



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

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ABSTRACT

Two naphthalenediimide (NDI)-C₆₀ 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 C₆₀ 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 C₆₀ unit. As a proof of concept, the dyads are used as *heavy-atom-free organic* triplet photosensitizers for triplet–triplet annihilation based upconversion. C₆₀-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 cost-efficient 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-dipyromethene (bodipy) and bromo-naphthalenediimide (NDI) have been used as triplet photosensitizers for sensitizing of singlet oxygen (¹O₂) or TTA upconversion [3d,7]. However, it is not always feasible for the organic chromophores to be derivatized with iodo- or bromo

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 ($\epsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$ in the range beyond 400 nm) [11–13]. The maximal absorption of C₆₀ is located at 337 nm (ϵ is ca. $52,350 \text{ M}^{-1} \text{ cm}^{-1}$). 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].

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Thereafter the C₆₀ moiety will undergo ISC and the triplet excited state will be populated. Therefore, we envisage that C₆₀ unit can be used as spin converter for ISC and these visible light-harvesting C₆₀-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 atom-free 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.

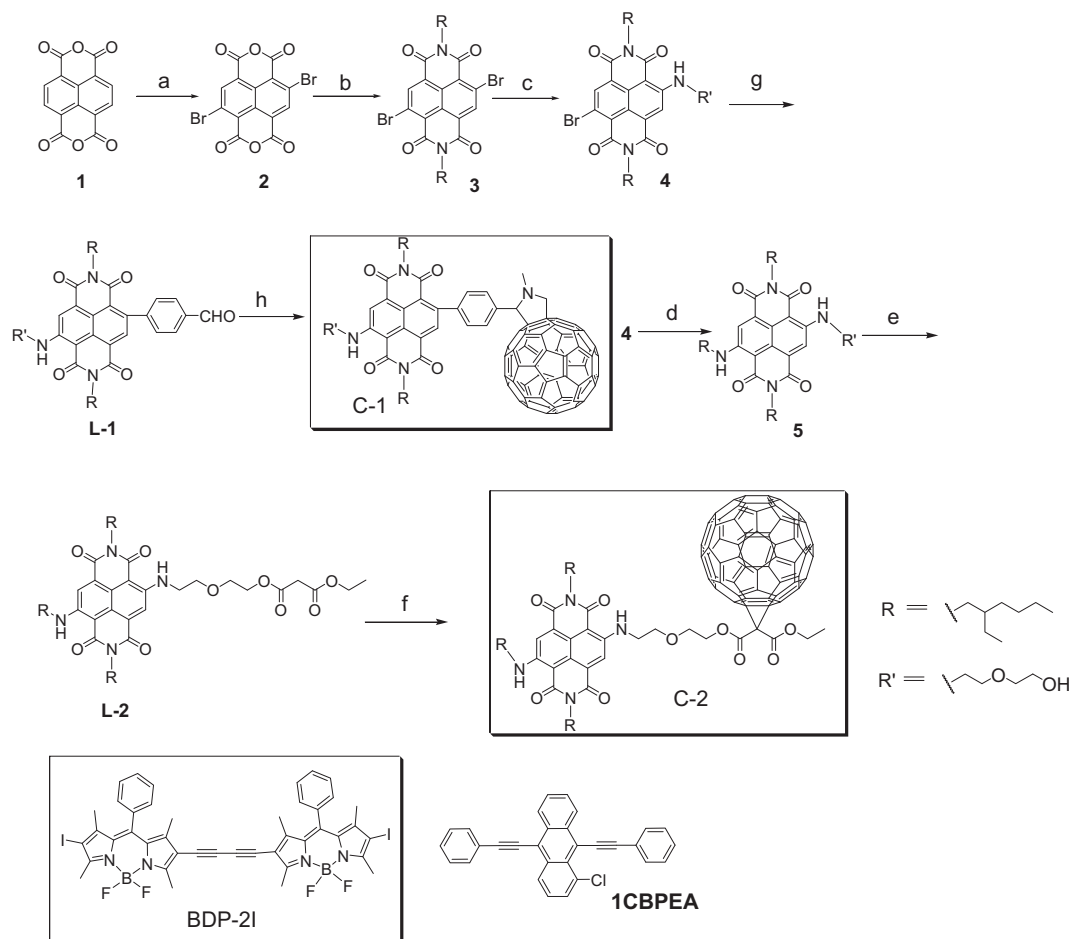
In order to address the above challenges, herein we prepared new C₆₀-naphthalenediimide (NDI) dyads and these dyads were used as organic triplet photosensitizers for TTA upconversion. NDI has been widely used as fluorophore [14], but its role in triplet

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 intramolecular 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-21** 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%.

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