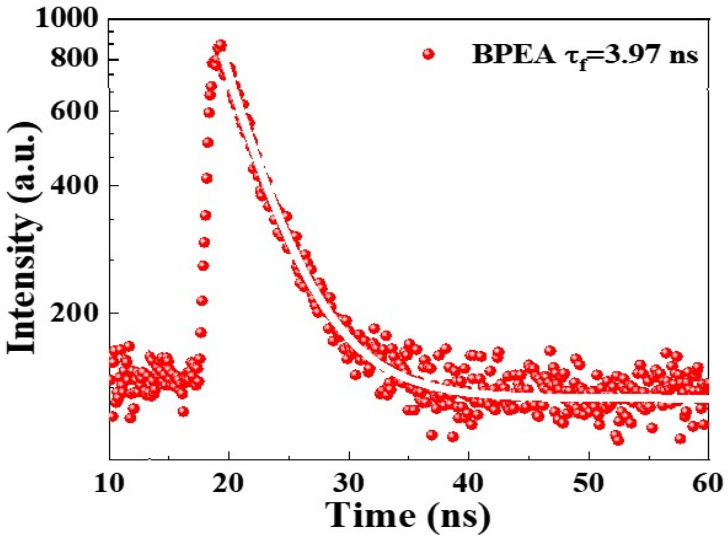

Fig. S9 Time-resolved fluorescence decay curve of **BPEA** (10 μM) under a pulsed excitation at 438 nm (detection at 504 nm, DMF).

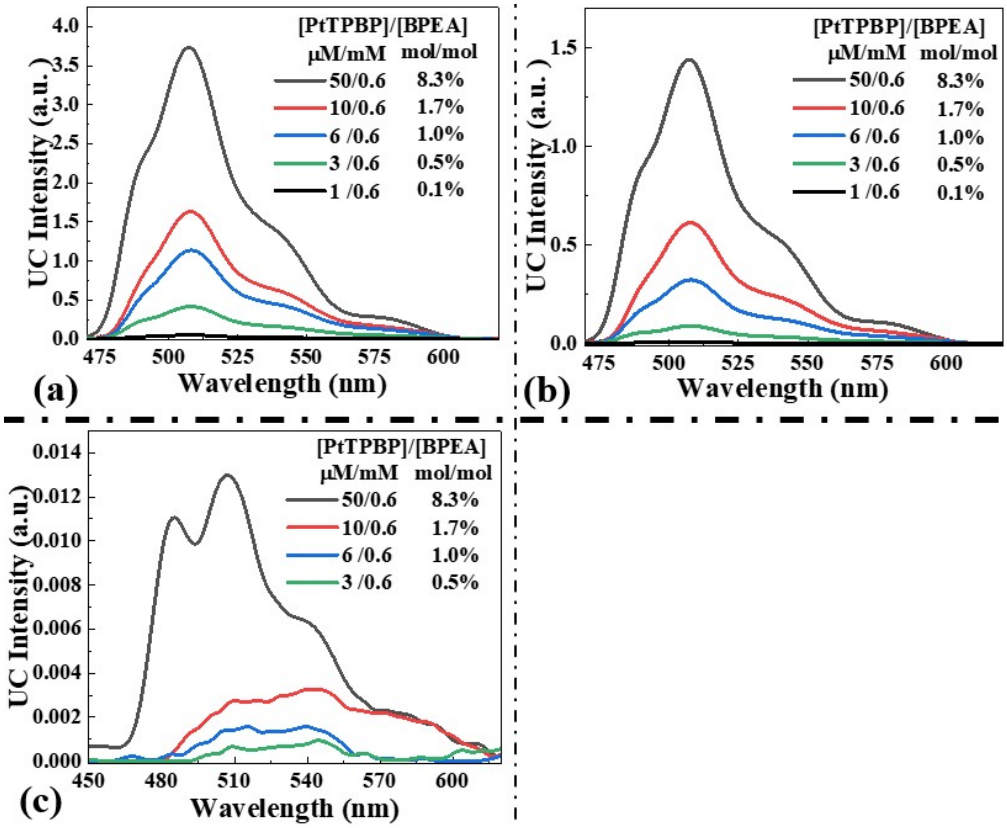

Fig. S10 TTA-UC spectra of **BPEA** (the concentration fixed at 0.6 mM) combined with **PtTPBP** (concentration: 1 μM ~50 μM), under the excitation of 635 nm **(a)**, 655 nm **(b)** and 785 nm **(c)** at power density of 1 W·cm^{-2} (with 600-short pass filter).

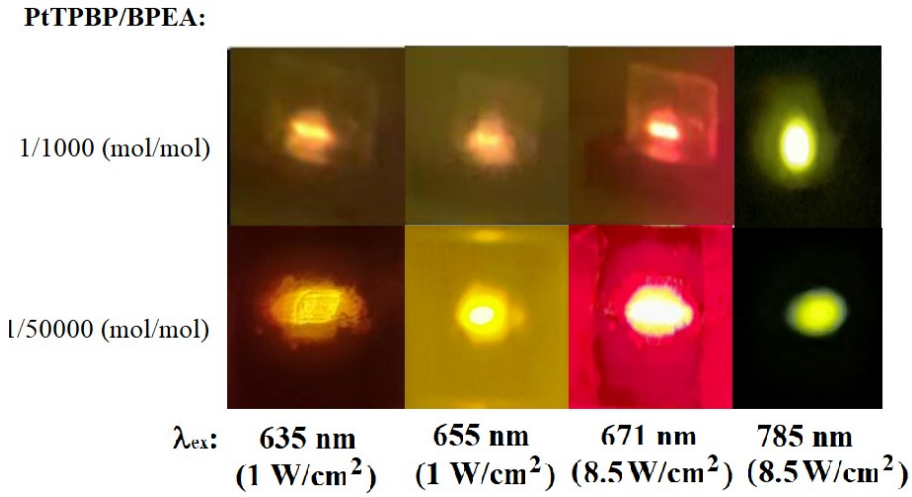

Fig. S11 Photographs of the upconverted fluorescence in solid **BPEA** crystallites doped **PtTPBP** as molar ratio of 1000/1 (up) and 50000/1 (down), under excitation of 635 nm (1 W·cm^{-2}) through a notch filter, 655 nm (1.7 W·cm^{-2}) through a notch filter, 671 nm (8.5 W·cm^{-2}) through a 650-short pass filter and 785 nm (8.5 W·cm^{-2}) through a 650-short pass filter.

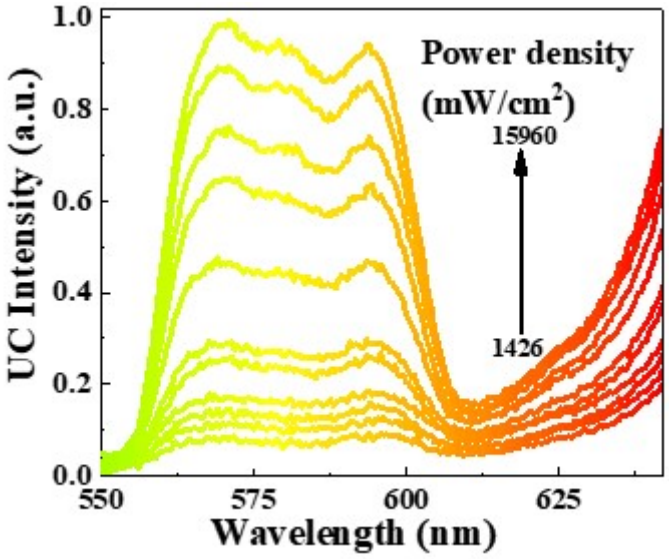

Fig. S12 power-dependent upconversion spectra **PtTPBP/BPEA** (1/1000, mol/mol) microcrystals under excitation of 671nm through a 650-short pass filter.

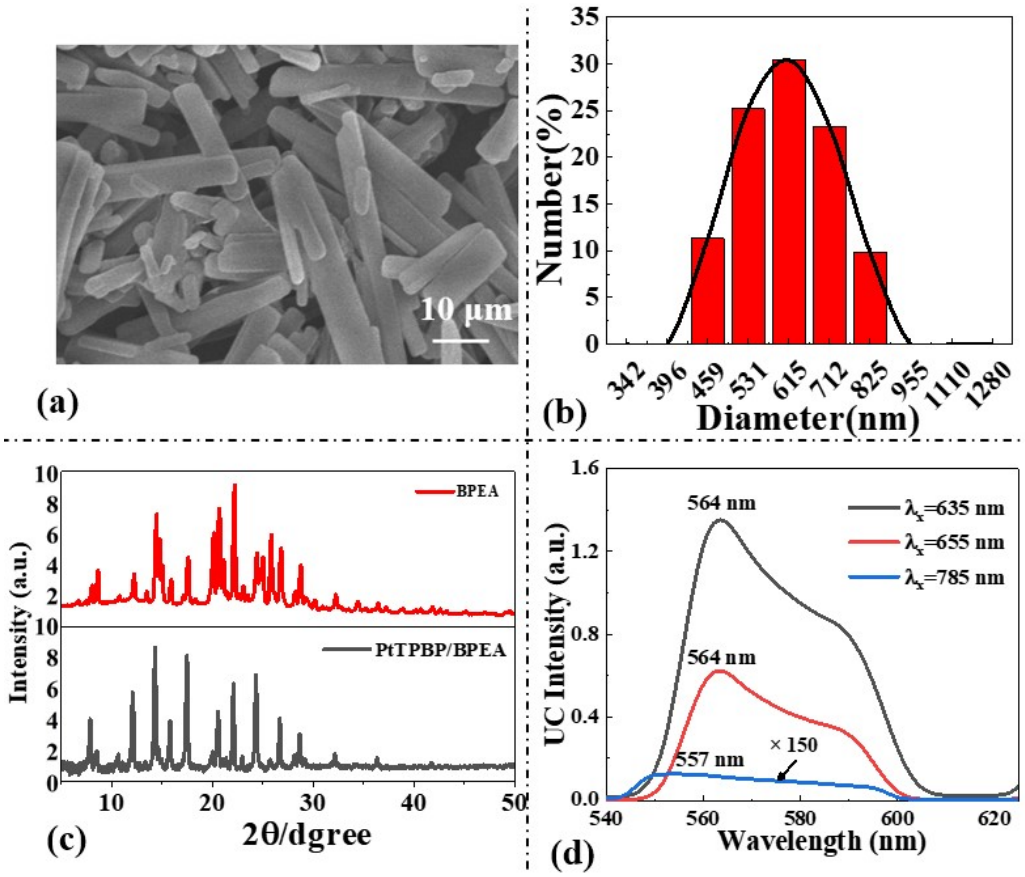

Fig. S13 **PtTPBP/BPEA** (1/1000, mol/mol) microcrystals obtained by fast-rate precipitation: SEM image (**a**), histograms of the size distribution (**b**), PXRD pattern (**BPEA** microcrystal presented for comparison) (**c**), and TTA-UC spectra obtained by exposure to air under 635 nm excitation (with a notch filter), 655 nm excitation (with a notch filter) and 785 nm excitation (with a 650-short pass filter) at the power dentisy at 1 W·cm^{-2} (**d**).

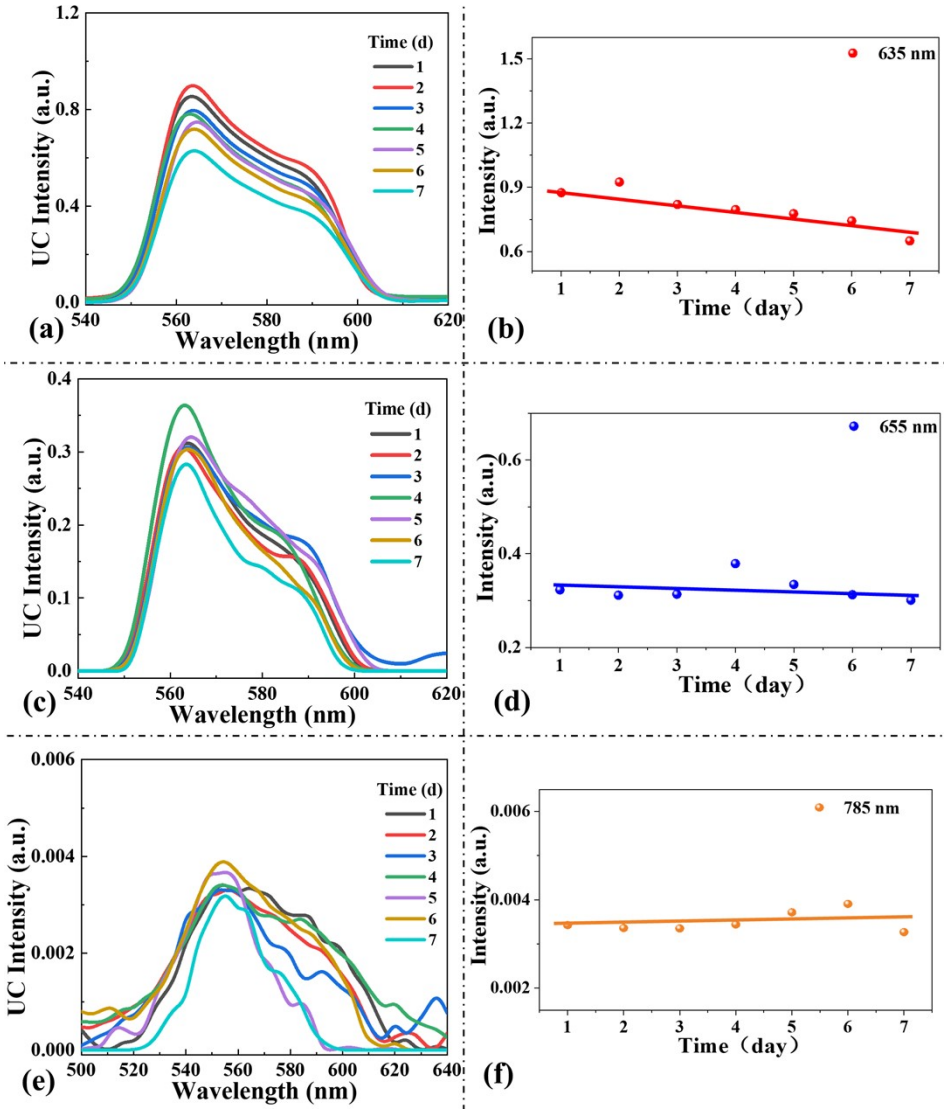

Fig. S14 Under the air atmosphere, the changes of upconversion spectra and upconversion intensities of **PtTPBP**/**BPEA** crystallites (1/1000, mol/mol), under excitation of 635 nm (1 W·cm^{-2}) through a notch filter (**a, b**), 655 nm (1 W·cm^{-2}) through a notch filter (**c, d**) and 785 nm (2 W·cm^{-2}) through a 650-short pass filter (**e**, **f**) from 1th day till to 7th days.

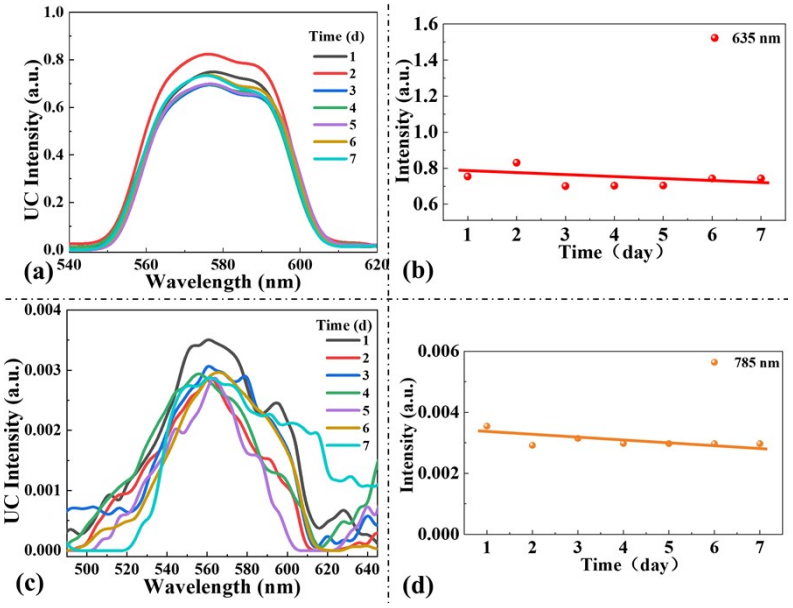

Fig. S15 Under the air atmosphere, the changes of upconversion spectra and upconversion intensities of **PtTPBP**/**BPEA** crystallites (1/50000, mol/mol), under excitation of 635 nm (1 W·cm^{-2}) through a notch filter (**a, b**) and 785 nm (2 W·cm^{-2}) through a 650-short pass filter (**c**, **d**) from 1th day till to 7th days.