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Towards 1D supramolecular chiral assemblies based on porphyrin–calixarene complexes†

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The design of functional chiral nanostructures in aqueous solution represents one of the most exciting challenges in supramolecular chemistry, offering potential applications in catalysis, sensing, and materials science. In this scenario, it has already been shown that the hierarchical step-by-step addition of porphyrins to calix[4]arene aqueous solutions yields porphyrin–calixarene supramolecular complexes with exact and tuneable stoichiometries and defined dimensionality. The present study reports the formation of novel 1D porphyrin–calix[4]arene assemblies, achieved through a hierarchical and stoichiometrically controlled self-assembly process in water using host–guest interactions between the anionic trisulfonated porphyrin, **H₂DPPS3**, and the cationic bis-calix[4]arene, **BC₄**. In addition, to obtain chiral 1D noncovalent assemblies, the copper(II) porphyrin, **CuDPPS3**, and the enantiomerically pure bis-calix[4]arenes, (*R,R*)- and (*S,S*)-**BC₄**, were also used in aqueous solution. The stepwise formation of linear noncovalent and chiral assemblies, based on porphyrin–calixarene complexes, was demonstrated by a number of different techniques such as: UV-vis spectroscopy, circular dichroism (CD), resonance light scattering (RLS) and scanning electron microscopy (SEM), revealing precise stoichiometries, sequence, dimensionality and induction of chirality.

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Introduction

In recent decades, the synthesis of large chiral supramolecular architectures derived from the self-assembly of simple molecular synthons has gained considerable interest owing to the increasing use of these species in various fields,^{1–7} ranging from light-harvesting^{8,9} and sensing^{10,11} to catalysis^{12,13} and photodynamic processes.¹⁴ In this context, porphyrins represent a relevant class of organic compounds exhibiting unique photophysical properties and synthetic versatility.^{15–19} Furthermore, under specific experimental conditions, porphyrins can self-organize into well-defined nanostructures with tuneable sizes, morphologies and properties.^{20–23} However, obtaining discrete porphyrin-based supramolecular complexes in aqueous medium requires careful selection of the reactants and rigorous control of the reaction conditions (*e.g.*, the sequence of the reactants addition) to prevent undesired aggre-

gation phenomena driven by electrostatic interactions, π – π stacking, and other weak forces.^{24–31} To this end, the choice of an appropriate molecular template is crucial for the successful synthesis of well-ordered self-assembled architectures.^{32–38}

In a pioneering study published in 1994,³⁹ M. C. Drain and J.-M. Lehn introduced an innovative one-pot synthetic method that took advantage of kinetically inert metal–ligand coordination between platinum or palladium ions and the pyridyl moieties of *meso*-substituted phenyl–pyridyl porphyrins. This approach allowed for rapid and efficient formation of porphyrin arrays with controlled stoichiometry and geometry, achieving yields close to 100%. Their work paved the way for metal ion-mediated synthesis of porphyrin assemblies with precise structural control.

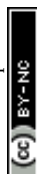
More recently, host–guest chemistry has emerged as a compelling approach to achieve precise control on the stoichiometry and sequence of these assemblies.^{40–46} In this context, the host molecule replaces the metal ion, contributing to the structural and electronic features of the resulting complexes. Cyclodextrins, for example, have been employed to form binary host–guest complexes with porphyrins, initially synthesised to mimic natural enzymes like myoglobin in aqueous environments.⁴⁷

The ability to form stable complexes in aqueous solutions is an intrinsic advantage of host–guest chemistry, enabling the

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simultaneous use of water-soluble and hydrophobic molecular components. In this regard, calixarenes have emerged as promising molecules capable of templating discrete porphyrin arrays in aqueous solutions with defined stoichiometry, sequence and high stability.^{36,48}

Studies have demonstrated that the interaction between *meso*-tetrakis(4-*N*-methylpyridyl)porphyrin and a tetracarboxylic *p*-sulfonate calix[4]arene results in a significant hypochromism and broadening of the Soret band, indicating strong host-guest interactions. By Job plot analyses and spectrophotometric titrations, the formation of discrete species at specific stoichiometric ratios has been revealed, highlighting the control of the assembly sequence of porphyrin units as well.^{43,49} The stability and kinetic inertness of these supramolecular complexes have also been confirmed by diffusion NMR and dynamic light-scattering experiments.⁵⁰ In addition it has been demonstrated that by using ditopic^{51,52} or tritopic⁵³ bis- or triscalix[*n*]arene it is possible to control the dimensionality of the assembly, hierarchically forming 2D and 3D noncovalent architectures of considerable size.

Such control over the stoichiometry, sequence and dimensionality of porphyrin assemblies is achieved by following rigid hierarchical rules and exploiting electrostatic interactions as driving force and solvophobic interactions as “non-covalent glue” to stabilize the complexes. Noteworthy, an electronic communication between the external components and the central core of the supramolecular system has been detected, opening new avenues for the development of functional materials with tailored optical and electronic properties. Previously, by exploiting the electronic communication between porphyrins, assembled *via* the calixarene-templated approach, we have induced chirality in the resulting porphyrin-calix[4]arene assemblies. In addition, we were also able to increase the distance between the central and peripheral porphyrin, demonstrating in such a way the presence of a long-range chirality transfer effect.^{54,55}

A further step towards a more complete understanding of the above-mentioned self-assembly processes involves the use of new molecular building blocks.

In the present study, we demonstrate that our approach, based on the hierarchical step-by-step addition of porphyrin to a calix[4]arene solution, allows the design of new architectures with desired properties. To this end, we have selected as building blocks the ditopic bis-calix[4]arene, 1,6-bis[5,11,17,23-tetrakis(trimethylammonium)-25,26,27-tripropoxy-28-(oxy)calix[4]arene]hexane octachloride⁵² (**BC₄**, Fig. 1b), and the novel anionic trisulfonated porphyrin, **H₂DPPS3**, (Fig. 1a) to assemble 1D noncovalent structures with tuneable properties. In addition, to induce chirality onto 1D porphyrin/bis-calixarene complexes we have synthesised a new chiral bis-calix[4]arene, *N,N'*-bis(5,11,17,23-tetraamino-25,26,27-tripropoxy-28-[3-carbonylpropoxy]calix[4]arene)-1,2-diaminocyclohexane octahydrochloride in both enantiomeric forms ((1*R*,2*R*)- and (1*S*,2*S*)-**BC4** respectively, Fig. 1c). With this study, we aim to contribute to the development of new chiral functional materials based on porphyrin systems, expanding their applicability in the field of molecular devices, catalysis, and materials science.

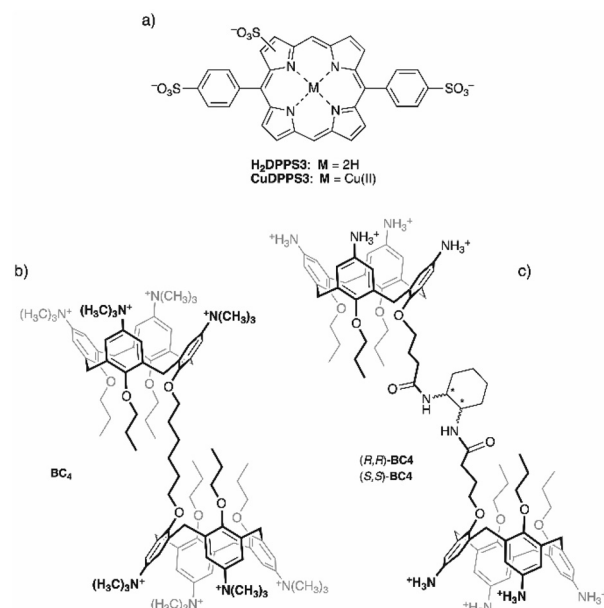


Fig. 1 Molecular structures of (a) **H₂DPPS3** and its Cu(II) derivative, (b) **BC₄**, and (c) (S,S)- or (R,R)-**BC4**.

Experimental section

Commercial reagent grade chemicals were used as received without any further purification. Solvents were dried by standard methods.

Trisulfonated porphyrin **H₂DPPS3** was synthesised according to a slight modification of Ribo's procedure,⁵⁶ using 5,15-diphenylporphine⁵⁷ as the starting material. The detailed synthetic procedure is reported in the ESI.†

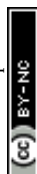
The copper(II) derivative of **H₂DPPS3**, **CuDPPS3**, was synthesised from the corresponding free-base by heterogeneous metal-insertion from copper(II) oxide (CuO) in water, according to a previous report.⁵⁸

BC₄ was available from previous studies.⁵²

The water soluble chiral bis-calix[4]arenes (*R,R*)-**BC4** and (*S,S*)-**BC4** were synthesised starting from the known acid chloride **1**⁵⁹ according to Scheme 1. Calix[4]arene **1** was reacted in turn with enantiomerically pure (1*S*,2*S*)-(+)- and (1*R*,2*R*)-(-)-1,2-cyclohexanediamine to produce *C₂*-symmetric enantiomerically pure octanitro-bis-calix[4]arene diamides (*R,R*)-**8NO₂-BC4** and (*S,S*)-**8NO₂-BC4**, in good yields. The reduction of the octanitro enantiomers afforded the corresponding octaamino derivatives (*R,R*)-**8NH₂-BC4** and (*S,S*)-**8NH₂-BC4**, which were directly converted to the corresponding hydrochlorides (*R,R*)-**BC4** and (*S,S*)-**BC4** (see the ESI for details†).

Ultrapure water at room temperature (18.2 MΩ cm, TOC 1 ppb), obtained from the PURELAB Flex 3 system (Elga Veolia company), was used to prepare all samples and stock solutions.

H₂DPPS3 and **CuDPPS3** stock solutions (about 4 × 10⁻⁴ M) were prepared by dissolving a given amount of the solid powder in ultrapure water. The concentrations of the porphyrin stock solutions were spectrophotometrically calculated



nated form of $\text{H}_2\text{DPPS3}$, undergoes a hypochromic effect, giving rise to a new band at 420 nm which is consistent with the formation of the core-protonated form of $\text{H}_2\text{DPPS3}$ (i.e., $\text{H}_4\text{DPPS3}$). In detail, by plotting the absorbance values at 405.5 nm and 420 nm against the pH values of each independent solution, it is possible to evaluate the pK_a values of $\text{H}_2\text{DPPS3}$ (Fig. 3). We observe only the equilibrium corresponding to the protonation step of the nitrogen core atoms of $\text{H}_2\text{DPPS3}$, with an estimated pK_a value of about 2.8. The protonation of the sulfonate groups cannot be obtained under these conditions, because it generally occurs in the presence of strong acidic solutions ($[\text{HCl}] > 4 \text{ M}$).^{24,61}

On the contrary, by slowly lowering the pH of a $\text{H}_2\text{DPPS3}$ solution (2 μM), in the 10.00–2.40 range, we were able to collect useful information on the porphyrin self-assembly process (Fig. S11†). During the pH titration, the absorption band of the deprotonated porphyrin ($\lambda = 405.5 \text{ nm}$) decreases in intensity and it becomes gradually broader. Moreover, Rayleigh scattering effect tends to increase over the titration course. Ultimately these phenomena can reasonably be ascribed to the formation of self-aggregates during the pH titration.⁶⁰

To test whether such intrinsic self-aggregation tendency of $\text{H}_2\text{DPPS3}$ could be controlled in the presence of an appropriate templating agent, we turned our attention to BC_4 . Namely, a homoditopic bis-calix[4]arene (Fig. 1b) bearing eight permanent cationic trimethylammonium groups and, consequently, fully soluble in water even at neutral pH and capable, in principle, of interacting with anionic counterparts such as the sulfonated porphyrins.

To evaluate the potential of ditopic BC_4 as a templating agent for the noncovalent assembly of porphyrin-based supramolecular structures, a 2.5 μM aqueous solution of BC_4 at neutral pH was gradually titrated (Fig. S13†) with increasing aliquots of an aqueous solution of $\text{H}_2\text{DPPS3}$ (0.25 μM per aliquot). The absorption data recorded over the course of the

titration displays hypochromicity and a broadening of the $\text{H}_2\text{DPPS3}$ Soret band as compared to the experiment performed in the absence of BC_4 (Fig. S14†). According to our previous observations,^{43,49} this represents a clear-cut evidence in favour of porphyrin/bis-calixarene interactions. Moreover, our earlier reports^{43,49,52} revealed the importance of electrostatic and hydrophobic interactions in the formation and stabilization of porphyrin/calix[4]arene assemblies. On this ground, we can reasonably state that the formation of porphyrin–calix[4]arene host–guest complexes is primarily driven by strong electrostatic interactions between the cationic moieties of BC_4 (host) and the anionic *meso*-phenyl sulfonate groups of $\text{H}_2\text{DPPS3}$ (guest). The additional sulfonate group present on one of the pyrrole moiety of $\text{H}_2\text{DPPS3}$ increases the water solubility and improves the charge balance, contributing to the formation and stabilization of such discrete complexes. Finally, the host–guest complexes are further stabilized by π – π stacking between the aromatic cores of the porphyrins and by solvophobic forces.

Several studies on other water-soluble calix[4]arenes,^{43,49} bis-calix[4]arenes,^{52,55} and tris-calix[4]arenes,⁵³ have demonstrated that discrete calixarene/porphyrin assemblies form in a stepwise, hierarchical fashion, as evidenced by distinct spectral changes in absorption or emission. More specifically, the formation of complexes or assemblies with well-defined stoichiometry are consistently marked by specific *break-points* in a plot of the absorbance values of the porphyrin Soret band vs. the [porphyrin]/[calixarene] ratio. On a titration curve, these *break-points* are highlighted by changes in slope greater than 10%. The presence of different slopes indicates distinct assemblies in solution, each characterised by its own molar extinction coefficient. Noteworthy, the occurrence of *break-points* confirms that the species formed are not in equilibrium with each other; otherwise, a continuous straight line would be observed throughout the titration experiment.⁶²

In analogy with other examples reported in the literature, the self-assembly process of $\text{H}_2\text{DPPS3}$ and BC_4 can be most effectively analysed by plotting the porphyrin absorbance values at 405.5 nm against the $[\text{H}_2\text{DPPS3}]/[\text{BC}_4]$ ratio (Fig. 4).

The titration plot reveals that the assembly process proceeds under stoichiometric control up to a $\text{H}_2\text{DPPS3}$ concentration of 10 μM . This is unambiguously demonstrated by the presence of several *break-points* (labelled as A, B, and C in Fig. 4, trace b), which correspond to $\text{H}_2\text{DPPS3}/\text{BC}_4$ complexes with precise stoichiometries—specifically, 0.5 : 1, 2 : 1, and 4 : 1 (refer to Fig. 4, trace b).[‡] These observations, coupled with the hypochromicity and broadening of the Soret band, indicate the presence of strong host–guest interactions.

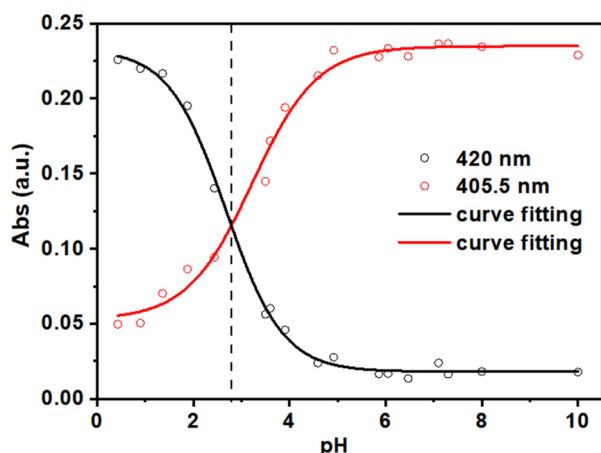
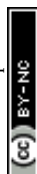


Fig. 3 Plot and experimental fit of the absorbance values at $\lambda = 405.5 \text{ nm}$ (red circles) and $\lambda = 420 \text{ nm}$ (black circles) as function of pH values (pH = 10.00; 8.00; 7.30; 7.10; 6.47; 6.05; 5.86; 4.92; 4.59; 3.91; 3.60; 3.50; 2.44; 1.88; 1.36; 0.9) during the independent solutions experiment of $\text{H}_2\text{DPPS3}$ (2 μM).

[‡]The absence of *break-points* at the 1 : 1- and 3 : 1- ($\text{H}_2\text{DPPS3}/\text{BC}_4$) ratios could probably be explained with the presence of a simultaneous equilibrium between two species with the same stoichiometry but different arrangement. For instance, in the 1 : 1- ($\text{H}_2\text{DPPS3}/\text{BC}_4$) complex two porphyrin could occupy the central core or, alternately, one porphyrin could be located between two bis-calixarene molecules while the second is bound to one of the external cavity of a bis-calixarene (Fig. S15†).



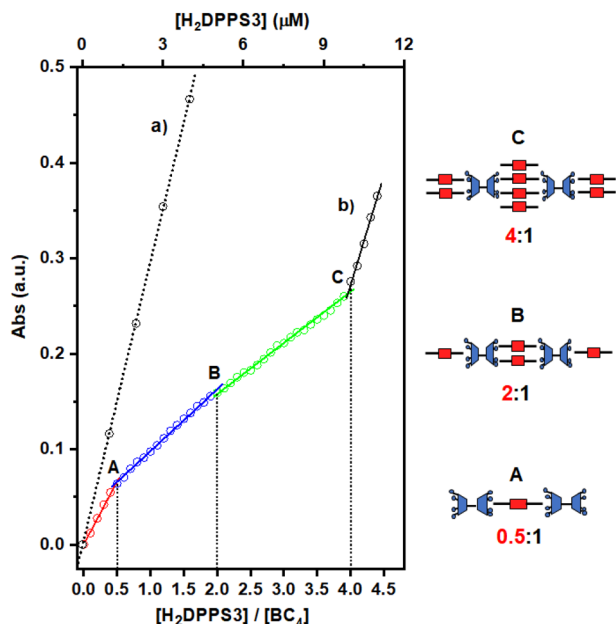


Fig. 4 Variation in the absorbance of the $\text{H}_2\text{DPPS3}$ Soret band ($\lambda = 405.5$ nm) observed upon: (i) increase of the porphyrin concentration in water at pH = 7.0 (dotted black trace labelled as (a)); (ii) portion-wise addition ($0.25 \mu\text{M}$) of $\text{H}_2\text{DPPS3}$ to a $2.5 \mu\text{M}$ aqueous solution of BC_4 at pH = 7.0 (multi-coloured trace labelled as (b)). Break-points are labelled as A, B, and C. The cartoons sketched on the right hand-side represent the likely structures of the complexes A, B and C, formed at the corresponding break-points.

As the titration progresses beyond the addition of the fourth equivalent of porphyrin (*i.e.*, for $[\text{H}_2\text{DPPS3}] > 10 \mu\text{M}$), the absorbance sharply increases and becomes almost identical to that observed for $\text{H}_2\text{DPPS3}$ on its own (compare trace (a) with the last segment of trace (b) in Fig. 4). These findings indicate that the excess of porphyrin molecules now present in the solution are no longer interacting with the supramolecular complex.

Such porphyrin/bis-calixarene complexes (Fig. 4) could further self-assemble to generate discrete 1D nanostructures. To promote the linear growth of porphyrin/bis-calix[4]arene assemblies, a solution of the 2 : 1 $\text{H}_2\text{DPPS3}/\text{BC}_4$ complex (structure B in Fig. 4) was initially treated with BC_4 (up to $5 \mu\text{M}$) and then, after 1 hour and in a step-wise manner, with $\text{H}_2\text{DPPS3}$ (up to $26.25 \mu\text{M}$) to produce a 10.5 : 2 $\text{H}_2\text{DPPS3}/\text{BC}_4$ complex where the interacting negative and positive charges of the porphyrin and the bis-calix[4]arene are roughly balanced. Finally, approximately $200 \mu\text{L}$ of an aqueous solution containing the 10.5 : 2 $\text{H}_2\text{DPPS3}/\text{BC}_4$ complex were drop-cast onto a silicon substrate. After a slow evaporation in the air, the substrate surface was subjected to SEM investigation (Fig. 5a and b). A low-magnification micrograph shows the presence of nanosticks on the silicon substrate surface (Fig. 5a). The darker appearance of the nanosticks is likely due to the lower conductivity of these nanostructures compared to that of the plain silicon substrate. Poorly conductive samples accumulate charges and, as a result, the signal output is reduced. Close examination of the micrograph at high magnification indicates

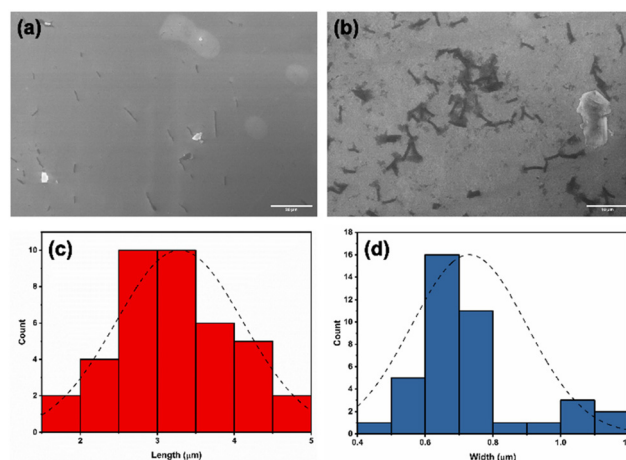


Fig. 5 SEM micrographs, at (a) low (scale bar = $20 \mu\text{m}$) and (b) high magnification (scale bar = $10 \mu\text{m}$), of nanosticks formed upon deposition of $\text{H}_2\text{DPPS3}/\text{BC}_4$ complexes onto a silicon substrate surface. Nanostick length (c) and width (d) distribution bars. Distribution curves are shown as black dashed lines.

the presence of nanosticks of similar shape and size (Fig. 5b), with an average length and width of $3.3 \pm 0.8 \mu\text{m}$ and $0.7 \pm 0.2 \mu\text{m}$, respectively. The length and width distribution of the nanosticks is shown in Fig. 5c and d, respectively.

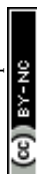
Given that the sizes of $\text{H}_2\text{DPPS3}$ and BC_4 are about $0.002 \mu\text{m}$, the length of the 2 : 1 complex should be around $0.01 \mu\text{m}$, it is reasonable to assume that an average of about 300 2 : 1 species are assembled to form a nanostick.

The successful formation of such porphyrin/bis-calix[4]arene assemblies not only demonstrates that self-assembly is hierarchically controlled and takes place in a stepwise manner, but also provides an opportunity to transfer electronic properties to the whole complex. In this context, recent studies have shown that stereogenic agents are able to induce chirality in porphyrin-calixarene assemblies, indicating electronic communication among the porphyrins in both 2D and 3D assemblies.^{53–55} For this reason, the use of novel enantiomerically pure bis-calix[4]arenes, namely (*R,R*)- BC_4 and (*S,S*)- BC_4 (Fig. 1c), as compared to the achiral BC_4 (Fig. 1b) might induce chirality to the entire supramolecular complex.

In water, bis-calix[4]arenes (*R,R*)- and (*S,S*)- BC_4 are soluble only under acid conditions upon protonation of the amino groups at the wider rims. For instance, acid aqueous solutions (pH = 2.0) of these chiral bis-calix[4]arenes ($50 \mu\text{M}$) exhibit two absorption peaks at about 275 nm and 300 nm (Fig. S16†). Consequently, an optical activity appears in their absorption range (see the inset of Fig. S16†).

Moreover, the spectrophotometric pH titration in aqueous solution (in the 1.50–10.70 pH range) confirmed that, at low pH values (*i.e.*, pH = 2.0), (*R,R*)- and (*S,S*)- $8\text{NH}_2\text{-BC}_4$, are converted to their fully protonated octaammonium forms (*R,R*)- and (*S,S*)- BC_4 , respectively ($\text{pK}_a \approx 5$, see Fig. S17†).

Thus, aqueous solutions of (*R,R*)- or (*S,S*)- BC_4 are stable only under acid conditions (pH < 4) and this evidence suggests that a free-base porphyrin, such as $\text{H}_2\text{DPPS3}$, cannot be



In analogy with the **H₂DPPS3/BC₄** system (Fig. 4), in the presence of (*R,R*)- or (*S,S*)-**BC₄** and **CuDPPS3** discrete complexes are also formed with similar structure (Fig. 6).§

Fig. 6 Variation in the absorbance of the **CuDPPS3** Soret band ($\lambda = 405.5$ nm) observed upon: (i) increase of the porphyrin concentration in water at pH = 2.0 (dotted black trace labelled as (a)); (ii) portion-wise addition ($0.25 \mu\text{M}$) of **CuDPPS3** to a $2.5 \mu\text{M}$ aqueous solution of (*R,R*)- or (*S,S*)-**BC4** at pH = 2.0 (multi-coloured trace labelled as (b)). The *break-points* are labelled as A, B, C, and D. The cartoons sketched on the right hand-side represent the likely structures of the complexes A, B and C, formed at the corresponding *break-points*.

No significant ICD signals were detected below 2 : 1 porphyrin/bis-calixarene molar ratio, likely due to a very low absorbance value. However, ICD signals appear at the 2 : 1 ratio, becoming even more evident at the 4 : 1 molar ratio (Fig. 7), highlighting the presence of an exciton coupling as well. These data are consistent with our proposed structures (see Fig. 6) where the porphyrin-stacking leads to a strong electric dipole-dipole coupling, which is also responsible for the CD couplet in the porphyrin absorbance region.⁶⁴ Finally, the efficiency of chirality induction was further quantified by calculating the dissymmetry *g*-factor which is related to the quality of the CD rotational oscillator and uncoupled with respect to the molar concentration.⁶⁵ The calculated *g*-factor is comparable for both enantiomeric complexes and it increases from $\approx 7.9 \times 10^{-5}$ to

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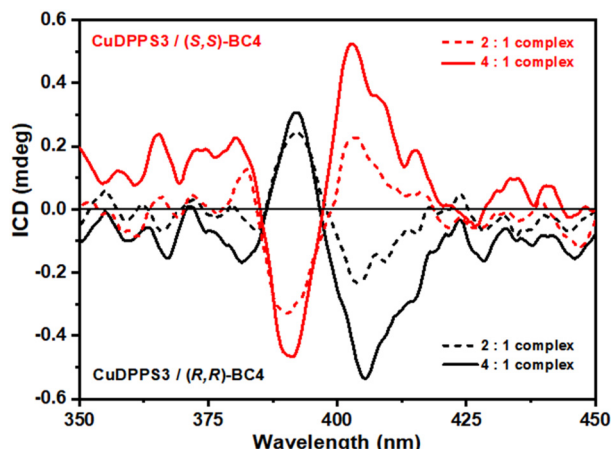


Fig. 7 ICD spectra of aqueous solutions at pH 2.0 of (i) **CuDPPS3** (5 μ M dashed red trace, 10 μ M solid red trace) in the presence of (*S,S*)-**BC4** (2.5 μ M), and (ii) **CuDPPS3** (5 μ M dashed black trace, 10 μ M solid black trace) in the presence of (*R,R*)-**BC4** (2.5 μ M).

$\approx 9.2 \times 10^{-5}$ at a porphyrin/bis-calix[4]arene molar ratio of 2 : 1 and 4 : 1, respectively. This increase further confirms the efficient transfer of chirality and supports the structural model proposed in Fig. 6. At higher porphyrin/bis-calix[4]arene molar ratios, the structural arrangement of the porphyrins promotes, *via* π - π stacking, a stronger exciton coupling amplifying the asymmetry of the supramolecular complexes and thus their *g*-factor.

Conclusions

By exploiting the versatility of porphyrin-calixarene complexes we have formed chiral linear noncovalent polymer in aqueous solution. Indeed, by selecting the appropriate building blocks with suitable functionalities, it is possible to drive the self-assembly towards the formation of a given desired structure with specific characteristics. In this work we employed a tri-anionic porphyrin and two cationic bis-calix[4]arenes to take advantage of the electrostatic forces to firstly induce the self-assembly; then, the hydrophobic interactions contribute to yield kinetically inert porphyrin/bis-calixarene assemblies. Moreover, the rigid hierarchical rules apply, so as only a step-wise addition of small aliquots of porphyrin to the solution of chiral bis-calix[4]arene provides complexes with precise stoichiometry, sequence, dimensionality and chirality.

Our approach shed further light on how to exploit noncovalent interactions in driving the self-assembly process and how to induce chirality through the electronic communication between external components and the central core of the supramolecular system. These data confirm the high potentiality of supramolecular chemistry and how hierarchical self-assembly allow to design functional supramolecular chiral material for several applications.

Author contributions

Conceptualization: A. D., M. G., R. P.; funding acquisition: A. D. A. N.; investigation: M. G., M. B., C. M. A. G., M. M., I. P., M. F. P., A. N., G. T.; methodology: A. D., R. P., M. E. F., M. F. P.; project administration: A. D., M. G.; resources: M. P., A. N., C. M. A. G.; supervision: A. D., M. G.; validation: M. B., M. G.; visualization; A. D., M. G.; writing – original draft: A. D., M. G.; writing – review & editing: M. F. P., A. N., R. P., M. E. F., C. M. A. G.

Data availability

Data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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