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Strong intramolecular chromophore interactions in novel bis([60]fullerene)–oligoporphyrin nanoarrays†

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Novel nanodimensional dyads were prepared by *Bingel* reaction of *meso, meso*-linked oligoporphyrin bis-malonates with C_{60}. Distinct conformational effects were observed as a result of strong fullerene–porphyrin interactions, which also lead to efficient quenching of the porphyrin luminescence.

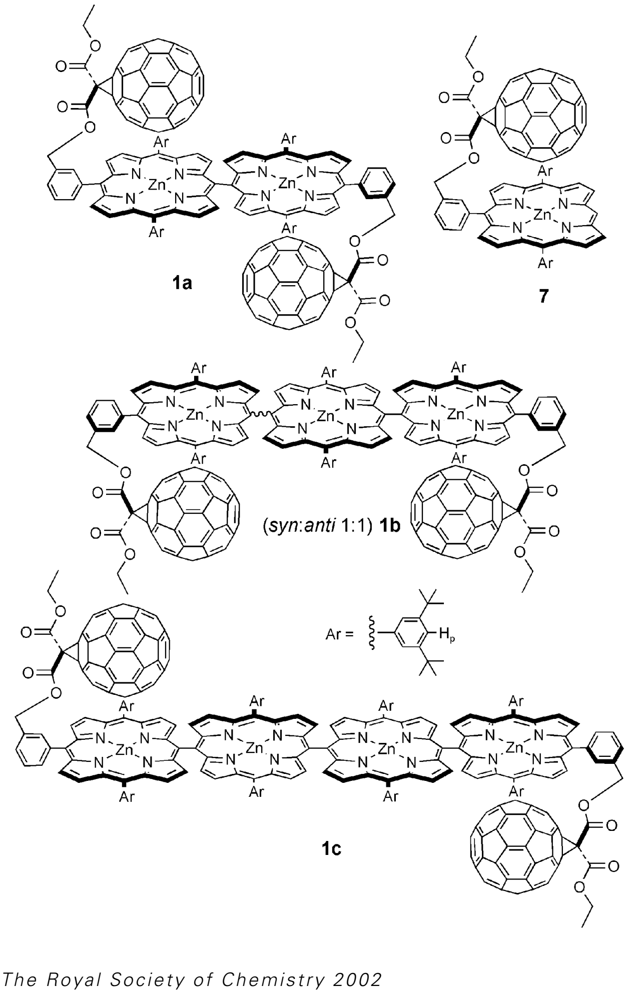
Covalent multiporphyrin arrays are attracting continuous attention in relation to investigation and modeling of electron and energy transfer in natural photosynthetic systems, as well as in the development of novel functional materials.[1] In particular, the *meso,meso*-linked, fully conjugated porphyrin rods, reported by Osuka and co-workers,[2,3] are exceptionally promising scaffolds for nanotechnology and optoelectronic applications, demonstrating highly efficient energy transfer along the array.[4]

For its part, [60]fullerene is one of the most widely used electron acceptor components in molecular dyads and much effort has been focused on the development of porphyrin–C_{60} adducts with the aim of studying photoinduced energy and electron transfer processes.[5] Saigo, Aida and co-workers showed that macrocyclic porphyrin dimers readily encapsulate C_{60} in organic solvents and in the solid state.[6,7] In earlier work, we had also obtained strong evidence for a high affinity between fullerenes and porphyrins.[8] We observed that the photophysical properties of a porphyrin connected to two fullerene moieties by single linkers were nearly identical to those of a macrocyclic *trans-1* bis-adduct of C_{60} with a porphyrin ring tangentially held in close proximity to the carbon sphere. Here, we describe a new family of fullerene–porphyrin dyads, **1a**–**c**, consisting of *meso,meso*-linked oligoporphyrin scaffolds with two C_{60} moieties attached to the outer porphyrins by short single linkers. We show that the attractive interactions between the molecular components substantially affect the conformational and photophysical properties of these systems.

The porphyrin oligomers **2a**–**c** were obtained by reaction of 5,15-bis(3,5-di(*tert*-butyl)phenyl)porphyrin with $AgPF_6$ (0.8 equiv.) in $CHCl_3$ following the protocol described by Osuka *et al.* (Scheme 1).[2] Iodination of **2a**–**c** (I_2, $AgPF_6$) afforded the diiodo derivatives **3a**–**c** with complete regioselectivity.[9] Suzuki coupling of **3a**–**c** with phenylboronic ester **4** gave **5a**–**c**. Silyl-deprotection followed by esterification with EtO_2CCH_2COCl provided bismalonates **6a**–**c**. The target compounds **1a**–**c** were finally obtained by Bingel reaction of **6a**–**c** with C_{60} in the presence of DBU and I_2 in toluene. All dyads were readily isolated by flash chromatography (SiO_2-*H*, toluene/cyclohexane 9:1) and fully characterised. The molecular mass of each compound was unambiguously established by high-resolution FT-ICR-MALDI-MS (DCTB as matrix), with the spectra depicting only the M^+ peak for **1a** and **1b**, and the MH^+ peak for **1c**.

The ^1H and ^{13}C NMR spectra of **1a** demonstrate that the dyad possesses C_2 symmetry. In the ^1H NMR spectrum (298 K, $C_6D_5CD_3$, Fig. 1), the *para*-protons Hp of the 3,5-di(*tert*-butyl)phenyl rings were detected as two *triplets* at δ 7.79 and 7.90 and the *tert*-butyl groups gave four *singlets*. Furthermore, the four β-protons close to the *meso, meso*-bond between the two porphyrins each showed a *doublet*, in agreement with the postulated chiral conformation (for a PM3-calculated structure, see graphical abstract in Contents list). A similar conformation was deduced for **5a**.

In the postulated preferred conformation of **1a**, each fullerene sits atop a porphyrin ring. Variable-temperature ^1H NMR spectroscopy was applied to quantify the tangential fullerene–porphyrin interactions in the dyad. By monitoring the coalescence of β- and *para*-protons Hp between 298 and 363 K, the activation free enthalpy $\Delta G^{\ddagger}_{298K}$ for racemisation (by turning around the single bond between porphyrin and $C_6H_4CH_2OR$ moieties) in $C_6D_5CD_3$ was estimated as 82.5 ± 2.1 kJ mol^{-1} for **1a**, and 69.9 ± 2.1 kJ mol^{-1} for **5a**.[10] Assuming no significant interactions between the $OSiBu^tMe_2$ groups (which appear at normal ^1H NMR chemical shift) and the porphyrin rings, we can deduce that the attractive interaction between a fullerene and a tangential porphyrin in **1a** increases the activation free enthalpy of racemisation by *ca.* 12 kJ mol^{-1} as compared with **5a**. In



1a

7

(*syn*:*anti* 1:1) **1b**

1c

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† Electronic supplementary information (ESI) available: selected physical and spectral data of **1a**–**c** and **7**, UV-Vis absorption spectra of **1a**–**c** and **7**, VT ^1H NMR spectra of **1a** and **5a** and fluorescence spectral comparisons for **1a**/**2a**, **1b**/**2b**, **1c**/**2c** and **7**/5,15-bis(3,5-di(*tert*-butyl)phenyl)porphyrin. See http://www.rsc.org/suppdata/cc/b2/b206624f/

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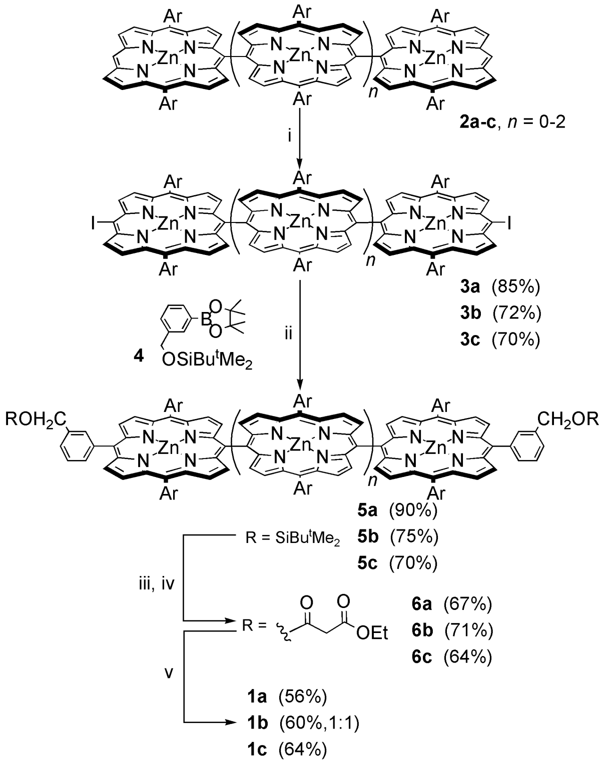

Scheme 1 *Reagents and conditions*: i, $AgPF_6$ (1 equiv.), I_2 (2 equiv.), $CHCl_3$, rt; ii, **4** (8 equiv.), Cs_2CO_3 (16 equiv.), $[Pd(PPh_3)_4]$ (0.2 equiv.), toluene, reflux, 18 h; iii, Bu_4NF (30 equiv.), CH_2Cl_2, rt, 3 h; iv, EtO_2CCH_2COCl (6 equiv.), Et_3N, CH_2Cl_2, rt, 1.5 h; v, C_{60} (4 equiv.), I_2 (2.2 equiv), DBU (6.6 equiv.), toluene, rt, 1 h. Ar = 3,5-di(*tert*-butyl)phenyl.

view of the flexibility of the benzylic malonate ester linker to the carbon sphere, it is reasonable to assume that this raise in $\Delta G^{\ddagger}_{298K}$ largely reflects the magnitude of the ground state interactions between the two chromophores in $C_6D_5CD_3$. All the considerations made for **1a** are also valid for **1c**, which adopts preferentially a C_2-symmetric conformation with the two carbon spheres resting on the outer porphyrin rings.

The relative position of the two carbon spheres on the *meso*,*meso*-triporphyrin oligomer **1b** was established by examining the ^{1}H NMR splitting pattern of the *para*-protons Hp of the middle 3,5-di(*tert*-butyl)phenyl rings, which showed two sets of signals (one at δ 7.80 and a group of 2 *multiplets* at δ 7.69 and 7.91) in a 1 : 1 ratio. These data suggest the presence of a 1 : 1 mixture of two conformers, an *anti* (C_{2h} symmetry) and a *syn* isomer (C_{2v} symmetry).

The fullerene–porphyrin adduct **7** was synthesised for comparison of its photophysical properties with those of **1a**–**c**. The UV-Vis absorption maxima of the four dyads are reported in Table 1. Fullerene absorption bands are visible below 350 nm, whereas the longer wavelength region is dominated by porphyrin-centred transitions. The bis-porphyrin dyads **1a**–**c** display excitonic splitting in the *Soret* band region, yielding two distinct maxima (at 428–420 and 465–489 nm, respectively). Whereas the fullerene-centred higher-energy transitions are not affected by the adjacent porphyrin arrays, the porphyrin bands in the dyads **1a**–**c** feature both a red shift and a strong intensity decrease, when compared to the corresponding absorptions in **2a**–**c**.[2]

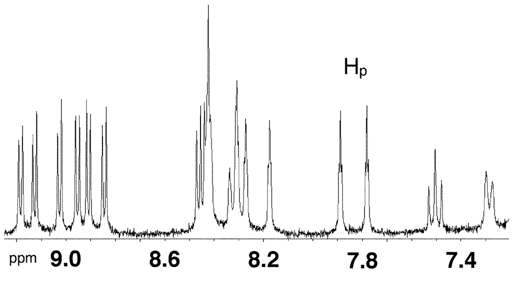

Fig. 1 ^{1}H NMR spectrum (aromatic region) of **1a** in $C_6D_5CD_3$ at 298 K.

Table 1 UV-Vis spectral data in $CHCl_3$

Compound	λ/nm (ε/M^{-1} cm^{-1})	λ/nm (ε/M^{-1} cm^{-1})	λ/nm (ε/M^{-1} cm^{-1})
7	422 (374000)	—	549 (18800)
1a	428 (115000)	465 (131000)	565 (29700)
1b	423 (167000)	481 (180000)	574 (56800)
1c	420 (218000)	489 (242000)	576 (93200)

The close spatial proximity between the carbon spheres and the tangential outer porphyrins causes a large decrease in fluorescence intensity of all dyads. The two characteristic porphyrin fluorescence bands of **7** at 596 and 644 and the broadened emission bands of **1a** (at 621 nm) and **1b**/**c** (at 634 nm) are *ca*. 100 times weaker compared to the emission bands of the starting porphyrin arrays **2a**–**c**. Thus, the porphyrin emission is also highly reduced for the dyads **1b** and **1c**, featuring one and two porphyrin moieties, respectively, that are not in direct contact with a fullerene. It remains to be clarified in time-dependent measurements whether the quenching of the luminescence results from photoinduced energy transfer and/or electron transfer along the porphyrin arrays.

In summary, the observed conformational effects together with the changes in the porphyrin-centered UV-Vis absorptions and the decrease in luminescence intensity provide good evidence for a strong attraction between the fullerenes and the porphyrin arrays in dyads **1a**–**c**. We are now conducting a quantitative investigation of the photophysical properties of these systems and explore their potential in the construction of novel hybrid materials.[11]

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