Triaminotriazines—photophysical investigations of a porphyrin-appended triazine receptor with a naphthalene diimide guest[†]

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ABSTRACT: A modular synthetic approach to preparing a family of triaminotriazine receptors bearing porphyrin chromophores is described. The porphyrin-appended triaminotriazines are prepared in a stepwise manner employing either cyanuric chloride or fluoride and 5-(4′-aminophenyl)-10,15,20-triphenylporphyrin in the first step. Reaction of the porphyrintriazine with excess 1-pentylamine leads to a triazine core programmed for three-point hydrogen bonding. Addition of a complementary naphthalene diimide yields a supramolecular donor–acceptor dyad. Photophysical studies in CH_2Cl_2 solvent show efficient quenching of porphyrin fluorescence within the dyad, consistent with an electron transfer process. Copyright © 2006 John Wiley & Sons, Ltd.
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KEYWORDS: triaminotriazines; porphyrins; naphthalene diimides; fluorescence quenching; electron transfer; hydrogen bonding

INTRODUCTION

One of the major aspects in designing artificial photosynthetic devices is the selection of an organising principle that will control the interactions and spatial disposition amongst chromophoric units.[1] Covalently bridged dyad systems in which bridge conformation and length have been changed in a systematic way have also been used effectively in the past as a means of elucidating the factors that govern energy transfer (EnT) and electron transfer (ET) processes.[2] However, applying these model systems to an application such as photovoltaic devices, optoelectronics or light harvesting is impractical due to their typically lengthy and inefficient syntheses. A building block approach, that employs simple and modular synthesis along with the potential to incorporate molecular recognition motifs is more pragmatic.[1a,3] In this way, changes in the connectivity of donors and acceptors, as well as the donors and acceptors themselves, can be achieved readily and the resulting assemblies can be formed on a large scale. In this respect, the potential of the 1,3,5-triazine core to act as an easily functionalised molecular and supramolecular scaffold has been recently realised.[4–10] Our approach is to adopt the triaminotriazines as an organising precept for the preparation and evaluation of discrete molecular dyads and supramolecular assemblies that undergo energy transduction. Here, we describe a supramolecular dyad bearing a porphyrin donor and naphthalene diimide acceptor and which employs complementary three-point hydrogen bonding between the triazine and the naphthalene diimide to effect the complexation. Formation of the supramolecular complex facilitates efficient quenching of porphyrin fluorescence, attributed to an ET from the photoexcited porphyrin to the naphthalene diimide.

RESULTS AND DISCUSSION

The synthesis of the porphyrin triazine receptor **7** followed the method outlined in Scheme 1. Reaction of aminoporphyrin **1**[11] with one equivalent of cyanuric chloride **2** or the fluoride equivalent **3** under ambient conditions yielded the monosubstituted products **4** and **5**, respectively, after chromatography. In our hands, the absence of base to remove any acid formed *in situ* best suited the formation and isolation of the monosubstituted triazines.[10,12] Reaction of **4** or **5** at elevated temperature with pentylamine **6**, whose role was to negate solubility issues, gave the target triaminotriazine receptor **7** in excellent yield.

The complementary diimide **8**, bearing one 3,5-di-*tert*-butylphenyl group, was prepared by literature procedures

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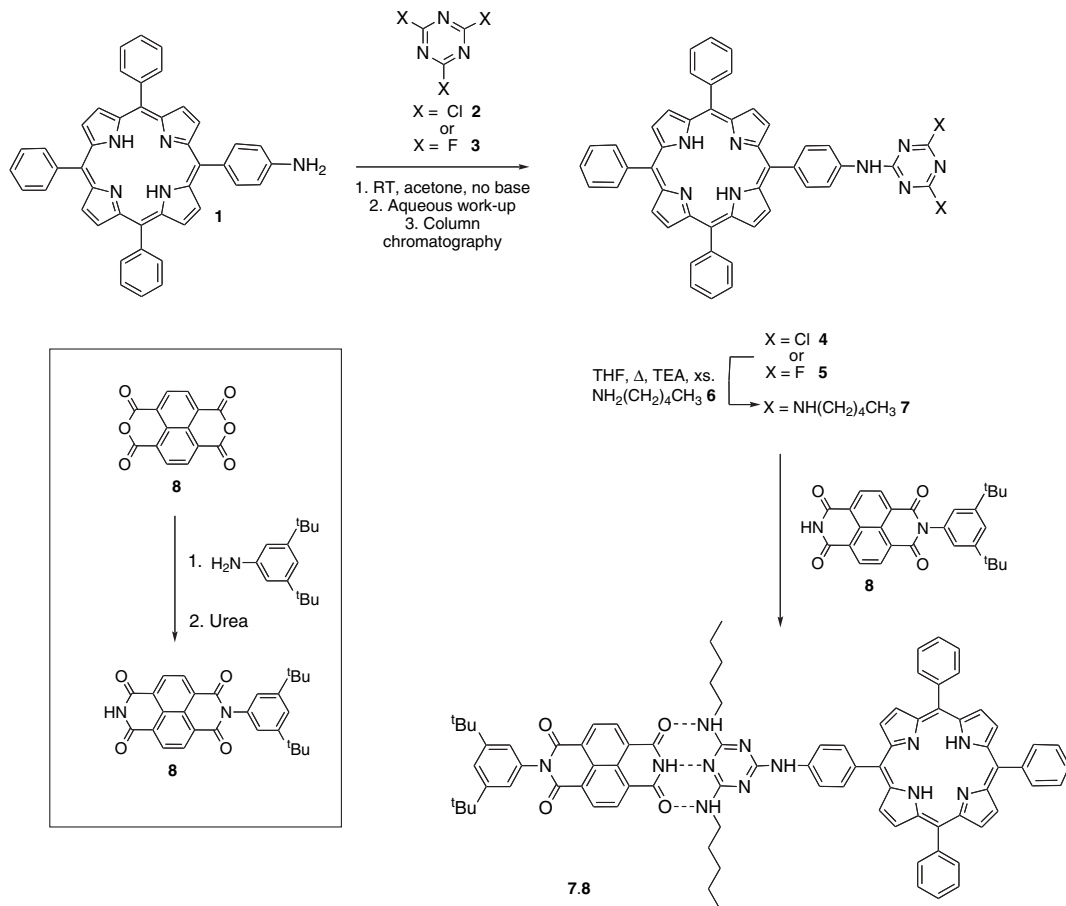
**Scheme 1.** Synthesis of triaminotriazine receptor 7, which is complementary to diimide 8. Upon mixing, the supramolecular dyad 7.8 forms *via* three-point hydrogen bonding

(Scheme 1).[13] The bulky nature of the *N*-substituent was chosen to overcome any possible stacking of diimide units and associated solubility problems we had encountered with other candidates. The ^{1}H-NMR spectrum of an equimolar mix of **7** and **8** in CDCl$_3$ exhibited a downfield shift for the N-H protons of the diimide and triaminotriazine when compared to the individual components.[14] This resonance shift is diagnostic for the three-point complementarity involving other triazines and supports the formation of the supramolecular dyad **7.8** in solution (Scheme 1).[5]

Fluorescence studies also support the formation of the supramolecular complex **7.8**. The absorption (Fig. S2) and fluorescence (Fig. 1a) spectra, the fluorescence lifetime (8.80 ns) and quantum yield (= 0.09) of the triaminotriazine **7** in de-aerated CH$_2$Cl$_2$ are typical of *meso*-tetraarylporphyrins, indicating that attachment of the aminotriazine substituent does not strongly effect the electronic properties of the porphyrin chromophore in **7**.[15] Fluorescence quenching studies were undertaken with excitation at 550 nm to selectively excite the porphyrin in solution. Fluorescence of **7** was quenched and slightly blue-shifted (*ca.* 2 nm) upon addition of **8** (Fig. 1c). The degree of quenching was considerably greater than that observed for the addition of the same

concentration of N,N′-dipentyl NDI **9**, which cannot form a complementary three-point hydrogen bond to the triazine core of **7** (Fig. 1b). The additional quenching observed in the solution of **7** and **8** is attributed to direct excitation of the supramolecular dyad **7.8**.
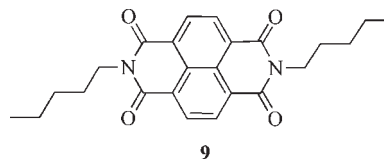
This conclusion is further supported by time-resolved fluorescence studies. The fluorescence decay profile of **7** became bi-exponential upon addition of **8**. A long lifetime component (τ_l) was observed, similar to the lifetime of **7** alone (8.80 ns), together with a second, short lifetime component (τ_S). The contribution to the decay of the short lifetime component increased with increasing solution concentration of **8**, while the lifetime remained constant at 0.27 ns. Thus, τ_S is attributed to the emission from the photoexcited supramolecular complex **7.8**. The long lifetime component was slightly reduced from 8.80 ns upon increasing the solution concentration of **8**, and is
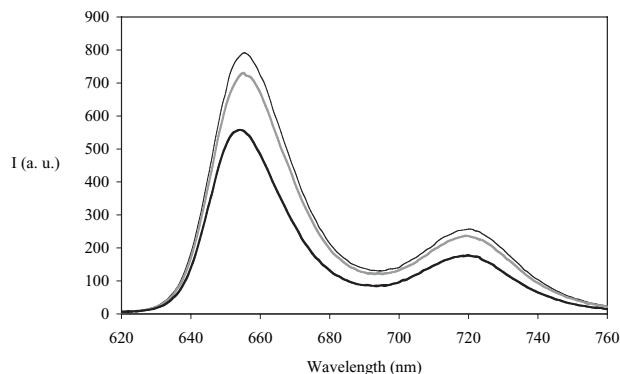
Figure 1. Corrected fluorescence spectra of optically matched solutions of (a) **7** (grey tin line), (b) **7** and 1 mM *N,N'*-dipentyl-NDI **9** (grey bold line) and (c) **7** and 1 mM **8** (black line) in CH_2Cl_2 ($\lambda_{ex} = 550$ nm)

attributed to photoexcitation of uncomplexed **7** in solution, which is then quenched by diffusive encounter with **8** during its excited-state lifetime.

In keeping with previous studies on porphyrin-naphthalene diimide dyads, the mechanism of fluorescence quenching of photoexcited **7** is attributed to an ET process.[7] The driving force for ET (ΔG_{CS}) in **7.8** was estimated using the Weller Eqn:[16]

$$\Delta G_{CS} = e(E_{OX}(D) - E_{RED}(A)) - E_{00}$$
$$- \frac{e^2}{4\pi\varepsilon_0\varepsilon_S R_{C-C}} \quad (1)$$

The gas phase, energy-minimised structure of **7.8**, calculated using *ab initio* B3LYP/6-31G methods (Fig. S1),[17] predicts a centre-to-centre inter-chromophore separation (R_{C-C}) of 18.4 Å.[18] Using the one-electron oxidation potential ($E_{OX}(D)$) of *meso*-tetraphenylporhyrin (0.95 V *vs.* SCE in CH_2Cl_2),[19] the one-electron reduction potential ($E_{RED}(A)$) of *N*-(2,5-di-*tert*-butylphenyl)-*N'*-hydrogen-4,8-dicarboxynaphthalenediimide (-0.61 V *vs.* SCE in CH_2Cl_2),[5] and the excited singlet energy (E_{00}) of **7** (1.90 eV), ΔG_{CS} was estimated to be -0.43 eV for **7.8** in CH_2Cl_2. The negative ΔG_{CS} value confirms that photoinduced ET is favourable in the complex.

The rate of ET quenching k_{ET} of the photoexcited porphyrin in the supramolecular complex **7.8** was calculated to be $3.59 \times 10^9 \, s^{-1}$ using:

$$k_{ET} = \frac{1}{\tau_s} - \frac{1}{\tau_0} \quad (2)$$

Nanosecond resolution transient absorption spectroscopy experiments on mixtures of **7** and **8** in de-aerated CH_2Cl_2 failed to detect any ionic intermediates, suggesting that charge recombination is an efficient process, occurring within the time resolution of the apparatus (*ca.* 8 ns). The excited triplet state lifetime of

the aminotriazine **7**, generated by excitation of the proportion of uncomplexed **7** in solution, was not quenched in the presence of **8**, suggesting that ET is not favoured in collisions between these two species. Given that the energy of the excited triplet state of *meso*-tetraphenylporphyrin is 0.45 eV lower than the excited singlet state, it is expected that ET from the triplet state of **7** to **8** is not thermodynamically favourable.[20]

In conclusion, we have described a method for the preparation of porphyrin appended triaminotriazines which allows for the isolation and characterisation of **3** and **4**. Addition of a complementary hydrogen bonding acceptor **8** to **7** formed the supramolecular dyad **7.8**. Fluorescence of **7** was efficiently quenched within the supramolecular dyad, however long-lived ET intermediates were not detected. Further photophysical studies are currently underway with the zinc(II) analogue of **7**. The modular nature of this synthetic approach unlocks the scope for other triaminotriazine systems and such examples will be reported in due course.

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