

# Synthesis and photophysics of a porphyrin–fullerene dyad assembled through Watson–Crick hydrogen bonding†

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A novel porphyrin–fullerene dyad assembled through Watson–Crick hydrogen bonds is described; this system undergoes photoinduced electron transfer upon irradiation with visible light to produce a charge separated state that is substantially longer lived than that of previous dyads of this type.

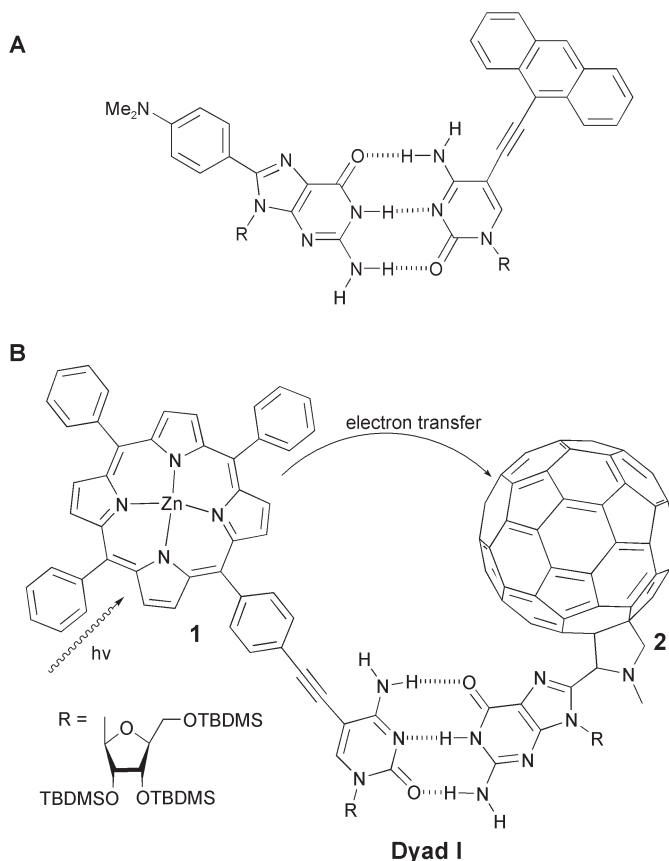
The study of photoinduced electron transfer (PET) in supramolecular assemblies is an area of rapid growth.<sup>1</sup> Many elaborate structures held together by hydrogen bonding interactions have been assembled<sup>2</sup> in order to mimic natural photosynthesis and for the design of photoactive devices. Our attention has been focused on the use of the Watson–Crick hydrogen bonding paradigm (specifically the three-point guanosine–cytidine couple) as a scaffold to assemble dyads that undergo PET.<sup>3</sup> Previous PET systems from our group include porphyrin–quinone<sup>3a,b</sup> and dimethylaniline–anthracene<sup>3c</sup> (shown in Fig. 1A) dyads. In an effort to improve further the PET process we have designed dyad **1** (Fig. 1B). This new self-assembled ensemble incorporates a porphyrin–fullerene donor–acceptor module. Fullerene, C<sub>60</sub>, was chosen as the acceptor because this species is known to act as an efficient acceptor in PET applications.<sup>4</sup> This key attribute is thought to be due, at least in part, to the low reorganization energy that results in rapid charge separation and rather slow charge recombination as a consequence of accessing the Marcus “inverted region”.<sup>5</sup>

The synthetic approach used to construct dyad **1** is shown in Scheme 1. The zinc porphyrin-appended cytidine **1** was synthesized via a palladium mediated cross coupling reaction of the appropriately protected iodocytidine **4**<sup>6</sup> with 5-(4-ethynylphenyl)-10,15,20-triphenylporphine **3**.<sup>7</sup> The key step in the preparation of fullerene appended guanosine **2** was the synthesis of 8-formyl guanosine **6**, which was synthesized by ozonolysis of vinyl-guanosine **5**<sup>9</sup> followed by a reductive work up with dimethyl sulfide. A cycloaddition of sarcosine and C<sub>60</sub> with **6** afforded the guanosine-linked-fulleropyrrolidine **7**.<sup>8</sup> Subsequent deprotection of the exocyclic amine under standard conditions<sup>9</sup> yielded target compound **2**.

Once nucleosides **1** and **2** were prepared, the energetics for PET were determined in CH<sub>2</sub>Cl<sub>2</sub> by cyclic voltammetry at room temperature using a micro-electrode. The first one electron

oxidation potential for **1** ( $E_{1/2}$  ZnP/ZnP<sup>+</sup>) and the first one electron reduction potential for **2** ( $E_{1/2}$  C<sub>60</sub>/C<sub>60</sub><sup>•-</sup>) determined versus an Fe/Fe<sup>+</sup> reference were found to be 0.32 V and –1.08 V, respectively. From these values, the driving force for the initial PET ( $\Delta G_{CS}^{\circ} = -0.81$  eV) and the subsequent charge-recombination ( $\Delta G_{CR}^{\circ} = -1.4$  eV) processes were estimated.<sup>10</sup>

The self-assembly of lipophilic guanosine–cytidine ensembles via Watson–Crick three-point hydrogen bonding has been well established in non-polar chlorinated organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>.<sup>3,11</sup> Thus, steady-state fluorescence spectroscopic analyses were carried out in this solvent. On the basis of such studies, initial evidence for the self-assembly of **1** and **2** to form dyad **I** was inferred from the decrease in the fluorescence emission of cytidine–porphyrin **1** observed as a function of increasing guanosine–fullerene **2** concentration (See Fig. 2). A non-linear least-squares



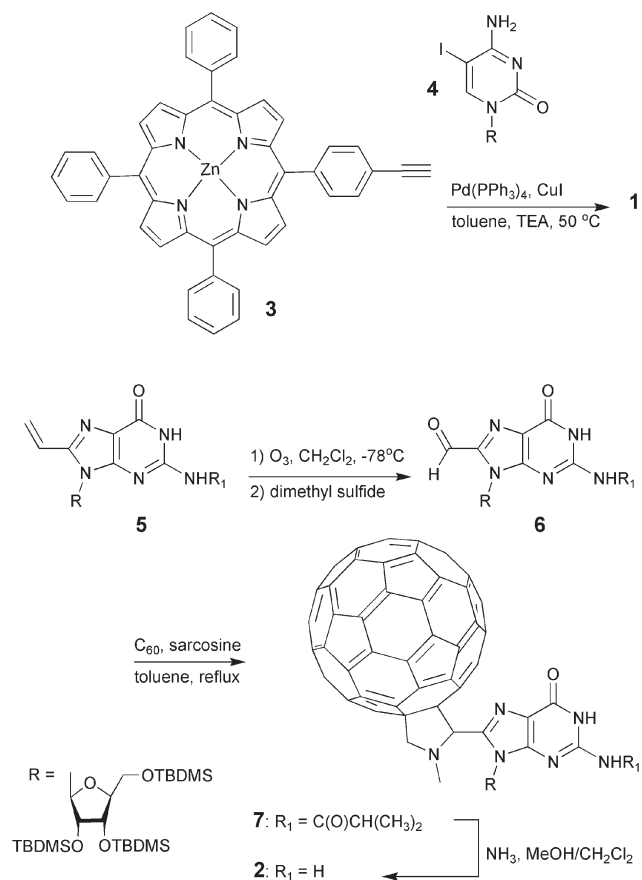
**Fig. 1** Self-assembly of dimethylaniline–anthracene (A) and porphyrin–fullerene (B) dyads through Watson–Crick hydrogen bonding interactions.

† Electronic supplementary information (ESI) available: Full synthetic experimental and electrochemical analysis. See <http://www.rsc.org/supp-data/cc/b4/b418345b/>

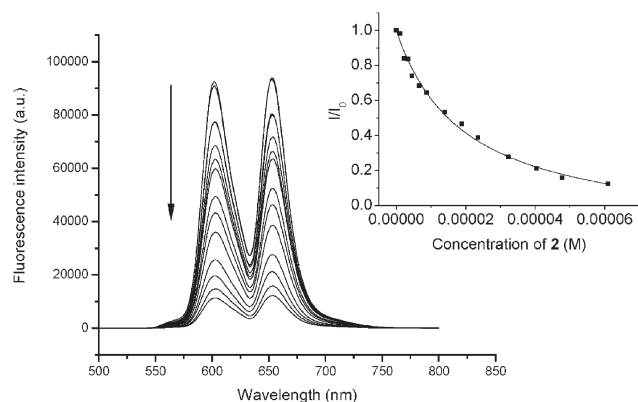
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**Scheme 1** Synthetic scheme for the preparation of nucleosides **1** and **2**.



**Fig. 2** Changes in the emission spectrum of **1** ( $5.6 \times 10^{-6} \text{ M}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$  seen upon increasing the concentration of **2** ( $0\text{--}6.1 \times 10^{-5} \text{ M}^{-1}$ ); excitation wavelength 425 nm. Inset: A plot of the change in fluorescence intensity as a ratio of  $I/I_0$  versus the concentration of guanosine–fullerene **2**. The solid line shows the estimated curve-fit (with an  $R$  value of 0.99) obtained by non-linear least-squares analysis.

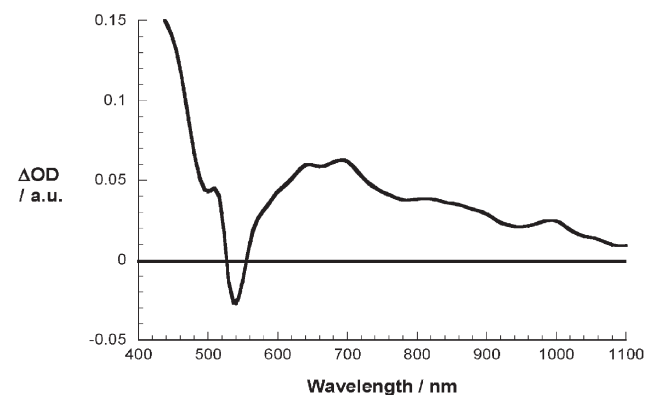
analysis<sup>12</sup> resulted in a binding constant of  $5.1 \pm 0.5 \times 10^4 \text{ M}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  (See Fig. 2; inset). This value is consistent with other GC dyads<sup>3,11</sup> in chlorinated solvents. Furthermore, upon addition of a known hydrogen bonding disruptor, hexafluoro-2-propanol,<sup>13</sup> complete restoration of the fluorescence of **1** is seen.

Time-resolved fluorescence measurements were undertaken to support the conclusion of dyad formation and intra-ensemble

quenching obtained from the steady state experiments. Specifically, the fluorescence emission of **1** ( $5.9 \times 10^{-6} \text{ M}^{-1}$ ) in the presence of varying concentrations of **2** (0–8 equiv.) in  $\text{CH}_2\text{Cl}_2$ , was monitored at 603 nm as a function of time. This revealed a fast rise and a subsequent bi-exponential decay. This bi-exponential decay is ascribed to the linear combination of two fluorescing species. The longer lived component ( $\tau_1 = 2.1 \text{ ns}$ ) is attributed to the uncomplexed excited state of **1** and the shorter lifetime ( $\tau_2 = 0.6 \text{ ns}$ ) is assigned to the PET derived quenching of the excited state of porphyrin **1** by fulleropyrroline **2** (i.e., via the formation of the Watson–Crick defined dyad **I**). Similar profiles have been seen for previous ET systems.<sup>2a</sup> From the derived lifetimes, a rate constant (ca.  $k_{\text{cs}} = 1.2 \times 10^9 \text{ s}^{-1}$ ) for the forward electron transfer was estimated.<sup>14</sup> The  $k_{\text{cs}}$  is within the range ( $10^8\text{--}10^{10} \text{ s}^{-1}$ ) of previous PET ensembles dictated by guanosine–cytidine H-bonded motifs.<sup>2a</sup>

Further support for PET as a result of the self-assembly of dyad **I** came from transient absorption spectroscopic measurements. Here, a solution of **1** and **2** in  $\text{CH}_2\text{Cl}_2$  was excited using a 532 nm laser. The resulting transient spectra revealed a weak band in the 600–800 nm region, which based on literature precedence, was assigned to the oxidized zinc–porphyrin radical cation ( $\text{ZnP}^+$ ).<sup>15</sup> Further confirmation of the charge separated state came from the observation of the fullerene radical anion ( $\text{C}_{60}^-$ ) at around 1000 nm (see Fig. 3).<sup>16</sup> Kinetic analysis of the transient absorption data resulted in a long lived charge separated radical ion pair (CSRIP) of 2.02  $\mu\text{s}$ , which is a dramatic increase in the lifetime for CSRIP within a Watson–Crick hydrogen bonded dyad (ca. three orders of magnitude larger than the previously determined value, in toluene, for the Watson–Crick based dimethylaniline–anthracene system<sup>3c</sup> (Fig. 1A); where the lifetime for the CSRIP = 705 ps).

In conclusion, the self-assembly and photophysics of a novel Watson–Crick tethered porphyrin–fullerene dyad **I** has been presented. The present study, in conjunction with previous work, highlights the fact that Watson–Crick base pairing provides a useful means of constructing self-assembled PET systems and that these natural base-pairs have an important role to play in the generation of functional supramolecular structures. On a different level, the present study illustrates how the basic PET dynamics of



**Fig. 3** Differential absorption spectrum for a solution of **1** ( $\sim 7.0 \times 10^{-5} \text{ M}^{-1}$ ) and **2** ( $\sim 1.0 \times 10^{-4} \text{ M}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$  at room temperature, obtained from flash photolysis (532 nm).

non-covalent ensembles can be enhanced through the judicious choice of the constituent donor–acceptor pairs.

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- From the derived lifetimes and their fractional amplitudes, the quantum efficiency for the forward electron transfer event, as well as the association constant between **1** and **2** were also estimated. These were found to be *ca.* 0.71, and  $3.3 \times 10^4 \text{ M}^{-1}$ , respectively. This latter value compares well with the association constant ( $5.1 \times 10^4 \text{ M}^{-1}$ ) derived from steady state fluorescence studies.
- For examples of ZnP<sup>+</sup> transient spectra see (a) H. Imahori, K. Yamada, M. Hasegawa, S. Taniguchi, T. Okada and Y. Sakata, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2626 and references therein; (b) Note: The fullerene triplet absorption is also seen in this region with a lifetime of *ca.* 45  $\mu\text{s}$ .
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