

View Article Online View Journal

# ChemComm

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: G. Pistolis, N. Karakostas, M. Fakis, K. Seintis, H. Oberacher, F. Pitterl Florian, E. Martinou, A. Kaloudi Chantzea and P. Giastas, *Chem. Commun.*, 2016, DOI: 10.1039/C5CC10335E.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/chemcomm

# **Journal Name**



Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Antonia Kaloudi-Chantzea,<sup>a</sup> Elisabeth Martinou,<sup>a</sup> Kostas Seintis<sup>b</sup>, Nikolaos Karakostas,<sup>a</sup> Petros Giastas,<sup>c</sup> Florian Pitterl,<sup>d</sup> Herbert Oberacher,<sup>d</sup> Mihalis Fakis<sup>b</sup>, and George Pistolis<sup>\*,a</sup>

A Highly – Ordered Rigid Multichromophoric 3D Supramolecular

Network by Combining Ionic and Coordination – Driven Self -

We present here the self-assembling of a green - emitting metallosupramolecular romboid into a rigid, highly - ordered 3D multichromophoric network through the mediation of a tetraanionic violet - blue molecular emitter. Control was obtained on the spatial topology, the electronic energy landscape and the fluorescence polarization of the interacting dipoles.

Assembly

The construction of extended networks via cooperative supramolecular interactions has become an ever - increasing challenge as can lead to the emergence of new functions and properties arising from the collective interactions between the proximal constituent sub-components<sup>1</sup>. From the perspective creation of photofunctional supramolecular of the architectures, rigidity, long-range molecular order and high periodicity are of great importance for both their fundamental photophysics and ability of enabling energy cascading / migration phenomena with controllable polarization for realworld applications<sup>2</sup>. As such, the implementation of self – assembled 3D rigid networks wherein the size / shape adjustable and color - tunable chromophoric building blocks would be predefined, suitably separated and precisely aligned through space, remains a challenging issue to be addressed.

Besides supramolecular structures,<sup>3</sup> polymers<sup>4</sup> and networks<sup>1</sup> that are built up by reversible and highly directional secondary interactions such as hydrogen bonds,  $\pi$ - $\pi$ interactions, hydrophobic interactions and metal - ligand binding, the molecular engineering of new functional supramolecular macrostructures via ionic self-assembly<sup>5</sup> of oppositely charged building blocks is gaining rapidly ground. We have recently reported that appropriately functionalized boron dipyrromethene dyes (Bodipys) can self-assemble via Ptpyridyl coordination chemistry to form various sizes of highly emissive distinct 3D metallosupramolecular polygonal hostarchitectures<sup>6</sup> and simple 1:1 host – guest supramolecular adducts<sup>7</sup>. Here, we combine coordination - driven with ionic self-assembly to demonstrate that the size and shape of the metallosupramolecular rhomboidal cavitand 3<sup>+4</sup> and the metal itself can play a decisive role in dictating the formation of a highly - ordered multichromophoric 3D supramolecular network with interesting photophysical properties, after being reacted with the tetra - anionic linker 1,3,6,8 tetrasulfonate pyrene (**4SPy**<sup>-4</sup>) exhibiting electrostatic binding capabilities at both sides of a symmetry plane (Scheme 1).

The synthesis of the romboidal cavitand 3(OTf)<sub>4</sub> was carried out by mixing the Bodipy-based acceptor 2 with the 90° platinum triflate Pt(dppp)(OTf)<sub>2</sub> donor in a stoichiometric ratio 2:2 in CH<sub>2</sub>Cl<sub>2</sub>. The product was characterized by ESI-MS, <sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C multinuclear NMR analysis and fluorescence spectroscopy methods (ESI). In obvious contrast to the simple (1:1) supramolecular adducts formed by the tetrameric Bodipys based rhomboidal<sup>7</sup> in the cavity of which **4SPy**<sup>-4</sup> can be precisely fitted, the smaller 3<sup>+4</sup> interacts with the "oversized" guest (**4SPy**<sup>-4</sup>) through an outside self-associative reaction mode which is fully consistent with directional





<sup>&</sup>lt;sup>a.</sup> NCSR "Demokritos" <sup>1</sup>Institute of Nanoscience and Nanotechnology, 153 10 Athens, Greece.

<sup>&</sup>lt;sup>b.</sup> Department of Physics, University of Patras, 26500 Patras, Greece. <sup>c.</sup> Hellenic Pasteur Inst, Dept Neurobiol, 11521 Athens, Greece.

<sup>&</sup>lt;sup>d.</sup> Inst. of Legal Medicine and Core Facility Metabolomics, Medical Univ. of Innsbruck, Müllerstraße 44, 6020 Innsbruck, Austria.

Electronic Supplementary Information (ESI) available: Synthesis, theory, additional NMR, ESI - MS, spectroscopic and crystallographic data. See DOI: 10.1039/x0xx00000x

#### COMMUNICATION

ion – pairing  $(SO_3 - Pt^{+2})$  between the complementary charged building blocks i.e.,  $3^{+4}$  and  $4SPy^{-4}$ . The supramolecular network is formed by mixing N,N - dimethylformamide (DMF) solutions of the reactants  $4SPy(NBu_4)_4$  and  $3(OTf)_4$  in a molar ratio > 0.5:1. Although the individual reactants exhibit negligible aggregation under these conditions, the mixture of the reactants immediately forms needle – shaped crystals which over time are increasingly becoming denser.

The crystal structure<sup>8</sup> reveals the formation of cross linked, parallel linear multichromophoric arrays wherein the linker's **4SPy**<sup>-4</sup> units are found to play a dual structural role as two distinct binding sites for  $4SPy^{-4}$  on  $3^{+4}$  were manifested in the asymmetric unit: one (site 1) with the  $4SPy^{-4}$  units to be coplanar (mauve) and a second one (site 2) where the above anionic linkers form a zig-zag arrangement across the rim of the linear chromophoric array (light blue; see Figure 1b). In the former arrangement (site 1) the coplanar **4SPy**<sup>-4</sup> units are aligned parallel the ac crystallographic plane, with their long and short molecular axes oriented parallel the crystallographic axes a and c, respectively. Each anionic unit (**4SPy**<sup>-4</sup>) is linked radially with four rhomboids via an equal number of pairwise electrostatic interactions between the sulfonate groups of **4SPy**<sup>-4</sup> and the apical position of the Pt (II) centers of  $3^{+4}$ . This leads to the linear multichromophoric arrangement pattern along the a crystallographic axis shown in Fig. 1a,b, in which the adjacent rhomboids in the unit cell are offset along axis a by 7.92 Å and position themselves from both sides of the glide plane on which the coplanar molecular linkers (**4SPys**<sup>-4</sup>) lie. The rhomboidal - shaped planar frame of  $\mathbf{3}^{+4}$  - defined by the least square plane  $\langle B...Pt^{*2}...B...Pt^{*2}\rangle$  - is parallel to the above plane of symmetry leading to a highly-ordered linear multichromophoric array (see Figure 1a) wherein the Bodipy dipoles of the alternate rhomboids face strictly parallel to each other and respectively are orthogonally aligned to the 4SPy-4 plane. At the second distinct binding site of **4SPy**<sup>-4</sup> (light blue; site 2) on  $3^{+4}$  (Fig. 1) the anionic linkers are appropriately positioned close to the rim of the rhomboidal cavitands



**Fig. 1** Crystal structure: A linear multichromophoric array (1D network) viewed down (a) *a* and (b) *b* crystallographic axis; the mauve  $4SPy^{-4}$  molecule lies on a symmetry plane (not shown) while the plane of the light blue  $4SPy^{-4}$  unit forms an angle of ~ 22° with the above symmetry plane (c) Unit cell packing viewed down *c* crystallographic axis showing cross-linked 1D networks. The Bodipy chromophore is colored green for clarity: C, grey; N, blue; Pt, magenta, P, orange; B, pink; O, red; S, yellow; F, light-green. Hydrogens atoms are not shown.

### Journal Name

at an angle of ~ 22<sup>0</sup> with respect to the symmetry plane formed by their coplanar counterparts (site 1)? This of the geometric placement allows bridging (cross-linking) of adjacent linear 1D multichromophoric arrays through pairs of  $SO_3 \dots Pt^+$  electrostatic interactions between two sulfonate groups comprising opposite sides of a planar linker (**4SPy**<sup>4</sup>) and the apical position of the Pt(II) centers of two interchain nearest – neighboring rhomboids (see Fig. 1c).

demonstrate the supramolecular То recognition capabilities between the oppositely charged reactants in solution, we studied the above system in DMF-d7 solution by means of 1D and 2D NMR methods as well as electrospray ionization mass spectrometry (ESI - MS). Figure 2 shows the partial <sup>1</sup>H NMR spectra by keeping constant the concentration of  $\mathbf{3}^{+4}$  ([3] = 0.2 mM) and varying the molar ratio R = [4SPy <sup>4</sup>]/[**3**<sup>+4</sup>]. The results clearly indicate strong binding leading to a substantial downfield shift of the axial and equatorial aromatic proton signals of **4SPy**<sup>-4</sup> by  $\Delta\delta H_{ax} = 0.730$  and  $\Delta\delta H_{eq} = 0.580$ ppm respectively for nearly all the molar ratios up to 0.4. All proton signals of  $\mathbf{3}^{+4}$  were shifted downfield with the exception of H<sub>b</sub> that shifted upfield and H<sub>1</sub> which was remained unaffected (ESI; Figure S5). When R reaches 0.5 the solution becomes slightly turbid over time while further addition of **4SPy**<sup>-4</sup> (R > 0.5) affords the rapid formation of needle – shaped crystals (Scheme 1 inset).

The formation of the supramolecular structure was confirmed with ESI-MS by keeping the mixing molar ratio R slightly less than 0.5 to block the formation of extremely insoluble highly extended 3D networks. When a mixture 0.4:1 of 4SPy.(NBu<sub>4</sub>)<sub>4</sub> and 3.(OTf)<sub>4</sub> in DMF/acetone (1:1 v/v) was sprayed in the positive-ion mode at 25 °C, various oligomeric supramolecular structures were observed. Characteristic signals were found at *m/z* 1339.6869, 2074.3948 and 2232.8808 which could be assigned to the ternary complex  $[(3)_2 .4SPy]^{4+}$  and the small oligometric assemblies  $[(3)_3 .$  $(4SPy)_2$ <sup>4+</sup> and  $[[(3)_4.(4SPy)_2](3OTf)]^{5+}$  respectively. The above peaks were isotopically resolved and found to agree very well with their theoretical distribution (SI; Figure S9, S10, S11). The presence of small - sized supramolecular adducts was also supported by 2D diffusion - ordered NMR spectroscopy (DOSY) in DMF-d7 (Figure S6). The diffusion coefficient of  $3^{+4}$  (0.2 mM) was estimated to be D =  $2.7 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$  which, after the addition of 0.4 equiv. of **4SPy**<sup>-4</sup>, was decreased to



**Fig. 2** Partial <sup>1</sup>H NMR spectra of  $3^{+4}$  [0.2 mM] vs the molar ratio R =  $[4SPy^{-4}]/[3^{+4}]$ . For the dependence of chemical shifts of all protons of  $3^{+4}$  vs R see ESI; Figure S5.

This journal is C The Royal Society of Chemistry 20xx

emcomm Accepted

Published on 25 January 2016. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 25/01/2016 15:57:07

### Journal Name

 $D = 2.4 \times 10^{-10} \text{ m}^2 \text{s}^{-1}$  indicating that the degree of complexation of  $3^{+4}$  was increased in the presence of the linker  $4SPy^{-4}$ . More detailed structural information were obtained by 2D nuclear Overhauser effect spectroscopy (NOESY, see ESI; Figure S7). Intermolecular cross peaks are observed between the axial  $(H_{ax})$  and  $\textit{equatorial}~(H_{eq})$  protons of  $\textbf{4SPy}^{\text{-4}}$  and those of the pyridyl ( $H_{\alpha}$  and  $H_{\beta}$ ) and phosphine aromatic groups ( $H_{Ph}$ ) of **3**<sup>+4</sup>. Moreover, additional intermolecular cross peaks are seen between the  $H_{eq}$  of  $4SPy^{-4}$  and the protons ( $H_e$ ) of the methyl groups of the Bodipy subunit of  $\mathbf{3}^{+4}$  heading toward the cavity of the rhomboid. These observations along with the absence of intermolecular cross peaks between the protons of 4SPy<sup>-4</sup> and the exocyclic protons of the Bodipy subunit  $(H_g, H_h, H_i, H_i)$ of the rhomboid cavitand provide clear indication that 4SPy<sup>-4</sup> binds so as to position itself toward the internal space of the cavitands.

Absorption and fluorescence spectroscopy was employed to gain more insights into electronic energy transfer (EET) phenomena between the closely spaced and fixed separated donor  $(4SPy^{-4})$  – acceptor  $(3^{+4})$  chromophoric subunits. Figure 3 shows the absorption and fluorescence spectra in DMF of (a)  $4SPy^{-4}$  alone and (b)  $3^{+4}$  (0.20 mM) versus added amounts of **4SPy**<sup>-4</sup>. As can be seen, despite the strong complexation between 3<sup>+4</sup> and 4SPy<sup>-4</sup> manifested above by NMR spectroscopy, the addition of  $4SPy^{-4}$  up to a molar ratio of R = 0.4 does not perturb the absorption spectrum of  $3^{+4}$  suggesting the absence of ground - state interchromophoric electronic interactions. (Figure S12). Excitation into the main  $S_0 \rightarrow S_1$  ( $\pi$ - $\pi^*$ ) absorption band of **4SPy**<sup>-4</sup> for all solution compositions up to R = 0.4 results to the disappearance of the strong violet emission of the pyrene moiety ( $\Phi_f$  = 0.42,  $\tau_f$  = 7.6 ns) and to the appearance of emission nearly completely dominated by  $\mathbf{3}^{\mathbf{+4}^*}$ . The above can be interpreted by means of efficient EET of  $4SPy^{-4^*}$  to  $3^{+4^*}$  (Figure 3b). The sensitization of the fluorescence of  $3^{+4^*}$  by  $4SPy^{-4^*}$  is also manifested by the recorded fluorescence - excitation spectrum (Figure 3b; left inset). It is worth noting that, in consistency with previous findings,<sup>€</sup>



**Fig. 3** (a) Absorption and fluorescence spectrum (exc: 356 nm) of **4SPy**<sup>-4</sup> in DMF. (b) Absorption and fluorescence spectra (exc: 356 nm) of **3**<sup>+4</sup> alone ( orange curve) and upon added amounts (blue lines) of **4SPy**<sup>-4</sup> (R = 0.13, 0.26 and 0.40). *Inset*: Fluorescence - excitation spectrum of **3**<sup>+4</sup> in the presence of 0.4 equiv. of **4SPy**<sup>-4</sup>.

#### COMMUNICATION

electronic energy flow from the S<sub>1</sub> state of **4SPy**<sub>iew</sub><sup>4\*</sup> toothening state of the Bodipys ( $\mathbf{3}^{+4^*}$ ) proceed With MC apparent quenching of the emissive state (S<sub>1</sub>) of the Bodipy subunit as clearly demonstrated by the invariability of the fluorescence lifetime of  $\mathbf{3}^{+4^*}$  as a function of added **4SPy**<sup>4</sup> (Figure S13).

The dynamics of EET from  $4SPy^{-4^*}$  to  $3^{+4^*}$  was studied by the femtosecond fluorescence upconversion method using 80 - fs excitation pulses at 380 nm and the results are shown in Figure 4a. The two fast decay times ( $au_1$  = 0.38  $\pm$  0.07 ps and  $au_2$  = 1.90  $\pm$  0.50 ps) found for the  $4 {
m SPy}^{-4^*}$  emission (residual fluorescence at 420 nm) were recovered as rise times at the Bodipy emission band of  $3^{+4^*}$  (530 nm). No rise – time of the fluorescence intensity at 530 nm can be detected when 3<sup>+4</sup> alone is excited with 380 nm fs-pulses, as clearly seen in Figure 4b. The finding of two different energy transfer processes could be rationalized by the assumption of two distinct binding sites of **4SPy**<sup>-4</sup> with respect to the **3**<sup>+4</sup>, associated with different distances between the donor - acceptor dipoles. This is not totally unexpected considering the fact that more than one binding site of  $4SPy^{-4}$  to the  $3^{+4}$  has been manifested in the crystal structure, with centroid – centroid distances between the donor – acceptor aromatic rings of ~ 11.5 Å (site 1) and ~ 7.4 Å (site 2) respectively.<sup>9</sup>



**Fig. 4** (a) Normalized fluorescence decays at 420 (residual emission of **4SPy**<sup>-4</sup>) and 530 nm (Bodipy emission of **3**<sup>+4</sup>) of the assembled forms (molar ratio R = 0.4) (b) Fluorescence dynamics at 530 nm of **3**<sup>+4</sup> alone and in the presence of **4SPy**<sup>-4</sup> (R = 0.4). (c) Fluorescence anisotropy decays for **3**<sup>+4</sup> alone and in the presence (R=0.4) of **4SPy**<sup>-4</sup>. Solid lines show fits.

ShemComm Accepted Manuscril

View Article Online

#### COMMUNICATION

To obtain orientation information between the donor – acceptor dipoles the fluorescence anisotropy depolarization dynamics r(t) at the Bodipy emission band (530 nm) of  $\mathbf{3}^{+4}$  was monitored in the absence and presence of  $4\mathbf{SPy}^{-4}$  upon excitation at 380 nm (Figure 4c and S14). The anisotropy r(t) of the  $\mathbf{3}^{+4}$  alone is found to be static over the 0-20 ps time window retaining a value of r(t) = r(0) ~ 0.07 as predicted by the limiting anisotropy<sup>10</sup> of Bodipys for excitation at 380 nm. The above invariability of r(t) can be rationalized by the fact that EET (homotransfer) between the two mutually parallel - aligned Bodipy dipoles in  $\mathbf{3}^{+4}$  does not induce a change in the direction of the oscillator dipole moment and thereby the emission is not depolarized<sup>6a</sup> (Figure 4c).

In obvious contrast to the above, in the presence of the donor **4SPy**<sup>-4</sup> (R =0.4) the anisotropy r(t) decays steeply with a mean lifetime of  $\tau_r = 0.95$  ps and soon levels off to a stable value of -0.02. Selective excitation with polarized light at the 0-0 band of the donor **4SPy**<sup>-4</sup> (380 nm) is expected to result in an excited state with the absorption and emission dipole moment vectors lying along the long molecular axis<sup>7</sup>. On the basis of the above results the fast decay of the fluorescence anisotropy r(t) detected at the emission band of the Bodipy subunit (acceptor) indicates a significant rotation of polarization between the donor – acceptor dipoles. Taking into account the fraction of direct acceptor (**3**<sup>+4</sup>) excitation obtained from the relative absorptivity of the subunits at 380 nm, an angle of ~ 70<sup>0</sup> between the donor – acceptor dipole moments was obtained<sup>2c,10</sup>.

To further elucidate the possible distortion from the perfect collinearity of the Bodipy dipoles in the oligomeric assemblies with respect to the single  $\mathbf{3}^{+4}$  unit, we monitored the fluorescence anisotropy decays of  $\mathbf{3}^{+4}$  at 530 nm in the free and complexed form after preferential excitation of the Bodipy subunit at 400 nm (ESI; Figure S15). No significant loss of r(t) can be seen, suggesting that the Bodipy dipoles retain their high collinearity in the oligomeric assemblies. The above results conclusively imply that the donor ( $4SPy^{-4}$ ) – acceptor ( $\mathbf{3}^{+4}$ ) chromophoric arrangement in the oligomeric structures in the solution should not differ remarkably by that manifested by the crystal structure.

To summarize, we demonstrate here the formation of highly - ordered multichromophoric supramolecular network formed by a self-associative reaction mode between a Bodipy dye – based metallosupramolecular rhomboid cavitand ( $3^{+4}$ ) and the tetra-anionic molecular linker 1,3,6,8 tetrasulfonate pyrene ( $4SPy^{-4}$ ). The results unveil that the Bodipy dipoles of the alternate rhomboids position themselves parallel to each other and are aligned nearly perpendicular to the linkers' ( $4SPy^{-4}$ ) plane. Highly efficient energy transfer and effective polarization switching from the linker ( $4SPy^{-4}$ ) to the Bodipy dyes of  $3^{+4}$  was manifested.

This work was performed in the framework of "IKY: Fellowships of Excellence for Postgraduate Students in Greece – Siemens Program". Part of this work also has been supported by Grant E.028 from the Research Committee of the University of Patras (Programme K. Karatheodori).

#### Notes and references

- DOI: 10.1039/C5CC10335E
  (a) J. R. Nitschke, Nature 2009, 462, 736; (d) M. Abel, S. Clair, O. Ourdjini, M. Mossoyan, L. Porte, J. Am. Chem. Soc. 2011, 133, 1203; (c) X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu, F. Huang, Adv. Mater. 2012, 24, 362; (d) P. Phuengphai, S. Youngme, I. Mutikainen, J. Reedijk, Inorg. Chem. Commun. 2012, 24, 129; (e) Z. B. Lim, H. Li, S. Sun, J. Y. Lek, A. Trewin, Y. M. Lama, J. Mater. Chem. 2012, 22, 6218; (f) M. Yamada, Y. Ootashiro, Y. Kondo, F. Hamada, Tetrahedron Lett. 2013, 54, 1510; (g) Y. Liu, P. Liu, Q. Liu, L.-Y. Pang, C.-Y. Ren, Y.-Y. Wang, Inorg. Chem. Commun. 2013, 35, 321; (h) X. Ji, Y. Yao, J. Li, X. Yan, F. Huang, J. Am. Chem. Soc. 2013, 135, 74.
- (a) S. McDowall, B. L. Johnson, D. L. Patrick J. Appl. Phys. 2010, **108**, 053508 (b) P. P. C. Verbunt, A. Kaiser, K. Hermans, C. W. M. Bastiaansen, D. J. Broer, M. G. Debije Adv. Funct. Mater. 2009, **19**, 2714 (c) C. Menelaou, J. ter Schiphorst, A. M. Kendhale, P. Parkinson, M. G. Debije, A. Schenning, L. M. Herz, J. Phys. Chem. Lett. 2015, **6**, 1170.
- (a) X. Yan, T. R. Cook, P. Wang, F. Huang, P. J. Stang, Nature Chem. 2015, 7, 342; (b) X. Yan, H. Wang, C. E. Hauke, T. R. Cook, M. Wang, M. Lal Saha, Z. Zhou, M. Zhang, X. Li, F. Huang, P. J. Stang, J. Am. Chem. Soc. 2015, 137, 15276.
- 4 (a) T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma, E. W. Meijer, Chem. Rev. 2009, 109, 5687; (b) W. L. Leong, J. J. Vittal, Chem. Rev. 2011, 111, 688; (c) M. M. Safont-Sempere, G. Fern\_andez, F. Würthner, Chem. Rev. 2011, 111, 5784; (d) X. Yan, S. Li, J. B. Pollock, T. R. Cook, J. Chen, Y. Zhang, X. Ji, Y. Yu, F. Huang, P. J. Stang, Proc. Natl. Acad. Sci. U.S.A. 2013, 110, 15585; (e) L. Yang, X. Tan, Z. Wang, X. Zhang, Chem. Rev. 2015, 115, 7196.
- (a) J. Lee, A. W. Schwabacher, J. Am. Chem. Soc. 1994, 116, 5 8382; (b) Z. Wang, C. J. Medforth, J. A. Shelnutt, J. Am. Chem. Soc. 2004, 126, 15954; (c) A. Hossain, P. Morehouse, D. Powell, K. Bowman-James, Inorg. Chem. 2005, 44, 2143; (d) E. Menozzi, M. Busi, R. Ramingo, M. Campagnolo, S. Geremia, E. Dalcanale, Chem. Eur. J. 2005, 11, 3136; (e) S. L. Craig, Angew. Chem. Int. Ed. 2009, 48, 2645; (f) G. H. Clever, S. Tashiro, M. Shionoya, Angew. Chem. Int. Ed. 2009, 48, 7010; (g) F. M. Menger, L. Shi, J. Am. Chem. Soc. 2009, 131, 6672; (h) M.-O. M. Piepenbrock, G. O. Lloyd, N. Clarke, J. W. Steed Chem. Rev. 2010, 110, 1960; (i) G. H. Clever, S. Tashiro, M. Shionoya, J. Am. Chem. Soc. 2010, 132, 9973; (j) G. H. Clever, W. Kawamura, M. Shionoya, Inorg. Chem. 2011, 50, 468; (k) J. H. Olivier, J. Barberá, E. Bahaidarah, A. Harriman, R. Ziessel, J. Am. Chem. Soc. 2012, 134, 6100; (I) T. Sendai, S. Biswas, T. Aida, J. Am. Chem. Soc. 2013, 135, 11509.
- 6 (a) A. Kaloudi-Chantzea, N. Karakostas, C. P. Raptopoulou, V. Psycharis, E. Saridakis, J. Griebel, R. Hermann, G. Pistolis, J. Am. Chem. Soc. 2010, **132**, 16327; (b) A. Kaloudi-Chantzea, N. Karakostas, F. Pitterl, C. P. Raptopoulou, N. Glezos, G. Pistolis, Chem.Commun. 2012, **48**, 12213.
- 7 N. Karakostas, I. M. Mavridis, K. Seintis, M. Fakis, E. N. Koini, I. D. Petsalakis, G. Pistolis, Chem. Commun. 2014, 50, 1362.
- 8 The molecular structure has been deposited at the Cambridge Crystallographic Data Centre: number CCDC 1434774.
- 9 Ultrafast energy transfer (< 2ps) which is several times faster<sup>7</sup> than the time predicted by Coulombic coupling calculations<sup>10</sup> has commonly been observed between closely spaced donor acceptor pairs (< 15 Å).</p>
- N. Karakostas, A. Kaloudi-Chantzea, E. Martinou, K. Seintis, F. Pitterl, H. Oberacher, M. Fakis, J. K. Kallitsis, G. Pistolis, Faraday Discuss. 2015, 185, 433.

4 | J. Name., 2012, 00, 1-3