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COMMUNICATION

Solvent-dependent amplification of chirality in assemblies of porphyrin trimers based on benzene tricarboxamide†‡

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Self-assembling achiral and chiral porphyrin trimers based on benzene tricarboxamide exhibit amplification of chirality only in solvents in which the assemblies are dynamic enough to rearrange their constituting components.

Amplification of chirality is a well-known phenomenon in solutions of helical supramolecular polymers and of non-covalently bound low molecular weight systems.[1] Initial studies by Green and co-workers distinguished two effects that influence the amplification of chirality and referred to them as the "sergeants and soldiers" principle[2] and "majority-rules" effect.[3] The "sergeants and soldiers" principle implies the control over the orientation of large number of cooperative achiral units (the soldiers) by a few chiral ones (the sergeants), whereas in the "majority-rules" effect, a slight excess of one enantiomer with respect to the other results in a strong bias toward the helical sense preferred by the enantiomer that is present in majority. Meijer and co-workers have performed systematic research on the chiral amplification of disk-shaped molecules based on benzenetricarboxamide (BTA), and revealed that the magnitude and kinetics of the effect can be strongly influenced by variations in the BTA side-chains,[4] temperature[5] and the choice of solvent.[6] We have previously described the self-assembly of porphyrin trimers based on benzenetricarboxy-amide (BTA), **1** and **2** (Fig. 1A), into helical columnar stacks, which are stabilised by a combination of threefold hydrogen bonding between the amide functions and π–π stacking interactions between the porphyrin planes (Fig. 1B).[7] While achiral trimer **1** yields a racemate of *P*- and *M*-helical stacks, the enantiopure trimer **2** yields stacks with one helical sense.[7b] Dropcasting micromolar solutions of these compounds in chloroform onto a mica surface yielded extended patterns of equidistant single columnar stacks of molecules, which were spontaneously formed by a fine balance between molecular self-assembly and dewetting.[7] In more apolar solvents like *n*-hexane, self-assembly of these compounds appeared to be much stronger,

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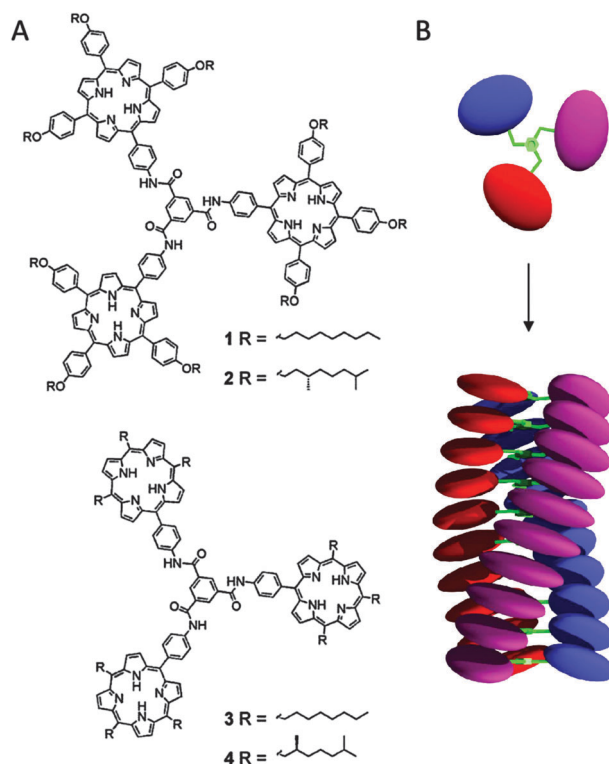

Fig. 1 (A) Molecular structures of the porphyrin trimers used in this study. (B) Schematic representation of the self-assembly of porphyrin trimers in helical columnar stacks.

resulting in the formation of stacks in solution already at very low concentrations ($< 10^{-8}$ M). Dropcasting these solutions onto mica gave irregular networks of micrometre long single molecule thick fibers.[7b]

Because of their resemblance to other BTA-based trimers, we expected that the chiral porphyrin trimer **2** would be able to act as a sergeant and dictate the overall helicity of a columnar stack consisting of soldiers of **1**. We here present these studies, and will show that a fine balance between the structure of the porphyrin trimers, their concentration, and the choice of solvent is essential for a successful amplification of chirality in assemblies of this type of compounds. In addition, we show that "sergeant and soldier" studies provide direct information about the kinetic stability of a supramolecular assembly in solution.
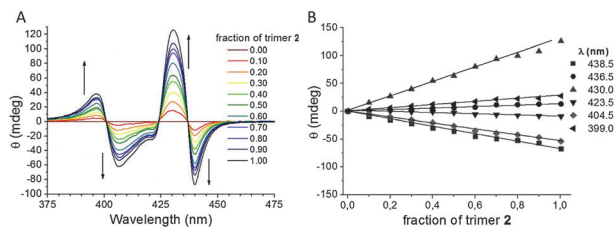
Fig. 2 (A) CD spectra of the "sergeant and soldiers" experiment in which solutions of varying concentrations of porphyrin trimers **1** and **2** in *n*-hexane were mixed. (B) Plots of the fraction of porphyrin trimer **2** *versus* the maximum intensity peaks in the CD spectra in (A).

The occurrence of a "sergeant and soldier" effect can be easily demonstrated using CD-spectroscopy: upon the introduction of progressive amounts of **2** into a solution of **1**, a non-linear increase of the CD-effect related to the quantity of added sergeant should be obtained. UV-vis spectroscopy revealed that, at micromolar concentrations required for the UV-vis and CD measurements, solutions of **1** and **2** in chloroform or toluene contained only molecularly dissolved species. In *n*-hexane, however, these trimers already self-assemble at concentrations below 10^{-8} M. Whereas the CD spectrum of the achiral trimer **1** in this solvent is CD-silent, the spectrum of chiral **2** shows strong CD-effects (Fig. 2A), indicating the assembly of the molecules in homochiral stacks.[7b] When solutions of **2** and **1** were mixed at different ratios (while keeping the total concentration of porphyrin trimers constant at 8.3×10^{-6} M), plots of the CD intensity *versus* the relative amount of **2** yielded straight lines (Fig. 2), which is evidence that no amplification of chirality occurs. Neither leaving the solutions to stand for many days, nor refluxing or sonicating them led to any changes in the CD spectra.

The total absence of amplification of chirality in this system is surprising, especially in the light of the behavior of many other disk-shaped molecules based on BTA, which generally exhibit strong amplification of chirality when the chiral components are mixed in solutions of the achiral analogues.[1a] Possibly, the interactions between **1** and **2** are not in the correct balance to express chirality from the sergeants to the soldiers, with respect to either strength and/or geometry. Alternatively, it might be thermodynamically unfavourable to exchange the components from the already formed homomolecular stacks of **1** and **2**.

To investigate the influence of the intermolecular interactions between the porphyrin trimers, the new derivatives **3** and **4** (Fig. 1A), which in comparison to trimers **1** and **2** lack three of the four *meso*-phenyl rings at the porphyrin moieties, were synthesised (ESI‡). It was reasoned that the intermolecular interactions between these molecules in the columnar assemblies would be stronger than between the molecules of **1** and **2** in their respective stacks, because of the enhanced ability of the porphyrins of **3** and **4** to approach each other and thus enhance the intermolecular π–π stacking interactions. Like in the case of **1** and **2**, UV-vis spectroscopy revealed that at micromolar concentrations trimers **3** and **4** were molecularly dissolved in chloroform and aggregated in *n*-heptane (Fig. 3A). And likewise, the addition of solutions of **4** to solutions of **3** in *n*-heptane in different ratios yielded straight lines in the plots of CD intensity *versus* the relative amount of the chiral component (Fig. 3C), and thus still a complete lack of chiral amplification was present.
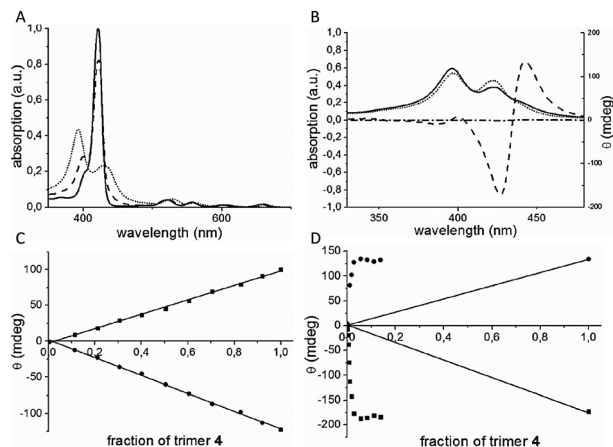

Fig. 3 (A) UV-vis spectra of porphyrin trimer **3** in chloroform (solid line, [**3**] = 1.1×10^{-6} M), in *n*-heptane (dotted line, [**3**] = 1.9×10^{-6} M), and toluene (dashed line, [**3**] = 2×10^{-6} M). (B) Normalised UV-vis spectra of **3** (1.7×10^{-5} M, dotted line) and **4** (1.6×10^{-5} M, solid line) and their respective CD spectra (**3**: dashed-dotted line; **4**: dashed line). (C) Plots of the fraction of **4** with respect to **3** *versus* the maximum intensity peaks in the CD spectra in *n*-heptane at 444 (squares) and 428 (dots) nm. (D) Plots of the fraction of **4** with respect to **3** *versus* the maximum intensity peaks, in toluene; the straight lines correspond to the expected behavior when amplification of chirality would be absent.

In contrast to porphyrin trimers **1** and **2**, trimers **3** and **4** were not molecularly dissolved in toluene at concentrations above 2×10^{-6} M, presumably as a result of stronger intermolecular interactions in stacks of the latter compounds. The UV-vis spectrum of **3** in toluene (Fig. 3A) is different from both the spectrum of this compound in chloroform, which shows a single intense Soret band at 423 nm corresponding to molecularly dissolved species, and from the spectrum in *n*-heptane, in which the band at 423 nm has completely disappeared and transformed into a blue-shifted and a red-shifted component. The spectrum of **3** in toluene indicates an intermediate situation, in which molecularly dissolved trimers are in equilibrium with aggregated ones: at 2.0×10^{-6} M concentration, the Soret band of **3** at 423 nm is flanked by a small blue-shifted component at 397 nm and a red-shifted shoulder. The intensity of these bands was strongly dependent on the concentration, which upon increase led to a rapid emergence of the blue- and red-shifted components at the expense of the band at 423 nm (Fig. 3B), indicating self-assembly of the disks. The addition of acetone to the solution caused their disassembly, which is proposed to be the result of the breaking of the hydrogen bonding between the amide groups of the trimers. In toluene, chiral trimer **4** appeared to start aggregating already at even somewhat lower concentration than that of **3**, implying that the increased steric bulk of the chiral alkyl chains apparently does not hamper self-assembly but even enhances it.

CD spectra of **4** in toluene showed that in the non-aggregated state ([**4**] < 1.2×10^{-6} M) no CD-effect is present. At higher concentrations, CD-effects emerge, which is attributed to the formation of homochiral stacks (Fig. 3B). Two Cotton effects, a strong signal centered around 436 nm and a much smaller signal centered around 397 nm, became apparent. When subsequently
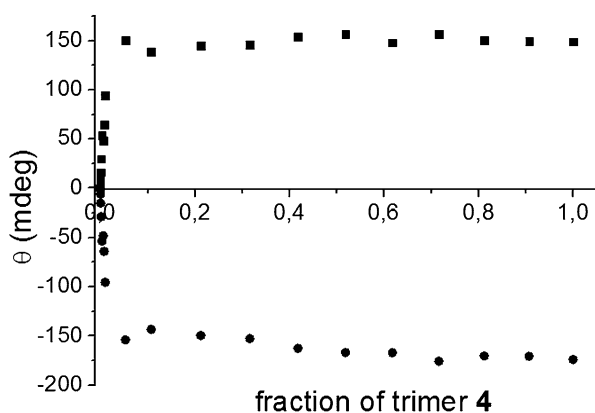
Fig. 4 Plots of the fraction of **4** with respect to **3** versus the maximum intensity peaks in the CD spectra in *n*-heptane, after premixing in toluene, at 444 (squares) and 428 (dots) nm.

toluene solutions of **3** and **4**, at a total concentration of porphyrin trimers of 1.7×10^{-5} M to ensure the presence of aggregated species, were mixed, a maximum in CD intensity was already reached when only 2.5% of chiral trimer **4** is present (Fig. 3D). This indicates that now the chiral sergeant is successfully incorporated in stacks of **3**, where it can transfer its chirality up to 40 achiral soldiers on average. The amplification of chirality in toluene is thus very successful, while in *n*-heptane it is completely absent. This behaviour is in support of the possibility that columnar stacks of porphyrin trimers in *n*-heptane are kinetically inert assemblies, and that chiral and achiral stacks cannot dynamically exchange their building blocks. However, it might still be possible that in the columnar stacks in *n*-heptane a structural imbalance exists between chiral and achiral trimers that inherently prevents chiral amplification. To investigate this possibility, different ratios of **3** and **4** were premixed in toluene at a total concentration of 1.7×10^{-5} M, the solvent in which dynamic reorganisation of the components can still occur, followed by slow evaporation of the solutions. The residues were subsequently redissolved in *n*-heptane so that the total concentration of trimers was the same as in the original toluene solutions. The plot of the CD intensity of the resulting solutions versus the relative amount of **4** (Fig. 4) now closely resembles the same plot that was recorded from the original toluene solutions (Fig. 3D), revealing a memory effect in which the amplified chirality of the stacks is retained upon a change of solvent.§

This observation confirms that in *n*-heptane stacks of porphyrin trimers based on BTA are very stable. Once formed, they are kinetically locked and do not allow dynamic interchange of their components anymore. The "sergeant and soldiers" experiments have proven to be an excellent method to reveal this behaviour. We expect that the unique stability of the assemblies of these porphyrin trimers in solution is of great interest for the future application of these systems in catalysis or photophysics devices. Work along these lines is currently in progress.

Notes and references

§ A detailed account about the thermodynamics and kinetics of stack formation by porphyrin trimers in different solvents will be given in a forthcoming full paper.

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