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Visible light-harvesting perylenebisimide–fullerene (C_{60}) dyads with bidirectional "ping-pong" energy transfer as triplet photosensitizers for photooxidation of 1,5-dihydroxynaphthalene[†]

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Visible light-harvesting perylenebisimide (PBI)– C_{60} dyads were prepared as organic triplet photosensitizers for photooxidation of 1,5-dihydroxynaphthalene and the efficiency of the dyads is 6-fold of the conventional Ir(III) complex triplet photosensitizer.

Photosensitized reactions, such as photocatalytic hydrogen (H₂) production, photooxidation and photodynamic therapy (PDT), have attracted much attention.^{1–3} Concerning these applications, design of efficient triplet photosensitizers showing strong absorption of visible light and long-lived triplet excited states is crucial.^{4,5} Transition metal complexes are usually used as triplet photosensitizers due to their efficient intersystem crossing (ISC), with which the triplet excited states of the chromophores are populated upon photoexcitation.⁶ For example, cyclometalated Ir(III) complexes have been used as a singlet oxygen (¹O₂) photosensitizer for photooxidation.² However, these conventional transition metal complex photosensitizers suffer from high cost, weak absorption of visible light, *etc.*²

Thus, similar to the development of dye-sensitized solar cells (DSCs), *organic triplet* photosensitizers with strong absorption of visible light are highly desired to replace the transition metal complex triplet photosensitizers.⁵ However, it is a challenge to design *organic* triplet photosensitizers because it is difficult to populate the triplet excited states of *organic* chromophores upon photoexcitation. In this case the heavy atom effect is very often indispensable.^{5,7} Although triplet photosensitizers without any heavy atoms do exist, their ISC property is almost unpredictable.^{6a} Thus design of heavy atoms-free organic triplet sensitizers with *predetermined* ISC capability will be the next milestone for the development of *organic* triplet photosensitizers.

Concerning this challenge, the efficient ISC capability of fullerene (*e.g.* C₆₀, triplet excited state quantum yield >95%) is particularly interesting.⁸ Although C₆₀ has been studied for more than a quarter of a century, the triplet manifolds of

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Fig. 1 Visible light-harvesting triplet photosensitizers $PBI-C_{60}$ and $NPBI-C_{60}$. The light-harvesting antenna precursors PBI-Ph and NPBI-Ph.

fullerene have been rarely applied in a photophysical process.⁸ Fullerene is known for its weak absorption in the visible range.⁸ Thus, C_{60} itself is not an ideal triplet photosensitizer. Herein we prepared visible light-harvesting C_{60} -chromophore dyads as organic triplet photosensitizers for photooxidation (**PBI-C**₆₀ and **NPBI-C**₆₀, Fig. 1, PBI = perylenebisimide, the visible light-harvesting antenna).⁹ In order to access absorption in the red range, we prepared dyad **NPBI-C**₆₀ (Fig. 1), which absorbs at 634 nm. Remarkably improved photooxidation of 1,5-dihydroxyl naphthalene (DHN) was found with these dyads as triplet photosensitizer, compared to the Ir(III) complex sensitizer Ir(ppy)₂(Phen)[PF₆] (Ir-1, see ESI[†]).

 C_{60} shows very weak absorption at *ca*. 700 nm,^{8,10–12} thus we propose that visible light-harvesting chromophores with an appropriate S₁ state energy level can be attached to C₆₀ and the singlet energy transfer (ET) from the light-harvesting antenna to C₆₀ will occur. Then the singlet excited state, and in turn the T₁ excited state of C₆₀ will be populated *via* ISC.⁸ Following this line, we designed dyads **PBI-C₆₀** and **NPBI-C₆₀** (Fig. 1).¹³ The visible-light harvesting antenna, perylenebisimide, was prepared with 2-ethylhexylamine. Prato reaction was used

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Fig. 2 UV-vis absorption spectra of (a) **PBI-C₆₀**, **PBI-Ph** and C₆₀, (b) **NPBI-C₆₀**, **NPBI-Ph** and C₆₀. In toluene, $c = 1.0 \times 10^{-5} \text{ mol } \text{L}^{-1}$, 20 °C.

to link the PBI unit to C_{60} and the dihydro-fullerenes were obtained (Fig. 1 and see ESI† for details).¹⁴

The UV-vis absorption of dyads was studied (Fig. 2). C_{60} shows strong absorption at 335 nm ($\varepsilon = 64400 \text{ M}^{-1} \text{ cm}^{-1}$), whereas the absorption in the visible range is very weak. For **PBI-Ph**, the absorption maximum is at 535 nm ($\varepsilon = 42000 \text{ M}^{-1} \text{ cm}^{-1}$). The absorption of **PBI-C**₆₀ is superimposable on the sum of the absorption spectra of C₆₀ and **PBI**. Thus the electronic interaction of C₆₀ and **PBI moieties in PBI-C**₆₀ at the ground state is weak. Notably the absorption of **PBI-C**₆₀ in the visible range is greatly enhanced *vs.* C₆₀ (Fig. 2a). Previously a dyad similar to **PBI-C**₆₀ was reported (the main difference is the alkyl chains) but only electrochemical, no photophysical properties were studied in detail.^{9a} **NPBI-C**₆₀ shows red-shifted absorption ($\lambda_{abs} = 634 \text{ nm}, \varepsilon = 25400 \text{ M}^{-1} \text{ cm}^{-1}$) (Fig. 2b).

To confirm the ET between the antenna (PBI) and the energy acceptor (C_{60}) in dyads, photoluminescence was studied (Fig. 3). **PBI-Ph** emits strongly at 575 nm ($\Phi_F = 36.0\%$). For **PBI-C₆₀**, however, the emission of the **PBI-Ph** moiety was quenched ($\Phi_F = 0.7\%$). Interestingly, weak emission at 707 nm was observed for **PBI-C₆₀**, which is attributed to the C₆₀ unit in **PBI-C₆₀**. Excitation of C₆₀ alone at 490 nm did not produce this emission band, which confirms the intramolecular ET between **PBI** and C₆₀ in **PBI-C₆₀**. The ET efficiency is estimated as 98% based on the Φ_F of **PBI-Ph** and **PBI-C₆₀**.¹³ The efficient ET of **PBI-C₆₀** is similar to a dyad based on C₆₀ and **PBI** with a flexible linker.¹³

The intramolecular ET of the red-absorbing **NPBI-C**₆₀ was also studied (Fig. 3b). Much lower ET efficiency was observed (*ca.* 62%) compared to **PBI-C**₆₀, probably due to the inappropriate S_1 energy level of **NPBI-Ph**, which is close to the S_1 energy level of C_{60} , thus the small ET driving force leads to inefficient ET.



Fig. 3 Emission of (a) **PBI-C₆₀**, **PBI-Ph** and C₆₀, $\lambda_{ex} = 490$ nm; (b) **NPBI-C₆₀**, **NPBI-Ph** and C₆₀, $\lambda_{ex} = 633$ nm. $c = 1.0 \times 10^{-5}$ mol L⁻¹ in toluene, 20 °C.

Fig. 4 (a) Nanosecond time-resolved transient difference absorption spectra of **PBI-C₆₀** upon pulsed laser excitation ($\lambda_{ex} = 532$ nm). Triplet excited state life (τ_{T}) is 105.9 µs (see ESI†). In deaerated toluene. $c = 1.0 \times 10^{-5}$ mol L⁻¹; 20 °C. (b) Spin density of **PBI-C₆₀**. Calculated at B3LYP/6-31G(d) level with Gaussian 09W.

This result is useful for design of *effective* visible-light harvesting C_{60} dyads.

The excited state of **PBI-C**₆₀ was studied with nanosecond time-resolved transient difference absorption spectroscopy (Fig. 4a). Upon pulsed laser excitation, bleaching at 540 nm was found. Concurrently, transient absorption at 400–650 nm was observed, which is characteristic for the PBI moiety, ^{13,15} indicating that the T₁ state of the dyad is localized exclusively on the PBI moiety, not on the C₆₀ unit. The population of the PBI-localized T₁ state is supported by the lack of characteristic transient absorption of the triplet state of C₆₀ at 720 nm. The T₁ excited state energy level of **PBI** (1.2 eV) is much lower than that of C₆₀ (1.50 eV).¹³ The lifetime of the T₁ state of **PBI-C₆₀** is 105.9 µs, much longer than that of a recently reported C₆₀–chromophore dyad (<40 µs).⁹⁶ The lifetime is also much longer than the intrinsic T₁ state lifetime of C₆₀ (40 µs).^{8a}

With the fluorescence data, we conclude that singlet ET from PBI to C_{60} is efficient. Since the triplet excited state is localized on the PBI moiety, instead of C_{60} , thus we propose that the backward *triplet* ET from C_{60} to the PBI moiety occurs. Overall, a "ping-pong" ET process (*singlet* energy transfer from PBI to C_{60} and then the backward *triplet* excited state energy transfer from C_{60} to PBI) occurs for the dyads upon photoexcitation.¹⁶ It should be pointed out that the intra-molecular charge transfer from the antenna to C_{60} cannot be completely excluded, especially for **NPBI-C_{60}**. The triplet excited state can also be populated by the charge recombination.^{12,13}

The population of the PBI-localized triplet excited state is confirmed by the spin density surface of the dyad **PBI-C₆₀** (Fig. 4b), which is exclusively localized on PBI, which is in full agreement with the transient absorption spectroscopy (Fig. 4a). Similar transient absorption and spin density profiles were found for **NPBI-C₆₀** (see ESI[†]).

To the best of our knowledge, light-harvesting C_{60} -dyads have been rarely used for triplet photosensitizing.^{9b,c} Recently fluorene– C_{60} dyads were used for ¹O₂ sensitizing, but the absorption is slightly blue-shifted *vs.* **PBI-C₆₀** and **NPBI-C₆₀**.^{9b} Previously ¹O₂ photosensitizing ability of dihydrofullerenes was studied, but those derivatives show absorption in the UV range.^{9b}

Herein the visible light-harvesting C_{60} dyads were used as an $^{1}O_{2}$ sensitizer for photooxidation of 1,5-dihydroxyl naphthalene (DHN) (Fig. 5).² Previously Ir(III) complexes were used for the same purpose, but Ir(III) complexes show weak absorption of visible light, which is a disadvantage.

Fig. 5 Absorption spectral change for the photooxidation of DHN using (a) **PBI-C₆₀**. (b) Plots of $\ln(A/A_0)$ vs. irradiation time (t) for the photooxidation of DHN using different sensitizers. c [sensitizers] = 2.0×10^{-5} mol L⁻¹, c [DHN] = 2.0×10^{-4} mol L⁻¹. In CH₂Cl₂-MeOH (9/1, v/v), 20 °C.

Upon irradiation of **PBI-C₆₀** in aerated solution, ${}^{3}O_{2}$ was sensitized to ${}^{1}O_{2}$ by the dyad, DHN was then oxidized by the reactive ${}^{1}O_{2}$, thus the characteristic absorption of DHN at 301 nm decreased and the absorption of the oxidation product juglone at 427 nm developed (Fig. 5a).²

The photooxidation reaction rate constants (k_{obs}) with **PBI-C**₆₀ (3.0 × 10⁻² min⁻¹) is much larger than that with **Ir-1** (4.5 × 10⁻³ min⁻¹), and C₆₀ (9.7 × 10⁻³ min⁻¹) (Fig. 5b and Table 1). We attribute the enhanced photosensitizing ability of **PBI-C**₆₀ to its strong absorption of visible light and a long-lived T₁ excited state. Previously C₆₀ derivatives were used for sensitizing reactive oxygen species, but the sensitizer worked well in the UV range.^{10,11} A slightly less efficient ¹O₂ sensitizing ability was found for **NPBI-C**₆₀, due to its lower intramolecular ET efficiency (Fig. 3). **PBI-C**₆₀ shows a better photosensitizing property than the typical organic triplet sensitizer methylene blue (MB) and its efficiency is comparable to that of TPP (Fig. 5b). No photobleaching was observed for the sensitizers (see ESI[†] for details).

In summary, perylenebisimide (PBI)– C_{60} dyads with strong absorption of visible light, a long-lived triplet excited state and efficient intramolecular energy transfer (ET) were prepared.

Table 1 Photophysical parameters of the compounds and the modeltriplet photosensitizer Ir-1, 5,10,15,20-tetraphenylporphyrin (TPP)and methylene blue $(MB)^a$

	$\lambda_{ m abs}$	ε^{b}	λ _{em}	$\Phi_{\mathrm{F}}^{c}(\%)$	$ au^d/\mu s$	k _{obs} ^e
PBI-C ₆₀	327, 537	5.98, 4.37	572	0.7	105.9	30.0
PBI-Ph	535	4.20	575	36.0	f	
NPBI-C ₆₀	286, 634	9.39, 2.54	735	0.5	12.6	22
NPBI-Ph	629	2.51	728	1.3	f	
C ₆₀	335	6.44	706	< 0.1%	40.0	9.7
Ir-1	371	0.70	584	0.5	0.77	4.5
ТРР	419	32.1	650	f	82.5	43.2
MB	533	2.0	654	f	f	23.1

^{*a*} In toluene. $c = 1.0 \times 10^{-5}$ mol dm⁻³. ^{*b*} Molar extinction coefficient at the absorption maxima. ε : 10⁴/M⁻¹ cm⁻¹. ^{*c*} Fluorescence quantum yields in toluene, with 4-dicyanomethylene-2-methyl-6-*p*-dimethylaminostyryl-4*H*-pyran (DCM) as the standard ($\Phi_{\rm F} = 0.1$ in CH₂Cl₂). ^{*d*} Triplet lifetimes, measured by transient absorption. ^{*e*} Pseudo-first-order rate constant. ln(C_t/C_0) = $-k_{\rm obs}t$. In 10⁻³ min⁻¹. ^{*f*} Not determined.

With nanosecond time-resolved transient absorption and spin density analyses, we confirmed that the triplet excited state of the dyads is exclusively localized on the PBI unit. Thus "ping-pong" ET from PBI to C_{60} and in turn backward from C_{60} to PBI produces the PBI localized T_1 state. The dyads were used as a singlet oxygen ($^{1}O_2$) photosensitizer for photooxidation of 1,5-dihydroxy-naphthalene. The photooxidation with C_{60} dyads is more efficient than with the conventional Ir(III) complex photosensitizer. Our result is useful for design of *universal* visible light-harvesting *organic* triplet photosensitizers and for the applications of these dyads in photocatalysis, photooxidation, photodynamic therapy (PDT), *etc.*

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