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Acceleration of the through space S_1 energy transfer rates in cofacial bisporphyrin bio-inspired models by virtue of substituents effect on the Förster *J* integral and its implication in the antenna effect in the photosystems†

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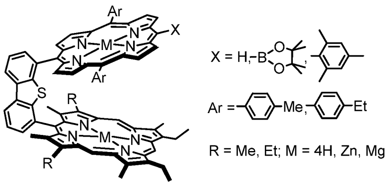
The singlet k_{ET} for cofacial β-octaalkylporphyrin/bis(*meso*-aryl)-porphyrin dyads increases linearly with the gap between the donor–acceptor 0–0 fluorescence peaks at 77 K.

Through space singlet energy transfer is one of the basic photophysical processes in the antenna effect (*i.e.* energy migration) in photosynthesis.[1] The theory explaining long distance singlet energy transfers was elaborated by Förster in the 1950's.[2] The singlet energy transfer rate, $k_{ET}(S_1)$, is found to be a function of the donor–acceptor distance (r), as $1/r^6$, their relative orientation of their dipole transition moments, κ^2, and on the spectral overlap between the donor fluorescence and the acceptor absorption band, also called the *J* integral. Osuka and collaborators demonstrated a quasi-linear relationship between $k_{ET}(S_1)$ and κ^2 (more accurately presented as κ^2/r^2).[3] Recently, we demonstrated the key role of the donor–acceptor distance in both through space $k_{ET}(S_1)$ and in $k_{ET}(T_1)$ cofacial *etio*-porphyrin free base (acceptor)/metal(II)-*etio*-porphyrin (donor) dyads (metal = Zn, GaOMe, Pd, Pt) held by different rigid spacers.[4] The increase in distance expectedly led to a steady decrease in $k_{ET}(S_1)$ but the plot of $k_{ET}(S_1)$ *vs* $1/r^6$ showed that two mechanisms took place; Förster[2] and Dexter.[5] To the best of our knowledge, no experimental report exists on relating this basic parameter (the *J* integral), even qualitatively, with $k_{ET}(S_1)$. The main reason for this important lack is that the exact absorbance contribution of the donor under the "donor + acceptor" spectral envelope is hard to establish with accuracy. However we find easy to demonstrate that the relative amplitude of the *J* area (spectral overlap between the donor fluorescence and that for the acceptor absorption band) is qualitatively but directly related to the wavelength difference between both the 0–0 absorption and fluorescence peaks of the donor and the acceptor. This 0–0 gap also represents the S_1–S_1 energy difference that is also proportional to the *J* integral. A qualitative demonstration for this relationship is given in the ESI† for convenience.

We now wish to report the dependence of $k_{ET}(S_1)$ on the S_1–S_1 energy gap for a series of dyads composed of an octa-β-alkylporphyrin (donor) and a bis-*meso*-arylporphyrin (acceptor), Scheme 1. The change of the 0–0 position is achieved using various substituents and metal atoms.

The synthesis of the target dyads **7**, **7Zn** and **7Mg** is achieved *via* the synthesis of **5**, a suitable synthon for C–C Suzuki coupling (Scheme 2; see ESI† for the experimental details).

First, bis(*meso*-tolyl)porphyrin **1** reacts with an excess of mesityl-lithium (10 eq.), then hydrolyzed and oxidized by DDQ to afford **2**, which is isolated in 45% yield after column chromatography. The subsequent bromination followed by metalation yields **4** in a nearly quantitative yield. The Suzuki–Miyaura cross-coupling[6] of **4** with pinacolborane affords **5**, which further reacts with 1.5 equivalent of **6Zn** in a toluene/DMF mixture in the presence of Cs_2CO_3 and of a catalytic amount of $Pd(PPh_3)_4$ providing **7Zn** in 66% yield. The demetalation of **7Zn** in acidic solution affords **7**. The Mg insertion proceeds easily in the presence of NEt_3 with an excess of $MgBr_2{\cdot}OEt_2$ in CH_2Cl_2.[7] The desired dyads **7**, **7Zn**, and **7Mg** were characterized by ^1H NMR, UV-vis and HRMS spectroscopy. Noteworthily, **7Mg** was isolated as a solvated adduct as evidenced by ^1H NMR and mass spectra (ESI†) showing the presence of coordinated water. This compound undergoes the undesired demetalation upon removal of the coordinating solvent, and consequently was studied as such. The synthesis



Scheme 1

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† Electronic supplementary information (ESI) available: Experimental details of the syntheses, measurements and the relation between *J* and the S_1–S_1 energy gap. See DOI: 10.1039/c1cc12839f

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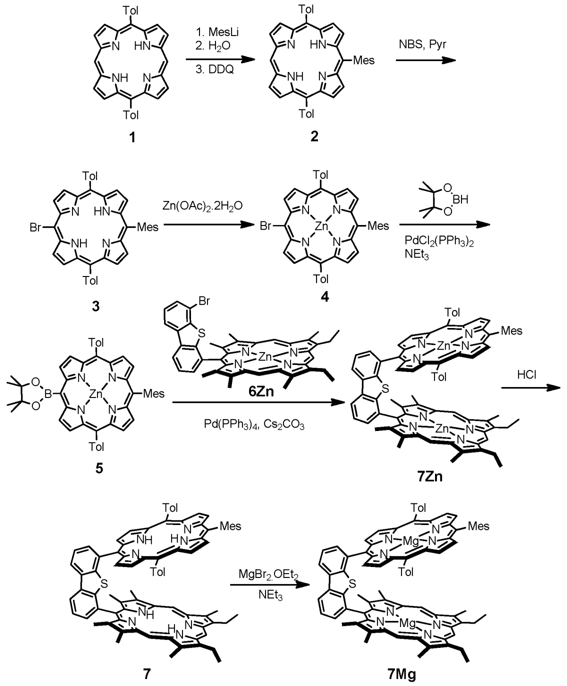
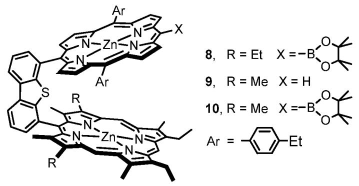


Scheme 2 General reaction paths.

of **8**, **9** and **10** (Scheme 3) proceeds similarly and will be reported in due course.

Typical examples of absorption, excitation and fluorescence spectra are shown in Fig. 1. The rest of all other spectra as well as spectroscopic and photophysical data are provided in the ESI.† The assignment of the donor–acceptor role is established from the position of the 0–0 peaks, λ(0–0), observed in the absorption and fluorescence spectra. The fluorescence envelope exhibits both emissions from the donor (zinc(II)-octaalkylporphyrin) and the acceptor (zinc(II)bis(*meso*-arylporphyrin)) where the fluorescence intensity of the donor is sensitively weaker than that of the acceptor suggesting S_1 energy transfer. Unambiguous evidence for energy transfer arises from the good superposition of the excitation and absorption spectra, meaning that excitation in the donor absorptions leads mainly to the fluorescence of the acceptor.

The $k_{ET}(S_1)$ values are obtained using $k_{ET} = (1/\tau_F) - (1/\tau_F^o)$ where τ_F and τ_F^o are the fluorescence lifetimes of the donor in the presence and absence of an energy acceptor, respectively.[1] For τ_F^o, **6Zn**, **12** and **6Mg** (Scheme 4), where no acceptor is present, are selected. This is justified by the close similarity in τ_F^o between **11Zn**,[4] **12Zn**[4] and **6Zn** (this work), and between **11**[4] and **12**.[4] The very small effect (if any) of the non-radiative internal conversion and intersystem crossing is specific to the dibenzothiophene spacer. The $k_{ET}(S_1)$ values (Table 1) exhibit a quasi-linear dependence on the difference between the 0–0 fluorescence peaks of the donor and the acceptor, Δ (Fig. 2).



Scheme 3

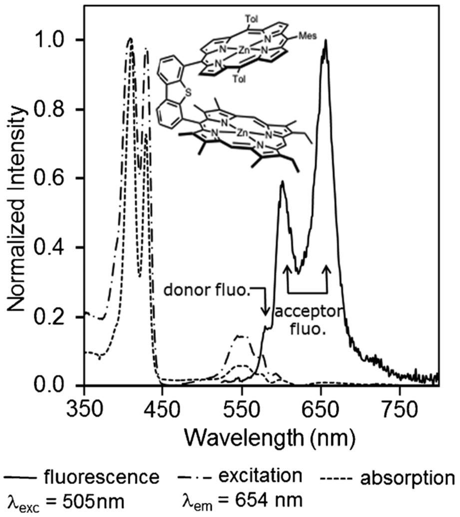
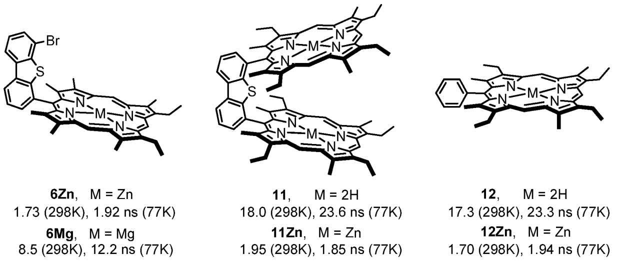


Fig. 1 Electronic spectra of **7Zn** in 2MeTHF at 298 K.



Scheme 4 τ_F^o data for **6Mg**, **6Zn**, **11–12** in 2MeTHF.

This linear trend is only depicted at 77 K and not at 298 K (ESI†) as the overall fluorescence intensity is weaker and that the absorption and fluorescence bands are broader at 298 K leading to larger uncertainties in the extraction of the position of the 0–0 peaks. This better defined trend at 77 K *vs.* 298 K was also previously observed by us for other cofacial dyads.[4] Moreover and perhaps having a more profound effect, the *meso*-substituted porphyrins exhibit flexibility about the dibenzothiophene/*meso*-substituted porphyrin C–C bond as recently shown for corrole-containing dyads,[8] leading to possible different conformations. Upon cooling to 77 K the lowest energy conformations are most likely to be obtained as indeed suggested in Fig. 2. Moreover, the linearity holds when the donor and the acceptor have very similar chemical structures.

This graph is very informative for two reasons. First, faster rate constants are obtained for larger Δ, and one can select the most appropriate substituents directed at accelerating the rate for energy transfer, here up to a factor of 3 (Table 1) by simply replacing H by a boronate group. Obviously, the rate constants should ultimately decrease again for larger values of Δ. Indeed, $k_{ET}(S_1)$ and Δ for the monometallic bis(*etio*-porphyrin) dyads at 77 K are 4.6 $(ns)^{-1}$ and 40 nm for M = GaOMe (donor), and 4.8 $(ns)^{-1}$ for M = Zn (donor) (the free base is the acceptor). These data points are similar to those for **8** and **10**, meaning that the maximum may be between a Δ of 30 and 40 nm.

Intuitively, nature would choose a given S_1–S_1 gap in order to maximize the rate constant *via* the maximization of

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Table 1 Fluorescence data in 2MeTHF at 77 K

Compounds[a]	Donor $\lambda(0\text{–}0) \pm 1$ nm	Accep. $\lambda(0\text{–}0) \pm 1$ nm	Δ^b	$\tau_F{}^c$ (donor)/ns	$\tau_F^{o\,d}$/ns	$k_{ET}{}^c/(\text{ns})^{-1}$
9 (6Zn)	576	594	18	0.47(7)	1.92	1.6(4)
7 (12)	623	644	21	0.32(4)	23.3	3.0(5)
7Mg (6Mg)	583	605	22	0.26(4)	12.2	3.8(4)
7Zn (6Zn)	576	600	24	0.24(3)	1.92	3.7(6)
8 (6Zn)	576	603	27	0.20(2)	1.92	4.5(5)
10 (6Zn)	574	602	28	0.18(1)	1.92	5.0(3)

[a] The numbers in parentheses are the reference molecules used to extract τ_F^o. [b] The uncertainties are ±2 nm. [c] The uncertainties are indicated in brackets. [d] ±0.3.

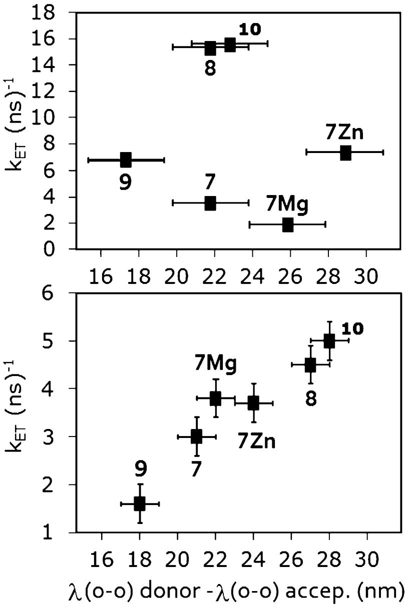

Fig. 2 Graph of Δ *vs* $k_{ET}(S_1)$ in 2MeTHF at 298 K (top) and 77 K (bottom). At 298 K, the uncertainties are the same as the box.

the *J* integral. For example, in the light harvesting complex LH2 of the purple photosynthetic bacteria, there is an efficient S_1 energy transfer (1.2 ps)[1] from B800 to B850 (composed of bacteriochlorophylls, and 800 and 850 means the position of the 0–0 peaks). This 50 nm gap means a better overlap between the donor fluorescence with the acceptor absorption. Again, this trend (Fig. 2) cannot go to infinity but it is noteworthy that the width of the porphyrin fluorescence band is ~100 nm (see Fig. 1). Second, since the *J* integral also plays an important role in $k_{ET}(S_1)$, using squeezed special pairs would further contribute to this effect since it is known that compressing the two macrocycles against each other induces an increase in the bandwidth and couplings.[9,10] Moreover, studies on supramolecular systems, where dynamics at the time scale of energy transfer have been shown to be important, have also been reported.[11] This work shows for the first time a dependence between $k_{ET}(S_1)$ and the position of the 0–0 fluorescence peaks or indirectly the S_1–S_1 energy gap between the donor and the acceptor, which is easily explained by the Förster theory based on the *J* integral. These observations also are found to be consistent with the universal conclusion that nature chooses her "ingredients" appropriately, including metals (Mg or Zn); substituents, and dimer formation (like the special pair in the reaction center) in order to maximize efficiency in $k_{ET}(S_1)$ as needed.

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