Facile synthesis of cofacial porphyrin dimer and trimer using a diarylurea linkage†

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Diarylurea-linked zinc porphyrin dimer and trimer were newly prepared: taking advantage of the structural characteristics of the diarylurea skeleton led to a convenient arrangement of the porphyrin chromophores in a cofacial manner.

Multi-porphyrin arrays and their photochemical properties have been attracting much attention from the viewpoint of the construction of suitable models for photosynthetic functions such as light gathering, excitation energy relay and long-range charge separation as well as their potential applications as molecular photonic devices such as solar cells, photon-gated molecular wires, and so on.[1] In multi-porphyrin arrays, photochemical processes, especially photo-induced energy and electron transfer are significantly affected by the inter-chromophore distance. Much effort has been devoted to regulating orientation among porphyrin chromophores by means of both covalent and non-covalent approaches,[2,3] but more convenient methods are still required to arrange the chromophores in various well-defined manners. In the present communication, we report the facile synthesis and conformational control of porphyrin dimer and trimer by using a diarylurea linkage, where the porphyrin chromophores are arranged in a cofacial manner.

As shown in Fig. 1a, *N*,*N*′-diarylurea predominantly adopts a *trans*,*trans*-conformation.[4] If porphyrin skeletons are introduced into the 5 and 5′ positions and the rotation of the N–C bonds (arrows a and a′ in Fig. 1a) is fixed by steric repulsion between the substituents introduced into the 2 and 2′ positions (*e.g.* methyls) and the carbonyl oxygen, the chromophores should be forced into a cofacial arrangement (Fig. 1b). In addition, diarylurea is easily obtained by the reaction of the corresponding amine and isocyanate in good yield. Thus, a diarylurea skeleton is a good candidate for the linkage in the construction of a cofacial porphyrin array. In Scheme 1 is shown the synthesis of diarylurea-linked zinc porphyrin dimer **1**, which is carried out in a similar manner to the preparation of urea-functionalized porphyrins reported by Collman.[5] Aminoporphyrin **3** was converted to the corresponding isocyanate **4** by treating with triphosgene in dry dichloroethane containing a small amount of dry pyridine. The reaction of **4** with another molecule of **3** followed by insertion of zinc(II) ions afforded zinc porphyrin dimers **1a** and **1b** in 73 and 49% yields from **3a** and **3b**, respectively. In the similar way, the reaction of 2 equiv. of **4a** with 1 equiv. of diaminoporphyrin **5** afforded trimer **2** in 44% yield from **3a**. The reference monomer **6** was also prepared from **3a** and aniline in 90% yield. Each compound was identified by ^{1}H NMR, ^{1}H–^{1}H COSY, electronic absorption, IR and FAB mass spectra and elemental analysis.†

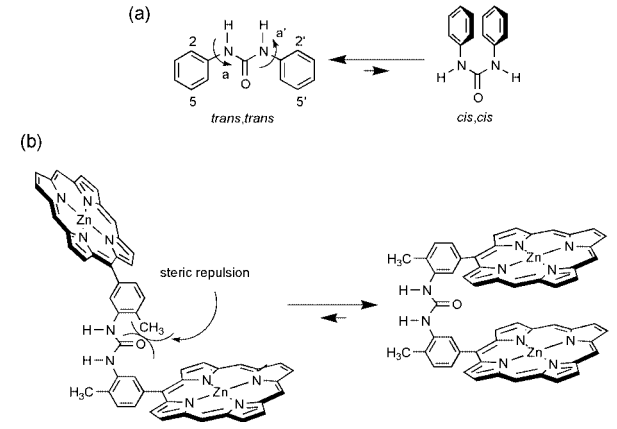
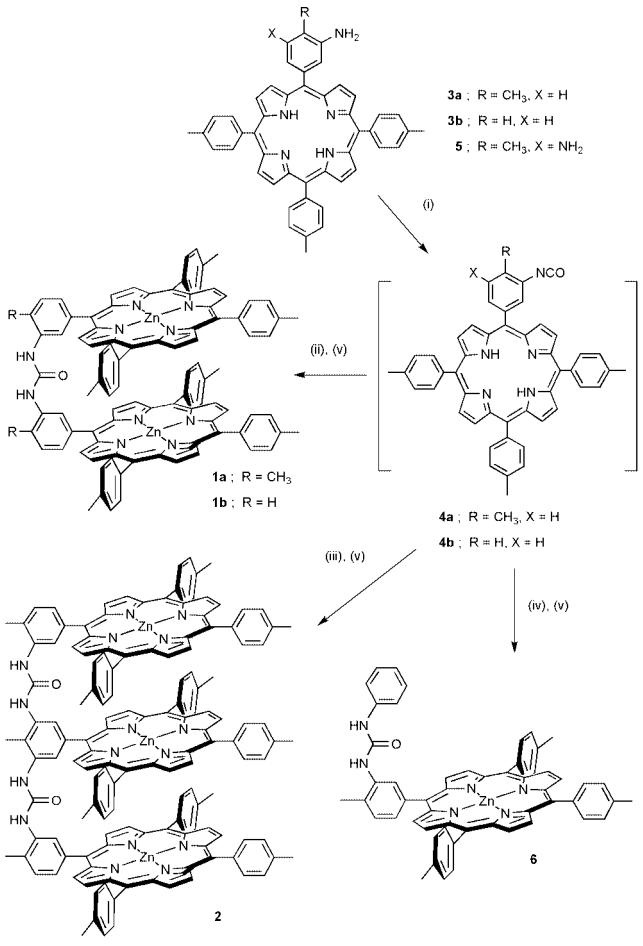


Fig. 1 (a) Conformational equiliblium in diarylurea. (b) An illustration of the conformational control of diarylurea-linked porphyrin dimer.



Scheme 1 *Reagents and conditions*: (i) triphosgene, dry pyridine, dry CH_2ClCH_2Cl, rt; (ii) **3** (1 eq.), reflux; (iii) **4a** (2 eq.) and **5** (1 eq.), reflux; (iv) aniline, reflux; (v) $Zn(OAc)_2$, CH_2Cl_2–EtOH, reflux.

† Electronic supplementary information (ESI) available: ^{1}H NMR, electronic absorption, IR and FAB mass spectra and elemental analysis data for **1a**, **1b**, **2** and **6**. See http://www.rsc.org/suppdata/cc/b0/b009578h/

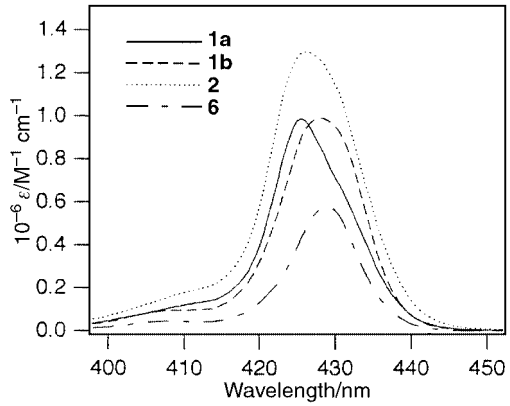


Fig. 2 Electronic absorption spectra of **1a**, **1b**, **2** and **6** in the Soret region in $CHCl_3$–DMSO (20/1, v/v) at 293 K.

Firstly, electronic absorption spectra gave us some information about the orientation between the chromophores in the zinc porphyrin oligomers **1** and **2**. The absorption spectra in the Soret region for **1**, **2** and **6** are shown in Fig. 2. The dimer **1b**, which possesses no substituents in the diarylurea skeleton except for the porphyrins, exhibited a similar absorption spectrum to **6**, whereas the absorption maximum of **1a** exhibited a slight blue shift of 4 nm compared to that of **6**, indicating an exitonic coupling between the transitions in the two porphyrin moieties adopting the cofacial arrangement.[6,7] The trimer **2** also exhibited the similar blue shift (λ_{max} = 426 nm), indicating a well-defined cofacial array of three porphyrin units, although the half band width is a little bit larger than that of **1a** (half band widths; 12 and 14 nm for **1a** and **2**, respectively).

The cofacial orientation between the porphyrin units in **1a** was also confirmed by formation of a complex with 1,4-diazabicyclo[2.2.2]octane (DABCO). The porphyrin face-to-face distance in **1a** estimated by a molecular modeling study was 7.0 Å,[8] suitable distance for binding of DABCO through two Zn–N coordination interactions. Addition of an equimolar amount of **1a** to a solution of DABCO in $CDCl_3$–DMSO-d_6 (20 : 1, v/v, 0.34 mM) induced a significantly large upfield shift of the $-CH_2CH_2-$ signal of DABCO from 2.80 to −4.75 ppm, which apparently originated from ring current anisotropy of the two porphyrin rings.[9] In Fig. 3 are shown absorption spectra of **1a** and **1b** in $CHCl_3$–DMSO (20 : 1, v/v) upon addition of varying concentrations of DABCO, and the titration data are summarized in Table 1. An isosbestic point observed in each spectral change (426 and 427 nm for **1a** and **1b**, respectively) indicates 1 : 1 complex formation in the present condition, which was supported by the Job plot. The spectra of **1a** and **1b** both exhibited blue shifts upon complexation with DABCO to

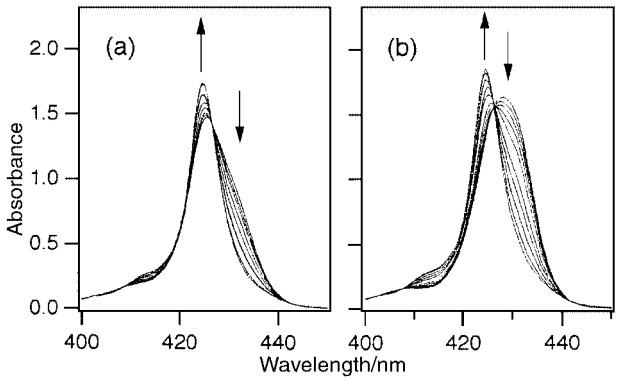


Fig. 3 Electronic absorption spectra of **1a** and **1b** in the presence of varying concentrations of DABCO in $CHCl_3$–DMSO (20/1, v/v) at 293 K. (a) [**1a**], 1.50 μM; [DABCO], 0, 1.22, 2.44, 4.83, 7.75, 11.7, 23.3, 34.8 μM. (b) [**1b**], 1.64 μM; [DABCO], 0, 0.0260, 0.0515, 0.0827, 0.125, 0.249, 0.372, 0.614, 2.50, 3.67 mM.

Table 1 Electronic absorption titration data for **1a**, **1b** and **6** with DABCO in $CDCl_3$–DMSO (20/1, v/v) at 293 K

Compound	λ_{free}[a]/nm	$\lambda_{complex}$[a]/nm	$\Delta\lambda$[b]/nm	K[c]/M^{-1} (s.d., %)
1a	425 (12)	424 (8)	−1	1.48×10^5 (11)
1b	428 (12)	424 (8)	−4	3.59×10^3 (7)
6	429 (10)	431 (9)	2	1.02×10^3 (5)

[a] Absorption maximum in the Soret region. λ_{free}; in the absence of DABCO, $\lambda_{complex}$; upon complexation with DABCO. Half band width in parenthesis. [b] $\lambda_{complex} - \lambda_{free}$. [c] Determined by computer-assisted least-squares analysis of the absorbance changes.

afford an identical narrow Soret absorption (λ_{max} = 424 nm; half band width, 8 nm), although monomer **6** exhibited a red shift upon complexation, induced by the coordination of DABCO's nitrogen to the central zinc of the porphyrin moiety.[10] This suggests that the blue shifts observed in **1a** and **1b** are due to the exitonic interaction between the porphyrin chromophores tightly fixed in a cofacial manner. It is emphasized that the binding constant K for **1a** was 41 times larger than that for **1b**, indicating that the introduction of methyl groups at the 2 and 2′ positions in the diarylurea skeleton of **1a** effectively forces the porphyrin moieties to adopt a cofacial orientation.

In summary, we have demonstrated here a facile method for construction of cofacial porphyrin oligomers by linking porphyrin units by a diarylurea linkage as well as the introduction of appropriate intramolecular steric interactions. As can be seen, alternative copolymerization of **5** with the corresponding porphyrin diisocyanate should afford a linear cofacial porphyrin array. This research is on going.

Notes and references

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7 The electronic absorption spectrum of **1a** did not exhibit any significant changes between temperatures 283–323 K. This suggests that **1a** predominantly adopts a cofacial conformation, and does not exist in equilibrium with other conformers.

8 The molecular modeling was performed at MOPAC PM3 level by using the PC Spartan *Pro* program package (Wavefunction Inc., Irvine, California, 1999).

9 In the presence of an excess of DABCO, no porphyrin ligands other than **1a** and **1a**·DABCO complex were observed in the ^1H NMR spectrum, indicating following complexation of DABCO to **1a**·DABCO scarcely occurs.

10 Although the possibility exists of the monomer **6** forming a 1 : 2 complex with two equivalents of DABCO, 1 : 1 complex formation is predominant under dilute conditions: P. N. Taylor and H. L. Anderson, *J. Am. Chem. Soc.*, 1999, **121**, 11 538.