Investigation of Heavy Atom Effect on the Low Power Upconversion†

Bao Wang, Changqing Ye[*], Zuoqin Liang, Yuyang Zhou, Ping Ding and Xiaomei Wang[*]

Jiangsu Key Laboratory for Environment Function Materials, College of Chemistry, Biology and Material Engineering, Suzhou University of Science and Technology, Suzhou 215009, P.R. China

*Corresponding author: E-mail: wangxiaomei@mail.usts.edu.cn; yechangqing@mail.usts.edu.cn

Selective low energy excitation of palladium(II)tetraphenylporphyrin (PdTPP) and palladium(II)tetrabromophenylporphyrin (PdBrTPP) in the presence of 2-chloro-9,10-di *p*-tolylanthracene (DTACl), respectively, can yield easily visualized upconversion fluorescence. The external and internal heavy atom effects were firstly found to significantly increase upconversion efficiency (Φ_{uc}) of emitter (DTACl) doped with PdTPP or PdBrTPP as much as 10 % under excitation of low power density at 60 mW/cm^2.

Keywords: Low-power upconversion, Triplet-triplet annihilation, Two-photon process, Photoelectrochemistry.

INTRODUCTION

Upconversion, that is, the processes of short-wavelength radiation from long-wavelength light sources, has been intensively studied due to its potential application in fields such as photovoltaics[1], photocatalysis[2-4], biological imaging and sensing[5] and photodynamic therapy of cancer[6,7]. A few techniques for upconversion have been well established, such as the two photon absorption. Two-photon absorption (TPA) is a nonlinear optical process of a molecule from the ground state to the excited singlet by simultaneous absorption of two photons, which needs to get across intra-molecular virtual state[8,9]. However, it has always been associated with the use of very high intensity light excitation on the order of MW-GM/cm^2 that has led to the serious application limitation[10-12]. In comparison to two-photon absorption upconversion (TPA-UC), a new upconversion technology that is triplet-triplet annihilation upconversion (TTA-UC) has been developed. Triplet-triplet annihilation upconversion requires a triplet sensitizer and an acceptor to accomplish the cascade processes of light-harvesting, triple-triplet energy transfer (TTT), TTA and upconverted fluorescence emission. It can be obtained at the very low intensity of excitation source (as low as 1 W/cm^2), which is of importance for the future applications. Over the past few years, tremendous advances have been made on the development of various sensitizers and acceptor to achieve higher upconversion efficiency[13-16].

Based on this idea, we studied two different Pd(II)phophyrins by peripheral substitution to examine the influence of heavy atom effect upon upconversion. Extensionally, the solvents with heavy atom such as bromobenzene (PhBr) is also used to examine the intermolecular heavy atom effect on the upconversion. The results obtained have shown that the substitution of Pd(II)tetrabromophenylporphyrin (PdBrTPP) for Pd(II)tetraphenylporphyrin (PdTPP) leads to 10 % enhancement of upconversion efficiency, due to effectively increasing phosphorescence lifetime (t_p) and phosphorescence quantum yield (Φ_p). For example, the upconversion values of bimolecular composition in DMF were obtained in the order of PdBrTPP/DTACl (16.88 %) PdTPP/DTACl (10.33 %) under low-powered density (532 nm, 60 mW/cm^2). On replacing internal heavy atom effect with external heavy atom effect (*i.e.*, solvent heavy atom effect), the upconversion values of bimolecular composition in bromobenzene (PhBr) are in the order of PdBrTPP/DTACl (27.21 %), PdTPP/DTACl (20.04 %). To the best of our knowledge, the current study represents the first example of the external heavy atom effect as a simple approach to increase the upconversion efficiency.

EXPERIMENTAL

Synthesis of Pd(II) tetra-(4-phenyl)-porphine (PdTPP): 2.5 g benzaldehyde was added to 45 mL dried propionic acid acid. After complete addition, they were reuxed at 140 ºC. 3 mL newly distilled pyrrole which was dissolved in 45 mL

dried propionic acid was spotted with slowly. After refluxing for 45 min, the turbid solution changed from white to purplish red, the solution is cooled to room temperature and filtered and the filter cake is washed thoroughly with methanol. Tetra-(4-phenyl)-porphine and palladium dichloride were mixed in benzonitrile (20 mL), the mixture was refluxed under the nitrogen atmosphere for 3 h. After extracting, the crude product was purified through flash column chromatography using petroleum/dichloromethane (v/v = 3:1) as eluent to give a purple solid (**Scheme-I**). Yield (2.11 g, 47.3 %). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm) δ: ^{1}H NMR (400 MHz, TMS): δ 8.83 (s, 8H, thiophene-H),8.19, 8.21(d, 8H, benzene-H), 7.76,7.78(d, 12H, benzene-H).

Synthesis of Pd(II) tetra-(4-bromophenyl)-porphine (PdBrTPP): A procedure analogous to the preparation of PdTPP was used, but instead of starting from 4-bromobenzaldehyde (1.84 g, 10.0 mmol). PdTPP was obtained as a purple solid (**Scheme-II**). Yield (1.32 g, 48.9 %). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm) δ: ^{1}H NMR (400 MHz, TMS): 8.83 (s, 8H, thiophene-H),8.04, 8.06 (d, 8H, benzene-H), 7.91,7.93(d, 8H, benzene-H).
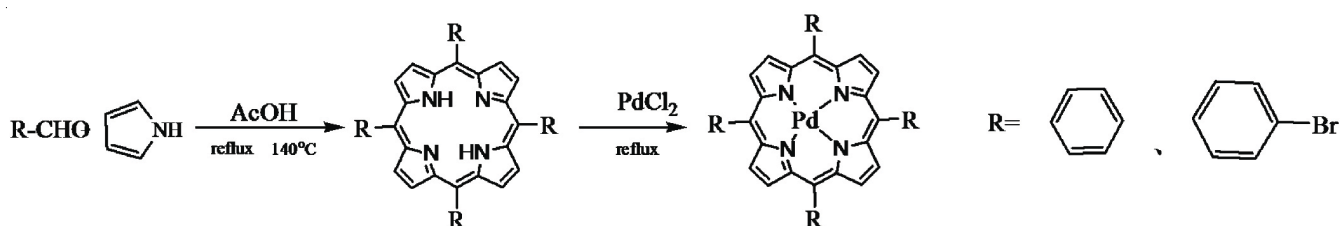
Synthesis of 2-chloro-9,10-di *p*-tolylanthracene (DTACl): Under N$_2$ atmosphere at -78 ℃, 1.6 M t-BuLi (25.0 mL, 62.0 mmol) was added with dropwise to a mixture of 1-bromo-4-methylbenzene (5.50 mL, 41.0 mmol) and 40 mL dried THF. After complete addition, stirring is continued for 0.5 h. At about 40-50 ℃, a solution of 2-chloroanthraquinone (5 g, 30.8 mmol) in 60 mL THF was injected through a syringe. The turbid solution changed from white to wine red. The mixture was allowed to warm to room temperature and maintained for 24 h. The reaction mixture was added to a saturated aqueous solution of NH$_4$Cl (120 mL). The organic solvent was evaporated and the suspension was extracted with ethyl acetate. The organic extracts were washed by water and brine and dried by anhydrous magnesium sulfate. Removing the solvent afforded a yellow oil, which was used without further purification.
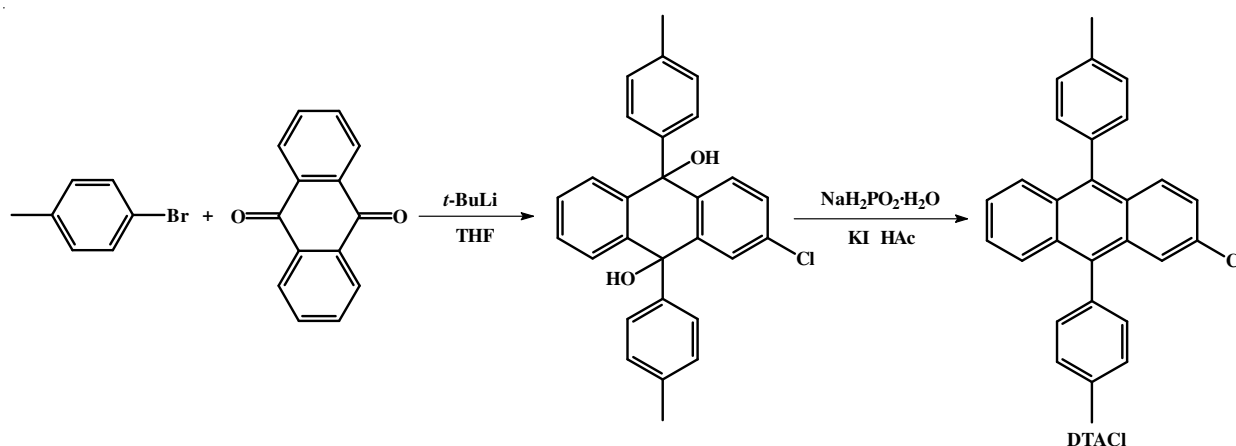
2-Chloro-9,10-di *p*-tolyl-9,10-dihydroanthracene-9,10-diol (4.05 g, 9.0 mmol), sodium phosphinate monohydrate (16.6 g, 157 mmol) and potassium iodide (15.8 g, 95.0 mmol) in acetic acid (40 mL) were reuxed at 120 ℃ for 3 h. After the mixture was cooled, water was added to it. The crude solid product was filtered and washed with water. The crude product was recrystallized using acetic acid to give a light yellow solid. Yield (3.27 g, 50.6 %). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm) δ: 2.35 (s, 6H, CH$_3$), 7.20-7.72 (d, 15H, Ar-H). Elemental analysis: calcd. (%) for C$_{28}$H$_{21}$Cl: C, 85.59; H, 5.39; Cl, 9.02. Found (%): C, 85.62; H, 5.52; Cl, 8.86.

Spectral characterization and triplet-triplet annihilation upconversion measurements: Solvent DMF and bromobenzene was purified before used. The ^{1}H NMR spectra was recorded at 25 ℃ using a Bruker Avance 300 MHz spectrometer. Elemental analyses were performed on an Elementar Vario EL-III instrument. Linear absorption measurements of dilute solution (8 mM) have been measured with Hitachi U-3500 recording spectrophotometer from quartz cuvettes of 1 cm path. Steady-state emission and time-resolved decay curves were measured on an Edinburgh FLS 920 fluorophotometer equipped with time-correlated single-photon counting (TCSPC) card. With the aid of nF 900 software, phosphorescence lifetime (τ_p) for sensitizers were measured under detection of nF-lamps; and then obtained by reconvolution fit analysis of the decay profiles. In the fluorescence and phosphorescence decay profiles, the monoexponential fit gives acceptable statistics parameters of $\chi^2 < 1.1$, where χ^2 is the "reduced chi-square". The phosphorescence lifetime (τ_p) measurements were done at the room temperature under nitrogen atmosphere.

Diode pumped solid state laser (emission wavelength: 532 nm, 60 mW cm^{-2}) was used as the excitation source for the

Scheme-I: Synthesis route of Pd(II) tetra-(4-phenyl)-porphine (PdTPP) and Pd(II) tetra-(4-bromophenyl)-porphine (PdBrTPP)

Scheme-II: Synthesis route of 2-chloro-9,10-di *p*-tolylanthracene (DTACl)

upconversion. The laser power was measured with photodiode detector. For the upconversion experiments, the mixed solution of the sensitizer and emitter was degassed for 10 min with N_2. Then the solution was excited with laser. The upconverted fluorescence was observed with PR655 SpectraScan colorimeter.

The upconversion efficiency (UC) of DTACl in presence of different sensitizers was obtained relative to rhodamine 6G in ethanol using 532 nm excitation according to the literature.

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

where the subscript "s" and "r" represent sample and reference respectively (here rhodamine 6G in ethanol at concentration of 0.5 mM was used as reference and DTACl as the sample). Φ_r is the fluorescence quantum yield of rhodamine 6G (0.88)[17,18] in ethanol using 532 nm excitation. F is the integrated emission of DTACl and rhodamine 6G under the excitation of 532 nm. A is the absorbance of both DTACl 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 emission properties: To investigate their photophysical properties, the absorption and fluorescence spectra of PdTPP (8.0 μM), PdTPP (8.0 μM) and DTACl $(10^{-6}$ M) were measured in DMF solution, as shown in Fig. 1a. Two Pd(II)porphyrins show the Q-band in the range of 500-540 nm that can overlap with the diode pumped solid state laser (532 nm). At the same time, the acceptor DTACl shows the characteristic vibronic pattern of the isolated anthracene group at 359, 380 and 400 nm in DMF solution. The molar extinction coefficient (ε) at 532 nm is in the order of PdTPP $(1.5 \times 10^4$ M^{-1} cm^{-1}) > PdBrTPP $(0.42 \times 10^4$ M^{-1} cm^{-1}) in DMF. Interestingly, the solvent heavy atom effect can be significantly increasing the ε values at 532 nm. As can be seen in Fig. 2, sensitizer PdBrTPP (ε 1.78×10^4 M^{-1} cm^{-1}) exhibit 4-5-fold increase in PhBr with respect to those in DMF, showing very high light harvesting (ε) to the excitation source in the solvent with heavy atom effect.

Their emission bands are centered at 441 nm for DTACl (Fig. 1b). Meanwhile, emission spectra of Pd(II)porphyrins in DMF shows that there are dual fluorescence (locating at 560 and 610 nm) and dual phosphorescence (locating at 650 and 720 nm) under the excitation of Q-band wavelength at room temperature and N_2 atmosphere. It is observed that the peripheral substitution from H to Br, the phosphorescence spectra are enhanced in the order of PdBrTPP > PdTPP. All of these have proven that Pd(II)tetraphenylphophyrins by peripheral substitution with bromine atom (internal heavy atom effect) and in the solvent with heavy atom (external heavy atom effect) exhibit significant improvement in phosphorescence behaviors. The emission quantum yield (Φp), lifetime (τp) are shown in Tables 1 and 2, respectively.

Triplet-triplet annihilated upconversion: Under the excitation of 532 nm at 60 mW cm^{-2}, the blue upconversion can radiate from the bichromophore solution mixed emitter
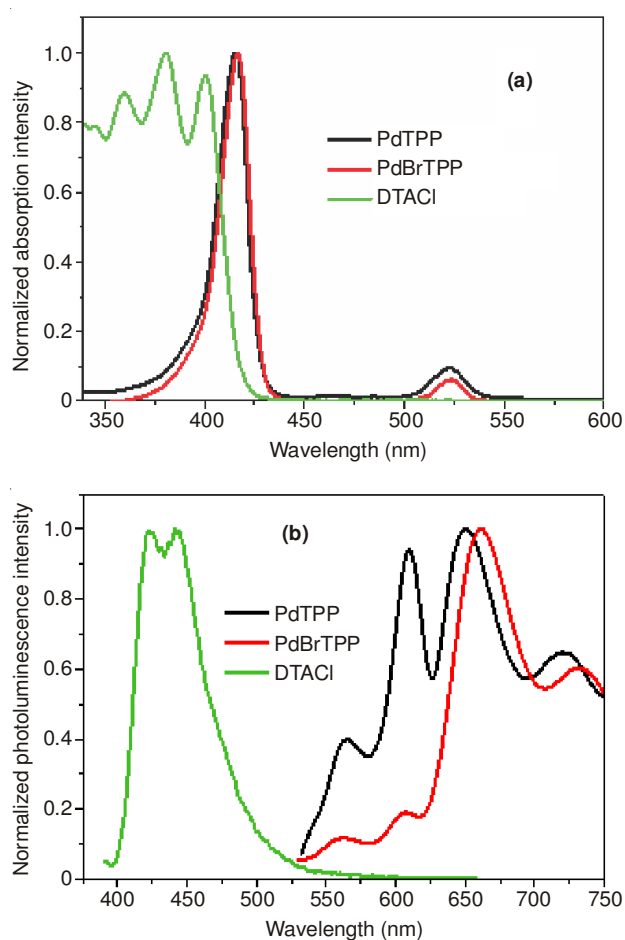

Fig. 1. Normalized absorption (a) and emission (b) spectra of PdTPP, PdBrTPP and DTACl (DMF solvent, 8 μM, 1 μM)
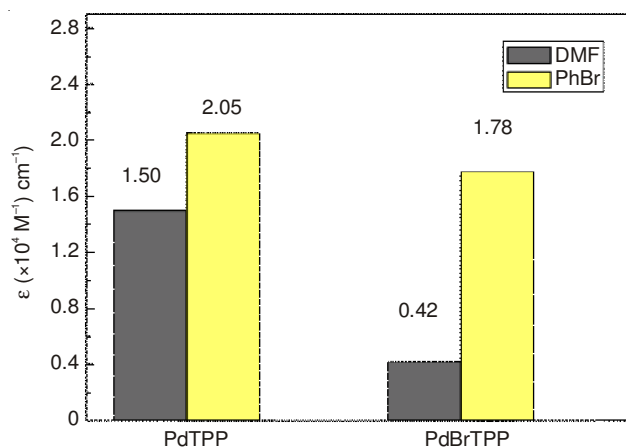

Fig. 2. Molar extinction coefficient in different solvents of sensitizers (the concentrations are at 8 μM)

TABLE-1 ABSORPTION AND FLUORESCENCE PROPERTIES OF SENSITIZER PALLADIUM(II) TETRAPHENYLPORPHYRINS IN DMF (8.0 μM)				
Sensitizer	Soret-band	Q-band	ε^* (M^{-1} cm^{-1})	λ_{max}^{fluo} (nm)
PdTPP	416 nm	522 nm	1.5×10^4	564, 609
PdBrTPP	417 nm	523 nm	4.2×10^3	561, 607

$^*\varepsilon$ is the molar absorbing coefficient at 532 nm; the emission spectra obtained at room temperature and N_2 atmosphere under the excitation of Q-band.

TABLE-2
TRIPLET PROPERTIES AND DYNAMICS DATA OF SENSITIZERS (8.0 μM) IN DIFFERENT
SOLVENTS UNDER ROOM TEMPERATURE AND NITROGEN ATMOSPHERE

Sen.	PdTPP			PdBrTPP		
	λ_{max}^{phos} (nm)	Φ_p (%)	τ_p (μs)	λ_{max}^{phos} (nm)	Φ_p (%)	τ_p (μs)
In DMF	650,725	0.45	9.92	673,697	0.96	10.95
In PhBr	696,773	0.99	10.88	690,767	1.25	15.52

[a]Fluorescence quantum yields, [b]Upconversion efficiency, [c]Stern-Volmer quenching constants, [d]Edelayed fluorescence.
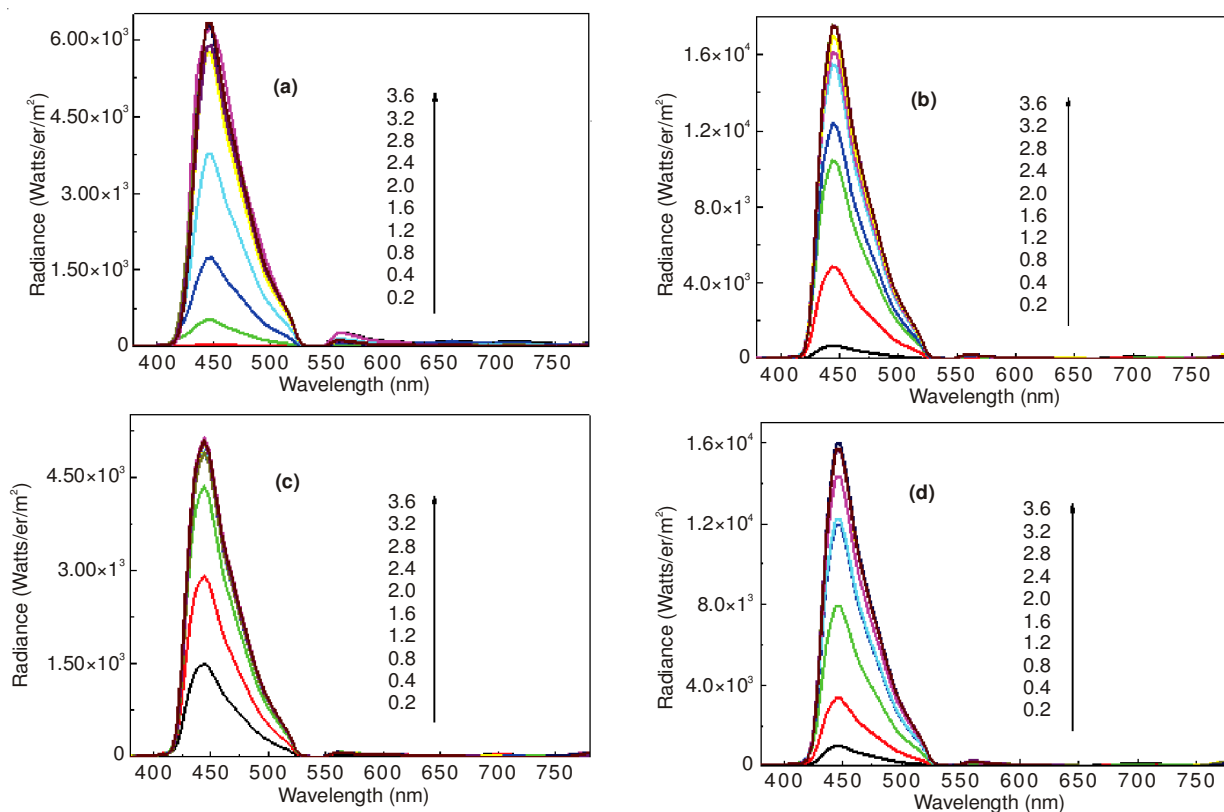

Fig. 3. Dependence of the upconversion intensity on concentration of PdTPP/DTACl in DMF (a), PdTPP/DTACl in PhBr (b), PdBrTPP/DTACl in DMF (c) and PdBrTPP/DTACl in PhBr (d) in degassed DMF and PhBr at fixed concentration of sensitizer (8 mM) upon excitation at 532 nm (60 mW cm^{-2})

and sensitizer, which shows strongly dependent on the concentration of the emitter. Thus, the relationship between upconversion intensity and the concentration of emitter was investigated (Fig. 3). With the concentration of emitter DTACl increasing from 0.2-3.6 mM, the corresponding upconversion intensity enhances rapidly at the beginning and then gradually stops to increase, showing 15.5-folds increasing (Fig. 3a).

Accordingly, the upconversion efficiency (Φ_{UC}) of different dual chromophores are calculated and presented in Fig. 4. For example, when the concentration of DTACl was increased to 3.6 mM, the Φ_{UC} of PdTPP/DTACl in DMF reached its maximum value as high as 10.33 %. Continuing to increase the concentration, the quantum yield started to remain constant. This is because that the increase of DTACl 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 DTACl exceeds the threshold value, the upconversion fluorescence can be suppressed due to the concentration quenching effect. The similar results for others were also obtained for their maximum upconversion efficiencies are at 16.88 % (PdBrTPP/DTACl, DMF). As anticipated, sensitizer PdBrTPP is more effective to DTACl upconversion.
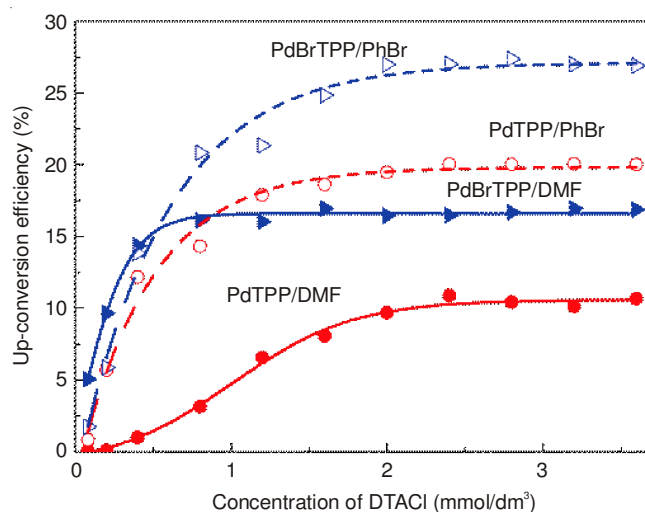

Fig. 4. Dependence of the upconversion efficiency (Φ_{UC}) on concentration of emitter at fixed concentration of sensitizer (8 mM) upon excitation at 532 nm (60 mW cm^{-2})

Since PdBrTPP possesses peripheral heavy atom substitution, phosphorescence dynamics measurements (Fig. 2 and

Table-2) have shown that PdBrTPP possesses the longest phosphorescence lifetime (τ_p 10.95 μs) and largest phosphorescence quantum yield (Φ_p 0.96 %). The most interesting thing is that the external heavy atom effect (solvent effect) can play much more important role than the internal heavy atom effect in enhancement upconverted efficiency. As seen in Table-3, the Φ_{UC} values of DTACl/sensitizer compositions are increased to more than 27.21 % in the solvent of PhBr. With respect to composition DTACl/PdTPP in DMF and DTACl/PdBrTPP presents about 10 % enhancements in Φ_{UC} values in DMF and PhBr, respectively. Evidently, the influence of external heavy atom effect (solvent heavy atom effect) on Φ_{UC} efficiency is larger than that of internal heavy atom effect (peripheral substitution by heavy atom) on Φ_{UC} efficiency. All sensitizers possess both increasing phosphorescence lifetime and increasing quantum yield, accompanied by decreasing non-phosphorescence decay rate constant, which are in good agreement with the internal heavy atom effect on the dynamics behaviors.

TABLE-3 UPCONVERSION EFFICIENCY (Φ_{UC}) OF BIMOLECULAR COMPOSITION IN DIFFERENT SOLVENTS AT POWER DENSITY OF 60 mW cm^{-2} (532 nm)		
Sensitizer (emitter)	PdTPP/DTACl (%)	PdBrTPP/DTACl (%)
DMF	10.33	16.88
PhBr	20.04	27.21

Conclusion

Two different Pd(II)phophyrins were reported about their low-power upconversions when doped with 2-chloro-9,10-di *p*-tolylanthracene (DTACl). Under the excitation of diode laser (532 nm, 60 mW cm^{-2}), blue upconversion locating at 444 nm can be observed from the bimolecular systems, which showed as a function (nearly double logarithm plot) of incident power intensity. The upconversion efficiencies were measured at 10.33 % for DTACl/PdTPP and 16.88 % for DTACl/PdBrTPP in DMF, which result from the triplet-triplet energy-reansfer efficiency, confirmed by long phosphorescence lifetime and long phosphorescence quantum yield. The current study has provided a simple approach that external heavy atom effect (solvent effect) can effectively increase the upconversion by very low intensity of excitation source (such as the sun).

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