Controlling energy and charge transfer in linear chlorophyll dimers†

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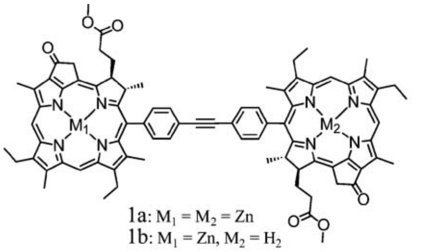
Received (in Cambridge, UK) 1st June 2007, Accepted 20th July 2007
First published as an Advance Article on the web 14th August 2007
DOI: 10.1039/b708318a

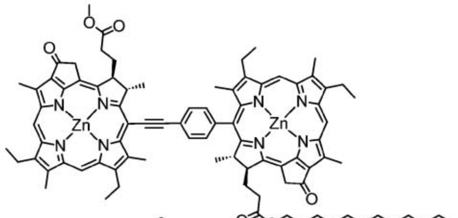
A series of linkers constructed from combinations of phenyl and ethynyl groups is shown to permit ultrafast energy transfer between two chlorophylls, while allowing control over radical cation migration between them.

The ability of chlorophylls (Chls) to act as donors *and* acceptors of both energy and charge in natural photosynthetic systems makes the incorporation of these molecules into artificial photosystems highly desirable. Artificial photosynthetic systems often require covalent linkages between their component chromophores and/or redox partners, so considerable effort has been devoted to understanding how through-bond energy and charge transfer occurs.[1] In studies where metalloporphyrins serve as the chromophore/redox centers, particular attention has been paid to understanding the effect of tetrapyrrole electronic structures on the rates of through-bond energy and charge transfer. We recently reported on a series of covalently-linked Chl trefoil systems in which the chromophores are connected to a central benzene scaffold either through a phenylethynyl linkage or directly with an ethynyl linkage.[2] Our results on the singly oxidized Chl trefoils suggested that sharing of the radical cation between the Chls in the trefoils on the ENDOR timescale is inhibited by the decrease in orbital overlap between the Chls resulting from the direct phenyl linkages. In order to deconvolute the effects of the direct phenyl linkage from the increased distances between the chromophores provided by the phenylethynyl linker, we now present data on a set of linear Chl dimers that shows how the detailed positioning of a phenyl spacer can be used to control charge sharing between Chls. The ability to control charge movement in multiple Chl systems is important for developing artificial photosynthetic systems.

Molecule **1a** was synthesized from methyl 3-ethyl-20-(4′-aminophenyl)-pyropheophorbide *a*[3] *via* a modified Sandmeyer reaction,[4] producing the 20-(*p*-iodophenyl)-derivative, followed by a copper-free Sonogashira coupling to zinc methyl 3-ethyl-20-(4′-ethynylphenyl)-pyrochlorophyllide *a* in DMF/Et_3N at room temperature.[2] Molecule **2** resulted from the direct Sonogashira coupling between zinc 2-octyl-1-dodecyl 3-ethyl-20-(4′-ethynylphenyl)-pyrochlorophyllide *a*[1] and methyl 20-bromo-3-ethylpyropheophorbide *a*,[5] and molecule **3** was the result of analogous coupling between zinc methyl 3-ethyl-20-ethynyl-pyrochlorophyllide *a* and 1,4-dibromobenzene.



1a: $M_1 = M_2 = Zn$
1b: $M_1 = Zn, M_2 = H_2$



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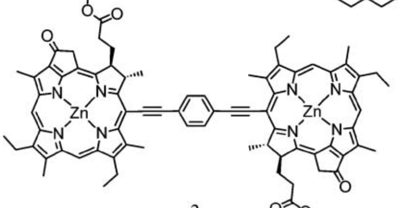

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The ground state absorption spectra of compounds **1a–3** in THF are compared to those of zinc methyl 3-ethyl-20-phenyl-pyrochlorophyllide *a* (ZCPh) and zinc methyl 3-ethyl-20-phenyl-ethynyl-pyrochlorophyllide *a* (ZCEPh) in THF in Fig. 1.[2,3] The spectrum of **1a** is nearly identical to that of ZCPh, with the Soret band at 430 nm and the Q bands at 577, 614 and 655 nm. The spectrum of **2** is essentially the linear combination of the spectra of

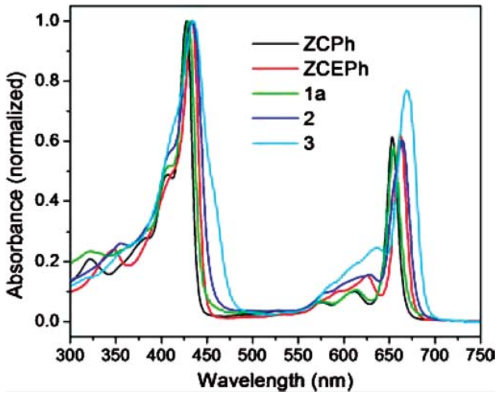

Fig. 1 Ground state absorption spectra of the Zn Chl derivatives in THF.

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† Electronic supplementary information (ESI) available: Details of synthesis and characterization, additional transient absorption data, and DFT atomic coordinants. See DOI: 10.1039/b708318a

ZCPh and ZCEPh. The overlapping Soret bands and $Q_y(0,0)$ bands are centered around 434 and 664 nm, respectively, with the remaining Q bands filling in between 550–640 nm. The similarity of the absorption spectra of **1a** and **2** to the spectra of their component chromophores indicates that relatively weak electronic coupling exists between the chromophores in these two dimers. The absorption spectrum of **3**, however, is noticeably different from the monomer ZCEPh. Both the Soret and Q bands are broadened and red shifted relative to those of ZCEPh. In addition to spectral shifting, the amplitude of the $Q_y(0,0)$ band is enhanced relative to that of the Soret band. This red-shift and increase in amplitude is indicative of further reduction of the electronic symmetry within both component chromophores and electronic delocalization along the long axis of the dimer.[6]

Excitation of **1a** in THF with 655 nm, 120 fs laser pulses yields transient absorption spectra of its lowest excited singlet state, ^{1*}**1a**, Fig. 2. Ground state bleaching of the $Q_y(0,0)$ band occurs at 660 nm, while ^{1*}**1a** exhibits broad absorption between 437 and 642 nm with local maxima occurring at 465, 504, 550, 590, and 632 nm. Stimulated emission from ^{1*}**1a** can be detected as the bleach centered around 726 nm. These spectra decay biexponentially with τ = 1.0 ± 0.2 ps and 3.7 ± 0.1 ns. Excitation of **2** in THF with 665 nm, 120 fs laser pulses yields transient absorption spectra of ^{1*}**2**, Fig. S1†. These spectra are very similar to those for **1a** with ground state bleaching at 667 nm, broad absorption between 451 and 649 nm and stimulated emission centered around 731 nm. The decay of ^{1*}**2** is biexponential with τ = 0.8 ± 0.1 ps and 3.6 ± 0.1 ns. Finally, excitation of **3** in THF with 665 nm, 120 fs laser pulses yields transient absorption spectra of ^{1*}**3**, Fig. S2†. These spectra are very similar to those for both **1a** and **2** with ground state bleaching at 455 and 667 nm, absorption between 472 and 655 nm (local maxima at 520, 591, 624 and 649 nm) and stimulated emission centered around 749 nm. Again, the decay of ^{1*}**3** is biexponential, this time with τ = 0.8 ± 0.2 ps and 3.2 ± 0.1 ns. The 3–4 ns components in the transient absorption kinetics of ^{1*}**1a**–^{1*}**3** match their fluorescence lifetimes in THF measured using an apparatus having a 20 ps instrument response time (Fig. S3–S5†).

The amplitudes of the picosecond components in the decays of ^{1*}**1a**, ^{1*}**2**, and ^{1*}**3** are laser power dependent and indicative of singlet–singlet annihilation, insets to Fig. 2, S1, and S2†, respectively. Assuming annihilation is the result of exciton transfer between adjacent chromophores, the time constant for exciton hopping (τ_h) within the dimers is simply twice the annihilation lifetime, τ_a. Using the measured values of τ_a, the values of τ_h for **1a**, **2**, and **3** were determined to be 2.0 ± 0.2 ps, 1.6 ± 0.1 ps, and 1.6 ± 0.4 ps, respectively. This approach for determining exciton hopping rates in the dimers was verified by preparation of **1b** having one Chl and one free-base pheophorbide (Pheo). Since the lowest excited singlet state of Pheo is lower in energy than that of Chl, selective excitation of the Chl with 656 nm, 120 fs laser pulses resulted in singlet–singlet energy transfer to Pheo with τ = 5.5 ± 0.5 ps, Fig. S6†. This lifetime is less than a factor three longer than that obtained for **1a** using τ_a. Although we do not expect the energy transfer rates for **1a** and **1b** to be identical because they are not chemically equivalent, this result shows that the annihilation analysis is reasonable.

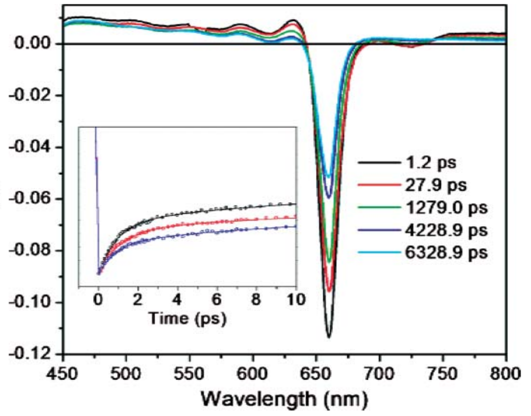

Fig. 2 Transient absorption of **1a** in THF following excitation with 655 nm, 120 fs laser pulses. Inset: power dependent transient absorption kinetics of **1a** monitored at 657 nm using 1.00 (black circles), 0.66 (red circles) and 0.33 (blue circles) μJ per 655 nm excitation pulse.

Previous measurements[2] involving the related trefoil Chl systems revealed that energy transfer between the covalently linked Chls occurred, at least in part, *via* the through-bond, Dexter mechanism as evidenced by the disparity between the observed energy transfer rates and those calculated for the through-space, Förster type mechanism.[7] The Dexter mechanism also contributes to energy transfer in the Chl linear dimers as the calculated Förster energy transfer rates for **1a** (13.1 ps)$^{-1}$, **2** (2.4 ps)$^{-1}$ and **3** (5.3 ps)$^{-1}$ again predict through space energy transfer should occur more slowly than what is observed in these systems.

Charge transport within the Chl dimers was studied by characterizing the radical cations of singly oxidized dimers using ENDOR spectroscopy. Solutions of **1a**$^{+\bullet}$–**3**$^{+\bullet}$ (2–5 × 10^{-4} M) in CH_2Cl_2 : THF (9 : 1)[8] were generated by addition of an acetonitrile solution containing I_2 and $AgClO_4$ to solutions of **1a**–**3**. The oxidation of **1a**–**3** was monitored using UV-vis spectroscopy to maximize the production of singly oxidized species (Fig. S7–S9†). Oxidized samples were loaded into quartz tubes and sealed under vacuum, following successive freeze–pump–thaw cycles. EPR and ENDOR[9] spectra were acquired at 250 K using a Bruker E-580 spectrometer fitted with an EN801 resonator, and an RF power amplifier (ENI A–500). The baseline of each ENDOR spectrum was corrected with a polynomial fit. The EPR spectra of **1a**$^{+\bullet}$–**3**$^{+\bullet}$ are inhomogeneously broadened into single unresolved lines due to the large number of electron–nuclear hyperfine interactions within each molecule. In such cases, ENDOR spectroscopy has been shown to provide a substantial improvement in spectral resolution of the hyperfine splittings of tetrapyrrole macrocycle radical cations.[10] The proton ENDOR spectra of **1a**$^{+\bullet}$–**3**$^{+\bullet}$ at 250 K each exhibit four line pairs with average isotropic hyperfine splittings of 7.7, 6.7, 3.4 and 0.5 MHz, Fig. 3, Table S1†. The similar hyperfine splittings for **1a**$^{+\bullet}$, **2**$^{+\bullet}$, and ZCPh$^{+\bullet}$ indicate that the radical cation is localized on a single chlorophyll in both dimers. Slight differences between the spectra of ZCPh$^{+\bullet}$ and those of dimers **1a**$^{+\bullet}$ and **2**$^{+\bullet}$ are indicative of the minor effect of the ethynyl linkages at the *para* position of the ZC phenyl group. The more significant differences between the hyperfine splittings of **2**$^{+\bullet}$ and ZCEPh$^{+\bullet}$ indicate that the radical cation in **2**$^{+\bullet}$ is localized on the ZC with the direct phenyl linkage and not the ZC with the direct ethynyl linkage. Cyclic voltammetry performed on ZCEPh and ZCPh, in butyronitrile with 1.0 M $n\text{-}Bu_4N^+BF_4^-$ and ferrocene/ferrocenium (Fc/Fc$^+$, 0.52 *vs.* SCE)

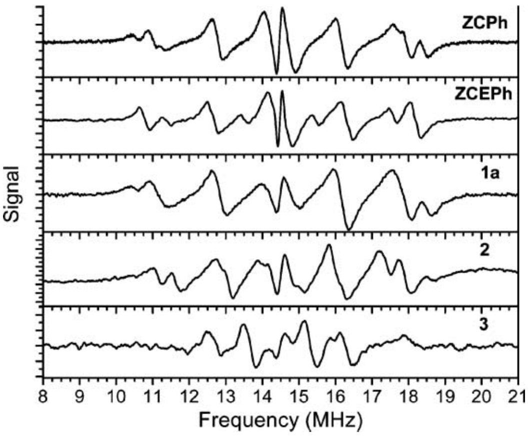

Fig. 3 Proton ENDOR spectra of $\mathbf{1a}^{+\bullet}$, $\mathbf{2}^{+\bullet}$ and $\mathbf{3}^{+\bullet}$ in DCM/THF (9 : 1) at 250 K. The proton ENDOR spectra of ZCPh$^{+\bullet}$ and ZCEPh$^{+\bullet}$ are also shown for reference. Microwave power was 63 or 100 mW; RF power was 230–400 W across the spectral window; frequency modulation depth was 50 or 100 kHz.

as an internal standard, reveals ZCEPh is 0.05 V harder to oxidize than ZCPh (0.71 and 0.66 V *vs.* SCE, respectively). While both chromophores can be oxidized by the I_2/$AgClO_4$ solution, ZCPh$^{+\bullet}$ is thermodynamically favored. The proton ENDOR spectrum of $\mathbf{3}^{+\bullet}$ at 250 K exhibits four line pairs with hyperfine splittings corresponding to those of ZCEPh reduced by a factor of two, indicating that, on the ENDOR timescale ($>10^7$ Hz), the unpaired electron is shared between *both* Chls in the dimer. The incidence of sharing between ethynyl-linked chlorophylls in $\mathbf{3}^{+\bullet}$ and the absence of sharing in the phenyl-linked $\mathbf{1a}^{+\bullet}$ and $\mathbf{2}^{+\bullet}$, confirms that the direct ethynyl linkage is responsible for cation sharing between chlorophylls on the ENDOR timescale. The distance dependence of charge transfer is ruled out as a factor given the distance between non-sharing chromophores in **2** is shorter than that between chromophores in the charge-sharing **3**.

In order to better understand the charge sharing within ethynyl-linked chlorophylls, the charge density distributions of the HOMOs of ZCPh$^{+\bullet}$ and ZCEPh$^{+\bullet}$ were obtained from DFT calculations performed with the Perdew–Wang 1991 nonlocal functional[11] and the 6-31G* basis set, Fig. 4. The electron density distributions within the HOMOs of ZCPh$^{+\bullet}$ and ZCEPh$^{+\bullet}$ indicate that both HOMOs maintain a_2 symmetry, which appear as mixtures of the distributions characteristic of metalloporphyrin a_{1u} and a_{2u} orbitals.[12] However, the HOMO of ZCEPh$^{+\bullet}$ shows charge density extending out of the macrocycle core, through the ethynyl linkage, and onto the terminal phenyl. The HOMO of ZCPh$^{+\bullet}$ shows only a slight presence of charge density on the phenyl carbon directly attached to the macrocycle. The difference in HOMO charge density distributions is due to the difference in orbital overlap between the chlorophyll and the linker functionality. In ZCPh$^{+\bullet}$, the dihedral angle between the phenyl ring and the chlorophyll macrocycle is 75°, which results in mediocre orbital overlap. The orbital symmetry of the ethynyl linkage in ZCEPh$^{+\bullet}$ provides optimal orbital overlap given the steric bulk of the attached chlorophyll.

Both ethynyl and phenyl groups provide for the rigid incoporation of chlorophyll into photoactive materials. The ability of these linkers to control whether the chromophores efficiently exchange both energy and charge or energy alone, allow these Chl derivatives to be tailored for different specific functions within artificial photosynthetic systems for solar energy conversion.

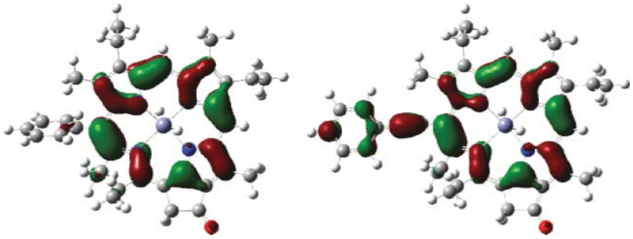

Fig. 4 The HOMOs of ZCPh$^{+\bullet}$ (left) and ZCEPh$^{+\bullet}$ (right) determined by DFT (PW91/6-31G*).

This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, DOE under grant No. DE-FG02-99ER14999. We thank Dr Ralph Weber (Bruker-Biospin, Inc.) for assistance with ENDOR experiments. M.J.T. acknowledges the donors of the American Chemical Society Petroleum Research Fund for partial support of this research.

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