

This article is part of the

Supramolecular Chemistry web-

based thematic issue

celebrating the International Year of Chemistry 2011

Guest editors: Professors Philip Gale, Jonathan Sessler and Jonathan Steed

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Cite this: Chem. Commun., 2011, 47, 6072-6074

www.rsc.org/chemcomm

COMMUNICATION

Singlet and triplet energy transfer rate acceleration by additions of clusters in supramolecular pigment-organometallic cluster assemblies[†]‡

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Received 28th February 2011, Accepted 23rd March 2011 DOI: 10.1039/c1cc11174d

Both S_1 and T_1 energy transfer rates (porphyrin \rightarrow cluster) increase from mono- to di- to tetracarboxylate[tetraphenyl-(zinc)porphyrin] adducts with $[Pd_3(dppm)_3(CO)]^{2+}$ clusters.

In past decades, tremendous efforts have been devoted to mimic natural photo-induced electron or energy transfer processes^{1,2} and the development of charge-separating devices.^{3–5} However, a large number of these models including porphyrin-based complex architectures, were based on covalent linkages.¹ Owing to the virtues of non-covalent systems, such as versatility, flexibility in design, and ease of synthesis, increasing attentions have recently been paid to the design and analysis of non-covalent systems, formed by hydrogen bonds,⁶ salt bridges,⁷ metal-ligand bonds⁸ to assemble donors and acceptors for energy transfers or charge separations. The assembling of carboxylate-porphyrins, which can bind cations, have widely been used as a convenient mean of forming noncovalent systems, including expanded porphyrins.9 The use of the unsaturated metal clusters $M_3(dppm)_3(CO)^{2+}$ $(M_3^{2+}; M = Pd, Pt; dppm = Ph_2PCH_2PPh_2)^{10}$ has not attracted attention in the context of energy transfer until recently.¹¹ These dicationic clusters, which also bind carboxylates via ionic interactions (as evidenced by the Pd...O separations measured by X-ray diffraction techniques for $Pd_3(dppm)_3(CO)(O_2CCF_3)^+$ that are too long to be coordination bonds but range in the typical window for ionic interactions),¹⁰ are attractive because of a "picket fences" like cavity built with dppm-phenyl groups (Fig. 1).

Nature uses the antenna effect where many energy donors, like chlorophylls, capture light and transport this excitation energy towards the special pair placed inside the reaction centre protein prior to the primary photo-induced electron transfer.¹ In the singlet state, the Förster theory states that the rate for energy transfer, $k_{\rm ET}$, is a function of the radiative rate constant of the donor, the relative orientation factor of the transition moments of the donor *vs.* acceptor, the donor–acceptor separation, and the

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‡ Electronic supplementary information (ESI) available: Experimental details. See DOI: 10.1039/c1cc11174d



Fig. 1 Left: space filling models showing two possible cavity sizes depending on the dppm-conformations. Right: drawing of the $Pd_3(dppm)_3(CO)^{2+}$ cluster.

J integral which is the surface between the donor fluorescence intensity and the absorptivity of the acceptor.¹²

The experimental verification of the relationship between $k_{\rm ET}$ and the donor–acceptor separation for zinc-porphyrin as the donor has been confirmed by us,¹³ but to the best of our knowledge not for this integral also called *J*. If the number of donors increases, as Nature strategically does, then *J* increases, but this should also be true for the acceptor. One easy way to increase the number of acceptors is to employ supramolecular assemblies organized *via* electrostatic interactions placing the donor and acceptors in a predictable manner. At the same time, one ensures that the energy transfer event takes place *via* a through space process (not through bond), as in Nature.

We now wish to report the design of three supramolecular donor-(acceptor)_n systems (n = 1, 2, 4), $MCO_2ZnP-(\mathbf{Pd_3}^{2+})$, $DCO_2ZnP-(\mathbf{Pd_3}^{2+})_2$ and $TCO_2ZnP-(\mathbf{Pd_3}^{2+})_4$ where the tetraphenyl-(zinc)porphyrin and cluster act as S₁ and T₁ energy donor and acceptor, respectively (Scheme 1). $k_{\rm ET}$ increases by about an order of magnitude going from $MCO_2ZnP-(\mathbf{Pd_3}^{2+})_2$ to $DCO_2ZnP-(\mathbf{Pd_3}^{2+})_2$, and from $DCO_2ZnP-(\mathbf{Pd_3}^{2+})_2$ to $TCO_2ZnP-(\mathbf{Pd_3}^{2+})_4$. See ESI for experimental details.

The host-guest interactions between carboxylates and $\mathbf{Pd_3}^{2+}$ was previously established from X-ray crystallography.^{10a} Moreover, the 1:1 binding constant, K_{11} , between MCO_2ZnP and $\mathbf{Pd_3}^{2+}$ ($MCO_2ZnP + \mathbf{Pd_3}^{2+} \leftrightarrow MCO_2ZnP$ -($\mathbf{Pd_3}^{2+}$)) was also



Scheme 1

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[†] This article is part of a ChemComm 'Supramolecular Chemistry' web-based themed issue marking the International Year of Chemistry 2011.



Fig. 2 Space filling model for TCO_2ZnP -(**Pd**₃²⁺)₄.

measured using UV-vis spectroscopic methods and these interactions are found to be strong and reversible ($K_{11} \sim 2 \times$ 10^4 M⁻¹).¹¹ The binding constants, K_{1n} , for DCO_2ZnP - $(\mathbf{Pd_3}^{2+})_2$ and $TCO_2ZnP-(\mathbf{Pd_3}^{2+})_4$ (*i.e.* DCO_2ZnP+2 $\mathbf{Pd_3}^{2+}$ $\leftrightarrow DCO_2ZnP-(\mathbf{Pd_3}^{2+})_2$ and $TCO_2ZnP + 4$ $\mathbf{Pd_3}^{2+}$ \leftrightarrow TCO_2ZnP -(**Pd**₃²⁺)₄) were measured and are also in the same range ($K_{1n} \sim 2 \times 10^4 \,\mathrm{M}^{-1}$; see ESI‡ for spectral changes, Scott and Scatchard graphs)¹⁴ indicating that K_{1n} for all clusters and sites is about the same. This means that the binding of the first cluster does not induce steric hindrance to the binding of the next ones. Careful attempts to detect other isosbestic points in the spectra upon the change in DCO_2ZnP/Pd_3^{2+} and TCO_2ZnP/Pd_3^{2+} ratio failed, clearly indicating that the binding sites are relatively electronically and sterically independent. Indeed, modeling was used in the absence of X-ray structure. Using X-ray data for O···Pd distances for related adducts,^{10a} a model for TCO_2ZnP -(Pd_3^{2+})₄ was built showing absence of steric $\mathbf{Pd_3}^{2+} \cdots \mathbf{Pd_3}^{2+}$ interactions (Fig. 2).

MALDI-TOF and ESI-TOF also failed to confirm the mass of these assemblies. Instead, the Pd₃²⁺ UV-vis spectra were monitored when it is added to a DCO_2ZnP and a TCO_2ZnP solution. The λ_{max} for the free $\mathbf{Pd_3}^{2+}$ and $\mathbf{RCO_2}$ - $\mathbf{Pd_3}^{2+}$ adducts are ~ 487 and ~ 467 nm, respectively. As the cluster is added, adducts are formed and the resulting band is located at \sim 467 nm. When the sites are saturated, the excess addition of Pd_3^{2+} to the solution adds a new feature at ~ 487 nm resulting in a gradual shift of the spectral envelope in the 465-490 nm range. The graph of λ_{max} vs. the number of $\mathbf{Pd_3}^{2+}$ equivalents for TCO_2ZnP - $(\mathbf{Pd_3}^{2+})_4$ (Fig. 3) gives a flat line for the number of equivalents lower than 4, and increases after this saturation point (see ESI[‡] for DCO_2ZnP -(Pd₃²⁺)₂). At large excesses, λ_{max} is 467 nm as expected. When the number of equivalents is 8 (meaning that the relative amount of free and associated Pd_3^{2+} is nearly the same), λ_{max} is precisely placed halfway between 467 and 487 nm. The Pd_3^{2+} UV-vis band spreads to 650 nm, whereas the

0–0 peak of DCO_2ZnP (see ESI‡) and TCO_2ZnP are seen at ~595 nm placing the cluster and the porphyrin unit as the energy donor and acceptor, respectively. The Pd_3^{2+} absorption and DCO_2ZnP and TCO_2ZnP fluorescences exhibit an overlap suitable for singlet energy transfer (Fig. 4).

Evidence for fluorescence quenching (and phosphorescence at 77 K; ESI‡) of the central zinc-porphyrin is observed when $Pd_3^{2^+}$ clusters bind the $-CO_2^-$ sites (Fig. 5; see the ESI‡ for the other examples). Quenching by intersystem crossing, isc, and internal conversion, ic, are most unlikely. A convincing argument comes from the comparison of the photophysical data of the free base in cofacial bis-*etio*-porphyrins using the



Fig. 3 Top: UV-vis spectra for the addition of Pd_3^{2+} (as PF_6^- salt) into a TCO_2ZnP 0.25 × 10⁻⁵ M methanol solution. Curves D–Z are obtained with successive additions of 0.1 ml of 7 × 10⁻⁵ M Pd_3^{2+} solution. Bottom: spectral shift of the Pd_3^{2+} band as a function of the Pd_3^{2+}/TCO_2ZnP ratio.



Fig. 4 Comparison of the UV-vis absorption spectrum of Pd_3^{2+} and fluorescence spectra of DCO_2ZnP and TCO_2ZnP in MeOH at 298 K.



Fig. 5 Comparison of the fluorescence spectra of TCO_2ZnP and $TCO_2ZnP-(Pd_3^{2+})_4$ in a 2MeTHF/MeOH mixture (20:1) at the same concentration at 298 K.

DPS spacer (diphenylthiophene, C_{meso} – C_{meso} distance = 6.33 Å) with phenyl-*etio*-porphyrin (P(2H); Scheme 2).¹⁵ Indeed, these show no changes between P(2H) and DPS(4H) and between DPS(4H) and DPS(Pd,2H) indicating that both ic and isc are not affected by these structure modification at this distance. For comparison purposes, the C_{meso} – Pd_3^{2+} distance is 9.0 Å in the TCO_2ZnP -($Pd_3^{2+})_4$ model (Fig. 2).

This quenching is therefore due to singlet energy transfer from the porphyrin to $\mathbf{Pd_3}^{2+}$ and k_{ET} (Table 1) is determined



Scheme 2

Table 1 $\tau_{\rm F}$, $\tau_{\rm F}^{\rm o}$ and singlet $k_{\rm ET}(S_1)$ data at 298 and 77 K

	$\tau_{\rm F}/{ m ns}$		$k_{\rm ET}/{\rm ns}^{-1}$	
	298 K	77 K	298 K	77 K
MCO ₂ ZnP	1.78 ± 0.01	1.59 ± 0.01		_
$MCO_2ZnP-(\mathbf{Pd_3}^{2+})$	1.74 ± 0.01	1.10 ± 0.25	0.016	0.28
DCO ₂ ZnP	1.83 ± 0.05	2.85 ± 0.06	_	
$DCO_2ZnP-(\mathbf{Pd_3^{2+}})_2$	0.78 ± 0.05	0.29 ± 0.05	0.73	3.1
TCO ₂ ZnP	1.65 ± 0.02	2.19 ± 0.01	_	
$TCO_2ZnP-(\mathbf{Pd_3}^{2+})_4$	0.17 ± 0.02	< 0.1	5.3	>10

according to $k_{\rm ET} = (1/\tau_{\rm e}) - (1/\tau_{\rm e}^{\rm o})$ where $\tau_{\rm e}$ and $\tau_{\rm e}^{\rm o}$ are the emission lifetimes of the donor in the presence and absence of energy acceptor, respectively.¹ First, $k_{\rm ET}(S_1)$ increases at 77 K contrasting with previous data on cofacial bis-etio-porphyrins similar to that shown in Scheme 2.13 Here, the donor-acceptor systems are help by electrostatic interactions whereas the cofacial bis-etio-porphyrins are more rigidly held by covalent bonds with the spacer. Upon cooling, the $RCO_2^{-} \cdots Pd_3^{2^+}$ interactions get stronger and the assemblies are in a more rigid environment. Second, $k_{\rm ET}(S_1)$ increases going from $MCO_2ZnP-({\rm Pd_3}^{2+})$ to DCO_2ZnP -($Pd_3^{2^+}$)₂ to TCO_2ZnP -($Pd_3^{2^+}$)₄. This trend appears to be due to the overlap integral J. As the number of acceptors increases, J is bound to increase. However, one expects a \sim 2- and ~4-fold increase in $k_{\rm ET}(S_1)$, respectively, but these are much larger. In an attempt to shine some light onto this question, the triplet state behaviour was studied as well. Because the donor porphyrin is not phosphorescent at 298 K, transient absorption spectroscopy was used to extract $k_{\text{ET}}(T_1)$ (Fig. 6 for DCO_2ZnP -(**Pd**₃²⁺)₂ for example and ESI[‡]).

The transient absorption spectra for DCO_2ZnP - $(\mathbf{Pd_3}^{2+})_2$ and DCO_2ZnP are identical meaning that the transient T_1-T_n signal belongs to the central unit. The T_1 lifetimes obtained from the transient decays indicate a large decrease upon complexation with $\mathbf{Pd_3}^{2+}$ (Table 2). The $k_{\rm ET}(T_1)$'s $(k_{\rm ET} = (1/\tau_e) - (1/\tau_e^{0}))$ show a large increase going from MCO_2ZnP - $(\mathbf{Pd_3}^{2+})$ to DCO_2ZnP - $(\mathbf{Pd_3}^{2+})_2$ to TCO_2ZnP - $(\mathbf{Pd_3}^{2+})_4$. Again, $k_{\rm ET}$ increases by approximately an order of



Fig. 6 Transient spectrum of DCO_2ZnP - $(Pd_3^{2+})_2$ in methanol at 298 K $\lambda_{exc} = 355$ nm. The pump and probe pulse delay times are in the inset.

Table 2 $\tau_{\rm T}$, $\tau_{\rm T}^{\rm o}$ and triplet $k_{\rm ET}({\rm T_1})$ data at 298 K

	$\tau_T{}^o/\mu s$		$\tau_T/\mu s$	$k_{\rm ET}/{\rm s}^{-1}$
MCO ₂ ZnP DCO ₂ ZnP TCO ₂ ZnP	125 603 617	$\begin{array}{l} MCO_2ZnP - (\mathbf{Pd_3}^{2+}) \\ DCO_2ZnP - (\mathbf{Pd_3}^{2+})_2 \\ TCO_2ZnP - (\mathbf{Pd_3}^{2+})_4 \end{array}$	35 8.8 0.072	$\begin{array}{c} 2.1 \times 10^{4} \\ 1.1 \times 10^{5} \\ 5.6 \times 10^{7} \end{array}$

magnitude per $\mathbf{Pd_3}^{2+}$ complexation. Since the Förster theory does not apply to triplet energy transfer (but the Dexter double electron exchange theory does),^{1,13} the *J* integral alone cannot explain the very large acceleration for $k_{\text{ET}}(\mathbf{S}_1)$.

While the exciton energy migration across energy donors is well known,¹ this same exciton behaviour for acceptors is not. Is there an exciton effect on $k_{\rm ET}$? This needs to be explored in detail in order to explain this current impressive acceleration in $k_{\rm ET}$ with the number of acceptors.

PDH thanks the Natural Sciences and Engineering Research Council of Canada for funding and the Agence National de la Recherche for the grant of a Research Chair of Excellence.

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