# Strongly coupled zinc phthalocyanine–tin porphyrin dyad performing ultra-fast single step charge separation over a 34 Å distance†

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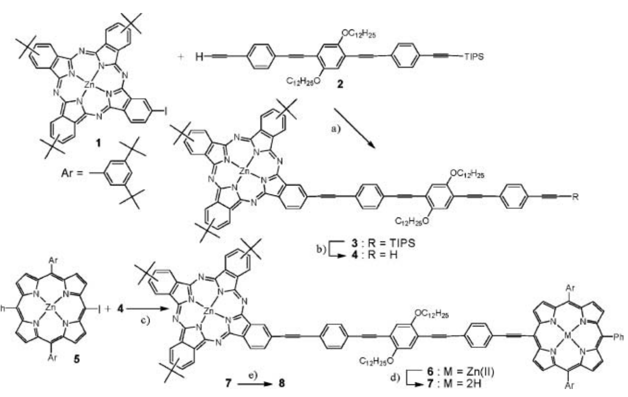
**A zinc(II) phthalocyanine–tin(IV) porphyrin dyad with a strong electronic coupling was synthesized and upon light excitation shown to exhibit ultra-fast, long-range electron transfer in a single step.**

The development of molecular systems that carry out rapid and directional energy or electron transfer over a long distance is an important research goal because these are key photofunctions needed for photovoltaic, artificial photosynthesis and molecular electronic applications. Although much attention has been paid to the preparation and study of porphyrin[1,2]- or phthalocyanine[3]-based molecular systems for energy or electron transfers, there are few examples of porphyrin–phthalocyanine dyads that perform electron transfer.[4] Multichromophoric systems containing both porphyrins and phthalocyanines are appealing because the distinct absorption bands of these two pigments permit harvesting of a large part of the solar spectrum and enable selective excitations. In most of the biomimetic porphyrin systems, the bridge is connected to the porphyrin *via* a *meso*-phenyl group that limits the electronic communication owing to poor frontier molecular orbitals overlap between the connected elements.[1,2,5,6] Alkynyl substituted phthalocyanines or porphyrins are attractive units for the design of systems with a strong electronic coupling. This feature has been previously used for the development of non-linear optical chromophores,[7,8] but it has rarely been tested for long-range electron transfer.[9] As part of our continuing interest in electronically coupled systems to perform long-range photoinduced energy or electron transfer,[5,6] we report here the preparation and the photophysical investigation of a strongly electronically coupled tin porphyrin–zinc phthalocyanine dyad that performs ultra-fast charge separation over a 34 Å centre-to-centre distance.

The synthetic route for the preparation of the dyad **8** is shown in Scheme 1. Zinc iodo phthalocyanine **1** was connected to the bridge **2** using the Heck ethynylation conditions.[10] The triisopropyl protecting group was removed by fluoride anion and the zinc iodoporphyrin **5** was then appended to compound **4** by a second cross-coupling reaction using the same conditions.



**Scheme 1** Synthetic route to the dyads **6–8**. *Reagents and conditions:* (a) piperidine, $Pd_2dba_3$–$CHCl_3$, $AsPh_3$, 40 °C, 15 h (43%); (b) $Bu_4NF$, THF (100%); (c) THF, $Et_3N$, $Pd_2dba_3$–$CHCl_3$, $AsPh_3$, 60 °C, 15 h (33%); (d) HCl, $CH_2Cl_2$ (91%); (e) pyridine, $SnCl_2$–$2H_2O$, 185 °C, 3 h (83%).

Zinc porphyrin in dyad **6** was selectively demetallated with hydrochloric acid and the corresponding free base porphyrin **7** was metallated by tin(II) chloride following the conditions reported by Arnold and co-workers.[11] It is noteworthy that during this reaction the triple bond directly connected to the porphyrin was reduced to a double bond to give **8**. Besides, unlike most tin porphyrins, the two chloro axial-ligands of **8** or **12** were not replaced by hydroxo ligands, neither during the reflux in ethanol solution of $K_2CO_3$, nor during the column chromatography on silica gel.[11,12] The symmetrical bis-porphyrin **12** was also prepared to serve as reference compound for the electrochemical and spectroscopic studies (Chart 1). Again, the metallation of the bis free base porphyrin **10** with tin(II) chloride gave the tin(IV) porphyrin dimer **12** in which the two triple bonds adjacent to the porphyrin were also transformed into double bonds (see ESI†). This is clearly evidenced by the $^1H$ NMR spectrum in which the

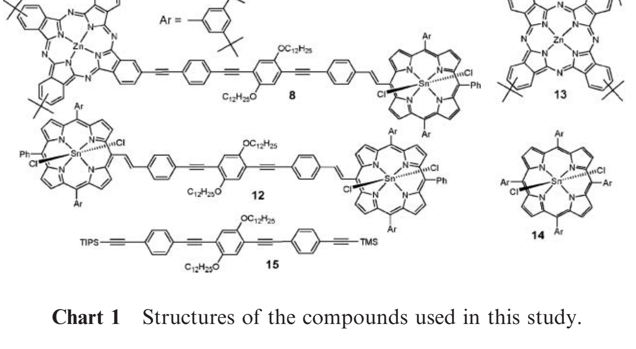


**Chart 1** Structures of the compounds used in this study.

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signals of the ethylenic protons came out as two doublets with a 16 Hz coupling constant and with chemical shifts that are in agreement with those of porphyrinic systems linked at the *meso* position with ethylenyl groups.[6,13] The mass spectrometric analyses of **8** and **12** also agreed with the reduced system.

The visible absorption spectra of dyad **8** can be well reproduced by a linear combination of the spectra of references **3** and **12** (Fig. 1). This indicates that the electronic properties of the porphyrin (SnP) and phthalocyanine (ZnPc) units are not significantly perturbed by each other. On the other hand, the presence of the OPE bridge reduces the symmetry of the SnP and ZnPc units and leads to a conjugated π-system involving the bridge. This results in red-shifted and broadened absorption bands, as compared to compounds **13** and **14** (Fig. S1†), and a split of the ZnPc Q-bands. Similar effects have been reported for phthalocyanines or porphyrins connected to a π-conjugated unit *via* a triple bond.[5,9,14] In coordinating solvents such as PhCN or pyridine, the spectra are well-resolved with narrow absorption bands and their intensities follow the Beer–Lambert law, indicating the absence of intermolecular interactions at low concentrations (below $10^{-6}$ $M^{-1}$).

The redox potentials of the dyad **8** in $CH_2Cl_2$ were determined by square wave voltammetry.[3,15,16] ZnPc is a good electron donor since its half-wave $ZnPc^+$/ZnPc-potential is found at 0.46 V *vs.* SCE. The bridge is oxidized at 1.3 V but its reduction occurs outside the solvent potential window ($E_{red} < -1.6$ V). SnP is a moderately good electron acceptor with a half-wave SnP/$SnP^-$-potential located at −0.82 V *vs.* SCE in dyad **8**. From these data and the spectroscopically determined excited state energies, the reaction driving force in PhCN was calculated as $\Delta G^\circ = -0.66$ eV for photoinduced charge separation from $^1$ZnPc and $\Delta G^\circ = -0.81$ eV from $^1$SnP.[17] The absorption spectra of the radical cation of ZnPc and of the radical anion of SnP were recorded by spectroelectrochemistry using the reference compounds **3** and **12**. The electrochemical reduction of SnP in **12** shows a spectrum featuring a bleaching of the Soret and the Q-bands and the appearance of a broad band between 650 nm and 850 nm (Fig. S2†). Upon oxidation of ZnPc, there is a strong bleaching of the Q-band at 700 nm and a modest one for the Soret band at 350 nm. New absorption bands build up between 470–600 nm and between 750–900 nm (Fig. S3†). These characteristics are in excellent agreement with the spectra of $SP^{-\bullet}$ and $ZnPc^{+\bullet}$ published previously.[15,16]

Selective excitation of the ZnPc Q-band was achieved by using 680 nm light, while 440 nm light selectively excited SnP in the Soret band. The steady-state fluorescence spectrum of the dyad **8** in PhCN showed a strong quenching of both $^1$ZnPc and $^1$SnP emission relative to the corresponding reference compounds (**3** and **12**) (Fig. S4†). Time resolved emission measurements of the dyad **8** showed a main lifetime component of less than 40 ps for both $^1$ZnPc and $^1$SnP, followed by slower components attributed to impurities. The main lifetimes of **8** are significantly shorter than those observed for **12** ($\tau_{^1ZnPc} = 2.2$ ns) and **3** ($\tau_{^1SnP} = 0.45$ ns).

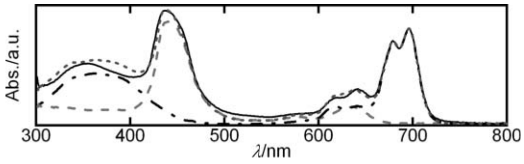

**Fig. 1** Spectra of dyad **8** (unbroken line) along with those of **3** (dashed-dotted line) and **12** (dashed line) recorded in PhCN. The dotted line is a linear combination of the spectra of **3** and **12**.

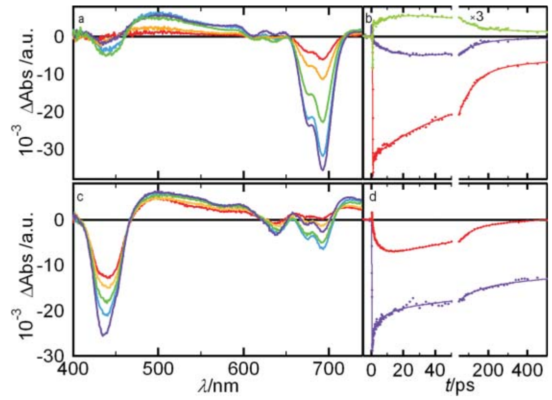

**Fig. 2** Transient absorption of dyad **8** in PhCN. The plot in (a) corresponds to excitation at 680 nm and that in (c) to an excitation at 440 nm. The delay times are 1 ps (purple), 10 ps (blue), 50 ps (green), 200 ps (orange) and 1000 ps (red). Plots (b) and (d) correspond to the kinetic traces at 440 nm (purple), 690 nm (red) and 730 nm (green, multiplied by 3 for clarity) for the respective excitations.

To further investigate the fast deactivation processes occurring in the dyad **8**, femtosecond transient absorption spectroscopy experiments were undertaken in PhCN. Upon excitation at 680 nm $^1$ZnPc is formed which rapidly decays to the charge separated state. This can be clearly seen from the SnP ground state Soret bleach that grows in with a 13 ps time constant, while most of the phthalocyanine bleach remains (Fig. 2a). At the same timescale there is a rise around 730 nm, due to the broad absorption band of $SnP^-$ and $ZnPc^+$ in that range (Figs. S5–6†). The transient spectra of both excited and radical states of porphyrins are often very similar, and the same is true for phthalocyanines. Nevertheless the observed spectrum ascribed to the charge separated state agrees well with simulated spectra constructed from the spectroelectrochemistry of oxidized **3** and reduced **12** (Fig. S7†). The spectrum is dominated by the bleach of *both* the SnP Soret band and the ZnPc Q-band. These two signals disappear with the same time constant ($\tau = 85$ ps), consistent with charge recombination (Fig. 3).

Excitation in the SnP Soret band at 440 nm results in a very short-lived $S_2$-state ($\tau_{IC} < 1$ ps in **12**), which undergoes internal conversion to the $S_1$-state. The latter is rapidly quenched ($\tau = 4$ ps)

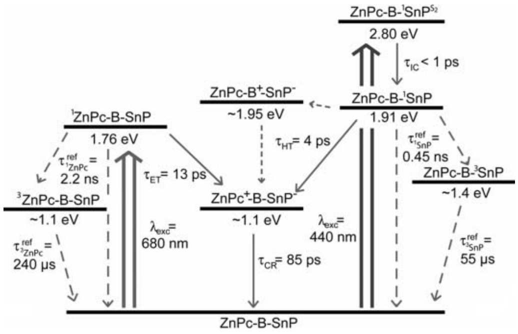

**Fig. 3** Summary of the relevant states and transitions (in PhCN[17]).

by a process that results in a bleach growing in around 690 nm, corresponding to the ZnPc Q-band (Fig. 2c). This process is ascribed to hole transfer from the $^1$SnP state, resulting in the same charge separated state as in the previously described electron transfer. The partial bleach recovery of the SnP Soret band is consistent with a smaller net bleach of the SnP$^-$-radical compared to $^1$SnP (Fig. S2, S5†). Recombination to the ground state occurs with the same time constant (85 ps) regardless of which chromophore is initially excited, further strengthening the conclusion that it is the same charge separated state.

Energy transfer from the $^1$SnP to $^1$ZnPc is energetically possible, but can be excluded since the subsequent charge separation from $^1$ZnPc is slower ($\tau_{ET}$ = 13 ps) than the observed decay of $^1$SnP. Thus a distinct intermediate state, with a 13 ps transient absorption component, would have been seen. There is also a fraction of the sample that is not quenched. The behaviour of this fraction is very similar to that observed in references **3** and **12**, starting with a singlet signal that over time evolves into a triplet that subsequently decays back to the ground state, on similar timescales (Fig. S4†). With 440 nm excitation, sample degradation during measurements made this component large, as seen by the significant porphyrin bleach remaining at 1000 ps (Fig. 2c).

Electron transfer from $^1$ZnPc has to proceed through the direct super-exchange mechanism,[18] as the bridge is too difficult to reduce for electron hopping to occur. Although similarly rapid single step charge transfer has been reported for dyads containing porphyrins or phthalocyanines with a direct ethynyl linkage,[8,9] there is to our knowledge no system with similar rates over a comparably long distance (34 Å, centre-to-centre). Studies of long-range electron transfer in similar systems, where the bridge binds to the porphyrins *via* a *meso*-phenyl unit, report rates that are two orders of magnitude slower than those reported here.[19]

Starting from $^1$SnP, a hole-hopping mechanism *via* a transiently oxidized bridge is energetically feasible (Fig. 3). Thus, it is conceivable that the very rapid charge separation ($\tau_{HT}$ = 4 ps) is due to a hopping mechanism, while the subsequent charge recombination can only occur *via* a long-range super-exchange mechanism and is therefore 20-fold slower. This is an interesting design principle for achieving rapid, long-range charge separation *via* transient states without losing energy in the intermediate steps, as is done in a conventional multi-step, exergonic charge separation approach demonstrated in triads and tetrads *etc.*[1,20] The close similarity in transient spectra and lifetime of the reference **12** to a simple SnP unit shows that the B$^+$–SnP$^-$ state lies higher in energy than the $^1$SnP state, as suggested in Fig. 3. The predicted activation energy for hopping and super-exchange are both very small so that temperature-dependent measurements would not be able to safely distinguish these mechanisms.[21] Instead further studies with new compounds, modifying the relative energy of the bridge state, are required to explore this interesting possibility.

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