Strong donor–acceptor couplings in a special pair-antenna model†

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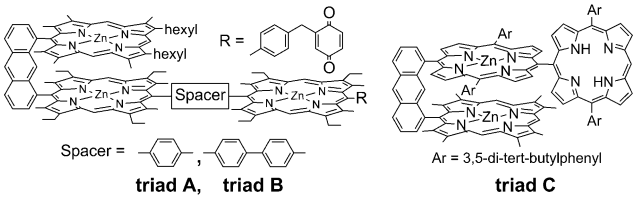
A special pair model composed of two cofacial zinc porphyrins (acceptor) linked to a free base (donor) acts as an energy transfer dyad. Despite the absence of conjugation, $\pi\pi^*$/charge transfer excited states and ultrafast energy transfer ($\sim$5 ps) are noted.

The mimicry of the special pair or the special pair flanked with electron and energy transfer accessories of photosystems PS I and II is still a topic of current interest.[1] In most cases, zinc porphyrins play the role of chlorophyll derivatives and the accessories are mostly changed for quinones, C_{60}, pyromellitdiimide or other acceptors.[2] In the purple photo-synthetic bacteria, bacteriochlorophylls and pheophytins are the electron acceptors and the electron transfer (et) occurs on the 0.9–2.3 ps time scale.[2] A model containing a special pair and electron acceptor groups was reported by Osuka *et al.* using benzene (**triad A**) and biphenyl (**triad B**) spacers to separate the special pair from the monoporphyrin residue and the quinone acceptor (Scheme 1).[3] The et takes place within 26–40 ps after excitation, which is $\sim$10 times slower than those cited above. We recently reported the anthracenyl-containing **triad C** (Scheme 1). The octamethylzinc(II)-, diarylzinc(II)- and free base porphyrins act as S_1 energy transfer (ET) donor 1, donor 2 and acceptor, respectively.[4] The noted ET between donor 1 and donor 2 raises the question whether the anthracenyl bite distance is short enough to adequately mimic the special pair. We now report a biphenylene-containing special pair directly linked to an ET accessory (**1**; Scheme 2). This system exhibits a spectacular role reversal with respect to **triad C** where the S_1 ET now occurs from the free base to the cofacial unit. The very close bite distance ($\sim$3.8 Å) of the bridge squishes the cofacial dimer to form an entity acting as a single unit. The three components are heavily coupled due to the close proximity and the ET time scale is ultrafast ($\sim$5 ps).



Scheme 1

Trimer **1** was prepared from three sequential Suzuki cross-coupling reactions (steps A, B and C in Scheme 2), applying our recently developed approach.[4] The coupling between **2** and **3** being performed with $Pd_2(dba)_3$ and KOH in the presence of Buchwald's SPhos ligand, known to suppress hydrodebromination in cross-coupling reactions,[5] led to the formation of the undesired product **4**. Alternatively, the use of a larger excess of **2** (2 eq.) in the presence of $Pd(PPh_3)_4$ and Cs_2CO_3 in DMF–toluene selectively provided product **5** in 94% yield. The latter was then reacted with the porphyrin diboronate **6** under optimized conditions with $Ba(OH)_2$ and $Pd(PPh_3)_4$ in DMF and gave the borylated face-to-face porphyrin dimer **7** in 48% yield. The coupling between **7** and **8** was attempted using different catalysts ($Pd(PPh_3)_4$, $Pd_2(dba)_3$, $PdCl_2(Ph_3P)_2$) and bases (KOH, Cs_2CO_3, $Ba(OH)_2$) in DMF or toluene–DMF (2 : 1) mixtures at 90–100 °C. The yield of the target trimer **1** was found to be critically dependent on the reagents ratio rather than on the catalytic system used. For instance, by using a stoichiometric amount or 2-fold excess of bromoporphyrin **8** with respect to boronate **7**, similarly to step A and other reported couplings,[4] only trace amounts of desired product **1** along with unreacted **7** and **8** were isolated despite increasing the reaction time or adding the catalyst. Such a result can be explained by the presence of steric hindrance, here caused by the cofacial dimer moiety, known to decrease the efficiency of the Suzuki reaction.[6] However, the use of 2 eq. of dimer **7** with respect to 1 eq. of **8** provided full conversion of **8** within 6–8 h and gave trimer **1** in up to 50% preparative yield when carried out with $Pd(PPh_3)_4/Cs_2CO_3$ in DMF/toluene. The excess of **7** was recovered from the reaction mixture. The product was purified by chromatography on silica and size-exclusion chromatography and was characterized by mass spectrometry and NMR spectroscopy. The profound effect of the reagents ratio on the coupling of **7** and **8** is not clear with respect to other sterically hindered Suzuki couplings, which are usually achieved by the use of specific ligands on Pd.[6] In an attempt to develop an alternative route towards **1** we prepared the borylated *meso–meso* dimer **9** which was subjected to coupling with **5** (Scheme 2, steps D and E) using the synthetic protocol developed for step C. However, regardless of the reaction conditions, no trimer was observed, while the starting material was converted to the corresponding *meso–meso* dimers **10**,

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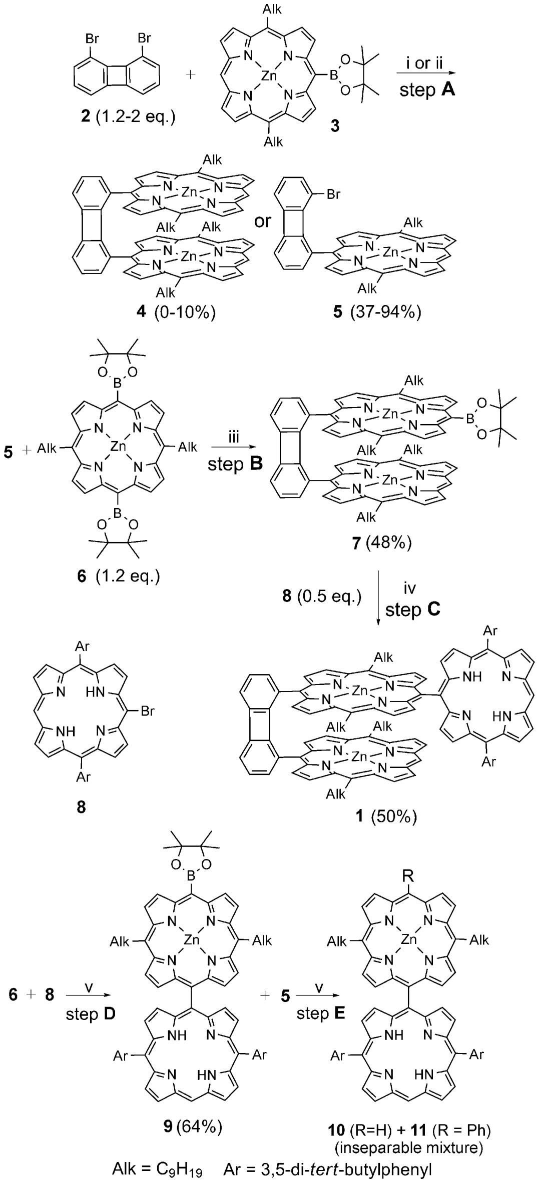

Scheme 2 (i) KOH, $Pd_2(dba)_3$, SPhos, PhMe, 90 °C, 15 h; (ii) $Pd(Ph_3P)_4$, Cs_2CO_3, PhMe/DMF, 90 °C, 15 h; (iii) $Ba(OH)_2$, $Pd(Ph_3P)_4$, DMF, 100 °C, 24 h; (iv) 5-bromo-5,15-di-(3,5-di-*tert*-butylphenyl)porphyrin (0.5 eq.), $Pd(Ph_3P)_4$, Cs_2CO_3, PhMe/DMF, 90 °C, 8 h; (v) $Pd(Ph_3P)_4$, Cs2CO3, PhMe/DMF, 90 °C, 20 h.

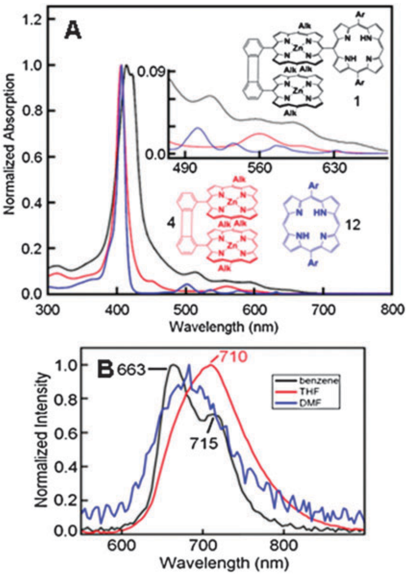

Fig. 1 (A) Comparison of the UV-vis spectra of **1**, **4** and **12** in THF. (B) Fluorescence spectra of **1** in various solvents (298 K).

resulting from a deborylation process, and **11** arising from an aryl–aryl interchange reaction.[7]

The comparison of the UV-vis spectra of **1** with those of **4** and **12** (Fig. 1A) showed broader Soret and Q-bands for **1** indicating interporphyrin interactions. Attempts to reconstruct this spectrum with the individual spectra of **4** and **12** failed to find a good fit (ESI†) hence providing evidence for interactions. Such interactions have also been previously demonstrated for a cofacial biphenylene–bisporphyrin,[8] but interactions for all three is new. In this respect, the absorption spectra of **9** were studied (ESI†) and the UV-vis bands were found to be broader than those observed for the mono-porphyrins. The fluorescence spectrum of **1** measured in three different solvents (Fig. 1B) exhibited a band centered at 680 nm. The excitation spectra superpose well the absorption spectra. In benzene, the 0–0 peak is visible at 663 nm. Because this value matches best that observed for **4** (667) and **7** (679 nm) with respect to **12** (635 nm; ESI†), this emission is due to the bis(zinc porphyrin) unit. This value also compares well with the low-energy Q-band in **1**. The lack of emission at 635 nm suggests an efficient S_1 ET from the free base (donor) to the cofacial unit (acceptor). The fluorescence lifetime of **1** in THF (2.27 ns) compares well to that for **4** (1.95 ns) but not with **12** (10.1 ns). One of the salient features is the change in emission intensity as a function of the medium polarity. The 0–0 peak is visible for **1** in benzene but the fluorescence band is unstructured and weak in DMF. At a first glance such behaviour may be assigned to a charge transfer (CT) excited state, however due to the lack of a red shift with increasing medium polarity, the exact nature of this state needs analysis.

The HOMO and LUMO for **1** are composed of π-systems primarily centered on the cofacial dimer indicating that the lowest energy excited state is dimer-centered (Fig. 2; DFT; ESI†). Moreover the LUMOs show atomic contributions arising from π-systems that spread over both the dimer and the free base, meaning that all these ππ* electronic transitions have some minor bis(zinc porphyrin) → free base CT character. This is consistent with the lack of a red shift of the fluorescence upon increasing the medium polarity. The computed UV-vis spectra of **1** (TDDFT, ESI†) compare well with the experimental one in Fig. 1. The individual calculated transitions and their major contributions (ESI†) also support the assignment of the S_1 states.

Transient absorption spectroscopy (TAS) was used to resolve the ultrafast dynamics of the excited states in **1** by tracking their photoinduced absorption (PA) profiles. The TA spectra of **1** (Fig. 3 top) are similar to that of the porphyrin dimer **4** (ESI†) but not the free base **12** (ESI†) indicating that the photo-induced absorption stems mainly from the acceptor unit, *i.e.* the cofacial dimer. A clear assignment of the spectral

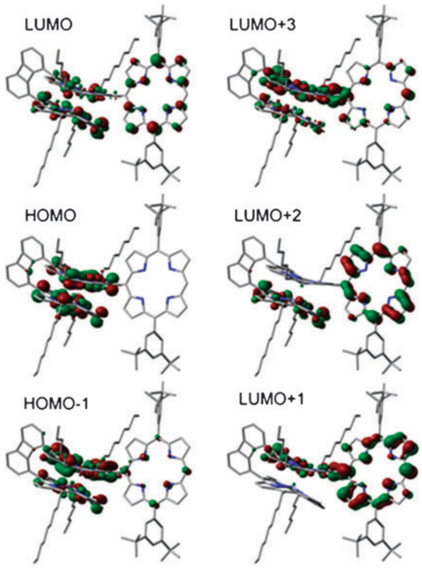

Fig. 2 MO drawings of selected frontier MOs of **1**.

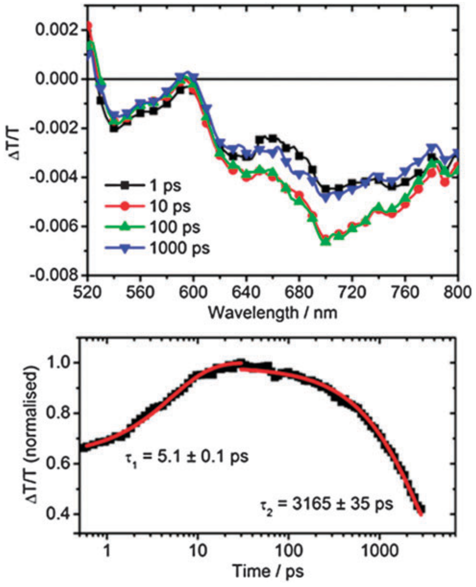

Fig. 3 Top: TA spectra of **1** in deaerated THF at delay times of 1, 10, 100 and 1000 ps. Note the increase of the photoinduced absorption between 1 ps (■) and 10 ps (red circles). Bottom: Kinetic traces of the photoinduced TA integrated between 700–750 nm. The red lines represent exponential fits to the experimental data with a rise (5.1 ps) and a decay time (~3.2 ns).

features is difficult since the transient absorption of compounds **4** and **12** overlaps in this spectral region. Moreover, the experiments are further complicated due to the overlap of the ground state absorption of **4** and **12**. In fact, it is not possible to exclusively excite one moiety in **1**. Consequently, a superposition of the signals from **4** and **12** can be expected for **1** and was indeed noted. Nevertheless, it is possible to extract information on the ultrafast ET processes occurring in **1**. The kinetic trace of the integrated spectral region 700–750 nm (Fig. 3 bottom) exhibits an exponential rise time of ~5 ps (±0.1 ps) and a significantly longer relaxation time of ~3165 ps (±35 ps). The latter is due to the excited state lifetime of the cofacial dimer (τ_F(**1**) = 2.27 ns). Considering that neither the PA signal of the free base **12** nor of the cofacial dimer **4** showed changes on the ps time scale (ESI†), it appears likely that the much shorter component seen for **1** is associated with an excited state ET process free base → cofacial dimer in **1** accompanied by a change in the excited state cross-section in the observed spectral region leading to the rise of the PA when going from an excited state on the freebase to an excited state on the dimer.

This ET is extremely fast and comparable to those seen in natural systems.[2] The very fast ET rate here is certainly aided by the short donor and acceptor distance, but the lack of large transition moments in porphyrins with respect to chlorophyll derivatives must slow down the rate. So these CT interactions appear to counter balance this effect. One of the key features is the biphenylene bridge which compresses the two cofacial aromatics. The resulting strong ππ-interactions form a true dimer with red-shifted absorptions, hence reversing the role of the energy donor and acceptor moieties. However, we find that the coupling between the frontier HOMOs and LUMOs is large with regard to special pair models, so models for et based on this spacer should also exhibit very fast rates. New systems with decoupled donors and acceptors are on the way.

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