



Low-Power Upconversion in Anthracene Derivatives Doped with Pd(II) Tetraphenylporphyrin†

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Selective low energy excitation of Pd(II) tetraphenylporphyrin in the presence of anthracene and anthracene-2-carboxylic acid, respectively, can yield easily visualized upconversion fluorescence at low excitation power. Anthracene-2-carboxylic acid shows about a two-fold increase in the upconversion quantum yield, relative to anthracene under the identical conditions. The higher fluorescence quantum of anthracene-2-carboxylic acid plays a crucial role in its effective upconversion fluorescence.

Keywords: Low-power, Upconversion, Sensitizer, Emitter, Quantum efficiency, Pd(II) tetraphenylporphyrin.

INTRODUCTION

Optical upconversion refers to a collection of process that permits the conversion of optical radiation into light of a shorter wavelength. This effect is potentially useful for a plethora of applications, including photovoltaics¹, photocatalysis², bio-imaging³, photodynamic therapy⁴ and frequency up-converted lasing⁵. A few techniques for upconversion have been well-established, such as two-photon absorption in organic molecules⁶ and sequential energy transfer upconversion in rare-earth ion-doped glasses⁷. Both of them need either a high power density (usually, in order of kW cm⁻² and MW cm⁻²) and/or a coherent excitation source. Recently, a different approach for upconversion, based on energetically conjoined triplet-triplet annihilation (TTA) was demonstrated. This upconversion process at low power densities (< 100 Wcm⁻²) and of non-coherent light can also be achieved in multi-chromophore systems that comprise a triplet sensitizer and an emitter⁸. The sensitizer firstly absorbs low-power light, then undergoes intersystem crossing and further transfers its triplet energy to the triplet of emitter. Secondly, the triplet emitters undergo triplet-triplet annihilation and then release the upconversion fluorescence.

The high upconversion efficiency is extremely desired from the viewpoint of applications. An efficient triplet-triplet

annihilation assisted photon upconversion has been observed for a broad variety of metal complexes, acting as sensitizers. Recently, it has been shown that metallated macrocycles such as platinum⁻⁹, palladium⁻¹⁰, zinc¹¹ and copper octaethylporphyrins¹² as well as Ru(II)¹³ and iridium complexes¹⁴ can serve as sensitizers in the bimolecular upconversion processes. Many experiments indicate that triplet sensitizers with intense absorption of visible light and long triplet excited state life times are helpful to improve the triplet-triplet annihilation upconversion efficiency. Compared to the development of triplet sensitizers, much less attention has been paid to the development of triplet emitters¹⁵. In this paper, two commercially available compounds anthracene (An) and anthracene-2-carboxylic acid (AnCOOH) were chosen as the emitter for low-power upconversion. Palladium(II) tetraphenylporphyrin (PdTPP) was used as the triplet sensitizer. The structures of the sensitizer and the emitters employed in the energy upconversion system are shown in Fig. 1. Their linear absorption, single-photon excited fluorescence and triplet-triplet annihilation upconversion fluorescence properties were studied.

EXPERIMENTAL

Palladium(II) tetraphenylporphyrin (PdTPP) was synthesized according to the procedure published¹⁶. The anthracene

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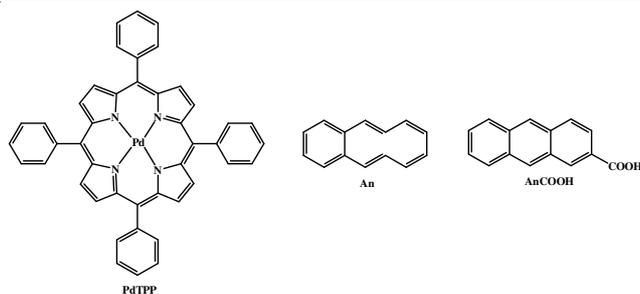


Fig. 1. Chemical structures of the sensitizer and the emitters

derivatives such as anthracene (An) and anthracene-2-carboxylic acid (AnCOOH) were commercially available. Solvent DMF at spectral reagent grade were used as received. UV-visible absorption spectra were recorded on Varian Cary 50 spectrophotometer. Fluorescence measurements were carried out with an Edinburgh FLS 920 fluorophotometer equipped with a 150 W Xe lamp.

Triplet-triplet annihilation upconversion measurements: Diode pumped solid state laser (emission wavelength: 532 nm) was used as the excitation source for the upconversion. The laser power was measured with photodiode detector. For the upconversion experiments, the mixed solution of the sensitizer and emitter was degassed for 0.5 h with N_2 . Then the solution was excited with laser. The upconverted fluorescence was observed with PR655 SpectraScan colorimeter. The upconversion efficiency of PdTPP in presence of different emitters was obtained relative to rhodamine 6G using 532 nm excitation according to the literature¹⁷.

$$\Phi_{UC} = 2\Phi_r \left(\frac{A_r}{A_s} \right) \left(\frac{F_s}{F_r} \right) \left(\frac{\eta_s}{\eta_r} \right)^2$$

where the subscript “s” and “r” represent sample and reference, respectively. Φ_r is the fluorescence quantum yield of rhodamine 6G (0.88) in ethanol using 532 nm excitation. F is the integrated emission of emitters and rhodamine 6G under the excitation of 532 nm. A is the absorbance of both PdTPP and rhodamine 6G at 532 nm, while η is the refractive index of solvent used. The factor 2 accounts for the fact that two absorbed photons are required to produce one upconverted photon.

RESULTS AND DISCUSSION

Absorption and fluorescence spectra: As shown in Fig. 2, the sensitizer PdTPP exhibits characteristic absorption bands at 522 nm correspond to the Q-band and 415 nm correspond to the Soret band. Upon excitation at 523 nm, PdTPP produces singlet fluorescence at 609 nm and long-lived triplet phosphorescence at 704 nm with a shoulder peak at room temperature under N_2 atmosphere. The emitter An shows four absorption bands at 327, 342, 360 and 379 nm. For AnCOOH, it also represents four absorption bands. Its longest absorption band is centered at 386 nm. Compared with the longest absorption band of An, the bands of AnCOOH represent a 7 nm red shift. The red-shift of absorption spectra for AnCOOH is due to the extension of conjugation and electron-withdrawing ability of the carboxylic acid group. The fluorescence spectrum of An in DMF has three emission bands located at 382, 403 and 427 nm (Fig. 2b). Anthracene-2-carboxylic acid exhibits two

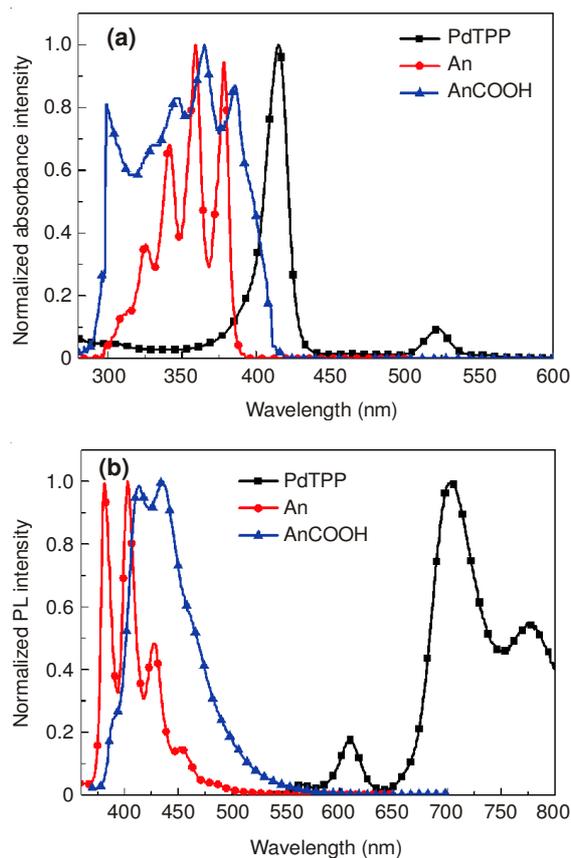


Fig. 2. Normalized absorption (a) and fluorescence (b) spectra of PdTPP, An, AnCOOH in DMF (1×10^{-6} M)

emission peaks centered at 413 and 436 nm. In addition, the fluorescence quantum yields of two emitters in DMF solution were measured by using quinine sulfate as standard. The fluorescence quantum yields of compounds An and AnCOOH are found to be 24.5 and 28.7 %, respectively.

Triplet-triplet annihilation upconversion: Blue upconversion from bimolecular PdTPP/An in degassed DMF can be observed upon excitation at 532 nm with power intensity at 0.5 W/cm^2 , as shown in Fig. 3a. With the increase of An concentration, the upconversion fluorescence intensity continues to increase. When the concentration of An is up to 1.4×10^{-3} M, the upconversion fluorescence intensity reaches its maximum. Continuing to increase the concentration of An, a decrease in the upconversion emission intensity is observed. At the same time, the emission intensity of PdTPP at 704 nm gradually becomes weak. Additionally, it is found that the emission of PdTPP at about 609 nm is not quenched in the presence of An. It is because that the triplet excited state, instead of the singlet excited state of the sensitizer, is involved in the triplet-triplet energy transfer process. PdTPP/AnCOOH system also exhibits a blue emission upon excitation at 532 nm, as shown in Fig. 3b. Its upconversion fluorescence spectra reveal the same change trend with that of PdTPP/An system. When the concentration of AnCOOH is up to 1×10^{-3} M, the upconversion fluorescence intensity reaches its maximum. Excitation of the sensitizer or the emitters alone at 532 nm does not produce the blue emission band in the range of 400–532 nm. The blue upconversion fluorescence is very similar to the fluorescence spectrum of corresponding emitter. Therefore,

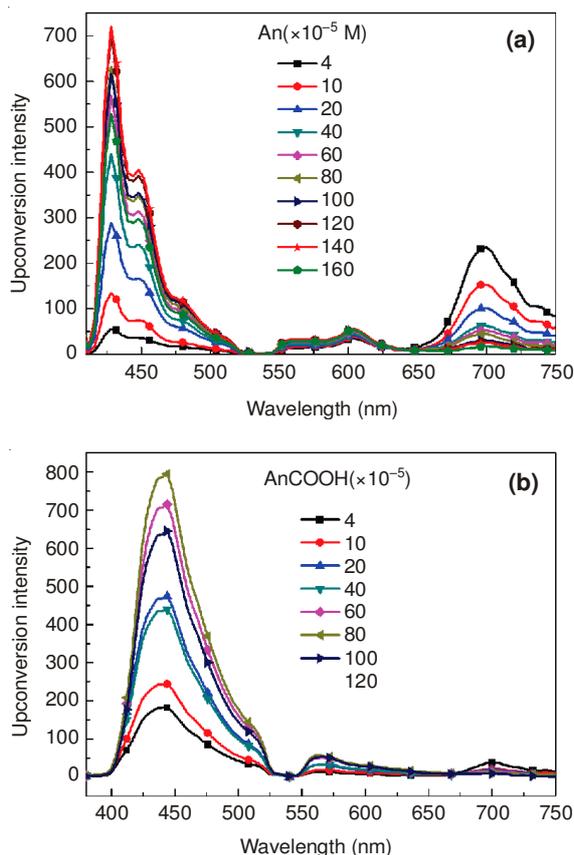


Fig. 3. Dependence of upconversion fluorescence intensity on the relative concentrations of the emitters An (a), AnCOOH (b) at fixed concentration of the sensitizer PdTPP (4×10^{-6} M) upon excitation at 532 nm with power density of 0.5 W/cm^2 in degassed DMF

the emission at 400-532 nm should be ascribed to the triplet-triplet annihilation upconversion. The green-to-blue photon upconversion can be easily visualized with a commercial green laser pointer ($< 5 \text{ mW}$ peak power) upon excitation at 532 nm, as shown by the digital photograph in Fig. 4. For PdTPP alone, no obvious emission is observed. The blue emission is obtained in the presence of An and AnCOOH, due to the significant triplet-triplet annihilation upconversion with the sensitizer PdTPP. It is evident that the upconversion based on triplet-triplet annihilation can be achieved at non-coherent light sources with power-densities.

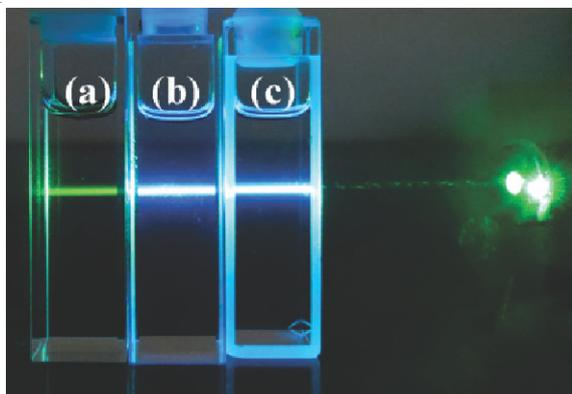


Fig. 4. Digital photographs of PdTPP (a), PdTPP/An (b) and PdTPP/AnCOOH (c) in deaerated DMF with a commercial green laser pointer upon excitation at 532 nm

The percent quantum efficiency of upconversion fluorescence was measured as a function of the concentration of both An and AnCOOH, determined relative to rhodamine 6G in methanol using 532 nm excitation. Fig. 5 displays the dependence of upconversion fluorescence quantum yield on the relative concentration of the emitters at a constant concentration (4×10^{-6} M) of the sensitizer. The upconversion quantum yield of An increases with increasing its concentration. When the concentration is increased to 1.2×10^{-3} M, the upconversion quantum yield reaches its maximum 1.4 %. Continuing to increase the concentration, the quantum yield starts to become weaker. This is because that the increase of An concentration can make the encounter of the sensitizer and the emitter more likely to enhance the yields of the energy transfer process. However, when the concentration of An exceeds the threshold value 1.2×10^{-3} M, the upconversion fluorescence can be suppressed due to the concentration quenching effect. The similar results are obtained across the AnCOOH concentration profiles. The maximum upconversion quantum yield of AnCOOH is 2.7 %. The upconversion quantum yield of PdTPP/AnCOOH system is about two times bigger than that of PdTPP/An. The relatively poor performance of PdTPP/An is probably because of the small fluorescence quantum of An. Following the mechanism for the upconversion based on triplet-triplet annihilation, the singlet excited state of the emitter decays radiatively to lead to upconversion fluorescence. Therefore, the fluorescence quantum of the emitter plays a crucial role in the upconversion quantum yield.

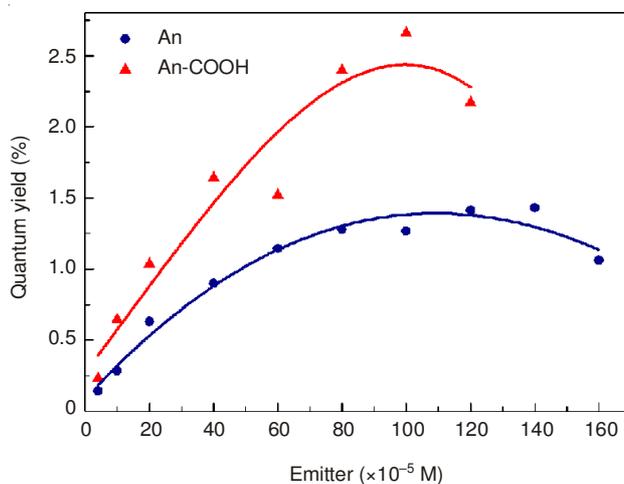


Fig. 5. Dependence of the upconversion quantum yield on the relative concentration of the emitters at a constant concentration (4×10^{-6} M) of the sensitizer upon excitation at 532 nm with power density at 0.5 W/cm^2

Conclusion

The linear absorption, fluorescence and triplet-triplet annihilation upconversion fluorescence properties of two emitters have been studied. Selective excitation of the sensitizer PdTPP in solutions containing An or AnCOOH at 532 nm with excitation power density of 0.5 W/cm^2 results in anti-Stokes blue emission. Green-to-blue photon upconversion can be easily visualized in the two sensitizer/emitter systems with a commercial green laser pointer. Comparison between An and AnCOOH

shows about a two-fold increase in the upconversion quantum yield for the latter. The higher fluorescence quantum of AnCOOH plays a crucial role in its effective upconversion fluorescence.

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REFERENCES

1. Y.Y. Cheng, B. Fückel, R.W. MacQueen, T. Khoury, R.G. Clady, T.F. Schulze, N.J. Ekins-Daukes, M.J. Crossley, B. Stannowski, K. Lips and T.C. Schmidt, *Energy Environ. Sci.*, **5**, 6953 (2012).
2. R.S. Khnayzer, J. Blumhoff, J.A. Harrington, A. Haefele, F. Deng and F.N. Castellano, *Chem. Commun.*, **48**, 209 (2011).
3. Q. Liu, T. Yang, W. Feng and F. Li, *J. Am. Chem. Soc.*, **134**, 5390 (2012).
4. A. Karotki, M. Khurana, J.R. Lepock and B.C. Wilson, *Photochem. Photobiol.*, **82**, 443 (2006).
5. G.S. He, P.P. Markowicz, T.-C. Lin and P.N. Prasad, *Nature*, **415**, 767 (2002).
6. X.M. Wang, F. Jin, Z.G. Chen, S.Q. Liu, X.H. Wang, X.M. Duan, X.T. Tao and M.H. Jiang, *J. Phys. Chem. C*, **115**, 776 (2011).
7. X.Y. Huang, S.Y. Han, W. Huang and X.G. Liu, *Chem. Soc. Rev.*, **42**, 173 (2013).
8. S. Balushev, T. Miteva, V. Yakutkin, G. Nelles, A. Yasuda and G. Wegner, *Phys. Rev. Lett.*, **97**, 143903 (2006).
9. (a) A. Monguzzi, R. Tubino and F. Meinardi, *Phys. Rev. B*, **77**, 155122 (2008); (b) T.N. Singh-Rachford and F.N. Castellano, *Inorg. Chem.*, **48**, 2541 (2009).
10. (a) V. Yakutkin, S. Aleshchenkov, S. Chernov, T. Miteva, G. Nelles, A. Cheprakov and S. Balushev, *Chem. Eur. J.*, **14**, 9846 (2008); (b) S. Balushev, J. Jacob, Y.S. Avlasevich, P.E. Keivanidis, T. Miteva, A. Yasuda, G. Nelles, A.C. Grimsdale, K. Müllen and G. Wegner, *Chem. Phys. Chem.*, **6**, 1250 (2005); (c) Y.Y. Cheng, B. Fückel, R.W. MacQueen, T. Khoury, R.G.C.R. Clady, T.F. Schulze, N.J. Ekins-Daukes, M.J. Crossley, B. Stannowski, K. Lips and T.W. Schmidt, *Energy Environ. Sci.*, **5**, 6953 (2012).
11. (a) T.N. Singh-Rachford, A. Nayak, M.L. Muro-Small, S. Goeb, M.J. Therien and F.N. Castellano, *J. Am. Chem. Soc.*, **132**, 14203 (2010); (b) S.K. Sugunan, U. Tripathy, S.M.K. Brunet, M.F. Paige and R.P. Steer, *J. Phys. Chem. A*, **113**, 8548 (2009).
12. C.E. Mccusker, F.N. Castellano, *Chem. Commun.*, **49**, 3537 (2013).
13. (a) R.R. Islangulov, D.V. Kozlov and F.N. Castellano, *Chem. Commun.*, **30**, 3776 (2005); (b) W.H. Wu, S.M. Ji, W.T. Wu, J.Y. Shao, H.M. Guo, T.D. James and J.Z. Zhao, *Chem. Eur. J.*, **18**, 4953 (2012); (c) G. Bergamini, P. Ceroni, P. Fabbrizi and S. Cicchi, *Chem. Commun.*, **47**, 12780 (2011).
14. L.H. Ma, H.M. Guo, Q.T. Li, S. Guo and J.Z. Zhao, *Dalton Trans.*, **41**, 10680 (2012).
15. (a) Z.Q. Liang, B. Sun, C.Q. Ye, X.M. Wang, X.T. Tao, Q.H. Wang, P. Ding, B. Wang, J.J. Wang, *Chem. Phys. Chem.*, **14**, 3517 (2013); (b) T.N. Singh-Rachford, A. Haefele, R. Ziessel and F.N. Castellano, *J. Am. Chem. Soc.*, **130**, 16164 (2008); (c) A. Turshatov, D. Busko, Y. Avlasevich, T. Miteva, K. Landfester and S. Balushev, *Chem. Phys. Chem.*, **13**, 3112 (2012); (d) S. Balushev, V. Yakutkin, T. Miteva, G. Wegner, T. Roberts, G. Nelles, A. Yasuda, S. Chernov, S. Aleshchenkov and A. Cheprakov, *New J. Phys.*, **10**, 013007 (2008).
16. L.B. Bolzon, H.R. Airoldi, F.B. Zanardi, J.G. Granado and Y. Iamamoto, *Micropor. Mesopor. Mater.*, **168**, 37 (2013).
17. T.N. Singh-Rachford and F.N. Castellano, *Coord. Chem. Rev.*, **254**, 2560 (2010).