

Decoupling the artificial special pair to slow down the rate of singlet energy transfer

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Dedicated to Professor Emanuel Vogel in memoriam

Received 2 April 2012 Accepted 16 April 2012

ABSTRACT: Trimer **2**, composed of a cofacial heterobismacrocycle, octamethyl-porphyrin zinc(II) and bisarylporphyrin zinc(II) held by an anthracenyl spacer, and a flanking acceptor, bisarylporphyrin free-base (Ar = $-3,5-(tBu)_2C_6H_3$), has been studied by means of absorption spectroscopy, "steady state and time-resolved fluorescence" and fs transient absorption spectroscopy, and density functional theory (DFT) in order to assess the effect of decoupling the chromophores' low energy MOs on the rate of the singlet, S₁, energy transfer, k_{ET} , compared to a recently reported work on a heavily coupled trimeric system, Trimer **1**, [biphenylenebis(*n*-nonyl)porphyrin zinc(II)]-bisarylporphyrin free-base (Ar = $-3,5-(tBu)_2C_6H_3$). The position of the 0–0 peaks of the absorption and fluorescence spectra of Trimer **2** indicates that these porphyrin units are respectively energy donor 1, donor 2, and acceptor. The DFT computations confirm that the MOs of the cofacial donor 1-donor 2 dyad are decoupled, but significant MO coupling between donor 2 and acceptor 1 is still present despite the strong dihedral angle between their respective average planes (77.5°: geometry optimization by DFT). The fs transient absorption spectra exhibit a clear S₁–S_n fingerprint of the bisarylporphyrin zinc(II) chromophore and the kinetic trace exhibits a slow rise time of 87 ps, due to a S₁ donor 1 \rightarrow donor 2 ET. The transient species donor 2 and acceptor decay respectively in the short (~1.5) ns and 6 ns time scale.

KEYWORDS: singlet energy transfer, DFT computations, molecular orbital coupling, fs transient absorption spectroscopy.

INTRODUCTION

Nature has designed efficient photosystems allowing microorganisms such as photo-bacteria to survive under

particularly difficult environment due to scarcity of light [1]. In the photosynthetic membranes of these organisms, exciton (energy excitation migration), energy and electron transfers occur with impressing rates [1], and numerous research groups around the world attempted to design chemical models, which were recently reviewed by us [2]. One of the key components in both the natural and synthetic systems is the special pair [3, 4]. Moreover, the various parameters controlling the rates for singlet energy transfer, $k_{\rm ET}$, in a general sense, was detailed

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by Förster well over 60 years ago [5] and is generally expressed by Equation 1:

$$k_{\rm ET} = \frac{\Phi_{\rm F}^{\,\rm o}\,({\rm D})\kappa^{\,2}}{\tau_{\rm F}^{\,\rm o}\,({\rm D})r^{6}} \left(\frac{9000\,(\ln 10)}{128\,\pi^{5}{\rm n}^{4}{\rm Na}}\right) \frac{\int F_{\rm D}\left(\lambda\right)\varepsilon_{\rm A}\left(\lambda\right)\lambda^{4}{\rm d}\lambda}{\int F_{\rm D}\left(\lambda\right){\rm d}\lambda} \tag{1}$$

where $\tau_{\rm F}^{\circ}$ and $\Phi_{\rm F}^{\circ}$ are the fluorescence lifetime and quantum yield of the donor chromophore in the absence of energy transfer, r is the distance between the donor and acceptor, κ^2 is an orientation factor relating the relative orientation of the transition moment of the donor and acceptor taking values between 0 and 4, $F_{\rm D}(\lambda)$ and $\varepsilon_A(\lambda)$ are the fluorescence intensity of the donor and the absorptivity of the acceptor as a function of the wavelength λ , *n* is the refractive index and N_a is the Avogadro's number. The integral represents the overlap between the donor fluorescence and acceptor absorption and is called the J integral. Osuka and collaborators demonstrated a quasi-linear relationship between $k_{\rm ET}(S_1)$ and κ^2 (more accurately presented as κ^2/r^2) [6]. Recently, we demonstrated the key role of the donor-acceptor distance on both through space $k_{\text{ET}}(S_1)$ [7] and in $k_{\text{ET}}(T_1)$ [8] cofacial etio-porphyrin free-base (acceptor)/metal(II)etio-porphyrin (donor) dyads (metal = Zn, GaOMe, Pd, Pt) held by different rigid spacers. Moreover, we also demonstrated for the first time that indeed $k_{\rm ET}$ varies linearly with the J integral [9].

During the course of this research program on the design of bio-inspired models exhibiting ultrafast processes of both energy and electron transfers, we recently reported the synthesis and the photophysical behavior of an artificial special pair flanked with an antenna held together by a direct single bond (see Trimer 1 in Scheme 1) [10]. In this system, the flanking free-base and the cofacial bis(zinc(II)porphyrin) units play the role of the singlet energy donor and acceptor, respectively, for which only the acceptor fluorescence is observed appearing as a poorly resolved band. The kinetic investigation of the ET process by ultrafast (femtosecond) transient absorption spectroscopy showed

that $k_{\rm ET}$ was very fast ($k_{\rm ET} = (5.1 \text{ ps})^{-1}$) as observed in ET between the natural special pair and its neighboring antennas [2] (*i.e.* 2–3 ps time scale). The solvent polarity dependent fluorescence of Trimer **1** urged us to investigate the nature of the excited states using DFT (Density Functional Theory) computations. The resulting MOs showed an astonishingly heavy mixing of the atomic contributions distributed all over the three porphyrin units for practically all frontier MOs (see Supporting information). This important information suggests that three chromophores are strongly coupled and consequently, $k_{\rm ET}$ is faster.

In order to verify this hypothesis, a study of the effect of decoupling the chromophores on $k_{\rm ET}$ is necessary. This decoupling can be achieved by using two different chromophores for the cofacial bis(porphyrin) unit, notably a β - and a *meso*-substituted porphyrin. The mixing (or coupling) of different MO wavefunctions would be rendered more difficult for symmetry reasons. This modification would then automatically create another cofacial dyad and two rates may be depicted. Consequently, a second modification is necessary in order to hope for easy extraction of two distinct $k_{\rm ET}$'s. This is performed by replacing the biphenylene spacer in Trimer 1 (Scheme 1) with an anthracenyl for example, which increases the Cmeso-Cmeso separation between porphyrins in the cofacial dimer unit from 3.80 to 4.98 Å [7].

We now report a preliminary study of the partially decoupled Trimer **2** (Scheme 2), as addressed by DFT calculations, along with a kinetic study by ultrafast (femtosecond) transient spectroscopy. This work shows that an ET cascade process occurs where two $k_{\rm ET}$'s are extracted, 1.1×10^{10} and $\sim 0.03 \times 10^{10}$ s⁻¹ between two distinct chromophores, showing that there is indeed a MO decoupling. These $k_{\rm ET}$'s are also significantly weaker than that observed for Trimer **1** ((5.1 ps)⁻¹; $k_{\rm ET} = 20 \times 10^{10}$ s⁻¹ [10]) despite its strong structural similarity with Trimer **2**. This preliminary study supports the hypothesis that the Förster theory is intrinsically accompanied by couplings of the individual chromophores.



Trimer 1

Scheme 1. Structure of Trimer 1 ($R = nC_9H_{19}$; Ar = -3,5-(tBu)₂C₆H₃)



Trimer 2

Scheme 2. Structure of Trimer 2 (Ar = $-3,5-(tBu)_2C_6H_3$)

EXPERIMENTAL

Materials

Trimer 2 (zinc(II) 5-{8-[zinc(II)-10,20-bis-(3,5-di-*tert*-butyl-phenyl)-15-(10,20-bis-(3,5-di-*tert*-butylphenyl)porphyrin-5-yl)porphyrin-5-yl]-anthracen-1-yl} 2,3,7,8, 12,13,17,18-octamethylporphyrin), Dimer 2 (zinc(II) 5-{8-[zinc(II)-10,20-bis-(3,5-di-*tert*-butylphenyl)-15-(4,4,5,5-tetramethyl[1,3,2]dioxaborolan-2-yl) porphyrin-yl]-anthracen-1-yl}-2,3,7,8,12,13,17,18octamethyl-porphyrin) and Dimer 1 (zinc(II) 5-[10,20bis-(3,5-di-*tert*-butyl-phenyl)-porphyrin-5-yl]-10,20-bis-(3,5-di-*tert*-butyl-phenyl)-15-(4,4,5,5tetramethyl-[1,3,2]dioxaborolan-2-yl)-porphyrin) were prepared as previously described [11].

Absorption and luminescence measurements

UV-vis spectra were recorded in solutions using Varian Cary 50 spectrophotometer (1 cm path length quartz cell). Emission and excitation spectra were measured by using a double monochromator Fluorolog FL-1039 instrument from HORIBA Jobin Yvon. The fluorescence lifetimes were measured using the same instrument but equipped with TCSPC module for time-resolved measurements (interchangeable NanoLED pulsed laser-diodes as sources and TBX-04 photomultiplier tube as a detector were used). Emission quantum yields of the compounds were measured relative to the fluorescence of free-base tetraphenylporphyrin ($\Phi_f = 0.11$, [12]) in deoxygenated toluene. Sample concentrations were chosen to obtain an absorbance of 0.03-0.07, at least three measurements were performed for each sample. All the measurements were performed using deoxygenated (by Ar bubbling) freshly distilled tetrahydrofuran (THF).

Ultrafast transient absorption measurements

Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (780 nm, 2 mJ/pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS which has optical frequency mixers resulting in tunable range from 285 nm to 1660 nm, while the rest of the output was used for white light generation. Prior to generating the probe continuum, a variable neutral density filter was inserted in the path in order to generate stable continuum, then the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at 410 nm of TOPAS output, which is fourth harmonic

of signal or idler pulses, was chosen as the pump beam. As this TOPAS output consists of not only desirable wavelength but also unnecessary wavelengths, the latter was deviated using a wedge prism with wedge angle of 18°. The desirable beam was irradiated at the sample cell with a spot size of 1 mm diameter where it was merged with the white probe pulse in a close angle (< 10°). The probe beam after passing through the 2 mm sample cell was focused on a fiber optic cable that was connected to a CCD spectrograph for recording the time-resolved spectra (410-800 nm). Typically, 2500 excitation pulses were averaged for 5 s to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at room temperature, 295 K.

DFT computations

Calculations were performed with Gaussian 09 [13] at the Université de Sherbrooke with the Mammouth supercomputer supported by *Le Réseau Québécois De Calculs Hautes Performances*. The geometries of the molecules were optimized first and then utilized to perform the final [14–17] DFT and TD-DFT [18–20] B3LYP [21–23]/3–21g* [24–29] calculations. The calculated absorption spectra and related MO contributions were obtained from GaussSum 2.1 [30].

RESULTS AND DISCUSSION

Synthesis

The synthesis of Trimer¹ was previously described [11] and recently reviewed [31]. Only the key points are presented here. The synthetic approach can be divided into two parallel strategies and is based on the Suzuki coupling as illustrated in Scheme 3.

This approach requires the use of 5-bromo-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin zinc(II), Monomer **3** [32, 33], 5,15-di-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-(3,5-di-*tert*-butylphenyl)porphyrin zinc(II), Monomer **1** [34], and 5-(8bromo-anthracen-1-yl)-2,3,7,8,12,13,17,18octamethylporphyrin zinc(II), Monomer **2**. Indeed, the Suzuki coupling of **1** with either the bromo-derivatives Monomers **2** and **3** gives Dimers **2** and **1**, respectively, in reasonable yields. Then, by subjecting Dimer **1** with Monomer **2**, and Dimer **2** with Monomer **3**, the same desired target Trimer **2** is obtained.

Demonstration of decoupling of the building blocks

Prior to the photophysical study, the building block Dimer 2 was qualitatively tested for interchromophore couplings. This testing was achieved by DFT computations and analyzing the frontier MOs from



Scheme 3. Two synthetic strategies to access target Trimer 2 (Ar = $-3,5-(tBu)_2C_6H_3$)

LUMO+3 to HOMO-3. These are provided in the SI as examples. These representations show no or almost no atomic contribution from the second chromophore and all the atomic contribution is concentrated on the macrocycle demonstrating clearly that the use of two different cofacial chromophores, here specifically using β - and *meso*-substituted macrocycles, along with elongating the separation a little is enough to decouple the system. This result contrasts with the computations obtained for Trimer **1** where heavy coupling was noted (these MOs are also placed in the SI for convenience). This rather

strong coupling was also experimentally confirmed by fluorescence spectroscopy where a charge transfer fluorescence was noted [10]. Due to DFT computations Trimer **2** exhibits no coupling between the two cofacial porphyrin zinc(II) macrocycles. However, a strong coupling is still calculated between the two *meso–meso* bonded bisarylporphyrin zinc(II) and bisarylporphyrin free-base fragments, particularly for the lowest energy MOs (Fig. 1). The individual contributions listed in Table 1 show that the fraction coming from the *meso–meso* bisarylporphyrin zinc(II)-bisarylporphyrin free-base unit

Table 1. Quantitative individual contributions of each fragments building Trimer 2^{a}

Fragment	MOs								
	HOMO-3	HOMO-2	HOMO-1	НОМО	LUMO	LUMO+1	LUMO+2	LUMO+3	
aryl substituents	2.07	11.29	2.41	3.67	11.75	2.31	2.79	12.10	
bisarylporphyrin zinc(II)	69.70	47.52	0.52	0.12	21.69	15.87	76.24	65.20	
octamethylorphyrin zinc(II)	0.54	0.37	90.50	94.80	0.09	0.08	0.11	0.08	
bisarylporphyrin free-base	20.40	38.47	0.89	0.09	66.24	81.00	15.79	21.85	
anthracenyl	7.29	2.35	5.68	1.32	0.23	0.74	5.07	0.77	
TOTAL	100	100	100	100	100	100	100	100	

^aThe fragments exhibiting more than 15% of the total contribution are put in bold.



HOMO; -0.1677



HOMO-1; -0.1745



HOMO-2; -0.1765



HOMO-3; -0.1795



LUMO; -0.0783



LUMO+3; -0.0692

Fig. 1. MO representations after geometry optimization of the frontier MOs for Trimer 2. The dihedral angle between the planes formed by bisarylporphyrin zinc(II) bisarylporphyrin free-base is 77.5° . This angle is 85.2° in Trimer 1

represents 85% or more of the total for the four first lowest empty orbitals along with HOMO-3 and HOMO-2. Some smaller residual contributions from the aryl substituents (which belong to the bisarylporphyrin zinc(II)-bisarylporphyrin freebase unit) and the anthracenyl are also computed. All in all, these calculations indicate that the bisarylporphyrin zinc(II) and bisarylporphyrin free-base units are electronically coupled, but the octamethylporphyrin zinc(II) is not coupled with the bisarylporphyrin free-base. This result greatly contrasts with the DFT computations reported for the Trimer **1** [10] where all three chromophore were heavily coupled (see also the SI).

Absorption and emission spectra

The role of the singlet energy donor and acceptor is assigned on the basis of the position of the 0-0 peaks in the absorption and emission bands reliably identifiable in the spectra (Fig. 2; Table 2). From the fluorescence spectra, the shoulder at 580 nm is indicative of the octamethylporphyrin zinc(II) unit, whereas the peak at 608 nm (also closely placed to the 595 nm band in the absorption) is associated with the bisarylporphyrin zinc(II) fragment. Finally, the strong fluorescence bands at 650 and 655 nm for Dimer 1 and Trimer 2, respectively, is indicative of the presence of the free-base macrocycle. In Dimer 2, the 580 nm component is significant weaker than that for the 608 nm one. This is strongly suggestive of an efficient singlet energy transfer.

The monitoring of the excitation spectra as a function of the fluorescence wavelength shows the same features observed in the absorption spectra (Fig. 2), indicating that the excitation in any of the two chromophores results in probably a weak and a strong fluorescence from bisarylporphyrin zinc(II) unit and bisarylporphyrin free-base, respectively. The same conclusion is also made for Dimer 2 and Trimer 2. One of the resulting key features is that the signals at 580, 610 and 610 nm for Dimers 2 and 1, and Trimer 2, respectively, are all very weak, and the fluorescence lifetime measurements are difficult.

These spectral measurements indicate that Trimer **2** can be assigned as a cascade donor 1–donor 2-acceptor system (as octamethylporphyrin zinc(II), bisarylporphyrin zinc(II) and slightly different substituents; Ar = *p*-ethylbenzene, and 4 methyls have replaced by ethyls), the $k_{\rm ET}$ values are found in the 1.6×10^9 to 5.0×10^9 s⁻¹ regime (*i.e.* the bisarylporphyrin free-base, respectively) as illustrated in Fig. 3. In previous studies of our group on related compounds to Dimer **2** (using a different spacer,



Fig. 2. Top: UV-visible spectra. Bottom: fluorescence spectra. Middle: excitation spectra using different monitoring excitation wavelengths. Solvent, THF at 298 K



Fig. 3. Representations of the various singlet energy transfer pathways in Dimers 1 and 2, and Trimer 2 ($Ar = -3, 5-(tBu)_2C_6H_3$)

dibenzothiophene, and fluorescence lifetime of the donor ranges from 180 to 470 \pm 30 ps) [9]. Predictions are not possible for this portion of the triad but based on $k_{\rm ET}$ reported for Trimer 1 ((5.1 ps)⁻¹) [10], this rate may be very fast, but must be experimentally verified.

Energy transfer dynamics

Both Dimer 1 and Trimer 2 show common photophysical features arising from the free-base

unit ($\Phi_{\rm F} = 0.062$ and 0.070, $\tau_{\rm F} = 6.1$ and 7.1 ns, respectively) in argon bubbled solutions at 298 K. Figure 2 indicates that the fluorescence lifetimes for the species associated with the peaks located at 580, 610 and 610 nm (donor 1, donor 2 and donor 2, respectively) are very difficult to extract with accuracy. In Trimer **2**, no fluorescence arising from donor 1 (*i.e.* octamethylporphyrin zinc(II) unit) is noted. Hence ultrafast absorption spectroscopy is used to extract the kinetic parameters of Trimer **2**.

Compounds	$\lambda_{\max} \ (\log \varepsilon)$				
Dimer 1	316 (4.34), 417 (5.28), 447 (5.13), 514 (4.44), 560 (4.45), 592 (4.06), 645 (w)				
Dimer 2	407 (5.53), 431 (5.22), 545 (4.29), 577 (4.06), 595 (w)				
Trimer 2	411 (5.34), 457 (4.93), 513 (4.28), 565 (4.30), 603 (sh), 645 (w)				

The femtosecond transient absorption spectra of Trimer **2** in benzonitrile at room temperature were investigated (Fig. 4). This solvent was selected as a suitable polar solvent to stabilize a charge-separated state if an electron transfer process took place, which turned out not to be the case. After 2 ps, the resulting transient spectrum is practically identical to that of ZnTPP, tetraphenylporphyrin zinc(II) [35–38], indicating that donor 2 in its S₁ excited state has been generated. The



Fig. 4. Top: transient absorption spectra of Trimer **2** in benzonitrile at 298 K taken at 2, 100 and 3000 ps after femtosecond laser excitation at 410 nm. Bottom: kinetic trace of the 640 nm transient as a function of time

latter transient species relaxes slowly with a rate of (~1.5 ns)⁻¹ (analyzed as a single exponential). This relaxation rate is faster than both S₁ lifetimes of the bisarylporphyrin zinc(II) chromophore (2.64 ns for bis(p-ethylbenzene)porphyrin zinc(II) in 2-methyltetrahydrofuran at 298 K [39]) and the bisarylporphyrin free-base (6–7 ns, see above). This slower rate indicates an enhanced excited state deactivation and is consistent with the presence of an energy transfer from donor 2 to acceptor of a modest rate. Because a limit of 3 ns exists on our instrument, accurate deconvolution was not possible. So the 7.1 ns component was not accessible. Assuming that the decay of ~ 1.5 ns mostly represents indeed the S₁ lifetime of donor 2 relaxing mainly via a singlet energy transfer from donor 2 to acceptor, then its correct rate can be evaluated from $k_{\rm ET} = (1/\tau_{\rm F}) - (1/\tau_{\rm F})$ [2] where $\tau_{\rm F}$ ° and $\tau_{\rm F}$ are the fluorescence of the donor (here donor 2 = bisarylporphyrinzinc(II)) in the absence (here $\tau_{\rm F}^{\rm o} \sim 2.6$ ns) and presence (here τ_{s_1} (donor 2) ~ 1.5 ns) of an acceptor. In this case, $k_{\rm ET}$ is qualitatively estimated to be in the order of ~2.8 × 10^8 s⁻¹, which is slow despite MO coupling between donor 2 and acceptor, but is fully consistent with the dihedral angle formed by the planes of donor 2 and acceptor ($\sim 80^{\circ}$; geometry optimization by DFT in Fig. 1), hence reducing κ^2 in Equation 1. One of the key features of this analysis is the presence of two rise times prior to 100 ps. The first one is very close to the laser pulse profile and represents the formation of the transient upon direct light excitation. The second rise is of $\tau = 87$ ps and is due to a process that generates the transient species donor 2 (in its S_1 state) from donor 1. In order to confirm this, the corresponding $k_{\rm ET}$ is compared to those reported to the related cofacial Dimers **3–6** (Scheme 4) [9].

In this previous work, a relationship between the gap between the 0–0 peaks of the donor and acceptor, Δ , with k_{ET} was observed. By using τ_{F}° from Monomer 3 (1.73 ns [9]), k_{ET} for Trimer **2** is ~1.1 × 10¹⁰ s⁻¹. In this work, the experimental conditions are very different from those used for Dimers 3–6 but the larger Δ and the shorter C_{meso} – C_{meso} distance in Trimer **2** (anthracenyl < dibenzothiophene) suggest that k_{ET} must be larger for the latter. This is exactly was is observed and this result strongly supports the rise time of 87 ps being associated with a S₁ energy transfer from donor 1 (octamethylporphyrin zinc(II)) to donor 2 (bisarylporphyrin zinc(II)). The conclusion of this analysis is that the three different chromophores are obviously decoupled to explain the presence of two rates.

FINAL REMARKS

The S₁ energy transfer rate, $k_{\rm ET}$, observed in Trimer 1 (Scheme 1; (5.1 ps)⁻¹; *i.e.* $k_{\rm ET} = 20 \times 10^{10} \text{ s}^{-1}$ [10]) is extraordinarily fast taking into account the quasi-right angle formed by the antenna free-base porphyrin and the linking *meso*-biarylporphyrin zinc(II) unit. In this case, DFT computations show strong MO couplings. This preliminary work reports that there are two relaxation



Scheme 4. Structures of the related comparative cofacial dimers from Ref. [9]

Table 3. Comparison of the k_{ET} data for Dimers **3–6**^a with Trimer **2**

Compounds ^a	donor $\lambda(0-0)$ $\pm 1 \text{ nm}$	accep. λ (0–0) ±1 nm	Δ^{b}	$ au_{\rm F}({ m donor})$ ns ^c	${\tau_{\rm F}}^{ m o}$ ns ^d	$k_{\rm ET}^{\ \ c}$ (× 10 ⁻⁹ s ⁻¹)
Dimer 3 [9]	576	594	18	0.47(7)	1.92	1.6(4)
Dimer 4 [9]	576	600	24	0.24(3)	1.92	3.7(6)
Dimer 5 [9]	576	603	27	0.20(2)	1.92	4.5(5)
Dimer 6 [9]	574	602	28	0.18(1)	1.92	5.0(3)
Trimer $2 (tw)^e$?	~610 ^f	38 ^g	0.087(-) ^h	1.73 ⁱ	~11(-)

^aIn 2MeTHF at 77 K. ^bThe uncertainties are ±2 nm. ^cThe uncertainties are indicated in brackets. ^d±0.3 ($\tau_{\rm F}^{\circ}$ is that from Monomer **3**). ^c*tw* = this work; solvent = benzonitrile, T = 298 K. ^fT = 298 K, in THF. ^gIn the absence of the 0–0 peak of in fluorescence of donor 1, the Δ values is extracted from the absorption spectra: 0–0 peaks for donor 1 and 2 are at 565 and 603 nm (Table 1). ^hFrom the rise time in the transient spectra in benzonitrile at 298 K. ⁱT = 298 K, in 2-MeTHF.

processes occurring *via* singlet energy transfer in Trimer **2**. These are in the order of $\sim 1.1 \times 10^{10} \text{ s}^{-1}$ (donor $1 \rightarrow \text{donor } 2$) and $\sim 0.03 \times 10^{10} \text{ s}^{-1}$ (donor $2 \rightarrow \text{acceptor}$) which is consistent of three distinct chromophores. Concurrently,

the MOs assessed by DFT are now decoupled within the cofacial portion of the trimer, but all three macrocycles are still interacting. This seems to mean that the effect of confining three chromophores closely together in Trimer 1 accelerates $k_{\rm ET}$ by virtue of strong MO coupling, including the non-directly bonded chromophores. Therefore, this investigation supports the hypothesis that the Förster theory is intrinsically accompanied by the nature of the MO couplings of the individual chromophores. In that respect, one question is if the short interplanar distance between the two identical porphyrin rings drives the MO coupling and the rate, between donor 1 and acceptor. In order to prove this, one can add a spacer between the special pair and the antenna as illustrated for Trimer 3 in Scheme 5, then measure $k_{\rm ET}$. This value should be slower, but the true question is how much smaller.

One more question is what is the contribution of the overall rate of transfer of the through space energy transfer between donor 1 and acceptor in the uncoupled Trimer **4** (Scheme 5)? Is it possible that the rate is faster in the trimer than in the cofacial heterodimer? This question is motivated by the comparison of Trimer **2** with Dimer **7** (Scheme 6). Indeed, for an identical spacer and geometry (r^6 and κ^2 are the same), and almost identical donors (*i.e.* Φ_F° and τ_F° are almost the same), a Δ of 45 nm is found for Dimer **7** [7]. This suggests a larger k_{ET} compared to that measured for Trimer **2**. This was,



Scheme 5. Structures and proposed energy transfer processes to be investigated



Scheme 6. Structures of Dimer 7 [7] and Trimer 2 along with a comparison of the ET parameters

in fact the opposite, and one can suspect a synergistic action between donor 1 and acceptor in Trimer **2** by the presence of the close proximity of this third chromophore. If this is the case, then the use of many chlorophyll molecules in the antenna around the central special pair in the Photosystems may be another strategy used by Nature to enhance the rate of energy migration and energy transfers. The results of these investigations will be published in due course [39].

Acknowledgements

PDH thanks the Natural Sciences and Engineering Research Council of Canada (NSERC), the Agence National de la Recherche (ANR) for the grant of a Research Chair of Excellence, the Fonds Québécois pour la Recherche en Sciences Naturelles et Technologie (FQRNT) for funding. The research by SF and KO was supported by Grant-in-Aid (Nos. 20108010 and 23750014) and KOSEF/MEST through WCU project (R31-2008-000-10010-0) of Korea.

Supporting information

MO representations of the frontier MOs of Trimer **2** according to Ref. 10, and those for Dimer **2**. This material is available free of charge *via* the Internet at http://www. worldscinet.com/jpp/jpp.shtml.

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