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Metallonaphthalocyanines as Triplet Sensitizers for Near-Infrared Photon Upconversion beyond 850 nm

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In triplet-triplet annihilation-based photon upconversion (TTA-UC), the utilization of near-infrared (NIR) light with a wavelength longer than 850 nm remains as an outstanding issue. We realized this by employing metallonaphthalocyanines as triplet sensitizers; upon excitation of NIR light (856 nm), upconverted emission was observed in the visible range with remarkable photostability.

Photon upconversion (UC), emitting higher energy photons with respect to incident light, has attracted much attention for various applications including renewable energy productions, bio-imaging and photodynamic therapy.[1-2] Especially the UC mechanism with triplet-triplet annihilation (TTA-UC) has been widely studied due to its occurrence with low-intensity, noncoherent incident light.[1-29] TTA-UC requires a bimolecular system consisting of a sensitizer (donor) and an emitter (acceptor), and its mechanism as follows: (1) a triplet excited state of the donor is formed by intersystem crossing (ISC) from a photo-excited singlet state, (2) two triplet excited states of the acceptor are populated by triplet-triplet energy transfer (TTET) from the donor triplets, and (3) a higher singlet energy level of acceptor is formed by collision and annihilation between two acceptor triplets, which consequently produces upconverted delayed fluorescence (Fig. 1a). The excitation and emission wavelength of TTA-UC can be regulated by independent selection of donors and acceptors.

Over the past years, many donor-acceptor combinations have been reported for TTA-UC, however the majority of investigations aimed at the UC of incident light in the visible region.[1-22] The effective utilization of near-infrared (NIR) light is of more significance since it is critical not only for enhancing the efficiency of photovoltaics devices[1-2, 15, 18, 23] but also for biological applications that take advantage of the high permeability of NIR light in living systems.[2, 12] Research groups of Castellano et al., Baluschev et al., and Schmidt et al. independently reported NIR-to-visible TTA-UC by employing derivatives of porphyrin,[23-26] texaphyrin,[27] and phthalocyanine[28]

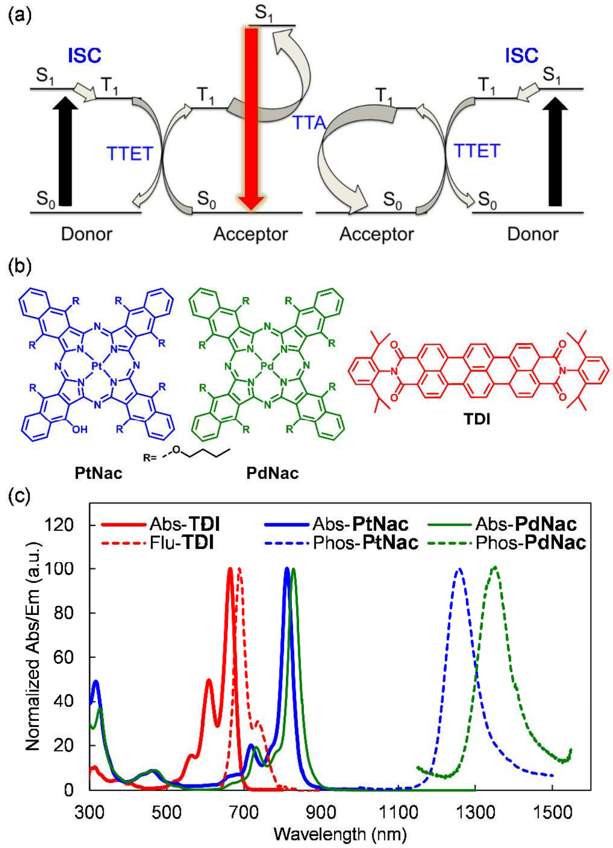

Fig. 1 (a) Outline of TTA-UC process, showing the energy levels involved in the TTA-UC (S=singlet, T=triplet). (b)Molecular structures and (c) normalized absorption and emission spectra (bottom) of **TDI**, **PtNac**, and **PdNac** in deaerated 1,2-dichlorobenzene (1,2-DCB).

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as sensitizers. In these reports, however, TTA-UC emissions were observed by using NIR excitation light with wavelengths below 800 nm. Although a TTA-UC system using 830 nm excitation light was reported by Schmidt et al., it utilized singlet oxygen as a mediator.[29] The system however suffered from severe photodegradation caused by the highly reactive singlet oxygen.[29] Therefore, it is crucial to develop stable TTA-UC systems that can convert the NIR light over 800 nm. In particular, the NIR light beyond 850 nm has been an untapped wavelength range for TTA-UC, which remains as an essential challenges to overcome the Shockley-Queisser limit.[30] For example, perovskite solar cells have recently attracted much attention for their remarkable efficiency, however, the bandgap of perovskite materials limit their absorption to visible light (< 800 nm).[31, 32] Therefore, in order to utilize NIR light over 800 nm, it is an urgent demand to develop TTA-UC systems that can convert NIR light over 800 nm to visible light.

Here we describe the first example of TTA-UC system that converts the NIR light (> 850 nm) to visible light. It consists of Pt(II)/Pd(II) octabutoxynaphthalocyanine (**PtNac**/**PdNac**, donor)[33, 34] and a terrylenediimide derivative (**TDI**, acceptor)[35] (Fig. 1b, c). These chromophores were synthesized according to the reported procedure.[33-35] As shown in Fig. 1, 1,2-dichlorobenzene (1,2-DCB) solutions of **PtNac** and **PdNac** exhibit strong Q-band absorption peaks at 812 nm ($\varepsilon = 2.6 \times 10^5$) and 828 nm ($\varepsilon = 2.5 \times 10^5$), respectively, with tails extending over around 900 nm. Phosphorescence peaks of **PtNac** and **PdNac** were observed at 1256 and 1348 nm, respectively. The energy difference between these phosphorescence bands (0.065 eV) is comparable to that between common Pd- and Pt-octaethylporphyrins (0.07 eV).[14] The observed strong NIR absorption and relatively small S_1-T_1 gap (0.54 eV for **PtNac** and 0.58 eV for **PdNac**) are suitable for sensitizers in the NIR-to-visible TTA-UC. **TDI** was chosen as an acceptor, because it has a good fluorescence quantum yield (Φ_{Em} = 32% in 1,2-DCB, 0.6 mM).

The TTA-UC emission of the **PtNac-TDI** and **PdNac-TDI** pairs was investigated in 1,2-DCB after deaeration by repeated freeze-pump-thaw cycles ([**Pt**/**PdNac**] = 0.05 mM, [**TDI**] = 0.6 mM). Under excitation at 856 nm, the mixed solutions clearly displayed upconverted emissions in the visible range (Fig. 2a, b). These upconverted emissions were not observed from the single-component solutions of donors or **TDI**. The UC emission at 690 nm observed for the **PtNac-TDI** and **PdNac-TDI** pairs showed microsecond-scale decay profiles, which are ascribed to the UC mechanism based on long-lived triplet species (Fig. 2c). Similar triplet lifetimes of acceptors ($\tau_{A,T}$) were observed for **PtNac-TDI** and **PdNac-TDI** pairs as 102 and 106 μs, respectively, based on the relationship of $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_{A,T})$ (τ_{UC}: UC emission lifetime, $\tau_{A,T}$: acceptor triplet lifetime). In this time domain, the annihilation efficiency becomes negligible compared with the spontaneous decay of the triplets.[36, 37]

The upconverted emission intensity from the **Pt/PdNac-TDI** pairs were measured as a function of excitation power density (Fig. 3). Slopes close to 2 were observed for the both systems in double logarithmic plot, which is consistent with the quadratic dependence of TTA process. Generally, the incident power dependence of UC emission intensity changes from quadratic to linear above a threshold excitation intensity (I_{th}), beyond that TTA becomes the main deactivation channel for the acceptor triplet.[4, 5, 8] The change in slope was observed at around 30 W cm^{-2} only for the pair of **PdNac-TDI**, suggesting that the I_{th} value is lower for **PdNac-TDI** as compared to that of **PtNac-TDI**. In the latter case, the slopes did not reach 1 within the

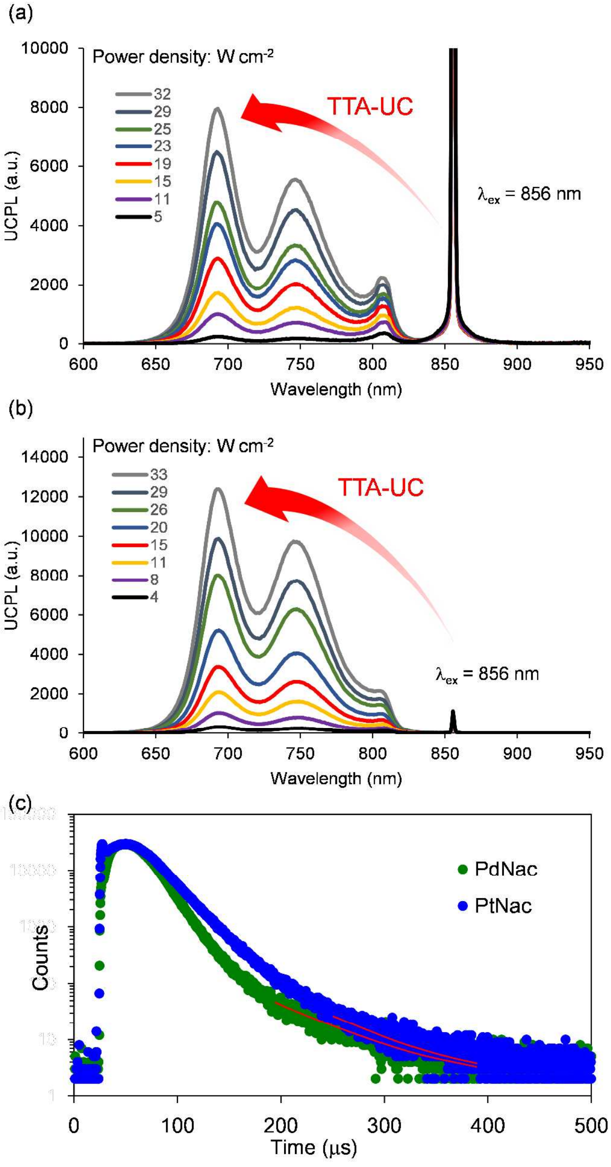

Fig. 2 Upconverted emission spectra of the (a) **PtNac**-**TDI** and (b) **PdNac**-**TDI** pairs in deaerated 1,2-DCB with different excitation power density of 856 nm laser. (c) Time-resolved upconverted emission at 690 nm of the **PdNac**-**TDI** and **PdNac**-**TDI** pairs in deaerated 1,2-DCB (λ_{ex} = 820 nm). The red fitting curves were obtained by considering the relationship of $I_{UC}(t) \propto \exp(-t/\tau_{UC}) = \exp(-2t/\tau_{A,T})$, where τ_{UC} is UC emission lifetime and $\tau_{A,T}$ is acceptor triplet lifetime. ([**Pt/PdNac**] = 0.05 mM, [**TDI**] = 0.6 mM, 810 nm short pass filter).

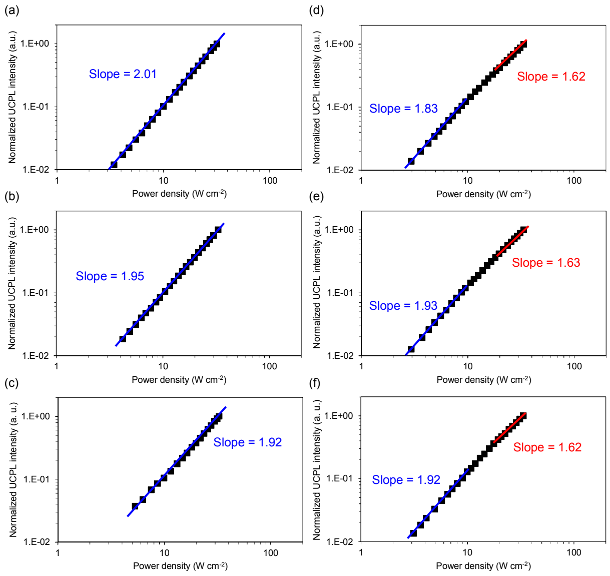

Fig. 3 Double logarithmic plots of the TTA-UC emission intensity of the (a) **PtNac-TDI** ([**PtNac**] = (a) 0.1 mM, (b) 0.05 mM, (c) 0.02 mM) and **PdNac-TDI** ([**PdNac**] = (d) 0.1 mM, (e) 0.05 mM, (f) 0.02 mM) pairs in deaerated 1,2-DCB as a function of excitation power density of 856 nm laser, [**TDI**] = 0.6 mM, 810 nm short pass filter).

examined power range regardless of donor concentrations (Fig. 3). The concentration of acceptor could not be increased above 0.6 mM due to the limitation in solubility.

We then quantified TTA-UC quantum yield Φ_{UC} of the UC pairs by using free-base octabutoxynaphthalocyanine (**Nac**) as a reference, whose fluorescence quantum yield was determined as $\Phi_{Em} = 3.4\%$ in 1,2-DCB (5 μM). Note that the quantum yield is generally defined as the ratio of emitted photon numbers to absorbed photon numbers, and thus the theoretical maximum of the TTA-UC quantum yield is defined as 50%, by considering that the absorption of 2 photons is required for generating 1 upconverted photon. With increasing the incident power density, the Φ_{UC} value increased up to 0.0089% and 0.067% for **PtNac-TDI** and **PdNac-TDI** pairs, respectively (Fig. S1, ESI†). It is to note that the observed Φ_{UC} value for **PdNac-TDI** is higher than the previous value ($\Phi_{UC} < 0.01\%$) of NIR (830 nm)-to-visible TTA-UC mediated by singlet oxygen.[29] With increasing the donor concentration, TTA-UC quantum yield once increased, then decreased (Table 1). This would be due to acceptor-to-donor triplet-triplet and/or singlet-singlet back energy transfer. Therefore, there are optimal donor concentrations.

To gain deeper insights into the Φ_{UC} of **PtNac-TDI** and **PdNac-TDI** pairs, we evaluated photophysical properties related to Φ_{UC}, which are represented by the following equation,

$$\Phi_{UC} = \frac{1}{2} f \Phi_{ISC}\, \Phi_{ET}\, \Phi_{TTA}\, \Phi_{Em} \quad (1)$$

where Φ_{ISC}, Φ_{ET}, Φ_{TTA}, and Φ_{Em} are efficiencies of donor ISC, donor-to-acceptor TTET, TTA, and acceptor fluorescence, respectively, and f is the statistical probability for obtaining a singlet excited state after the annihilation of two triplet states.[11,15] The estimated parameters were summarized in Table 1. We estimated the Φ_{ISC} values of **PtNac** and **PdNac** as 56% and 29%, according to the reported method of fitting the dependence of transient absorbance upon incident pulsed laser intensity (Fig. S2,ESI†).[38] The Φ_{ISC} value of **PtNac** was higher than **PdNac** due to the heavier metal centre. The Φ_{ET} values were determined by the ratio between the donor phosphorescence intensity with and without the acceptor **TDI** (Figs. S3 and S4, ESI†). Under the identical donor-acceptor concentration ([donor] = 0.05 mM, [**TDI**] = 0.6 mM), the Φ_{ET} value obtained for **PdNac-TDI** (31%) was higher than that for **PtNac-TDI** (16%), probably due to the longer triplet lifetime of **PdNac** (0.88 μs) as compared to **PtNac** (0.15 μs) (Figs. S5 and S6, ESI†). This difference in triplet lifetime might come from larger spin-orbit coupling for heavier Pt ion than Pd ion. The development of triplet sensitizer with higher triplet energy level would be beneficial to further elongate the triplet lifetime and TTET efficiency. It seems therefore important to develop donors with longer triplet lifetime in order to improve these Φ_{ET} values.[7,18] By assigning the Φ_{UC}, Φ_{ISC}, Φ_{ET}, and Φ_{Em} values in equation (1), a $f\Phi_{TTA}$ value of 5% was calculated for the **PdNac-TDI** pair under the excitation power density of 30 W cm^{-2}. The generation of acceptor singlet state following the triplet-triplet annihilation is thus characterized by low efficiency. To understand this low $f\Phi_{TTA}$ value observed for **TDI**, we performed density functional theory (DFT) calculations of T_1 and S_1 energy levels of **TDI** (ESI†). The S_1 energy level (1.89 eV) was found to be higher than 2 times of the T_1 energy level (0.85 eV × 2 =1.70 eV), suggesting that the formation of S_1 state by TTA is thermodynamically unfavourable for **TDI** (Figure S7 ESI†). The improvement of Φ_{UC} is expected by proper optimization of the chemical structure of acceptors and their energy levels.

Table 1 Photophysical parameters of the **PtNac/TDI** and **PdNac/TDI** pairs in deaerated 1,2-DCB.[a)]

System	[Donor] (mM)	Φ_{UC} (%)	Φ_{ISC}[b)] (%)	Φ_{ET} (%)	Φ_{Em} (%)
PtNac/TDI	0.1	0.0030	56	6	32
	0.05	0.0089	56	16	32
	0.02	0.0022	56	12	32
PdNac/TDI	0.1	0.041	29	13	32
	0.05	0.067	29	31	32
	0.02	0.056	29	24	32

[a] [**TDI**] = 0.6 mM, [b] Estimated in toluene by using transient absorbance measurements (Fig. S2) [c] fluorescence quantum yield of **TDI** 1,2-DCB (0.6 mM) was determined by using an integrating sphere.

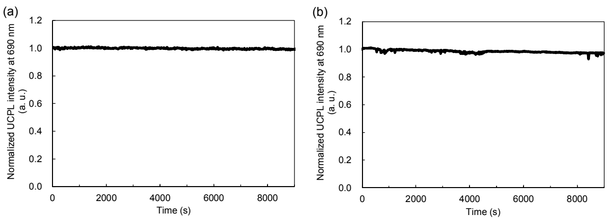

Fig. 4 Time dependence of upconverted emission intensity at 856 nm of (a) **PtNac-TDI** and (b) **PdNac-TDI** pairs in deaerated 1,2-DCB at room

temperature ([Donor]=0.05 mM, [**TDI**]=0.6 mM). Excitation power was 15 W cm^{-2}.

Meanwhile, we found a remarkable photochemical stability for the present NIR-to-visible UC systems (Fig. 4). The TTA-UC emission spectra of the **PtNac**-**TDI** and **PdNac**-**TDI** pairs remained unchanged even after a prolonged irradiation for 150 min of high power density laser (15 W cm^{-2}). This is the first demonstration of stable TTA-UC of NIR light over 850 nm to visible light.

Conclusions

We accomplished the stable TTA-UC of NIR light with a wavelength longer than 850 nm to visible light by employing new chromophore combinations of the donor **Pt**/**PdNac** and acceptor **TDI**. The metallonaphthalocyanines display excellent features such as simple structure, easy synthesis, and superior photostability, and therefore they would play an important role in the development of efficient NIR-to-visible UC. The structural tuning of donor and acceptor molecules and accordingly their energy landscapes towards efficient NIR-to-visible upconversion are currently underway in this laboratory. The controlled assembly of the optimized donor and acceptor chromophores would be important for photovoltaic applications based on fast triplet energy migration and TTA-UC under low-power excitation, i.e., solar irradiance.[13, 21, 22]

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