ChemComm

Porphyrins & Phthalocyanines
web themed issue

Guest editors: Jonathan Sessler, Penny Brothers and Chang-Hee Lee

ChemComm

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Cite this: *Chem. Commun.*, 2012, **48**, 2671–2673

www.rsc.org/chemcomm

COMMUNICATION

Organometallic multiads of zinc(II) porphyrins with interchromophoric cooperativity in S_1 and T_1 energy transfers†‡

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Received 2nd November 2011, Accepted 11th January 2012
DOI: 10.1039/c2cc16804a

Three different S_1 and T_1 energy donors are linked onto a central zinc(II) porphyrin acceptor and the rates for energy transfers show evidence for cooperativity.

Platinum(II) acetylides have been widely used for the design of photonic materials,[1] and their connection to porphyrins led to the designs of photocells,[2] and molecular, oligomeric, polymeric and dendrimeric devices exhibiting exciton coupling,[3] red emission,[4] singlet, S_1, and triplet, T_1, energy transfer,[5] host–guest,[6] self-assembly,[7] optical limited and nonlinear optical properties.[8] Recently, we[9] and others[10] reported the synthesis and emission properties of truxene-containing zinc(II) porphyrins. From the study on the antenna properties of truxene (**Tru**) and tritruxene,[9] it was deduced that despite modest rates of S_1 and T_1 energy transfers, the fluorescence and phosphorescence intensity of **Tru** donor was strongly quenched and that the fluorescence and phosphorescence quantum yields of the central zinc(II) porphyrin or free base were enhanced compared to the tetraphenyl-porphyrin analogues, even at 298 K. Moreover, the rates were found independent of the nature of the antenna, **Tru** or tritruxene, indicating that the closest unit played the main role in the energy transfer rate. We now wish to report multiads containing 3 different S_1 and T_1 energy donors around a central zinc(II) porphyrin (see **5**, **8** and **9** in Chart 1). The energy transfer rates are significantly dependent upon the number of donors (2 *vs.* 4).

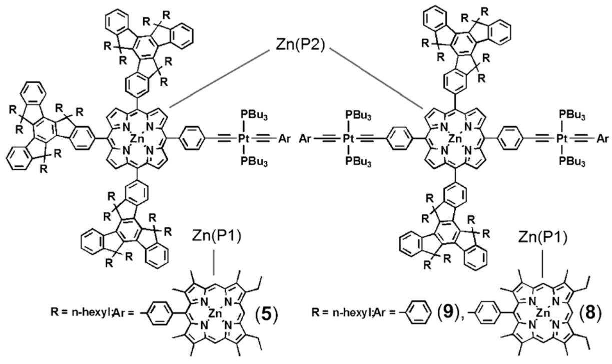
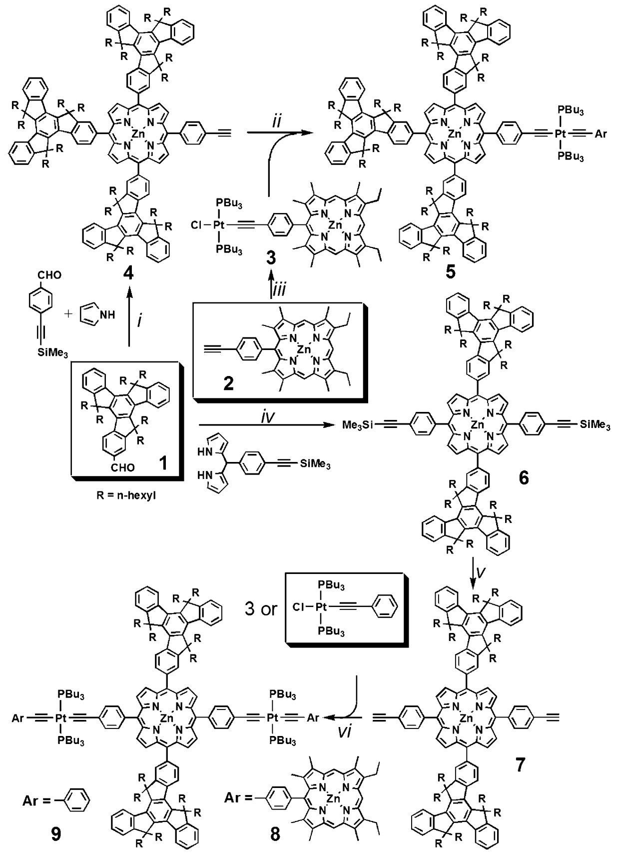


Chart 1 Structures of the multiads **5**, **8** and **9**.

The general procedure for the syntheses of the target multiads involves a converging approach of the **Tru**/zinc(porphyrin)-containing core with the flanking *trans*-bis(phosphine)-(ethynylaromatic)s (Scheme 1; see the ESI‡ for experimental details). The main precursor 2-carbaldehyde-5,5′,10,10′,15,15′-hexahexyltruxene,[9] **1**, is condensed with 4-trimethylsilylethynylbenzaldehyde (~3 : 1 ratio) and pyrrole, followed by a metallation with zinc acetate providing the mono-ethynyl derivative **4** in



Scheme 1 Synthesis paths for **5**, **8** and **9**: (i) (a) CH_2Cl_2, $BF_3{\cdot}OEt_2$, DDQ; (b) $Zn(OAc)_2$, THF/MeOH; (c) TBAF, THF. (ii) CH_2Cl_2/*i*Pr_2NH, CuI. (iii) CH_2Cl_2/*i*Pr_2NH, CuI, *trans*-$[Pt(P(n\text{-}Bu)_3)_2Cl_2]$. (iv) (a) $CHCl_3$, $BF_3{\cdot}OEt_2$, DDQ; (b) $Zn(OAc)_2$, THF/MeOH. (v) THF/MeOH, K_2CO_3, RT. (vi) CH_2Cl_2/*i*Pr_2NH, CuI.

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† This article is part of the ChemComm 'Porphyrins and phthalocyanines' web themed issue.

‡ Electronic supplementary information (ESI) available: Experimental section and all photophysical data for **5–9**. See DOI: 10.1039/c2cc16804a

10% yield. In parallel, the monoethynyl-zinc(II) porphyrin species **2**[5b] is reacted with *trans*-[Pt(P(*n*-Bu)$_3$)$_2$Cl$_2$] to afford **3** in 35% yield. The reaction of **3** and **4** in the presence of *i*Pr$_2$NH and CuI provides target **5** in 30% yield. For the preparation of targets **8** and **9**, **1** is first condensed with 5-4-trimethylsilylethynylphenyldipyrromethane[10] in the presence of the oxidizing agent DDQ to generate **6** in 11% yield.

The latter is desilanated with potassium carbonate to form **7** in excellent yield (98%). The latter is then reacted with **3** or with *trans*-[Pt(P(*n*-Bu)$_3$)$_2$Cl(C$\equiv$CC$_6$H$_5$)],[5b] in the presence of CuI and *i*Pr$_2$NH to give **8** and **9**, in 10 and 75% yield, respectively.

The energy level for each component has been determined using the position of the 0–0 peaks in the absorption, fluorescence and phosphorescence spectra of truxene,[9] *trans*-Pt(P(*n*-Bu)$_3$)$_2$-(C$\equiv$CC$_6$H$_5$)$_2$ **[Pt]**,[11] **7** (Fig. 1) and **2**.[5b] The relative positions of the 0–0 peaks (Table 1) indicate that the energy levels vary as **Tru** > **[Pt]** > **2** > **7** for S$_1$ and as **[Pt]** > **Tru** > **2** > **7** for T$_1$.

Previous transient absorption and emission spectroscopic studies from our group and others on dyads containing **[Pt]** and *meso*-aryl substituted zinc(II) porphyrin,[5c] **[Pt]** and **2**,[5a] **Tru** and **7**,[9] and β-alkyl (**Zn(P1)**) and *meso*-aryl substituted zinc(II) porphyrin (**Zn(P2)**)[12] provided evidence for S$_1$ or T$_1$ energy transfers, excluding the possibility of charge separated states. Hence using these building blocks, any excited state quenching of the donor is a consequence of energy transfers. The fluorescence (Φ_F) or phosphorescence (Φ_P) quantum yields for these chromophores are truxene, Φ_F = 0.07 in toluene at 298 K,[13a] substituted truxenes 0.18 < Φ_F < 0.56, in THF at 298 K,[13b,c] substituted **[Pt]** complexes 0.17 < Φ_P < 0.38, in 2-MeTHF at 77 K,[11b] **2** 0.047 and 0.045 at 298 and 77 K, respectively, in 2-MeTHF,[5a] and **7** (Φ_F = 0.019 in 2-MeTHF at 298 K; this work). The emission spectra of **5** and **8** exhibit strong fluorescence and phosphorescence bands of the *meso*-aryl substituted zinc(II) porphyrin central acceptor but those for **Tru** (350–450), **[Pt]** (450–550) and *octa*-alkyl-zinc(II) porphyrin (575 nm) are very weak (Fig. 2). This anticipated quenching is associated to efficient S$_1$ and T$_1$ energy transfers.

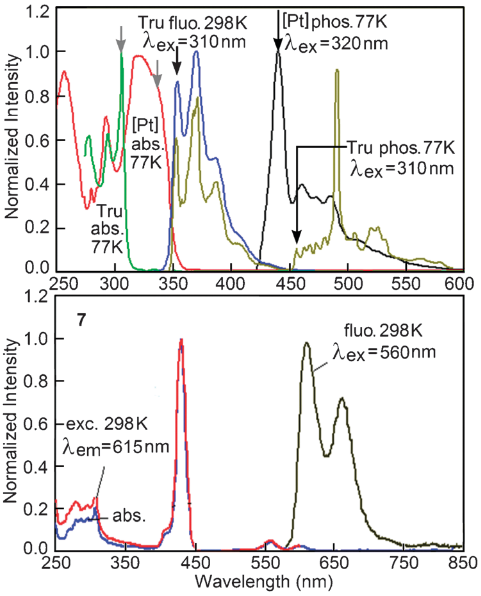

Fig. 1 (top) Absorption, fluorescence and phosphorescence spectra of truxene (**Tru**) and *trans*-Pt(P(*n*-Bu)$_3$)$_2$(C$\equiv$CC$_6$H$_5$)$_2$ **[Pt]** in 2-MeTHF. The arrows point the 0–0 transitions. (bottom) Absorption (blue), excitation (red) and fluorescence (black) spectra of **7** in 2-MeTHF.

Table 1 Positions of the 0–0 peaks in the absorption, fluorescence and phosphorescence spectra of the model compounds in 2-MeTHF (tw = this work)

	Abs./nm, 298 K	Fluo./nm, 298 K	Fluo./nm, 77 K	Phos./nm, 77 K	Ref.
Tru	306	354	356	457	9
[Pt]	340	346	—	445	11
2	575	597	575	703	5*b*
7	605	610	610	797	tw

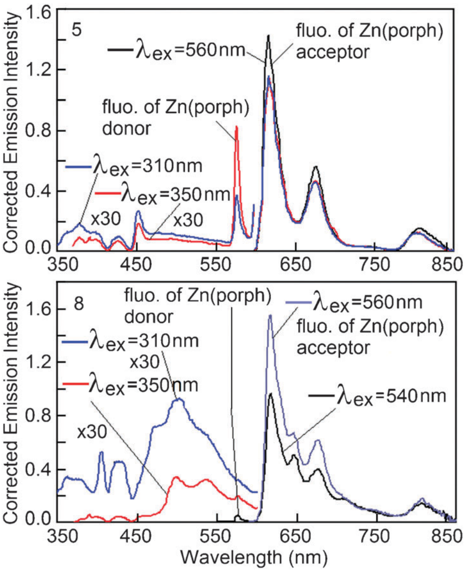

Fig. 2 Emission spectra of **5** and **8** in 2-MeTHF at 77 K.

The rates for S$_1$ and T$_1$ energy transfers, k_{ET}, are obtained using $k_{ET} = (1/\tau_e) - (1/\tau_e^{\circ})$ where τ_e and τ_e° are the fluorescence (S$_1$) and phosphorescence (T$_1$) lifetimes of the donor chromophore (**Tru**, **[Pt]** or **Zn(P1)**) in the presence and absence of an energy acceptor (**Zn(P2)**), respectively (**Zn(P1)** and **Zn(P2)** are defined in Chart 1). The τ_e and τ_e° data, measured at the emission maximum, indicate quenching in the presence of the energy acceptor by 1 to 2 orders of magnitude (Tables 2 and 3). In comparison with compound **10** (Chart 2),[9] k_{ET}(S$_1$) for **5**, **8** and **9** are all in the same vicinity meaning that the replacement of **Tru** by **[Pt]** 1 or 2 times has little effect on k_{ET} at both temperatures.

In order to verify this hypothesis, k_{ET}(T$_1$) **Tru** → **Zn(P2)** for **7** and **9** was measured and compared these to **10** and **11** (Table 3). k_{ET} increases going from **7** to **10** by two orders of magnitude further supporting the presence of cooperativity between the donors.

The replacement of two **Tru** in **10** by **[Pt]** gives **9** and an increase is noted going from **7** to **9** as well but by one order of magnitude meaning the cooperativity between **Tru** and **[Pt]** is not as good as between **Tru** and **Tru** in the T$_1$ state. To support this, k_{ET}(T$_1$) **[Pt]** → **Zn(P2)** is also compared for **9** and **11**. Both cases exhibit rates in the same range. We also note that k_{ET}(T$_1$) for **[Pt]** → **Zn(P2)** is larger than that for **Tru** → **Zn(P2)**. This is explained by the fact that only the Dexter mechanism operates in the T$_1$ state,[14] whereas both, Dexter[15] and Förster,[16] operate in the S$_1$ states. The former involves a double

Table 2 τ_F data for **Tru**, **2**, **5**, **7**, **8** and **9** in 2-MeTHF (tw = this work)

	Chromophore	τ_F/ns, 298 K	k_{ET}/ns^{-1}, 298 K	τ_F/ns, 77 K	k_{ET}/ns^{-1}, 77 K	Ref.
Tru	**Tru**	56.3 ± 0.2	—	64.6 ± 0.5	—	9
2	**Zn(P1)**	1.45 ± 0.06	—	1.71 ± 0.03	—	5*b*
5	**Tru**	0.54 ± 0.02	1.8	0.20 ± 0.09	4.9	tw
	Zn(P1)	0.26 ± 0.08	3.2	0.29 ± 0.05	2.9	
	Zn(P2)	1.67 ± 0.02	—	1.88 ± 0.03	—	
7	**Tru**	1.68 ± 0.56	0.58	1.17 ± 0.21	0.84	tw
	Zn(P2)	1.57 ± 0.05	—	1.65 ± 0.04	—	
8	**Tru**	0.89 ± 0.17	1.1	0.19 ± 0.04	5.0	tw
	Zn(P1)	0.31 ± 0.05	2.6	0.19 ± 0.05	4.7	
	Zn(P2)	1.80 ± 0.02	—	1.88 ± 0.06	—	
9	**Tru**	0.77 ± 0.24	1.3	[a]	—	tw
	Zn(P2)	1.66 ± 0.02	—	[a]	—	
10	**Tru**	0.80 ± 0.03	1.2	0.39 ± 0.06	2.6	9
	Zn(P2)	1.68 ± 0.02		2.25 ± 0.03		

[a] Not Measured

Table 3 τ_P data for **Tru**, **[Pt]**, **7** and **9–11** in 2-MeTHF (tw = this work)

	Chromophore	τ_P, 77 K	k_{ET}/s^{-1}, 77 K	Ref.
Tru	**Tru**	620.2 ± 0.3 ms	—	9
[Pt]	**[Pt]**	35.0 ± 1.3 μs	—	11*b*
7	**Tru**	12.6 ± 1.0 ms	7.8×10^1	tw
	Zn(P2)	12.5 ± 1.6 ms	—	
9	**Tru**	2.1 ± 0.2 ms	4.7×10^2	tw
	[Pt]	15.6 ± 4.8 μs	3.6×10^4	
	Zn(P2)	11.2 ± 0.5 ms	—	
10	**Tru**	0.71 ± 0.04 ms	1.3×10^3	9
	Zn(P2)	25 ± 0.4 ms	—	
11	**[Pt]**	12.6 ± 0.8 ms	5.1×10^4	5*c*
	Zn(P2)	11.8 ± 0.8 ms	—	

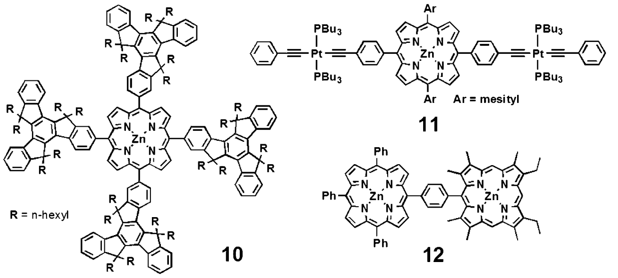

Chart 2 Structures of **10–12**.

electron exchange stressing the need for a good donor–acceptor orbital overlap and is bound to be sensitive to the dihedral angle between the truxene and porphyrin planes. The *n*-hexyl groups on the **Tru** unit render this aryl bulky and *n*-hexyl/*n*-hexyl steric interactions increase the dihedral angle towards a poorer orbital overlap as previously demonstrated using computer modeling for **10**.[9] Such a steric situation does not exist with **[Pt]** and the smaller dihedral angle is driven by the β- and *ortho*-hydrogen contacts of the phorphyrin and phenyl groups. Therefore, **[Pt]** is most likely to exhibit a better donor–acceptor orbital overlap, and a faster $k_{ET}(T_1)$ **[Pt]** → **Zn(P2)** value.

The $k_{ET}(S_1)$ **Zn(P1)** → **Zn(P2)** data in **5** and **8** are similar to each other ($2.6 < k_{ET} < 4.7$ (ns)$^{-1}$), but are slower than that found in **12** (25 (ns)$^{-1}$).[12] This is consistent with the shorter donor–acceptor distance in **12**. However, no change in $k_{ET}(S_1)$ **Zn(P1)** → **Zn(P2)** between **5** (1 **Zn(P1)**) and **8** (2 **Zn(P1)**) is noted, which may be due to the long separation between the two **Zn(P1)** in **8**, and may act independently. No **Zn(P1)** phosphorescence (703 nm)[5b] was detected and no $k_{ET}(T_1)$ **Zn(P1)** → **Zn(P2)** data are available.

This work showed an increase in $k_{ET}(S_1)$ and $k_{ET}(T_1)$ going from 2 to 4 antennas around a central unit. This effect is relevant to photosystems where excitation energy delocalization (exciton) takes place efficiently bringing the collected light energy to the special pair in the reaction center. The observed cooperativity may well be due to an excitonic effect like in the natural systems.

PDH thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding.

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