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Intersystem crossing and triplet excited state properties of thionated naphthalenediimide derivatives

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ABSTRACT

Thionated naphthalenediimide (NDI) derivatives with 2,6-dibromo and diaminoalkyl substituents are prepared by treating of 1,4,5,8-naphthalenetetracarboxylic dianhydride with Lawesson's reagent. Red shifted absorption was obtained for all thionated derivates as compared to the respective oxo-compounds. Thionated NDI derivative with 2,6-diamino substituents shows strong absorption at 674 nm. Nanosecond time-resolved transient absorption spectroscopy confirmed the population of triplet excited state of the thionated compounds upon photoexcitation and the triplet state quantum yield was determined as $\Phi_T = 58\%$. Thionated derivatives were used for singlet oxygen ($^1O_2$) photosensitizing, the compound shows high singlet oxygen quantum yield ($\Phi_\Delta = 56\%$) with excitation at 675 nm. With femtosecond transient absorption spectroscopy, the intersystem crossing (ISC) of the thionated NDI was found to take 32 ps. Based on TD-DFT computations, the ISC of these heavy atom-free NDI is attributed to the $S_1 \rightarrow T_2/T_3$ transition, which is in $^1(\pi\text{-}\pi)^* \rightarrow {}^3(n\text{-}\pi)^*$ feature, which obeys with El-Sayed rule. Moreover, the S_1/T_3 state energy gap is 0.02 eV, much smaller than that of S_1/T_1 energy gap (0.86 eV). These results are useful for the design of heavy-atom-free triplet photosensitizers.

1. Introduction

Triplet photosensitizers (PSs) are versatile compounds which have been widely used in photodynamic therapy (PDT) [1–3], photocatalysis [4–6], and triplet–triplet annihilation (TTA) upconversion [7–9] etc. These applications are dependent on the visible light-absorption capabilities of the PSs, the efficiencies of production of triplet excited states and the triplet state lifetimes. Thus preparation of efficient triplet PSs is crucial for the above mentioned areas [10–12].

Normally the triplet PSs include the porphyrin free ligands and their corresponding transition metal complexes e.g. Ir(III), Pt(II), Ru(II) complexes, and the halogenated organic chromophores, such as iodinated Bodipy and naphthalenediimide [10–13]. On the other hand, the heavy atom-free triplet PSs were rarely reported [14]. Recently, we proposed to use intramolecular spin converter to access the triplet excited states of organic chromophores [14]. C_{60} is one of the spin converters. Concerning this aspect, C_{60}-Bodipy dyads and triads were prepared and were demonstrated efficient in upconversion and photocatalysis [15–17]. These compounds not only represent a unique molecular structural profile, but also offer an approach for minimal modification of the chromophores, or to reduce the dark toxicity in PDT studies [10]. Moreover, it is also interesting to study the fundamental photophysical properties of the heavy atom-free triplet PSs.

Recently it was reported that thionated perylenebisimide (PBI) compounds show triplet state production upon photoexcitation [18]. Its triplet state property was not studied in detail, such as the triplet state quantum yields and the triplet state lifetimes. Inspired by this work, we assume that naphthalenediimide (NDI), a popular fluorophore [19], may be used for the approach of thionation to prepare heavy atom-free triplet PSs. Previously the ISC of brominated NDI was studied [20–22], but the ISC of the thionated NDI was not reported. NDI can be easily modified with amino substituents to tune the absorption wavelength. Following this line we prepared a few thionated NDI derivatives (**D-S-NDI**, **Br-S-NDI**, **T-S-NDI**, Scheme 1), the photophysical properties were studied in detail with steady state and nanosecond/femtosecond transient absorption spectroscopies, as well as DFT computations. Amino-substituted thionated NDI derivatives show strong absorption at 674 nm and the triplet state quantum yield is higher ($\Phi_T = 58\%$) as compared to corresponding non thionated NDI ($\Phi_T = 27\%$), which shows absorption in UV region.

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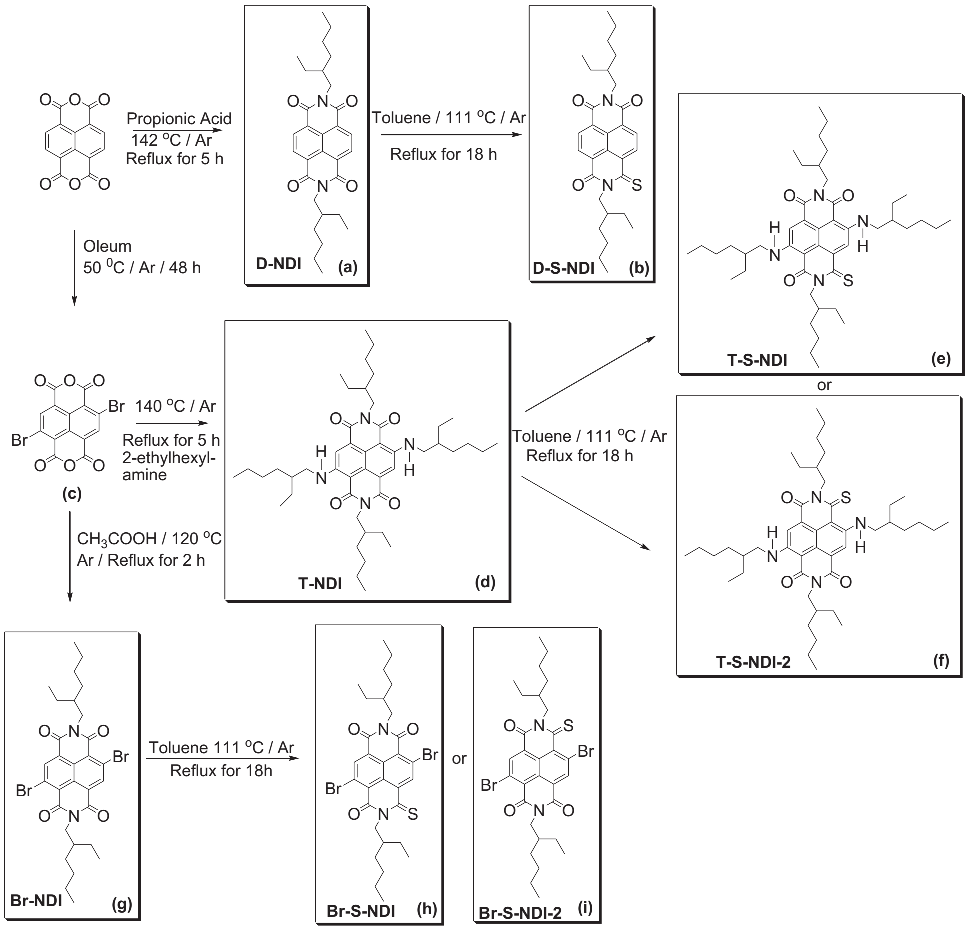

Scheme 1. Synthesis of di and tetra substituted thionated naphthalenediimide: (a) 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA), 2-Ethylhexyl amine (b) D-NDI, Lawesson's reagent (c) NDA, I_2, Br_2(d) compound c, 2-ethylhexyl amine (e, f) T-NDI, Lawesson's reagent (g) Compound c, 2-ethylhexylamine (h, i) Br-NDI, Lawesson's reagent.

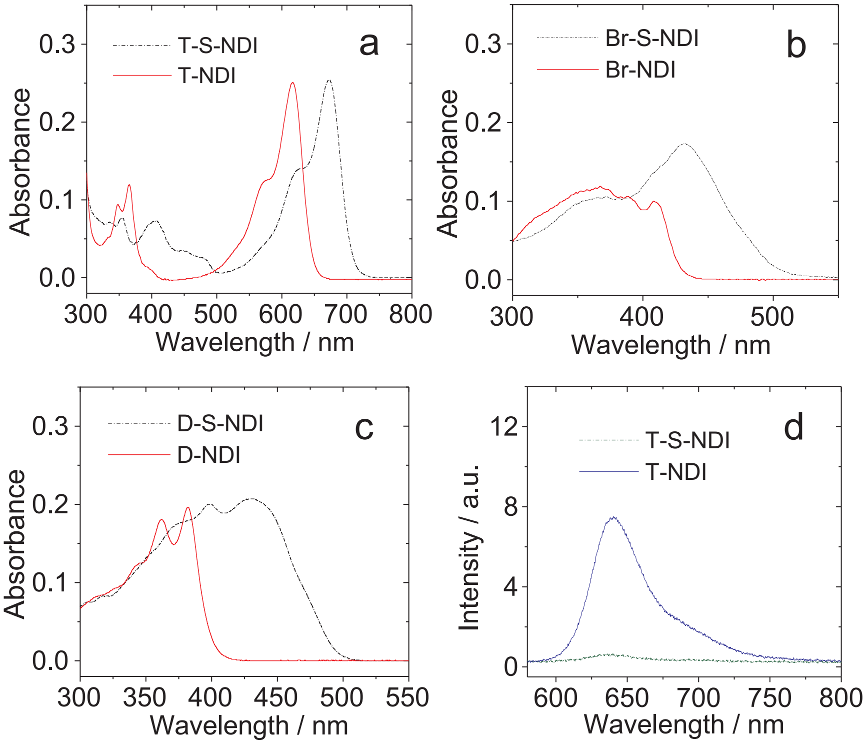

Fig. 1. UV–vis absorption spectra of the compounds. (a) **T-S-NDI** and **T-NDI**; (b) **Br-S-NDI** and **Br-NDI**; (c) **D-S-NDI** and **D-NDI**. $c = 1.0 \times 10^{-5}$ M in toluene, 20 °C. (d) Fluorescence spectra of **T-NDI** at $\lambda ex = 570$ nm. Optically matched solutions were used. $c =$ ca. 1.0×10^{-5} M in toluene, 20 °C.