Energy Transfer across a Hydrogen-bonded, Cytosine-derived, Zinc–Free-base Porphyrin Conjugate

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A novel approach to construction of multi-chromophoric arrays is described in which the self-association of cytosine residues in aprotic solvents is used to assemble complexes containing 2–4 porphyrin subunits.

In an attempt to mimic the essential features of photosynthesis, many supramolecular systems have been characterized.[1] Weakly coupled donor and acceptor moieties have been assembled at predetermined sites using (semi)rigid spacer groups to form covalent, multifunctional macrocycles. Photo-induced vectorial energy or electron transfer can proceed through σ-bonds in the spacer, even over large distances, to produce highly energetic metastable entities. We have developed a novel approach to the assembly of supramolecular donor–acceptor systems in which the inherent molecular recognition features of nucleic acid bases are used to self-assemble, spontaneously, individual donor and acceptor molecules in a regular pattern.† Our approach is

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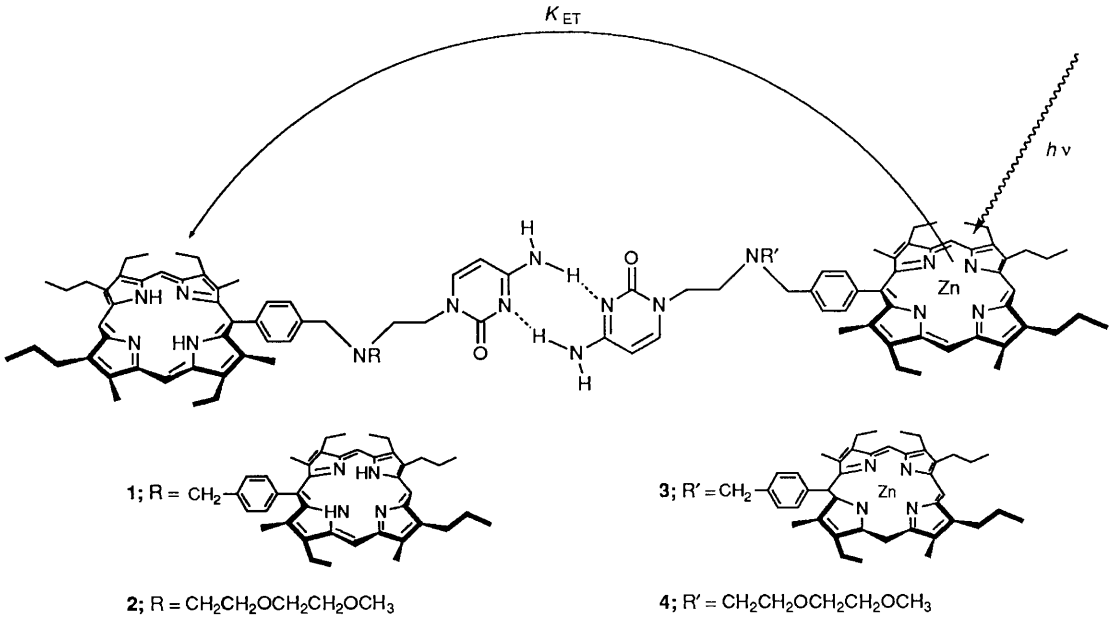


Fig. 1 Structures of the compounds and schematic representation of energy transfer across the hydrogen bonded supramolecular heterodimer

outlined in Fig. 1 whereby a nucleic acid base has been covalently bound to a porphyrin such that the optical or redox properties of the porphyrin can be modulated by insertion of different cations into the central cavity. Upon mixing in aprotic solvents, self-association of the nucleic acid base occurs *via* multiple hydrogen bonding[2] to generate a (non-covalent) porphyrin ensemble. Illumination of one porphyrin subunit could then be followed by energy or electron transfer to the second porphyrin, as has been demonstrated for covalently linked porphyrin dimers.[3] As an illustration of our approach, we describe here the specific case of zinc–free-base porphyrins linked to cytosine as in Fig. 1.

Two **1**, **3** or one **2**, **4** porphyrin molecules were bound to cytosine through a tertiary aliphatic amino function connected at cytosine N_1 (Fig. 2) using a synthetic method described previously.[4]‡ This facilitates self-association of cytosine in aprotic solvents *via* an 8-membered double hydrogen-bonded ring structure (Fig. 1) containing two, three or four porphyrins. Association, which is dynamic, has been followed by ^{1}H NMR spectroscopy for non-porphyrinic analogues of **1–4** and leads to the formation of a range of both homo- and hetero-porphyrin ensembles. The various aggregates formed in this manner differ from each other by virtue of the fact that electronic energy transfer can occur only from zinc to free-base porphyrins over short distances.[3]

Photophysical properties measured for the porphyrin subunits in compounds **1–4** have been compared to those measured for the corresponding separated porphyrins; namely, free-base (H_2oep) and zinc (Znoep) octaethylporphyrin. In dilute ($<10^{-5}$ mol dm^{-3}) $CHCl_3$, fluorescence quantum yields (Φ_f) and excited singlet state lifetimes (τ_s) for the cytosine-bound porphyrins are reduced relative to the model compounds (Table 1). Quenching decreases the triplet quantum yield (Φ_t) and the triplet lifetime (τ_t) is also reduced relative to the models. These quenching effects are attributed to intramolecular electron abstraction from the tertiary amino function in the spacer; rate constants for singlet (k_s) and triplet (k_t) state electron abstractions are included in Table 1. Under these conditions, **1** and **3** exhibit no detectable level of excitonic coupling between the porphyrin rings.[3]

Table 1 Photophysical properties measured for the various compounds in dilute $CHCl_3$ solution; estimated errors on all values ±10%

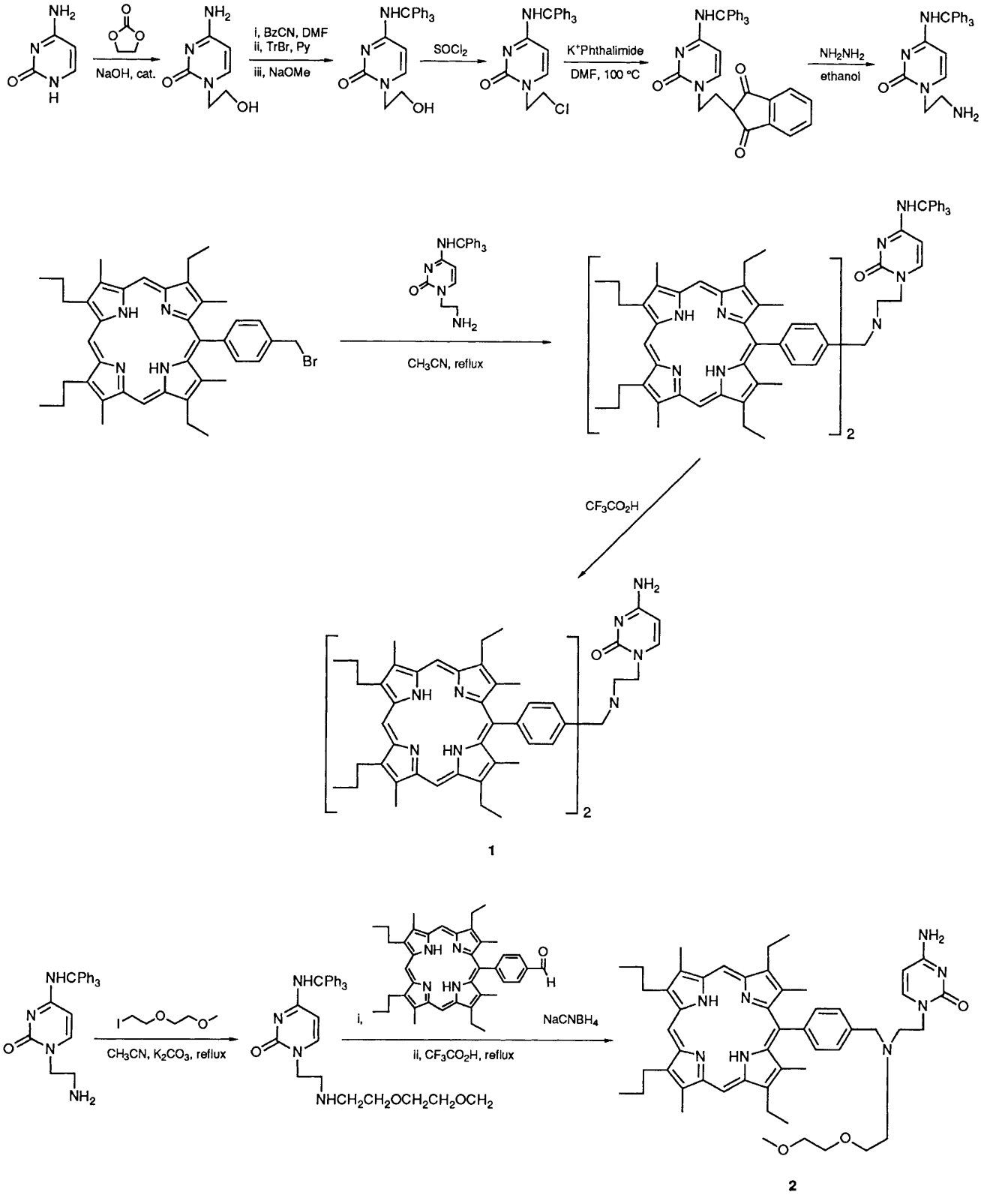
Compound	Φ_f	τ_s/ns	Φ_t	τ_t/μs	$10^{-8}\,k_s$/s^{-1}	$10^{-5}\,k_t$/s^{-1}
1	0.052	5.4	0.32	4.0	0.73	2.5
2	0.064	6.0	0.38	4.7	0.56	2.1
3	0.028	1.4	0.58	4.3	1.9	2.2
4	0.027	1.5	0.56	5.0	1.4	1.9
H_2oep	0.105	8.9	0.58	200	—	—
Znoep	0.035	1.9	0.69	95	—	—

Table 2 Singlet excited state lifetimes measured for the Znp subunits comprising equimolar mixtures of cytosine conjugates in $CHCl_3$ solution; total cytosine concentration was 2×10^{-3} mol dm^{-3}.

Mixture	τ_1/ns	τ_2/ns	K/dm^3 mol^{-1}
1–3	1.42	0.61	40
1–4	1.60	0.77	48
2–3	1.37	0.80	41
2–4	1.58	1.16	51

Photophysical properties measured at much higher concentration (*ca.* 2×10^{-3} mol dm^{-3}) are similar to those given in Table 1. At such concentrations, there was no broadening of the Soret bands and this is taken to indicate the absence of intermolecular association of porphyrins. There was no indication of bimolecular electron-abstraction processes such that the rate constants must be $<10^8$ dm^3 mol^{-1} s^{-1}. Similarly, equimolar mixtures of Znoep and **1** or **2** and of H_2oep and **3** or **4** behaved exactly as expected for separated, non-interacting species, even at 10^{-3} mol dm^{-3}. Equimolar mixtures of **1** and **3** or **4** and of **2** and **3** or **4** also behaved as non-interacting species at concentrations $<10^{-5}$ mol dm^{-3}. In all such cases, the various porphyrin subunits function independently even under conditions where we expect partial self-association of cytosine.[2] In particular, fluorescence emanating from the zinc porphyrin (Znp) and free-base prophyrin (H_2p) subunits

‡ All compounds gave satisfactory ^{1}H NMR and mass spectral analyses.



Scheme 1 Synthesis of compounds **1** and **2**. Zinc ions were inserted into the porphyrin rings to produce compounds **3** and **4**, using conventional methods.

could be resolved clearly, a result which is supported by the corresponding excitation spectral analyses.

Time-resolved fluorescence studies were made with these latter systems at a much higher equimolar concentration (*ca.* 2 × 10^{-3} mol dm^{-3}) using a mode-locked, synchronously pumped, cavity-dumped dye laser operating in the single-photon-counting mode. Following excitation at 570 nm, where the Znp subunit absorbs *ca.* 85% of the incident photons, fluorescence from the H_2p subunit (λ 685 nm) decayed monoexponentially with a lifetime corresponding to that of monomer species. Fluorescence from the Znp subunit (λ 600 nm), however, showed dual exponential decay profiles. The longer lifetime (τ_1), which accounts for ≥80% of the total fluorescence, corresponded to that given in Table 1 whereas

the shorter lifetime (τ_2), accounting for ≤20% of the total fluorescence, is attributed to a Znp subunit within a hydrogen bounded cytosine dimer. The quenching is assigned to Forster energy transfer from Znp to H_2p subunits within the same ensemble since the fraction of shorter-lived component increased with increasing concentration and was observed only with the mixed porphyrin–cytosine conjugates. Average porphyrin centre-to-centre separation distances, as estimated from space-filling models, are in the range 1–3 nm while the Förster critical distance is calculated to be *ca.* 1.8 nm. From the measured lifetimes (Table 2), we derive rate constants for energy transfer ($k = 1/\tau_2 - 1/\tau_1$) of 9.4, 6.8, 5.2 and 2.3 × 10^8 s^{-1} for the **1–3**, **1–4**, **2–3** and **2–4** ensembles, respectively. The apparent increase in the rate of energy transfer with the number of porphyrins within an ensemble is due to the greater probability of finding a porphyrin donor–acceptor pair in close proximity. From the fractional amplitudes of τ_1 (A_1) and τ_2 (A_2), we have derived self-association constants (K) for cytosine base pairing (Table 2). The average value found ($K = 2A_2C/[(1 - 4A_2)C]^2$) at a total cytosine concentration of C was 45 ± 15 dm^3 mol^{-1}.

We have also observed triplet energy transfer from Znp to H_2p subunits within the hydrogen-bonded cytosine dimers, albeit at very slow rates. This process is apparent from nanosecond laser flash photolysis studies conducted in a thin-layer cell using collinear excitation at 532 nm where the Znp subunit absorbs strongly. These experiments were carried out using a high concentration (2×10^{-3} mol dm^{-3}) of **3** or **4** and adding low concentrations ($0–50 \times 10^{-6}$ mol dm^{-3}) of either **1** or **2**. Under such conditions, all incident photons are absorbed by the Znp subunit. Measurements made at 585 nm, an isosbestic point for the differential triplet absorption spectrum of Znp, showed that the triplet of the H_2p subunit grew in after the laser pulse by first-order kinetics. The rate of formation was independent of H_2p concentration (<10^{-4} mol dm^{-3}) but the final absorbance increased with increaasing concentration. This process is attributed to triplet energy transfer across a hydrogen-bonded cytosine-derived dimer and the derived rate constants for the triplet energy transfer steps were 9.2×10^6, 4.9×10^5, 8.4×10^5 and <2×10^5 s^{-1} for **1–3**, **1–4**, **2–3** and **2–4** ensembles respectively, after correction for any bimolecular effects as determined from concentration dependence studies (using **1** or **2** and Znoep). In all cases, the lifetime of the H_2p triplet state remained close to the appropriate values given in Table 1. Triplet energy transfer most probably involves a through-bond Dexter-type mechanism in which the conformation of the spacer affects the rate of transfer.[5]

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