# Photophysical characterization of a cytidine–guanosine tethered phthalocyanine–fullerene dyad†

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**A new non-covalent electron transfer model system, based on the use of cytidine–guanosine hydrogen bonding interactions, is described that incorporates a phthalocyanine photodonor and a $C_{60}$ fullerene acceptor.**

Non-covalent interactions play critical roles in a variety of complex biological processes, including the photoinduced electron- and energy-transfer events associated with photosynthesis. The particular importance of the latter reactions, which range from fundamental theory to practical efforts at light-harvesting, has inspired the development of a new, supramolecular approach[1] to generating so-called photosynthetic model systems. The strength of this approach is that it relies on the use of simple building blocks, often borrowed from nature, to effect assembly of the individual model components (*e.g.*, photodonor, spacer, acceptor, *etc.*) *via* non-covalent means, including metal coordination[2] or hydrogen bonding.[3] It is also conceptually appealing in that, at least in principle, the properties of a given system, including such key parameters as driving force and overlap, may be "fine tuned" *via* the "mixing and matching" use of slightly different self-associating building blocks.

For many years, we have been studying photoinduced electron transfer (PET) using Watson–Crick hydrogen bonding as a scaffold to assemble electron donor–acceptor ensembles.[3d] Recently,[4] we reported on the synthesis and the photophysical characterization of a tethered porphyrin-fullerene dyad (ZnP–C:G–$C_{60}$) constructed by means of a guanosine–cytidine scaffold. The lifetime of the radical-ion pair state for this dyad (2.02 μs) proved substantially higher than those reported for related covalently tethered porphyrin–fullerene dyads,[5] as well as all other non-covalent PET model systems studied in our laboratories. Inspired by this finding, we prepared ensemble **1** (Fig. 1) using a phthalocyanine in order to take advantage of the good optical properties of this class of macrocyclic compounds.[6]‡ However, initial UV-vis studies indicated that the key phthalocyanine-cytidine "building block" **2** (ZnPc–C) self-associates to form aggregates in organic media.[7] Nonetheless, it was also found that addition of guanosine–$C_{60}$ **3** (G–$C_{60}$), leads to de-aggregation of **2** through putative formation of ZnPc–C:G–$C_{60}$ dyad **1** and that its formation is accompanied by a substantial fluorescence quenching of the phthalocyanine chromophore. In the current report, we provide support for the conclusion that this quenching reflects photoinduced intra-complex charge separation mediated by the formation of ensemble **1**. Previously, only a few examples of PET in non-covalent Pc–$C_{60}$ dyads had been reported;[6d,h,i] none of these involved base-pairing as the key supramolecular motif.

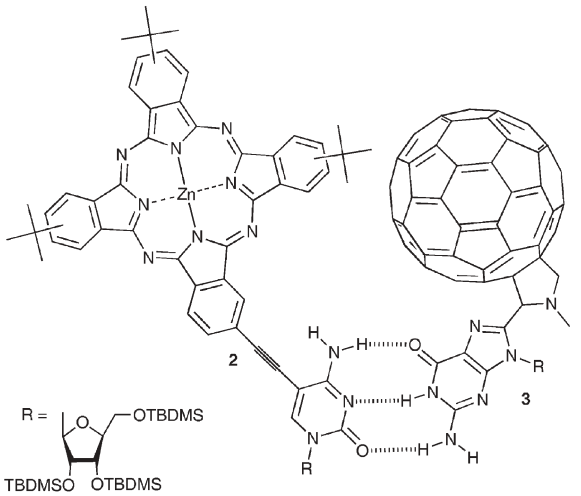

**Fig. 1** Structure of ZnPc–C:G–$C_{60}$ dyad **1**.

To extend our previous analyses of the ZnPc–C monomer **2** and ensemble **1**, new sets of titration experiments were carried out. As illustrated in Fig. 2 adding increased concentrations of the G–$C_{60}$ subunit **3** to a dichloromethane solution of cytidine functionalized phthalocyanine **2** (ZnPc–C), leads to a non-linear decrease in the fluorescence intensity of this latter chromophore. Over the concentration range employed in these studies (*i.e.*, $1.18 \times 10^{-7}$ to $1.18 \times 10^{-5}$ M) no final fluorescence value was reached. From this we infer that the fluorescence quenching in **1** exceeds 80%.§ Such quenching is similar to what is seen in the case of many other non-covalent electron transfer model systems, including specifically the analogous base-pair linked ZnP–C:G–$C_{60}$ ensemble reported earlier,[4] and leads to the proposal that photoinduced intra-complex charge separation takes place within ensemble **1**. Notably, the absorption features of ZnPc–C:G–$C_{60}$ reveal broadening, suggesting electronic interactions between ZnPc and $C_{60}$.

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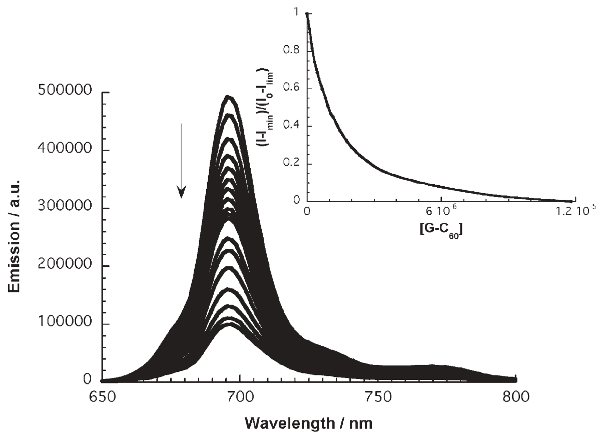

**Fig. 2** Steady-state fluorescence spectra ($\lambda_{exc}$ = 662 nm) of ZnPc–C ($1.21 \times 10^{-6}$ M) and variable concentration of G–$C_{60}$ (0–$1.18 \times 10^{-5}$ M) in nitrogen saturated toluene–dichloromethane solutions (4 : 1 v/v) at room temperature – arrow indicates the progression of the titration. Inset displays $I/I_0$ *vs.* [G–$C_{60}$] relationship used to determine the association constant.

The exponential concentration/fluorescence relationship enabled the affinity constant, corresponding to the formation of ensemble **1** from ZnPc–C (**2**) and G–$C_{60}$ (**3**), to be calculated. The resulting value, determined to be $(2.6 \pm 0.2) \times 10^6\ M^{-1}$, is several orders of magnitude larger than what has been established for the analogous ZnP–C:G–$C_{60}$ dyad (*i.e.*, $(5.1 \pm 0.7) \times 10^4\ M^{-1}$). A possible rationalization for the strength of the interaction is that the base-pair bonding is further augmented by π–π interactions and/or charge-transfer interactions. Evidence for such ground state interactions involving subunits **2** and **3** came from absorption and electrochemical analyses (*vide infra*).

The electrochemical behaviour of the ZnPc–C:G–$C_{60}$ dyad **1** and its constituents **2** and **3** were studied using cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) in dichloromethane–tetrabutylammonium hexafluorophosphate (DCM–TBAP$F_6$) solution. The CV results from these experiments are shown in Fig. 3. In the cathodic scan, compound **2** reveals two one-electron quasi-reversible reduction waves at around −1.14 and −1.37 V, respectively. Subsequent experiments using Osteryoung square wave voltammetry (OSWV) revealed a third peak at around −2.22 V for compound **2** (see ESI,† Fig. S1 and Table S1). In the anodic scan, compound **2** exhibits two redox processes; the first one is a poorly resolved two-electron quasi-reversible wave, at *ca.* 0.53 V and the second, at around 1.42 V, is chemically irreversible ($v$ = 100–600 mV $s^{-1}$). In contrast, compound **3** presents three one-electron quasi-reversible reduction waves at around −0.83, −1.26 and −1.83 V, respectively, on the cathodic direction scan. A chemically irreversible oxidation peak was observed for **3** at around 1.25 V ($v$ = 100–600 mV $s^{-1}$) and is ascribed to the pyrrolidine fragment.

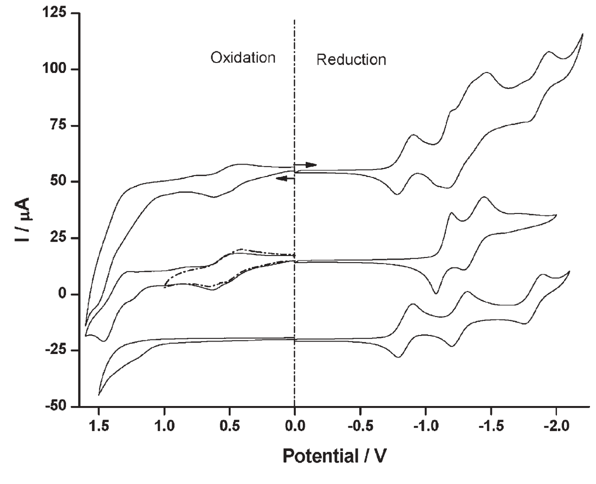

**Fig. 3** CVs (sweep rate 0.1 V $s^{-1}$) for (from top to bottom) **1**, **2** and **3** as recorded in dichloromethane–tetrabutylammonium hexafluorophosphate (DCM–TBAP$F_6$) solution at room temperature (V *vs.* Ag/AgN$O_3$).

The CVs of dyad **1** (1 : 1 molar mixture of the ZnPc–C and G–$C_{60}$ components in DCM–TBAP$F_6$) are similar to those of its constituents **2** and **3**. For instance, two one-electron quasi-reversible waves and three poorly resolved one-electron waves are observed in the cathodic scan that are the sum of the corresponding redox processes ascribed to **2** and **3**. The first and fifth waves at around −0.85 and −1.90 V, respectively, could be assigned easily as $C_{60}$-based processes (based on analogy to the G–$C_{60}$ monomer). However, the other three peaks, corresponding to the two Pc-based reduction processes and the second $C_{60}$-based reduction, respectively, could only be assigned based on OSWV measurements (ESI,† Fig. S1 and Table S1). In the anodic scan, two groups of redox processes are seen; the first one is a two-electron poorly resolved quasi-reversible process at around 0.51 V that can be assigned as Pc-based. The second, a chemically irreversible process ($v$ = 100–600 mV $s^{-1}$) at around 1.4 V, can be resolved by OSWV measurements into two peaks at 1.31 and 1.50 V, respectively, is thought to reflect contributions from both individual components.

A careful comparison of the assigned redox potentials for dyad **1** reveals that the $C_{60}$-based reduction potentials are negatively shifted with respect to those of **3** by about −20, −60 and −70 mV for the first, second and third processes, respectively. Likewise, the first and second anodic ZnPc-based potentials are less positive than those of **2** by about 20 and 10 mV, respectively. On this basis, we conclude that there are significant ground-state interactions between the phthalocyanine donor and the fullerene acceptor under ambient conditions. Nonetheless, it proved possible to estimate the driving force for a putative PET event based on these potentials (*i.e.*, radical ion pair state at 1.36 eV) and an analysis of the optical properties of **2** (*i.e.*, singlet excited state at 1.78 eV); such an analysis gave a predicted $-\Delta G^\circ$ of 0.42 eV.

In an effort to elucidate the nature of the photoexcited state deactivation, transient absorption measurements were performed with **1** and **2** with 150 fs laser pulses at 387 nm being used as the excitation source.¶ A corresponding analysis of the photophysical properties of G–$C_{60}$, **3**, has been carried out and reported previously.[4] In the toluene/dichloromethane solvent mixture the following singlet attributes are gathered for ZnPc–C (**2**): transient maxima at 430, 550 and 800 nm; transient minima at 685 and 695 nm. In this reference compound, these singlet excited state features decay slowly ($3.1 \pm 0.2$ ns) to yield **2** in the corresponding triplet manifold.‖

When dyad **1** was examined subsequent to laser excitation the same singlet excited state features observed in the case of ZnPc–C were immediately seen to develop (*cf.* Fig. 4 and ESI,† Fig. S2).

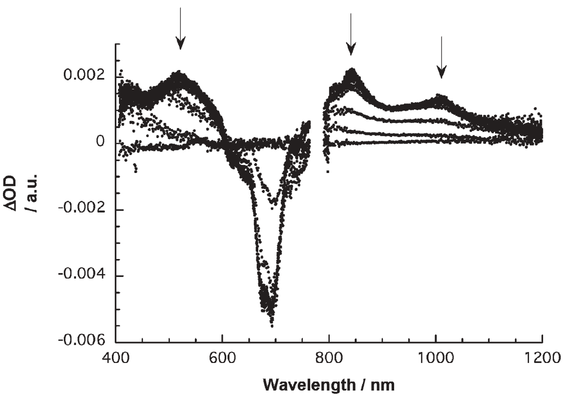

**Fig. 4** Differential absorption spectra (visible and near-IR) obtained upon femtosecond flash photolysis (387 nm) of ZnPc–C ($1.3 \times 10^{-5}$ M) and G–$C_{60}$ ($5.1 \times 10^{-5}$ M) in nitrogen saturated toluene solutions with several time delays between 0 and 20 ps at room temperature. arrows indicate the spectral character of the radical ion pair state. See time-absorption profiles in Fig. S3 (ESI†).

However, these features were found to decay rather rapidly, a finding that is ascribed to intraensemble charge separation (35 ± 5 ps). Consistent with this conclusion, characteristics of the radical ion pair state were observed, including transient maxima at 525, 850 and 1000 nm, in addition to ground state bleaching with minima at 685 and 695 nm. The maxima at 525 and 850 nm are attributed to the one-electron oxidized ZnPc–C, while the 1000 nm peak bears resemblance to the fingerprint absorption of the one-electron reduced G–$C_{60}$ and is ascribed to such a species. Interestingly, the radical ion pair state decays with lifetimes of 3.0 ± 0.5 and 1.2 ± 0.5 ns in toluene and toluene–dichloromethane, respectively, and, in turn, reinstates the ground state. Such a stabilizing trend with decreasing solvent polarity points to dynamics that are located in Marcus inverted region.**

In summary, system **1** acts as a functioning PET model system displaying clear evidence for charge separation. However, the significantly shortened lifetimes with respect to the ZnP–C:G–$C_{60}$ ensemble (3.0 ns for ZnPc–C:G–$C_{60}$ in toluene *vs.* 2.02 μs for ZnP–C:G–$C_{60}$ in dichloromethane) is thought the reflect pronounced coupling between the ZnPc and $C_{60}$ moieties in the present dyad, **1**. This is corroborated by a surprisingly large association constant. There is thus an appreciable difference between the present system and its previous, porphyrin-based analogue. As such, the present study serves to highlight how ostensibly small changes in the choice of "building blocks", in this case substitution of a phthalocyanine for a porphyrin, can lead to profound differences in both the ground- and excited-state properties of the corresponding ensemble. It also helps underscore the utility of using Watson–Crick base-pairs as scaffolds for PET model systems, while illustrating in a more general sense the benefits of employing a non-covalent "mix and match" strategy, wherein various putative photo-donor–acceptor pairs are constructed and evaluated rapidly.

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## Notes and references

‡ Recently, we have described the preparation of strongly coupled covalent ZnPc–$C_{60}$ dyads; *cf.* ref. 6*g*.

§ Probing Pc–C with *N*-methylfulleropyrrolidine resulted in only slight increase in fluorescence.

¶ For a description of the photoexcited properties of **3** the reader is referred to ref. 4.

‖ Bleaching in the differential absorption spectra (*i.e.*, pure toluene and in a toluene–dichloromethane solvent mixture), although resembling the ground-state absorption, is much broader than that of the ZnPc Q-bands.

** The small reorganization energy of fullerenes in electron transfer reactions is mainly responsible for this trend. See for example, ref. 8.

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