ChemComm

RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Is the special pair structure a good strategy for the kinetics during the last step of the energy transfer with the nearest antenna? A chemical model approach†

Cite this: *Chem. Commun.*, 2013, **49**, 2228

Received 5th December 2012,
Accepted 26th January 2013

DOI: 10.1039/c3cc38740b

www.rsc.org/chemcomm

Jean-Michel Camus,[a] Adam Langlois,[b] Shawkat M. Aly,[b] Roger Guilard*[a] and Pierre D. Harvey*[ab]

A cofacial bis(Mg(II)porphyrin)–C_6H_4-free base ($[Mg_2]$–bridge–FB) dyad shows S_1 energy transfer in both directions and much slower rates than similar monoporphyrin systems are observed.

The photosynthetic membranes in plants and photosynthetic bacteria are equipped with reaction center proteins within which a cofacial slipped dimer of chlorophylls or bacteriochlorophylls called the special pair is placed.[1] It is surrounded by antennas that play a role in absorbing light and funneling this excitation energy to it (antenna* → special pair).[1] The natural special pair exhibits many structures depending on the organism (Fig. 1),[2] and the S_1 energy transfer, $k_{ET}(S_1)$, between the nearest antenna and the central special pair occur in the 25–50 ps time scale.[3] Noteworthily, a special pair* ↔ antenna* ET equilibrium was also reported to occur at the 100 ± 50 fs time scale for photo-system II (special pair P680 ↔ antenna C670),[4a] and using selective excitations, at the 25 ps (k_1, antenna B875* → special pair P865) and 8 ps (k_{-1}, special pair P865* → antenna B875) time scales for purple photosynthetic bacteria.[4b] This process was shown to regulate the subsequent oxidation of the special pair (*i.e.* charge separation step).[4c,d] To the best of our knowledge, no artificial special pair–antenna model providing evidence for equilibrium has been reported. We now report chemical model **1** (Fig. 2, top), built upon a cofacial bis(magnesium(II)-porphyrin), $[Mg_2]$, held by a biphenylene-spacer DPB ($C_{meso}\cdots C_{meso}$ distance = 3.80 Å) as the artificial special pair, a 1,4-benzene bridge, and a free base porphyrin, FB, as an antenna. The $k_{ET}(S_1)$'s for $[Mg_2]^*$ → FB extracted from the rise time seen in transient absorption kinetic traces are about one order of magnitude slower than that reported for dyads strictly built on monoporphyrins (**3–5**; Fig. 2). This unexpected result also applies for a dyad bearing no bridge (**2** *vs.* **5**). At first glance, this $k_{ET}(S_1)$ decrease for the special pair-containing species is counterintuitive, but can be explained by the Förster theory.[5] Moreover, a $[Mg_2]^*$ → FB energy transfer was observed from the fluorescence data indicating the presence of $[Mg_2]^*$ ↔ FB* equilibrium.

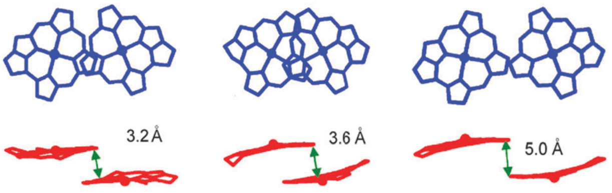


Fig. 1 Top (blue) and side views (red) of the special pairs included in the purple photosynthetic bacteria (left) and in photosystems I (middle) and II (right) in plants. Modified from ref. 3.

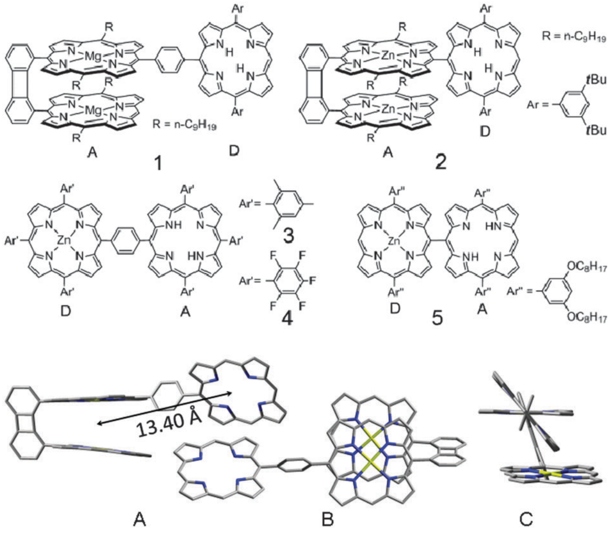


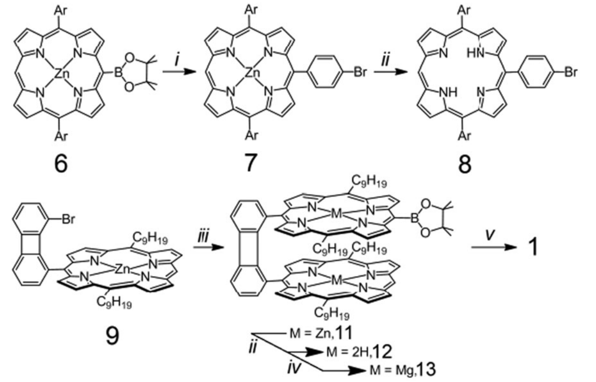
Fig. 2 Top: structures of several ET dyads (D: donor; A: acceptor). Bottom: front (A), top (B) and side (C) views of the optimized geometry of **1**. The substituents have been removed for clarity. The dihedral angles formed by the $[Mg_2]/C_6H_4$, $[Mg_2]$/FB and FB/C_6H_4 and average planes are 69.1°, 45.3° and 65.6°, respectively.

---

[a] *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB,UMR 6302), Université de Bourgogne, Dijon, France*

[b] *Département de Chimie, Université de Sherbrooke, 2550 Boulevard de l'Université, Sherbrooke, Québec, Canada J1K 2R1. E-mail: Pierre.Harvey@USherbrooke.ca; Fax: +1-819-821-8017; Tel: +1-819-821-7092*

† Electronic supplementary information (ESI) available: Complete experimental section, all photophysical spectra and data, and graphs showing the total energy (DFT) against the dihedral angles. See DOI: 10.1039/c3cc38740b



Scheme 1 Synthesis of **1**. (i) 1,4-BrC$_6$H$_4$I, Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$; (ii) HCl; (iii) zinc(II) 5,15-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis-(nonyl)porphyrin **10**, Pd(PPh$_3$)$_4$ Cs$_2$CO$_3$; (iv) MgBr$_2$(OEt$_2$), NEt$_3$; (v) **8**, Pd$_2$(dba)$_3$, S-PHOS, Cs$_2$CO$_3$. (Ar = 3,5-di(*t*-butyl)phenyl).

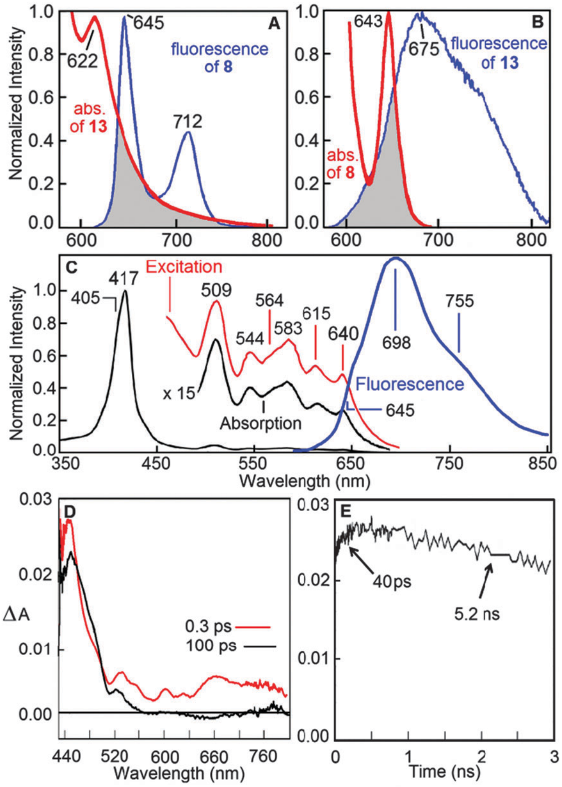


Fig. 3 (A) Absorption spectrum of **13** (ε: 7080 M^{-1} cm^{-1}) normalized with the fluorescence band of **8**. (B) Absorption spectrum of **8** (ε: 1950 M^{-1} cm^{-1}) normalized with the fluorescence band of **13**. (C) Absorption, fluorescence and excitation spectra of **1**. (D) Transient absorption spectra of **1**. (E) Kinetic trace of the 450 nm transient peak of **1**. λ_{exc} = 388 nm. The component of 5.2 ± 1.0 ns is due to the [Mg$_2$] unit in air as checked with **13** and **8** in air by fluorescence. The instrument time scale is limited to 3 ns so the longer component was not accessible. All frames are in 2 MeTHF at 298 K in air.

The strategy to prepare polyads exhibiting a rigidly held cofacial unit flanked with a side arm using stepwise Suzuki couplings was recently reviewed by us.[6] It allows tuning of the synthesis of mimicking models by controlling the spacer and metallation in the cofacial dimer and the anchoring of a suitable monomer. This approach is also used for the synthesis of **1** (Scheme 1 and ESI†). It consists of two converging paths to first prepare precursors **8** and **11** from the known macrocycles **6**, **9**, and **10**.[7] The anchoring of the benzene bridge on **6** proceeds *via* a Suzuki coupling with BrC$_6$H$_4$I forming **7**. The latter is demetallated using HCl providing precursor **8** (92% yield). Concurrently, **9** and **10** are coupled in the same manner to afford the borane-containing bisporphyrin **11**. The coupling of **11** with **8** gives a bis(zinc(II)porphyrin)–C$_6$H$_4$-(free base) dyad, analogous to **1**, but could not be obtained pure enough for reliable photophysical analyses. **1** is then obtained by the demetallation of **11** with HCl (affording **12** in 62% yield), followed by the metallation with MgBr$_2$(OEt$_2$) (forming **13** in 80% yield),[8] and by a Suzuki coupling with **8**. No intra-molecular transmetallation or demetallation was detected by mass spectrometry and **1** was isolated with a satisfactory yield after repetitive SEC purifications (28%). A resonance at −2.6 ppm characteristic of the FB flanked to the cofacial dimer was detected (^{1}H NMR). **1**, **8**, and **11–13** were characterized by ^{1}H NMR, ESI-TOF mass and UV-vis spectroscopy (ESI†). In the absence of X-ray data, the geometry of **1** was optimized by DFT (B3LYP; Fig. 2) to extract the center-to-center [Mg$_2$]–FB distance, *r*. Rotations about the C$_6$H$_4$–[Mg$_2$] and C$_6$H$_4$–FB single bonds lead to dissymmetric double potential wells for which the deepest minima are placed 3.0–3.5 kJ mol^{-1} below the activation barriers (ESI†).

The energy donor and acceptor cannot be directly assigned from the 0–0 peak positions of **8** and **13** as the absorption and emission data suggest opposite roles (ESI†). Moreover, the comparison of the absorption trace of **13** with the fluorescence spectra of **8** and *vice versa* show clear overlaps (see grey area in Fig. 3, frames A and B) indicating that both can act as donors and acceptors based on the *J*-integral of the Forster's theory.[5] This is caused by the broad signals of the DPB-[Mg$_2$] unit, well-known for DPB-containing bisporphyrins, which is due to the cofacial π-systems' interactions.[9] The fluorescence spectrum of **1** shows a shoulder at ~645 nm matching that of the 0–0 peak of **8** but its rather weak intensity indicates quenching. The good match of the excitation and absorption spectra indicates efficient ET. This double ET role should generate two unquenched and two quenched emissions (graphic art). The fluorescence lifetimes, τ_F (quantum yields, Φ_F), for **13** and **8** are 7.3 ± 0.1 (0.019), and 13.9 ± 0.1 (0.067) ns, respectively, consistent with those reported for magnesium(II)tetraphenylporphyrin (8.1 ns) and 10,20-bis(3,5-di(*t*-butyl)phenyl)porphyrin (11.3 ns) at 298 K.[10]

The decay for **1** (Φ_F = 0.023) monitored at 670 nm, where both units emit (using λ_{exc} = 510 nm, where both absorb), exhibits three components (τ_F = 0.21 ± 0.06, 7.6 ± 0.5 and 11.2 ± 1.2 ns; ESI†). These are assigned to the quenched and unquenched fluorescence of [Mg$_2$] and unquenched emission of the FB, respectively. The relative intensity of the two slowest components decreases as the monitoring wavelength is shifted to the blue where the FB emits more. Then τ_F for the unquenched FB is accurately extracted (11.0 ± 0.1 ns). The quenched component of the FB was not accessible from emission decays due to the large pulse width of the laser (fwhm ~ 1.6 ns; detection limit ~ 100–150 ps). Therefore, the S$_1$ lifetime of the FB donor was obtained from fs transient absorption spectroscopy (frames D and E; Fig. 3). The spectra show the typical porphyrin S$_1$ → S$_n$ signal,[11] which evolves between 0.3 and 100 ps. The transient absorption trace, ΔA *vs.* time, monitored at

Table 1 Comparison of the $k_{ET}(S_1)$ data for **1–5**

Compd	$k_{ET}(S_1)$ ($\times 10^{10}$ s^{-1})	Time scale (ps)	Reference
1	2.5 (FB* → [Mg$_2$]) 0.46 ([Mg$_2$]* → FB)	40 210	This work This work
2	20	5.1	7*b*
3	29	3.4	12*a*
4	10	10	12*a*
5	180	0.55	12*b*

450 nm exhibits two clear rises; the first one due to the direct excitation of both chromophores by the laser pulse (<1 ps), and the second one of 40 ps, associated with a clear ET process feeding the acceptor S_n level. Attempts to extract the 210 ps rise time of the [Mg$_2$]* → FB process at 450 and 480 nm failed (ESI†). This is due to the strong overlap of the $S_1 \rightarrow S_n$ bands of both units and its likely weaker intensity relative to the noise level. $k_{ET}(S_1)$ is obtained from $k_{ET}(S_1) = (1/\tau_{S1}) - (1/\tau^{o}_{S1})$ with τ_{S1} and τ^{o}_{S1} being the S_1 lifetimes of the donor, respectively, in the absence and the presence of an acceptor.[1b] $k_{ET}(S_1)$ (FB* → [Mg$_2$]) is 2.5×10^{10} s^{-1} (τ^{o}_{S1} = 11 ns; τ_{S1} = 40 ps). This time scale clearly differs from those of the monoporphyrin dyads shown in Fig. 1 and Table 1.[8,12]

Four comparisons can be made from Table 1's data. First, $k_{ET}(S_1)$ for **2** is smaller than that for **5** (species exhibiting no bridge). Second, $k_{ET}(S_1)$ for **1** is smaller than those for **3** and **4** (with bridge). Third and fourth, $k_{ET}(S_1)$ for **1** is smaller than that for **2** and $k_{ET}(S_1)$ for **3** and **4** are smaller than that for **5**, both by approximately an order of magnitude. Despite limitations of the Forster theory,[13] the change in $k_{ET}(S_1)$ upon introducing a bridge between the acceptor and the donor is qualitatively explained from this,[5] which states that k_{ET} is proportional to r^{-6}. Computer modelling evaluates the center-to-center distances to be r = 8.41 for **2** and **5**, r = 12.75 for **3** and **4**, and r = 13.40 Å for **1**, allowing for the determination of r^{-6} ($r^{-6} = 2.83 \times 10^{-6}$ (**2** and **5**), 2.33×10^{-7} (**3** and **4**), and 1.73×10^{-7} Å^{-6} (**1**)). This one order of magnitude decrease in r^{-6} does indeed corroborate the decrease in $k_{ET}(S_1)$. Changing a monoporphyrin for a cofacial bis(metalloporphyrin) unit, in both bridged and non-bridged systems, unexpectedly causes a decrease in $k_{ET}(S_1)$ by about an order of magnitude. This can be explained using the Forster theory.[5] First, $k_{ET}(S_1)$ is proportional to k^{o}_{F}(donor). The zinc(II)-porphyrin is the donor in **3–5**, and the FB in **1** and **2**. k^{o}_{F} (Φ_F/τ_F) for **8** is 4.8×10^{6} s^{-1}. For tetraphenylzinc(II)porphyrin, ZnTTP (in 2 MeTHF, 296 K), $k^{o}_{F} = 0.030/1.9 \times 10^{-9}$ s^{-1} = 16×10^{6} s^{-1}.[14] This means that k_{ET} for ZnTTP-type donors are prone to being 3.33 faster than that for the FB. Moreover, the r^{-6} zinc(II)porphyrin/r^{-6} [Mg$_2$] ratio is 2.33/1.73 = 1.35. Combined with the above parameter, **3** and **5** (*i.e.* ZnTTP-type donors) are prone to being 4.5 faster than the FB (**1**). The $k_{ET}(S_1)$ **4**/$k_{ET}(S_1)$ **1** ratio is 4 and matches this prediction. Finally, it was recently shown that the modification of the substituents and metal on the porphyrin rings could change $k_{ET}(S_1)$ up to 4-fold.[15] However, the *J*-integrals for **3–5** are not available. Nonetheless, the product of 4.5 × 4-fold is 18-fold, so the $k_{ET}(S_1)$ decrease of about an order of magnitude (from FB such as in **8** to ZnTTP-type donors) is not unreasonable.

Based on the fluorescence data (τ^{o}_{F} = 7.3 ns; τ_F = 210 ps), the $k_{ET}(S_1)$ value for [Mg$_2$]* → FB is 4.6×10^{9} s^{-1}. This 6.3-fold slower rate relative to FB* → [Mg$_2$] (25×10^{9} s^{-1}) is again explained using the Forster theory. Using the surface of the grey area of **13** and **8** in M^{-1} cm^{-1} nm^{-1} units (Fig. 3; frames A and B), the ratio k^{o}_{F} × grey area (FB* → [Mg$_2$])/k^{o}_{F} × grey area ([Mg$_2$]* → FB) is 6.5, which is consistent with 6.3.

This work shows that **1** and **2** exhibit no kinetic benefit in using a cofacial bisporphyrin structure. However, the presence of an artificial special pair* ↔ antenna* process is observed ($25 \times 10^{9}/4.6 \times 10^{9}$ s^{-1}). To the best of our knowledge, evidence for an artificial special pair* ↔ antenna* equilibrium is provided for the first time using chemical models. Not only are these observations consistent with literature findings of natural special pair-antenna's,[4] but more importantly open the door for further model designs in order to establish structure–property relationships for this behaviour relevant for the regulation of the charge separation process in natural systems.

PDH thanks the Agence National de la Recherche (ANR) for the grant of a Research Chair of Excellence. JMC and RG thank the Centre National de la Recherche Scientifique.

References

1 (*a*) *Light-Harvesting Antennas in Photosynthesis* in *Advances in Photosynthesis and Respiration*, ed. B. R. Green and W. W. Parson, Kluwer, Boston, 2003, vol. 13; (*b*) P. D. Harvey, C. Stern and R. Guilard, in *Handbook of Porphyrin Science With Applications to Chemistry, Physics, Materials Science, Engineering, Biology and Medicine*, ed. K. M. Kadish, K. M. Smith and R. Guilard, World Scientific Publishing, Singapore, 2011, vol. 11, pp. 1–177.

2 Y. Kobuke, *Struct. Bonding*, 2006, **121**, 49.

3 (*a*) M. L. Groot, N. P. Pawlowicz, L. J. G. W. van Wilderen, J. Breton, I. H. M. van Stokkum and R. van Grondelle, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 13087; (*b*) A. N. Melkozernov, J. Barber and R. E. Blankenship, *Biochemistry*, 2006, **45**, 331; (*c*) J. R. Durrant, G. Hasting, D. M. Joseph, J. Barber, G. Porter and D. R. Klug, *Biochemistry*, 1993, **32**, 8259.

4 (*a*) J. R. Durrant, G. Hastings, D. M. Joseph, J. Barber, G. Porter and D. R. Klug, *Proc. Natl. Acad. Sci. U. S. A.*, 1992, **89**, 11632; (*b*) T. Ritz, S. Park and K. Schulten, *J. Phys. Chem. B*, 2001, **105**, 8259; (*c*) T. Rech, J. R. Durrant, D. M. Joseph, J. Barber, G. Porter and D. R. Klug, *Biochemistry*, 1994, **33**, 14768; (*d*) L. Valkunas, J. Chmeliov, G. Trinkunas, C. D. P. Duffy, R. van Grondelle and A. V. Ruban, *J. Phys. Chem. B*, 2011, **115**, 9252.

5 T. Forster, *Ann. Phys.*, 1948, **2**, 55.

6 P. D. Harvey, M. A. Filatov and R. Guilard, *J. Porphyrins Phthalocyanines*, 2011, **15**, 1150.

7 (*a*) C. Maeda, S. Yamaguchi, C. Ikeda, H. Shinokubo and A. Osuka, *Org. Lett.*, 2008, **10**, 549; (*b*) M. A. Filatov, F. Laquai, D. Fortin, R. Guilard and P. D. Harvey, *Chem. Commun.*, 2010, **46**, 9176.

8 J. S. Lindsey and J. N. Woodford, *Inorg. Chem.*, 1995, **34**, 1063.

9 F. Bolze, C. P. Gros, M. Drouin, E. Espinosa, P. D. Harvey and R. Guilard, *J. Organomet. Chem.*, 2002, **643–644**, 89.

10 (*a*) R. Shediac, M. H. B. Gray, H. T. Uyeda, R. C. Johnson, J. T. Hupp, P. J. Angiolillo and M. J. Therien, *J. Am. Chem. Soc.*, 2000, **122**, 7017; (*b*) D. Kowalska and R. P. Steer, *J. Photochem. Photobiol., A*, 2008, **195**, 223.

11 V. A. Waiters, J. C. de Paula, B. Jackson, C. Nutaitis, K. Hall, J. Lind, K. Cardozo, K. Chandran, D. Raible and M. Phillips, *J. Phys. Chem.*, 1995, **99**, 1166.

12 (*a*) S. I. Yang, R. K. Lammi, J. Seth, J. A. Riggs, T. Arai, D. Kim, D. F. Bocian, D. Holten and J. S. Lindsey, *J. Phys. Chem. B*, 1998, **102**, 9426; (*b*) H. S. Cho, D. H. Jeong, M.-C. Yoon, Y.-H. Kim, Y.-R. Kim, D. Kim, S. C. Jeong, S. K. Kim, N. Aratani, H. Shinmori and A. Osuka, *J. Phys. Chem. A*, 2001, **105**, 4200.

13 (*a*) Y. R. Khan, T. E. Dykstra and G. D. Scholes, *Chem. Phys. Lett.*, 2008, **461**, 305; (*b*) G. D. Scholes, *Annu. Rev. Phys. Chem.*, 2003, **54**, 57; (*c*) C. Curutchet, B. Mennucci, G. D. Scholes and D. Beljonne, *J. Phys. Chem. B*, 2008, **112**, 3759; (*d*) D. Beljonne, C. Curutchet, G. D. Scholes and R. J. Silbey, *J. Phys. Chem. B*, 2009, **113**, 6583.

14 S. Gentermann, N. Y. Nelson, L. Jaquind, D. J. Nurco, S. H. Leung, G. J. Medforth, K. M. Smith, F. Fajer and D. Leung, *J. Phys. Chem. B*, 1997, **101**, 1247.

15 J.-M. Camus, S. M. Aly, C. Stern, R. Guilard and P. D. Harvey, *Chem. Commun.*, 2011, **47**, 8817.