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Visible light-harvesting naphthalenediimide (NDI)-C₆₀ dyads as heavy-atom-free organic triplet photosensitizers for triplet—triplet annihilation based upconversion

Song Guo, Jifu Sun, Lihua Ma, Wenqin You, Pei Yang, Jianzhang Zhao*

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, E-208 West Campus, 2 Ling-Gong Road, Dalian 116024, PR China

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ABSTRACT

Two naphthalenediimide (NDI)- C_{60} dyads that show strong absorption of visible light were prepared as *heavy atom-free organic* triplet photosensitizers. Alkylamino substituted NDI was used as the light-harvesting antennas and the C_{60} unit was used as *spin converter* for the intersystem crossing (ISC) from singlet excited state to triplet excited state. Upon visible light photoexcitation, triplet excited states of the dyads are populated (lifetime is up to 90.1 µs). Nanosecond time-resolved transient difference absorption spectroscopy indicated that the triplet excited state of the dyads is localized on either the NDI or the C_{60} unit. As a proof of concept, the dyads are used as *heavy-atom-free organic* triplet photosensitizers for triplet—triplet annihilation based upconversion. C_{60} -organic chromophore dyads can be used as a *general* molecular structural motif of heavy-atom-free organic triplet photosensitizers, for which the photophysical properties can be readily changed by using different light-harvesting antennas, and the ISC property of these dyads is *predictable*.

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1. Introduction

Triplet photosensitizers are widely used in photocatalysis [1], photoirradiation initialized reaction [2], photodynamic therapy [3], and more recently triplet-triplet annihilation (TTA) upconversion [4]. Triplet photosensitizers can be divided into a few categories. The first is transition metal complex photosensitizer. The intersystem crossing (ISC) of these compounds is usually efficient, due to the heavy atom effect of the Pt(II), Pd(II), Ir(III) or Ru(II) atoms in the complexes [5]. However, these complexes are not costefficient and their synthesis and purification is usually difficult. Furthermore, the molecular structure of these complexes cannot be readily changed to optimize the photophysical properties [5,6]. The second kind of triplet photosensitizers are the organic compounds which contain heavy atoms such as bromine or iodine [3d,4f,7]. For example, iodo- or bromo boron-dipyrromethene (bodipy) and bromo-naphthalenediimide (NDI) have been used as triplet photosensitizers for sensitizing of singlet oxygen $({}^{1}O_{2})$ or TTA upconversion [3d,7]. However, it is not always feasible for the organic chromophores to be derivatized with iodo- or bromo

E-mail address: zhaojzh@dlut.edu.cn (J. Zhao).

substituents, and at the same time, to ensure efficient ISC [5a,7,8]. Another kind of triplet photosensitizer is the organic compounds that contain *no* heavy atoms, for example, 2,3-butanedione [9], porphyrins, perylenebisimide derivatives, etc [5a,10]. However, the disadvantage of these organic triplet photosensitizers is their elusive photophysical property, e.g., subtle alternation of the molecular structures may eliminate the ISC property completely, and it is *impossible* to predict whether or not a *derivative* of these compounds will undergo ISC upon photoexcitation.

As a result, the challenge facing the photochemical community is how to *design* a heavy-atom-free *organic* triplet photosensitizer with *predictable* ISC. Furthermore, the molecular structures of these heavy atom-free triplet photosensitizers should be readily derivatizable, and at the same time, with the ISC be *persistent* upon derivatization. Concerning this aspect, we noticed the ISC property of fullerene C₆₀ is in particular interesting [11]. It was known that C₆₀ undergoes efficient ISC upon photoexcitation, and the fluorescence quantum yield of C₆₀ is very low ($\Phi_F < 0.1\%$)[11a]. However, C₆₀ itself is *not* an ideal triplet photosensitizer due to its very weak absorption in visible range ($\varepsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$ in the range beyond 400 nm) [11–13]. The maximal absorption of C₆₀ is located at 337 nm (ε is ca. 52,350 M⁻¹ cm⁻¹). Light-harvesting organic chromophores with appropriate singlet state energy levels can be attached to C₆₀, so that singlet energy transfer from antenna to C₆₀ moiety can occur [13].





^{*} Corresponding author. Tel./fax: +86 411 3960 8007.

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Thereafter the C_{60} moiety will undergo ISC and the triplet excited state will be populated. Therefore, we envisage that C_{60} unit can be used as spin converter for ISC and these visible light-harvesting C_{60} -organic chromophore dyads can be used as *heavy-atom-free organic* triplet photosensitizers in photocatalysis, photodynamic therapy (PDT) and TTA upconversion.

Although the C₆₀-organic chromophores have been studied for the basic photophysical properties [13], very few application of these dyads as triplet photosensitizers have been reported [11]. On the other hand, heavy atom-containing triplet photosensitizers have been widely used for TTA upconversion [4], but heavy atomfree organic triplet photosensitizers that show strong absorption of visible light were not reported for TTA upconversion [4a-4c]. Although 2,3-butadione was used as triplet photosensitizer for TTA upconversion, its absorption is in UV-blue range and the derivatization cannot be readily accomplished without compromising the ISC ability of the chromophore [9]. Recently we reported a visible light-harvesting C₆₀-chromophore dyads as triplet photosensitizers for TTA upconversion, with the Bodipy as light harvesting antenna, but the diversity of the antenna structure needs to be extended [11d-11f]. The information obtained with different C₆₀-chromophore dyads will be useful for future design of these novel heavy atom-free triplet photosensitizers.

In order to address the above challenges, herein we prepared new C_{60} -naphthalenediimide (NDI) dyads and these dyads were used as organic triplet photosensitizers for TTA upconversion. NDI has been widely used as fluorophore [14], but its role in triplet excited state manifold was rarely been studied [7c,13d,15]. Its photophysical properties, such as the absorption wavelength, can be readily changed by modification [14c,16]. We prepared two different NDI moieties with mono and bis-amino substituents, thus the two NDI antenna of the dyads (Scheme 1) give different absorption wavelength [7c]. Both antennas give fluorescence in the range 500–700 nm, indicated the S₁ state levels, thus the intra-molecular energy transfer from the NDI moieties to C₆₀ moiety is possible [11b,13c,17]. The photophysical properties of the dyads were studied with steady state and time-resolved spectroscopy. It was proved that the triplet state of the dyads was populated upon photoexcitation. As a proof of concept, the dyads were used as organic triplet photosensitizers for TTA upconversions [4].

2. Experimental section

2.1. General information

NMR spectra were taken on a 400 MHz Varian Unity Inova spectrophotometer. Mass spectra were recorded with a Q-TOF Micro MS spectrometer. UV–vis spectra were taken on an HP8453 UV–visible spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF5301 spectrofluorometer and a Sanco 970 CRT spectrofluorometer. Luminescence quantum yields were measured with 4,4-Difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (bodipy) as the standard ($\Phi_F = 72\%$ in THF). Luminescence lifetimes were measured on OB920 luminescence



Scheme 1. Preparation of the C₆₀-NDI dyads C-1 and C-2. The triplet acceptor 1CBPEA and quantum yield standard BDP-2I were also presented. (a) DBI, oleum (20% SO₃), 40 °C, 5 h; yield: 83.2%; (b) 2-ethylhexylamine, 120 °C, under N₂, 2 h; yield: 33.4%; (c) DGA, 2-methoxyethanol, 120 °C, 8 h, 71.0%; (d) 2-ethylhexylamine, 2-methoxyethanol, 120 °C, 7 h, 52.1%; (e) ethyl malonyl chloride, pyridine, CH₂Cl₂, 8 h, 92.2%; (f) C₆₀, I₂, DBU, toluene, 8 h, 62.1%; (g) 4-formylphenylboronic acid, Pd(PPh₃)₄, NaCO₃, 94%; (h) C₆₀, sarcosine, toluene, reflux, 20 h, 58.8%.

lifetime spectrometer (Edinburgh, UK). Compound **2** was prepared according to literature method [18].

2.2. TTA upconversion

Diode pumped solid state laser (continuous wave) was used for the upconversion. The samples were purged with N₂ or Ar for 15 min before measurement. The upconversion quantum yields were determined with 2,6-diiodo-4,4-difluoro-1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene as the quantum yield standards ($\Phi_F = 2.70\%$ in CH₃CN) [7b]. The upconversion quantum yields were calculated with modified equation (Eq. (1)), where Φ_{unk} , F_{unk} , and I_{unk} represent the quantum yield, absorbance correction factor ($F = 1-10^{-0.D.}$), integrated photoluminescence intensity of the samples. η_{unk} stands for the refractive index of solvents [4a]. The photography of the upconversion was taken with Samsung NV 5 digital camera.

$$\Phi_{\rm unk} = 2\Phi_{\rm std} \left(\frac{F_{\rm std}}{F_{\rm unk}}\right) \left(\frac{I_{\rm unk}}{I_{\rm std}}\right) \left(\frac{\eta_{\rm unk}}{\eta_{\rm std}}\right)^2 \tag{1}$$

The density functional theory (DFT) calculations were used for optimization of the singlet states and triplet states of the antennas. All the calculations were performed with Gaussian 09W [19].

2.3. Delayed fluorescence of the TTA upconversion

The delayed fluorescence of the upconversion was measured with nanosecond pulsed laser OpoletteTM 355II UV nanosecond pulsed laser, typical pulse length: 7 ns. Pulse repetition: 20 Hz. Peak optical parametric oscillator (OPO) energy: 4 mJ. Wavelength is tunable in the range of 210–355 nm and 410–2200 nm (OPOTEK, USA). The laser is synchronized to FLS 920 spectrofluorometer (Edinburgh, UK). The pulsed laser is sufficient to sensitize the TTA upconversion. The decay kinetics of the upconverted fluorescence (delayed fluorescence) was monitored with FLS920 spectrofluorometer (synchronized to the OPO nanosecond pulsed laser). The prompt fluorescence lifetime of the triplet acceptor 1-chloro-bisphenylethynylanthracene (1CBPEA) was measured with EPL picosecond pulsed laser (445 nm) which is synchronized to the FLS 920 spectrofluorometer.

2.4. N,N'-Di-(2-ethylhexan-1-amine)-2,6-dibromonaphthalene-1,4,5,8-tetracarboxy-dianhydride (**3**) [18]

A mixture of compound **2** (1.06 g, 2.5 mmol), 2-ethylhexylamine (0.97 g, 7.5 mmol), and acetic acid (25 mL) was stirred at 120 °C for 2 h under N₂ atmosphere. After cooled to room temperature, the mixture was poured into 100 mL cold water. The solid was collected with filtration, and was washed with water. After drying under vacuum, the resulting reddish solid was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether = 1:1, v/v). Compound **3** was obtained as yellow crystalline solid (530 mg). Yield 33.4%. M.p. 245.2–248.6 °C. ¹H NMR (400 MHz, CDCl₃/CD₃OD) δ 8.99 (s, 2H), 4.11–4.20 (m, 4H), 1.93–1.96 (m, 2H), 1.25–1.43 (m, 16H), 0.94 (t, 6H, *J* = 7.2 Hz), 0.89 (t, 6H, *J* = 7.2 Hz). HR-MALDI-MS: Calc (C₃₀H₃₆N₂O₄Br₂) *m/z* = 646.1042, found, *m/z* = 646.1032.

2.5. N,N'-Di-(2-ethylhexan-1-amine)-2-(diethyleneglycolamino)-6-bromonaphthalene-1,4,5,8-tetra-carboxydianhydride (**4**)

The mixture of compound **3** (500.0 mg, 0.75 mmol), 2-ethylhexylamine (51.6 mg, 0.4 mmol), and methoxyethanol (5 mL) was stirred at 120 $^{\circ}$ C for 6 h. After removal of

methoxyethanol under reduced pressure, the residue was purified with column chromatography (silica gel, dichloromethane/ methanol = 100:1, v/v) to give 358.0 mg of a red solid. Yield: 71.0%. M.p. 112.2–114.1 °C. ¹H NMR (400 MHz, CDCl₃/CD₃OD) δ 10.35 (s, 1H), 8.78 (d, 1H, *J* = 3.2 Hz), 8.34 (d,1H, *J* = 3.2 Hz), 4.03–4.16 (m, 4H), 3.90 (t, 2H, *J* = 4.8 Hz), 3.80 (d, 4H, *J* = 4.8 Hz), 3.70 (t, 2H, *J* = 4.8 Hz), 1.87–1.93 (m, 2H), 1.25–1.38 (m, 16H), 0.93 (t, 6H, *J* = 7.2 Hz), 0.88 (t, 6H, *J* = 7.2 Hz). HR-MALDI-MS: Calc (C₃₄H₄₆N₃O₆Br + Na⁺) *m*/*z* = 694.2468, found, *m*/*z* = 694.2462.

2.6. N,N'-Di-(2-ethylhexan-1-amine)-2-(diethyleneglycolamino)-6-(2-ethylhexan-1-amine)naphthalene-1,4,5,8-tetracarboxy dianhydride (**5**)

The mixture of compound **4** (100.0 mg, 0.15 mmol), 2-(2-aminoethoxy)ethanol (125.0 mg, 1.2 mmol), and methoxyethanol (20 mL) was stirred at 120 °C for 8 h. After removal of methoxyethanol in vacuum, the residue was purified with column chromatography (silica gel, dichloromethane/methanol = 100:1, v/v) to give 56.3 mg of a blue solid. Yield: 52.1%. M.p. 189.7–191.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.63 (s, 1H), 9.44 (s, 1H), 8.20 (s, 1H), 8.12 (s, 1H), 4.05–4.16 (m, 4H), 3.86 (t, 2H, *J* = 24.2 Hz), 3.80 (t, 2H, *J* = 24.2 Hz), 3.68–3.73 (m, 4H), 3.42–3.39 (m, 2H), 2.87 (s, 1H), 1.88–1.92 (m, 2H), 1.74–1.80 (m, 1H), 1.25–1.55 (m, 24H), 0.88–1.00 (m, 18H). HR-MALDI-MS: Calc (C₄₀H₆₁N₄O₅ + H⁺) *m/z* = 677.4672, found, *m/z* = 677.4642.

2.7. L-1 [20]

A mixture of aqueous 0.24 M Na₂CO₃ (1 mL) and dioxane(3 mL) was degassed by purging with Ar, and into it the 4formylphenylboronic acid (36.0 mg, 0.24 mmol), 4 (83.1 mg, 0.12 mmol) and 2 mol% of Pd(PPh₃)₄ (1.3 mg) were added. The mixture was heated in darkness under Ar atmosphere for 12 h. The reaction was then guenched with the addition of 10% aqueous HCl. The organic layer was extracted with dichloromethane, washed with water and brine before being dried over MgSO₄. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM/ hexane = 2/1, v/v) to afford 77.8 mg of red solid. Yield: 93.1%. M.p. 105.4–106.3 °C. $^1\mathrm{H}$ NMR (400 MHz, CDCl_3) δ 10.45 (s, 1H), 10.11 (s, 1H), 8.45 (s, 1H), 8.43 (s, 1H), 7.99 (s, 1H), 7.97 (s, 1H), 7.53 (s, 1H), 7.51 (s, 1H), 4.07–4.18 (m, 2H), 3.98–4.00 (m, 2H), 3.89–3.91 (m, 2H), 3.81-3.86 (m, 4H), 3.70 (t, 2H, J = 24.1 Hz), 2,80 (s, 1H), 1.89-1.95 (m, 1H), 1.81-1.85 (m, 1H), 1.25-1.37 (m, 16H), 0.84–0.94 (m, 12H). HR-MALDI-MS: Calc (C₄₁H₅₂N₃O₇) m/ z = 698.3085, found, m/z = 698.3839.

2.8. L-2 [21]

Compound **5** (50.4 mg, 0.07 mmol) was dissolved in 20 ml CH₂Cl₂ and pyridine (7 µl, 0.85 mmol) was added under Ar atmosphere. The mixture was cooled on an ice bath and methyl malonyl chloride (9 µL, 0.09 mmol) in 10 ml CH₂Cl₂ was added dropwise. The mixture was stirred for 12 h at room temperature. Compound **6** was purified by column chromatography (silica gel, CH₂Cl₂/ethyl acetate = 20:1, v/v) to afford 52.7 mg of blue solid (yield: 92.2%). M.p. 94.8–96.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.48 (s, 2H), 8.18 (s, 2H), 4.36 (s, 2H), 4.10–4.22 (m, 6H), 3.84 (t, 2H, *J* = 24.3 Hz), 3.78 (t, 2H, *J* = 24.3 Hz), 3.71–3.73 (m, 2H), 3.41–3.44 (m, 4H), 1.90–1.97 (m, 2H), 1.75–1.80 (m, 1H), 1.25–1.57 (m, 30H), 0.87–0.99 (m, 18H). HR-MALDI-MS: Calc (C₄₇H₇₀N₄O₉Na) *m*/*z* = 857.5041, found, *m*/*z* = 857.5121.

452

2.9. C-1

Under N₂ atmosphere, compound **7** (35.0 mg, 0.05 mmol) and sarcosine (24.0 mg, 0.27 mmol) were added to the solution of C₆₀ (36.0 mg, 0.05 mmol) in toluene (40 mL). The mixture was heated to 113 °C, and was refluxed for 20 h. The reaction mixture was cooled to ambient temperature. The solvent was then removed under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane/methanol = 40:1, v/ v). Red solid was obtained. 42.5 mg, yield: 58.8%. M.p. 247.6–249.8 °C. ¹H NMR (400 M Hz, CDCl₃) δ 10.39 (s, 1H), 8.51 (s, 1H), 8.40 (s, 1H), 7.89 (s, 2H), 7.41 (s, 1H), 7.39 (s, 1H), 5.02–5.05 (m, 2H), 4.31–4.34 (m, 1H), 4.06–4.15 (m, 2H), 3.78–3.96 (m, 8H), 3.67–3.69 (m, 2H), 2.94 (s, 3H), 2.75 (s, 1H), 1.90–1.93 (m, 1H), 1.78–1.83 (m, 1H), 1.26–1.40 (m, 16H), 0.85–0.93 (m, 12H). HR-MALDI-MS: Calc (C₁₀₃H₅₆N₄O₆) *m/z* = 1444.4200, found, *m/z* = 1444.4177.

2.10. **C-2**

lodine (10.2 mg , 0.04 mmol) were added to a solution of C₆₀ (26.4 mg , 0.04 mmol) in toluene (30 mL). The malonate **6** solution in toluene was added and the mixture was degassed with Ar for 30 min. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (15 μ L, 0.06 mmol) in toluene (20 mL) was added dropwise within 1 h and the reaction mixture was stirred over night. **C-2** was purified with column chromatography (silica gel, DCM) to yield 35.6 mg of blue solid, 62.1%. M.p. 138.2–140.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.52 (s, 1H), 9.47 (s, 1H), 8.14 (s, 1H), 8.12 (s, 1H), 4.73 (t, 2H, *J* = 24.2 Hz), 4.54–4.59 (m, 2H), 4.03–4.15 (m, 4H), 3.94–3.96 (m, 2H), 3.85–3.86 (m, 2H), 3.69 (t, 2H, *J* = 24.2 Hz), 3.40–3.43 (m, 2H), 1.89–1.94 (m, 2H), 1.74–1.80 (m, 1H), 1.26–1.37 (m, 24H), 0.87–0.97 (m, 18H). HR-MALDI-MS: Calc (C₁₀₇H₆₈N₄O₉) *m*/*z* = 1552.5055, found, *m*/*z* = 1552.4986.

3. Results and discussion

3.1. Design and synthesis of C₆₀-NDI dyads

The design of the dyads is based on the rationales that the energy level of S_1 state of light-harvesting antenna (NDI moieties) must be higher than the C_{60} moiety (1.72 eV) [13c,17a,17b,22]. Thus the intramolecular energy transfer from NDI antenna to C_{60} moiety is allowed. Furthermore, it was known that the absorption of NDI can be readily changed by derivatization [14a,14d]. Therefore NDI was selected as the light-harvesting antenna. It should be pointed out that the triplet excited state of the dyads can be located on

either the NDI moiety or C_{60} unit, dependent on the relative energy levels of the T₁ excited states of the two moieties [13a,13b,23b]. We prepared two different NDI moieties as the light harvesting antennas (compounds L-1 and L-2, Scheme 1), one is with mono amino substituent (L-1), and another is with bisamino substitutions (L-2). These light harvesting ligands give absorption at 526 nm (L-1) and 612 nm (L-2), respectively. Recently we used Bodipy to construct C_{60} dyads [11d–11f], which contain rigid linker between the antenna and C_{60} moiety. Herein flexible linker was used.

The synthesis is with 1,4,5,8-naphthalenetetracarboxylic acid dianhydride as the starting material (Scheme 1) [14a–14d]. The bromination was carried out with the dibromoisocyanuric acid. With two bromo substituents at 2,6-position were introduced, then the monoamino substitution was carried out. Suzuki coupling reaction between the resulted 2-amino-6-bromo imide and the 4-formylbenzene boronic acid leads to intermediate **7**. Bingle reaction was used to produce the dyads **C-1** (Scheme 1). In order to prepare the bisamino substituted **NDI-C**₆₀ dyad, a slightly different method was used. The 2-amino-6-bromo imide **4** was treated with 4-formylphenylboronic acid to give intermediate compound **L-1**. Bingle reaction of compound **6** with C₆₀ gives the dyad **C-2**. All the compounds were obtained in moderate to satisfying yields.

3.2. Steady state UV-vis absorption and fluorescence spectra

The UV–vis absorption spectra of the dyads and the light harvesting antennas were studied (Fig. 1). C_{60} gives very weak absorption in the visible range [11a,13a,13b]. The maximal absorption of C_{60} is located at ca. 336 nm (Fig. 1a). The light-harvesting antenna **L-2** shows absorption at 612 nm ($\varepsilon = 20,500 \text{ M}^{-1} \text{ cm}^{-1}$), whereas the monoamino-substituted light-harvesting antenna **L-1** gives absorption at blue-shifted range (526 nm, $\varepsilon = 12,700 \text{ M}^{-1} \text{ cm}^{-1}$).

Both the C_{60} dyads **C-1** and **C-2** give strong absorption, which are similar to the light harvesting antennas. Furthermore, the absorption profile of the dyads in the visible range is roughly the sum of absorption of C_{60} and the antennas (Fig. 1). Thus, the electronic interaction between the C_{60} and the light harvesting antennas in the dyad is weak at the ground state [13a,13b]. It should be noted that the tunability of the absorption wavelength of dyads **C-1** and **C-2** are more significant that the Bodipy based C_{60} dyads used for TTA upconversion [11d–11f].

The emission of the dyads and the light-harvesting antennas were also studied (Fig. 2). It was known that the fluorescence quantum yields of C_{60} is very low ($\Phi_F < 0.1\%$), due to its efficient ISC [11a,13b]. Experimentally, very weak fluorescence emission was



Fig. 1. UV–vis absorption spectra of (a) **C-1**, **L-1** and **C**₆₀. (b) **C-2**, **L-2** and **C**₆₀. $c = 1.0 \times 10^{-5}$ M in toluene. 20 °C.



Fig. 2. The fluorescence spectra of the C₆₀ dyads. (a) The emission spectra of **C-1**, **L-1** and C₆₀. Inset is the magnified emission spectra of **C-1** and C₆₀. $\lambda_{ex} = 526$ nm. (b) The emission spectra of **C-2**, **L-2** and C₆₀. Inset is the magnified emission spectra of **C-2** and C₆₀. $\lambda_{ex} = 591$ nm. $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C.

observed for C₆₀ (Fig. 2). In comparison, the light harvesting antenna **L-1** and **L-2** give intense fluorescence emission at 561 nm and 634 nm, with fluorescence quantum yields (Φ_F) of 85.7% and 44.7%, respectively (Table 1).

Interestingly, the C_{60} dyads **C-1** and **C-2** give much weaker fluorescence emission than the light-harvesting antennas (Fig. 2). Since the emission of the antenna is in blue-shifted range compared to that of the unsubstituted C_{60} (ca. 720 nm, can be approximated as the S₁ state energy level of C_{60}) [11a,13b], we propose the quenched emission of antenna in the dyads is due to the photo-induced intramolecular energy transfer from the antenna to the C_{60} moiety.

Table 1

Photophysical parameters of the C₆₀ dyads and the components.^a

	$\lambda_{abs}{}^a$	ε ^b	λ _{em}	$\Phi_{\mathrm{F}}(\mathrm{\%})^{\mathrm{c}}$	τ
C ₆₀	336	6.19	_	_	46.0 μs ^d
L-1	526	1.27	561	85.7% ^c	10.5 ns ^e
L-2	612	2.05	636	44.7% ^c	10.4 ns ^e
C-1	526	1.43	555/710	<0.1%	37.2 μs ^d
C-2	612	2.08	634	<0.1%	90.1 μs ^d

^a In toluene (1.0 \times 10⁻⁵ M).

^b Molar extinction coefficient at the absorption maxima. ϵ : 10⁴ M⁻¹ cm⁻¹.

^c With Bodipy as the standard ($\Phi_{\rm F} = 72\%$ in THF).

^d Triplet state lifetimes, measured by transient absorptions.

^e Fluorescence lifetimes.

As a proof of this intramolecular energy transfer, enhanced fluorescence emission of C_{60} moiety was observed for **C-1** at 708 nm, in comparison to C_{60} itself (inset of Fig. 2a) [13a,13b]. Similar intramolecular energy transfer was found for Bodipy derived C_{60} dyads [11d–11f]. The intramolecular energy transfer is probably not Föster resonance energy transfer (RET) mechanism, because the spectral overlap between the emission of the antenna and the absorption of the energy acceptor C_{60} is neglectable. We propose that the energy transfer process can be considered as internal conversion [5a]. Photo-induced electron transfer (charge separation) may be also responsible for the quenching of the antenna emission [13a,13b].

3.3. Nanosecond time-resolved transient difference absorption spectra

Based on the relative energy levels of the singlet excited states of antenna and C_{60} unit, we envisaged that photo-induced intramolecular energy transfer from the antenna to C_{60} moiety will firstly produce the singlet excited states of C_{60} moiety [13a,13b]. In turn the triplet excited states of C_{60} will be populated, due to the intrinsic ISC property of C_{60} [11a,13a–13c]. In order to prove the population of triplet excited states of **C-1** and **C-2**, the nanosecond time-resolved transient difference absorption spectra of the dyads were studied (Fig. 3).

The time-resolved transient absorption of **C-1** was studied (Fig. 3a). Upon pulsed laser excitation, no bleaching was observed at the ground state absorption of antenna at 526 nm. Instead, the characteristic transient absorption band of the triplet excited state of C_{60} at 710 nm was observed (Fig. 3a) [13a]. Thus we propose the T_1 excited state of **C-1** is localized on C_{60} , and the light-harvesting antenna is not involved in the T_1 excited state of **C-1**. As a proof, the lifetime of the dyad was determined as 37.2 µs, which is close to the intrinsic triplet state lifetime of C_{60} (40.6 µs Table 1) [11a].

Upon pulsed laser excitation of **C-2** at 532 nm, bleaching of the absorption of ground state of antenna **L-2** at 612 nm was observed, as well as the bleaching of C_{60} at 350 nm (Fig. 3c). Furthermore, the characteristic absorption of the triplet excited state of the C_{60} moiety at 707 nm was also observed [13a]. Recently we prepared Bodipy- C_{60} dyads for TTA upconversion, but the triplet excited states were found to be localized on C_{60} units [11d–11f]. The location of the triplet excited state in dyads may have effect on the properties such as the triplet–triplet energy transfer efficiency.

Based on these results, we propose that for C-2, both the triplet excited states of C₆₀ moiety and the NDI moiety were populated, in other words, the triplet excited states of L-2 and C₆₀ moieties are in equilibrium. The calculated T₁ state energy level of the antenna L-2 is at 1.57 eV (See Supporting Information, Table S1), which is very close to the T_1 state energy level of the C_{60} moiety (1.51 eV). The triplet state lifetime of C-2 was determined as 90.1 µs, much longer than the T_1 state lifetime of C_{60} itself, indicates that the triplet excited state of C-2 is drastically different from that of C-1. The triplet state lifetime of C-2 is also much longer than that of the Bodipy-C₆₀ dyad reported recently [11d–11f]. This result indicated that the localization of the triplet excited state of dyad has significant effect on the photophysical properties of dyad. The lifetime of the transient of C-2 was reduced to 0.5 µs in aerated solution, which confirms that the transients are mainly due to the triplet excited state, not charge-separated state [13a,13b]. The photophysical properties of the dyads and the light harvesting antenna are summarized in Table 1.

3.4. Visible light-harvesting C_{60} dyads as organic triplet

photosensitizers for triplet-triplet annihilation based upconversion

TTA upconversion has attracted much attention, due to the advantages of its low excitation power requirement, strong



Fig. 3. Nanosecond time-resolved transient difference absorption spectra of compound **C-1** and **C-2**. Transient difference absorption spectra with different delay times: (a) **C-1**, (c) **C-2**. Decay trace of the transient of (b) **C-1** at 700 nm and (d) **C-2** at 610 nm. Excited with 532 nm nanosecond pulsed laser. $c = 2.0 \times 10^{-5}$ M in deaerated toluene, 20 °C.

absorption of the excitation light, and the high upconversion quantum yields [4a-4c,4e,4g,24]. Other upconversion methods, such as those with rare earth metal materials [25], show relatively weak absorption of excitation light. For the two-photon absorption dyes [26], however, coherent excitation with much higher power density is required. TTA upconversion was reported by Parker et al. half a century ago [27]. But those organic triplet sensitizers show weak absorption in visible range and non-efficient ISC, thus the upconversion capability is limited. Currently the triplet photosensitizers for TTA upconversion are limited to the transition metal complex photosensitizers, such as the Pt(II), Ir(III) and Ru(II) complexes [4a-4c]. However, these metal complex photosensitizers are not cost-efficient. Therefore, similar to the development of the dye-sensitized solar cells (DSCs), to replace the transition metal complex photosensitizers with organic photosensitizers will be important for the development of TTA upconversion [4b].

From a photochemistry point of view, it is very difficult to develop *heavy atom-free* (such as Pt, Ir, Ru, Or Br, I, etc.) *organic* triplet photosensitizers because without the heavy-atom effect, the ISC property of an organic chromophore is unpredictable. Derivatization of a known heavy atom-free organic triplet photosensitizer is not a reliable method to prepare new triplet photosensitizers. For example, subtle derivatization of a triplet photosensitizer may eliminate the ISC property, this is true for anthracene. Anthracene shows ISC efficiency ($\Phi_{\rm ISC}$) of 72%, but for 9,10-diphenylanthracene,

the ISC efficiency is decreased significantly ($\Phi_{\rm ISC} < 5\%$) [5a,28]. Thus, it is highly desired to develop a *general molecular structural motif* for heavy-atom-free organic triplet photosensitizers that show the *predictable* ISC property, and more importantly, the molecular structure motif should be readily *derivatizable*. To the best of our knowledge, *no* such general molecular structural motif for heavy-atom-free organic triplet photosensitizers have been reported [4a–4c,5a].

As discussed above, the C_{60} -NDI dyads are ideal triplet photosensitizers for TTA upconversion. As a proof of concept, the dyads **C-1** and **C-2** were used as triplet photosensitizers for TTA upconversion (Fig. 4). Upon 589 nm laser excitation (continuous wave), **C-2** gives emission at 634 nm, which is due to the residual emission of the antenna. **C-1** did not show any emission under the same experimental conditions, due to its blue-shifted absorption.

In the presence of triplet acceptor of 1-chloro-9,10bis(phenylethynyl)anthracene (1CBPEA, Scheme 1), green emission in the range of 470–600 nm was observed with **C-2** as the triplet photosensitizer (Fig. 4b). Excitation of the photosensitizer **C-2** or 1CBPEA alone did not produce this emission band. Thus, the emission band in the 470–600 nm range is due to the TTA upconversion. **C-1** did not give TTA upconversion under the same experimental conditions, due to the unmatched excitation and the absorption wavelength (Fig. 4b). With 532 nm laser excitation, at which **C-1** shows stronger absorption, TTA upconversion was



Fig. 4. TTA upconversions with triplet photosensitizers C-1, C-2 and C_{60} . (a) Fluorescence emission of the photosensitizers (dyads) alone. (b) Emission of dyads in the presence of triplet acceptor **1CBPEA**. Excited with 589 nm laser (5.2 mW, power density 70 mW cm⁻²). c [dyads] = 3.0 × 10⁻⁵ M. c [1CBPEA] = 6.7 × 10⁻⁴ M. In deaerated toluene. 20 °C.

Table 2

Triplet excited state lifetimes ($\tau_{\rm T}$), Stern–Volmer quenching constant ($K_{\rm SV}$) and bimolecular quenching constants ($k_{\rm q}$) of the C₆₀-NDI dyads photosensitizers by triplet acceptor (1CBPEA). In deaerated toluene solution 20 °C.

	$\tau_{\rm T}/\mu s^{\rm a}$	K _{sv} ^b	k_q^c	$\Phi_{UC} \left(\% \right)^{d}$	η^{e}	$\tau_{DF}/\mu s^{f}$
C-1	37.2	_	_	0.46 ^g	62.6	16.5
C-2	90.1	25.7	2.9	0.33	47.4	32.3
C ₆₀	40.6	1.01	0.25	0.81 ^g	0.5	43.9

^a Triplet state lifetime. Determined with the nanosecond time-resolved transient absorption spectroscopy.

^b Quenching constants. 10³ M⁻¹.

^c Bimolecular quenching constants. $k_q = K_{sv}/\tau_T$. In 10⁹ M⁻¹ s⁻¹.

^d Upconversion quantum yield.

^e $\eta = \varepsilon \times \Phi_{\text{UC}}$.

^f Lifetime of the delayed fluorescence (upconverted fluorescence).

^g Perylene as acceptor.

observed for **C-1** (see Supporting Information). The upconversion quantum yields (Φ_{UC}) with the C₆₀ dyads **C-2** and **C-1** were determined as 0.33% and 0.46%, respectively (Table 2). C₆₀ itself is also effective for TTA upconversion. These Φ_{UC} values are lower than that with visible light-harvesting transition metal complex triplet photosensitizers. However, the Φ_{UC} values are comparable to that with the conventional transition metal complex triplet photosensitizers [4h]. Considering the strong absorptions of **C-1** and **C-2** in the visible range, the TTA upconversion with the C₆₀ dyads are still significant, the upconversion capability ($\eta = \varepsilon \times \Phi_{UC}$, where ε is the upconversion quantum yield and Φ_{UC} is the molar extinction

coefficient of the triplet photosensitizer) of C_{60} dyads are much higher than C_{60} alone. Previously a ferrocene-NDI- C_{60} triad was reported [13d], but the application of the triplet excited state was not studied [13d]. Furthermore, the NDI moiety in the reported ferrrocene-NDI- C_{60} triad was without any amino substitution on the π -core of the chromophore, thus the absorption of the triad is in UV range [13d]. It should be pointed out that compared to a single-chromophore triplet photosensitizer, the potential drawback of the approach based on dyad is the loss of energy due to multiple energy transfer process. We noticed that the upconversion quantum yield of the present C_{60} dyads is lower than that of the C_{60} -Bodipy dyads [11d]. The exact reason for the decreased upconversion quantum yields is unknown, although the TTET efficiency difference can be excluded (Table 2).

The excitation power-dependency of the upconverted emission intensity was studied (see Supporting Information Figure S22 and Figure S23). Nonlinear quadratic dependence was observed for the upconversion with **C-1** and **C-2** as the triplet photosensitizers, which is in agreement with the typical TTA upconversion [4d].

In order to unambiguously prove that the green emission observed for the dyad/triplet acceptor mixed solutions (Fig. 4b) is due to the TTA upconversion, the lifetime of the green emission in Fig. 4b was measured. With **C-2**, the lifetime of the emission band at 500 nm was determined as 32.3 μ s (Fig. 5a). The lifetime of the prompt fluorescence of 1-CBEPA, measured in a different experiment, was determined as 4.3 ns (Fig. 5b). The exceptionally long-lived luminescence of the dyad/1-CBPEA mixed solution unambiguously confirms TTA



Fig. 5. (a) Delayed fluorescence observed in the TTA upconversion with **C-2** as triplet photosensitizer and 1CBPEA as the triplet acceptor. Excited at 589 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and the decay was monitored at 500 nm. Under this circumstance **C-2** is selectively excited and the emission at 500 nm is due to the upconverted emission of 1CBPEA. (b) The decay of the prompt fluorescence of acceptor 1-CBPEA determined in a different experiment. Excited with picosecond 475 nm laser, the decay of the emission was monitored at 500 nm. $c[Sensitizers] = 3.0 \times 10^{-5}$ M. $c[1CBPEA] = 6.7 \times 10^{-4}$ M. In decarated toluene, 20 °C.



Fig. 6. Upconversions with photosensitizers **C-1**, **C-2** and C₆₀. Photographs of the emission of (a) photosensitizers alone and (c) the upconversion. b) CIE diagram of the emission of sensitizers alone and (d) the upconversion. Excited with 589 nm laser (5.2 mW, power density is 70 mW cm⁻²). c[Photosensitizers] = 3.0×10^{-5} M c [1CBPEA] = 6.7×10^{-4} M. In deaerated toluene, 20 °C.

upconversion [4g,11d–11f]. Similar long-lived delayed fluorescence with **C-1** and C₆₀ as triplet photosensitizer were also observed, 16.5 μ s and 43.9 μ s, respectively (Table 2 and see Supporting Information). The delayed fluorescence lifetime with **C-1** and **C-2** as the triplet photosensitizer are much shorter than that with the Bodipy-C₆₀ dyads as the triplet photosensitizer [11d].

The TTA upconversion is clearly visible to un-aided eyes (Fig. 6). Orange color (in the web version) was observed for the emission of the dyad alone, mainly due to the scattering laser (589 nm). In the presence of triplet acceptor (**1CBPEA**), green color (in the web version) was observed for the emission, which is in agreement with the spectroscopy studies (Fig. 4).

The photophysical processes with C_{60} dyad as the triplet photosensitizers for TTA upconversion are summarized in Scheme 2 [4a,4b,4f–4h]. Firstly the **NDI** antenna in the dyad **C-2** was



Scheme 2. Jablonski diagram of photophysics of the C_{60} -NDI dyads and the application of dyads as triplet photosensitizers for triplet-triplet-annihilation (TTA) upconversion (the triplet states of the sensitizers and acceptors are non-emissive). Exemplified with **C-2** as the triplet photosensitizer. The effect of the light-harvesting ability and the lifetimes of the sensitizers on the efficiency of TTA upconversion are shown (please note that the vibration energy levels of each electronic state are omitted for clarity). *E* is energy. GS is ground state (S₀). ¹(*NDI-C₆₀) is singlet excited state localized on NDI, and ¹(NDI-*C₆₀) is singlet excited state localized on fullerene. IC is inner conversion. ISC is intersystem crossing. ³(NDI-*C₆₀) is the triplet excited state localized on fullerene. TTET is triplet—triplet energy transfer. ³1CBPEA* is the triplet excited state of 1CBPEA. The emission band observed in the TTA experiment is the ¹1-CBPEA* emission (fluorescence).

photoexcited and the singlet excited state was populated. Then the intramolecular energy transfer from L-2 moiety to the C₆₀ unit occurs, with which the singlet excited state of C₆₀ unit was produced. In turn the triplet excited state of C₆₀ was populated via the intrinsic ISC of C₆₀ unit. It should be pointed out that the triplet excited state of the dyad does not necessarily localize on the C₆₀ unit. A backward triplet state energy transfer from C_{60} to antenna is also possible [13]. For example, the nanosecond time-resolved transient difference absorption spectroscopy of the dyads (Fig. 3) shows that the triplet excited state is localized on C₆₀ for C-1, but the triplet excited of dyad C-2 is localized on antenna L-2. This different localization of the triplet excited is due to the different triplet excited state energy level of the antennas relative to C₆₀ unit. Triplet-triplet-energy-transfer (TTET) between the photosensitizers and the triplet acceptor produces the acceptor molecules at the triplet excited state. TTA of the acceptor molecules at the triplet state produce the acceptor at the singlet excited state and the radiative decay from the singlet state to the ground state gives the upconverted fluorescence, i.e. the delayed fluorescence of the triplet acceptor.

4. Conclusions

In conclusion, naphthalenediimide (NDI)-C₆₀ dyads with strong absorption of visible light were prepared. The UV-vis absorption wavelength of the dyads was readily tuned by using different light-harvesting antennas in the dyads. C₆₀ unit was used as the spin converter. Upon visible light photoexcitation, intramolecular energy transfer from the light-harvesting antenna to the C₆₀ unit occurs, in turn the triplet excited state of C₆₀ was produced via the intrinsic ISC property of C₆₀. Nanosecond time-resolved transient absorption spectroscopy indicated that the triplet excited state is localized on either NDI antenna or C₆₀ unit, dependent on the energy levels of the triplet excited state of the antennas and the C₆₀ unit. Triplet-triplet annihilation (TTA) upconversion was observed with the dyads are triplet photosensitizer. We propose that the C_{60} organic chromophore dyads can be used as a general molecular structure motif for heavy atom-free organic triplet photosensitizers, for which the structure of the light-harvesting antennas can be readily changed, so that the absorption wavelength can be tuned. These molecular structure variable organic triplet photosensitizers can be used to replace the currently used precious metal complex triplet photosensitizers or the heavy atom-containing (such as Br, I) organic triplet photosensitizers in areas such as photocatalysis, photooxidation, photodynamic therapy or TTA upconversion.

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Appendix A. Supplementary data

Supplementary data related to this article can be found in the online version at http://dx.doi.org/10.1016/j.dyepig.2012.09.008.

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