Transformation, memorization and amplification of chirality in cationic Co(III) complex–porphyrin aggregates

Jian Wang,[a] **Dongdong Ding,**[b] **Lixi Zeng,**[a] **Qian Cao,**[a] **Yujian He***[ac] **and Hui Zhang***[b]

Λ- and Δ-enantiomers of *cis*-[CoBr(NH$_3$)(en)$_2$]Br$_2$ were obtained by absolute asymmetric synthesis. The interactions between the achiral 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) and two chiral cationic Co(III) complexes were studied by UV-vis spectroscopy, circular dichroism (CD), fluorescence spectroscopy and atomic force microscopy (AFM). It was found that the cationic Co(III) complexes can induce the formation of chiral porphyrin J-aggregates, that the metal-centered chirality can be transferred to the J-aggregates, and that the chirality was able to be memorized and amplified in the porphyrin J-aggregates. Therefore, this should be a good chiral model for understanding similar processes in physical and biological systems.

Introduction

The origin of homochirality has aroused great interest since the discovery of the predominance of L-amino acids in protein and D-sugars in both DNA and RNA.[1–4] The spontaneous generation of biomolecular homochirality is one of the most important steps to understanding the origin of life.[5–8]

In 1995, Asakura discovered random symmetry breaking in the synthesis of chiral octahedral cobalt complex (*cis*-[CoBr(NH$_3$)(en)$_2$]Br$_2$), *i.e.* a spontaneous preferential generation of one enantiomer.[9–11] Recently, Purrello *et al.* reported that the chiral [Ru(1,10-penanthroline)]$^{2+}$ and [(Ru(phen)$_3$)]$^{2+}$ enantiomers could act as a guide to induce the chiral assembly of the achiral anionic porphyrin derivatives.[12] The chirality of the inorganic complexes could be transferred and amplified to the supramolecules during the assembly process.[13–15]

Owing to their unique and tunable spectroscopic and electronic properties, *meso*-substituted water-soluble porphyrins are excellent building blocks for such hierarchical molecular systems.[16–20] Achiral porphyrins have been used to form chiral supramolecular systems by the induction of chiral compounds. For example, amino acids, water-soluble charged biopolymers, DNA, polypeptides, polysaccharides and chiral inorganic complexes could be used as chiral templates for the induction of chiral porphyrin J-aggregates, respectively.[21–30] In some cases, the kinetic inertia of the chiral porphyrin J-aggregates can lead to the so-called "memory" phenomenon.[31–36] Another intriguing property of these supramolecular systems is the self-amplification of their own chirality.[37–39] Moreover, some contributions have shown that the supramolecular system of porphyrin J-aggregates could be used as a chiroptical switch.[40–42] Much effort has been devoted to the investigation of chiral memorization and amplification functions in the supramolecular porphyrin system.

What we are interested in is whether the random symmetry breaking in the synthesis of chiral cobalt complexes could be transferred into other hierarchical molecular systems. In this paper, we report that the chiral aggregation of achiral anionic porphyins can be induced by chiral cationic Co(III) complexes (Scheme 1). The supramolecular chirality in the porphyrin aggregates can be memorized even after the addition of an excess of the cationic Co(III) complex of opposite chirality. More interestingly, the ICD signal of the cationic Co(III) complex–porphyrin aggregates induced by Δ- (or Λ-) Co(III) complex enantiomers could be amplified by the addition of Λ- (or Δ-) enantiomers, respectively (Scheme 1). Using the chiral porphyrin aggregates from which the Co(III) complex enantiomer inducer was removed, the chirality could be amplified by adding the porphyrin monomers to the system. The chiral porphyrin aggregates were characterized by UV spectroscopy, circular dichroism (CD) spectroscopy, fluorescence and atomic force microscopy (AFM). The system may be seen as a guiding model to understanding the biologically relevant aggregates, and gives some insights into the mechanisms of chirality transfer from the molecular to supramolecular level.

Experimental section

1. Materials

5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) was purchased from Fluka. Ethylene diamine, CoSO$_4$·7H$_2$O, NH$_4$Br, hydrobromic acid (48%), synthetic camphor (C$_{10}$H$_{16}$O), Br$_2$(l), NH$_3$·H$_2$O (25%), fuming sulfuric acid (20%) and Na$_2$SO$_3$ were purchased from Sinopharm Chemical Reagent Co., Ltd (SCRC, P. R. China). (+)-Ammonium α-bromocamphor-π-sulfonate [NH$_4$(*d*-BCS)] and (−)-ammonium

[a] *College of Chemistry and Chemical Engineering, Graduate University of Chinese Academy of Sciences, Beijing 100049, China. E-mail: yujianhe@hotmail.com; Fax: (+86) 108 825 6093; Tel: (+86) 108 825 6141*
[b] *College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail: huizhang@xmu.edu.cn; Tel: (+86) 592 218 3910*
[c] *State Key Laboratory of Natural and Biomimetic Drugs, Peking University, Beijing 100083, China*
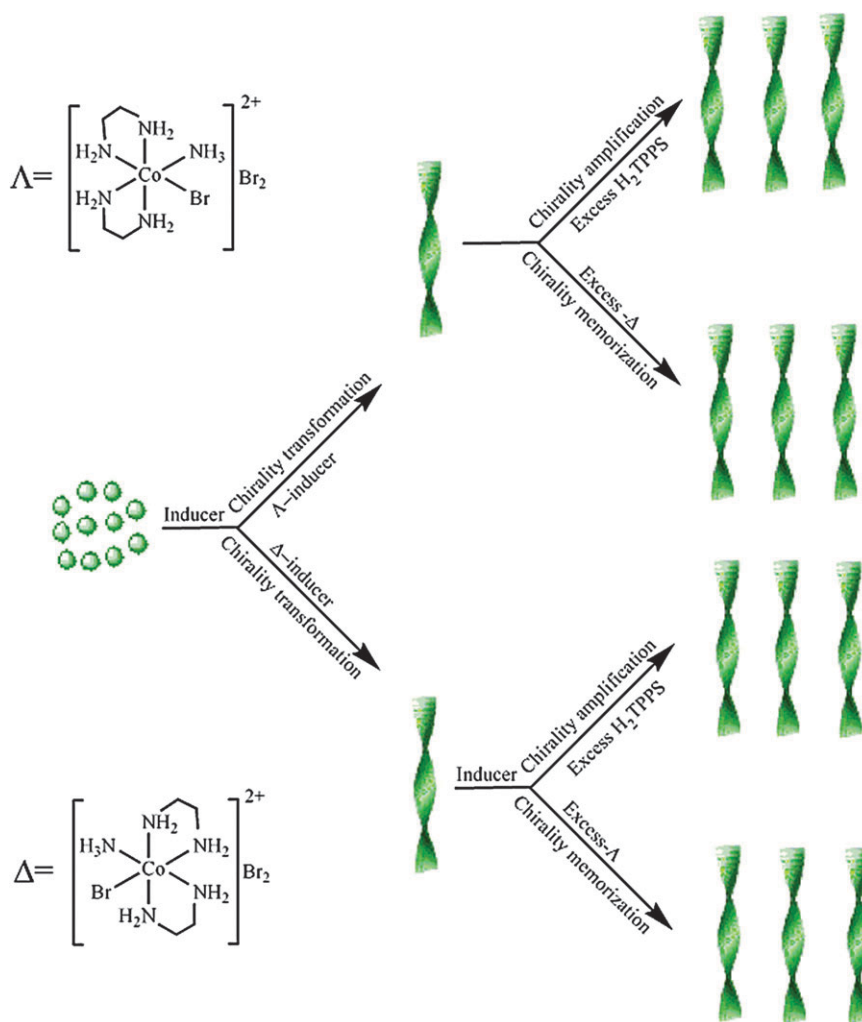
Scheme 1 Schematic illustration of the induction, memory, and amplification of chirality in H_2TPPS with Λ- or Δ-Co(III) complexes.

α-bromocamphor-π-sulfonate [NH_4(*l*-BCS)] were supplied by Acros. SP-Sephadex C-25 was purchased from Aldrich. All the chemicals were used as received.

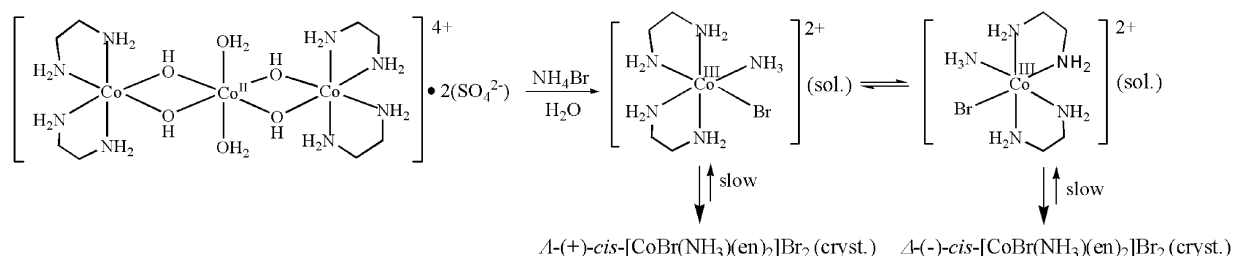### 2. Absolute asymmetric synthesis of *cis*-[CoBr(NH₃)(en)₂]Br₂

The chiral *cis*-[CoBr(NH_3)(en)$_2$]Br$_2$·nH$_2$O (n = 0, 2) was prepared by the reported method (Scheme 2).[43,44] The Co(III) complexes were characterized by UV and CD spectroscopy to determine their purity and concentrations (light path 1 cm).

3. Porphyrin assembly induced by Co(III) complexes

(1) Preparation of solutions. Stock solutions of Δ- and Λ-Co(III) complex were prepared by dissolving the Co(III) complex in HCl solution (pH = 2.0). A solution of H_2TPPS (10 μM) was freshly prepared by dissolving the TPPS crystals in distilled water, adjusted to pH 2.0 by 0.1 M HCl solution.

(2) Chiral induction. The Co(III) complex was added to the TPPS (10 μM) (pH = 2.0) to make cationic Co(III) complex–porphyrin complexes at molar ratios of H_2TPPS:Co(III) complex

Scheme 2 Absolute asymmetric synthesis of Δ- or Λ-*cis*-[CoBr(NH_3)(en)$_2$]Br$_2$.

from 1 : 4 to 1 : 10. These solutions were kept at RT overnight before characterization.

(3) Chiral memory. The above stock solutions of chiral H_2TPPS aggregates induced by Co(III) complex enantiomers at 1 : 4 molar ratio of H_2TPPS:Co(III) complex were incubated at RT for 12 h and were characterized by both UV and CD spectroscopy. Then, the opposite configurational Co(III) complexes with different concentrations were added to these samples. After stabilizing overnight, these solutions were characterized by UV and CD spectroscopy again to investigate the "chiral memory" effect.

(4) Chiral amplification. The stock solutions of chiral H_2TPPS aggregates (TPPS monomer concentration: 2.5 μM) were induced by the Λ- and Δ-Co(III) complexes (final concentration: 40 μM), respectively. After stabilizing overnight, these samples were characterized by both UV and CD spectroscopy. Then, Λ- and Δ-Co(III) complexes were removed by centrifugal separation at 10 000 rpm for 30 min, the supernatant was carefully removed and an isometric HCl solution (pH 2.0) was added to disperse the precipitate of H_2TPPS aggregates, with vigorous shaking for 5 min. The same operation was performed three times to remove as much Co(III) complex as possible.

The H_2TPPS aggregates without the Co(III) complex were diluted in HCl solution (pH 2.0), and were divided into four aliquots. After these samples were characterized by both UV and CD spectroscopy, the H_2TPPS monomer (2.5 μM) was added to each sample to make a different ratio of H_2TPPS to Co(III) complex. These solutions were characterized by UV and CD spectroscopy again to investigate the chiral amplification.

(5) Characterizations. The adsorption and CD spectra were measured using a UV-2550 spectrophotometer (Japan) and a Jasco J-810 spectropolarimeter (Japan), respectively. Fluorescence spectra were obtained on a LS 55 fluorescence spectrometer (Perkin-Elmer). AFM measurements were performed on a Nanoscope IIIa microscope (Digital Instruments, Santa Barbara, CA, USA) in air at room temperature using standard silicon tips in the tapping mode.

Results and discussion

1. Chiral formation of H_2TPPS J-aggregates induced with Λ- and Δ-Co(III) complexes

The structures of the chiral octahedral cobalt complexes and the achiral porphyrin derivative (H_2TPPS) are shown in Fig. 1. It is well known that when the pH is <3, the protonated species of H_2TPPS is zwitterionic and can be self-assembled to form edge-to-edge aggregates (J-aggregates) by both electrostatic attraction and the hydrophobic effect.[45] Much effort has been devoted to the investigation of the assemblies of these molecules.[46–50]

The CD spectrum of the Λ- and Δ-Co(III) complexes are shown in Fig. 2. The CD spectra of the Λ-Co(III) complex ($\Delta\varepsilon_{564} = 0.333$) and the Δ-Co(III) complex ($\Delta\varepsilon_{564} = -0.336$) are approximately perfect mirror-images, and thus the complexes must be enantiomers of each other.
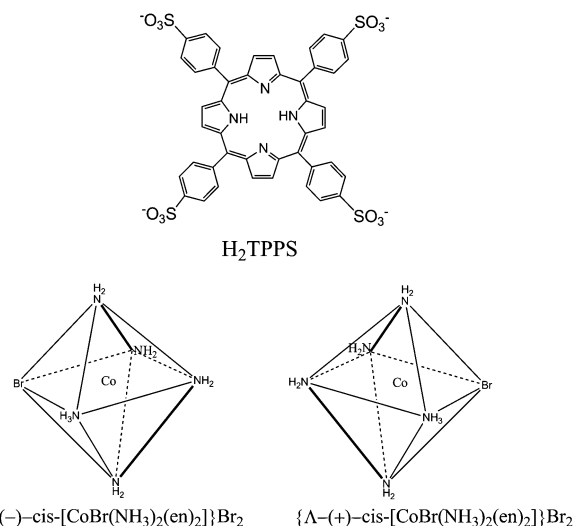

Fig. 1 Schematic structures of H_2TPPS and Δ- or Λ-Co(III) complexes.
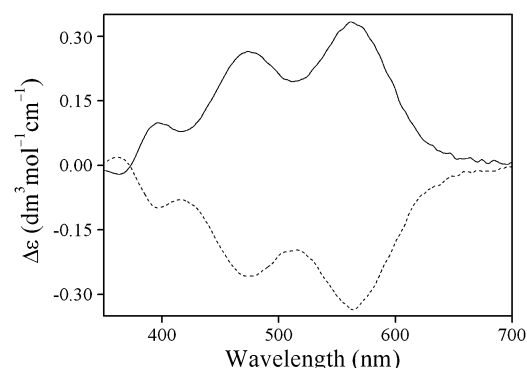
Fig. 2 CD spectra of Λ-cis-[CoBr(NH₃)(en)₂]Br₂ (solid line) and Δ-cis-[CoBr(NH₃)(en)₂]Br₂ (dashed line). The sample concentration of Co(III) complexes was 22.0 mg in 15.00 mL.

The interaction between H_2TPPS and Λ-/Δ-Co(III) complexes can be verified by the change in the UV-vis spectra of the H_2TPPS. The H_2TPPS monomer has an absorption at 434 nm, and there are absorptions at both 491 nm and 707 nm when self-assembled to J-aggregates.[51] In the presence of Λ- and Δ-Co(III) complexes, the H_2TPPS solution demonstrated new absorptions at both 491 nm and 707 nm (Fig. 3A), indicating that the H_2TPPS J-aggregates might be induced by Λ- and Δ-Co(III) complexes, respectively.

To see whether the H_2TPPS J-aggregates are chiral or not, the induced circular dichroism (ICD) band of porphyrin J-aggregates at around 484 nm was determined.[52] In Fig. 3B, the porphyrin J-aggregates induced by the Δ- and Λ-Co(III) complexes showed a positive signal around 484 nm and a negative signal around 484 nm, respectively, while the racemic Co(III) complex did not cause any signal in the CD spectra. According to the CD spectral data of Δ- and Λ-Co(III) complexes, there is no ICD signal around 484 nm. Thus, it strongly suggests that the chiral H_2TPPS J-aggregates can be correspondingly induced with Λ- and Δ-Co(III) complexes, respectively.
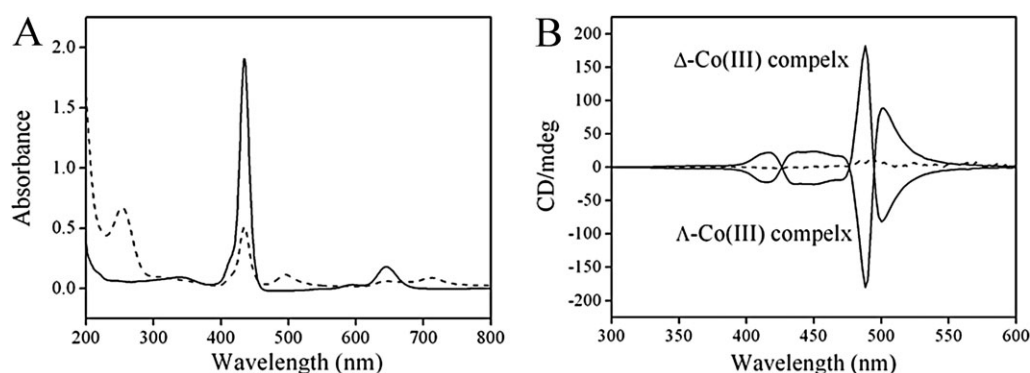
Fig. 3 A: UV-vis spectra of the H_2TPPS (10 μM) before (solid line) and after (dashed line) the addition of Co(III) complexes (100 μM); B: CD spectra of H_2TPPS (10 μM) at pH = 2.0 in the presence of Δ-, Λ- and racemic Co(III) complexes (dashed line). Spectra were recorded about 12 h after the addition of Co(III) complex.

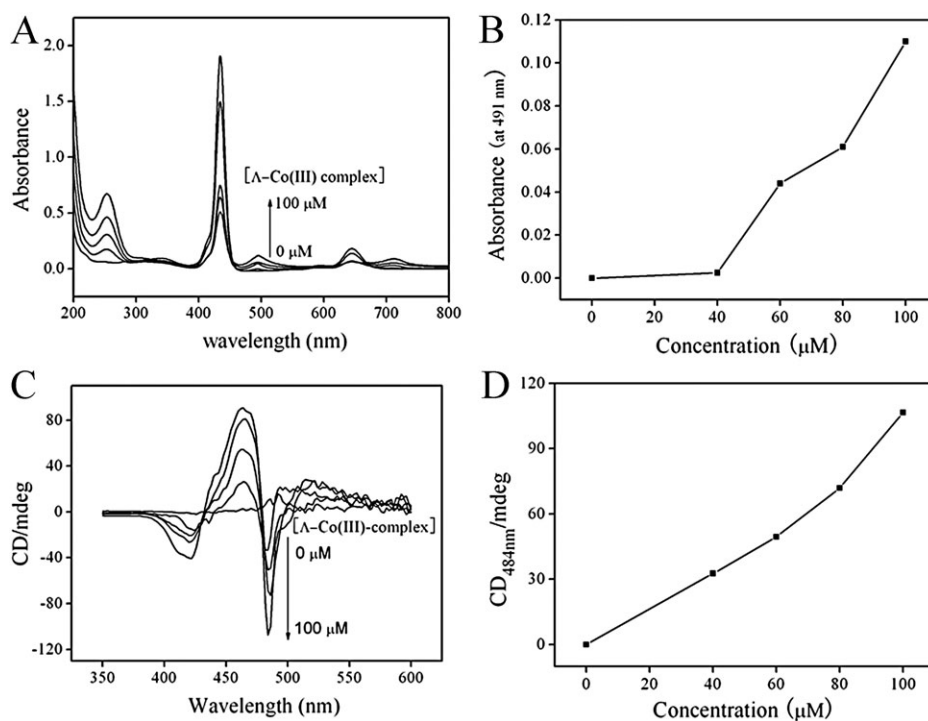## 2. Effect of concentration of the Co(III) complex on chiral induction in H_2TPPS J-aggregates

Fig. 4A shows that the intensity of the Soret band (434 nm) of 10 μM porphyrin decreased by 24%, 56%, 69% and 74% after the Λ-Co(III) complex was added at 40 μM, 60 μM, 80 μM and 100 μM, respectively. And, with increasing concentration of the Λ-Co(III) complex, the absorption band of the J-aggregates at 491 nm correspondingly increased, this change was smaller than that at 434 nm; the absorption at 648 nm decreased and the new band at 705 nm increased. Fig. 4B further shows the obvious induction effect of the Λ-Co(III) complex on the formation of H_2TPPS J-aggregates (10 μM porphyrin).

Fig. 4C and D show that the exciton-coupled CD intensity at 484 nm of the H_2TPPS J-aggregates also gradually

increased with increasing concentration of the Λ-Co(III) complex. This indicates that the formation of the chiral H_2TPPS J-aggregates is strongly dependent on the concentration of chiral Λ-Co(III) complex.

The UV-vis and CD data also demonstrated that there were similar effects of the Δ-Co(III) complex on chiral induction in H_2TPPS J-aggregates (data not shown).

Fluorescence spectra were then performed under the same aforementioned experimental systems. Since absorbance changes were observed in the mixed solution, the fluorescence emission for 10 μM H_2TPPS in the presence of Co(III) complexes with different molar ratios was excited at 434 nm and 491 nm respectively.[53] As shown in Fig. 5A, under excitation at 434 nm, the fluorescence of H_2TPPS in the

Fig. 4 A: Absorption spectrum of a 10 μM H_2TPPS solution in the absence and in the presence of different concentrations of the Λ-Co(III) complex; B: Absorption increase (at A_{491} nm) versus Λ-Co(III) complex concentration; C: ICD spectra of 10 μM H_2TPPS in the presence of different concentrations of Λ-Co(III) complex; D: ICD spectra increase (at CD_{484} nm) versus Λ-Co(III) complex concentration.
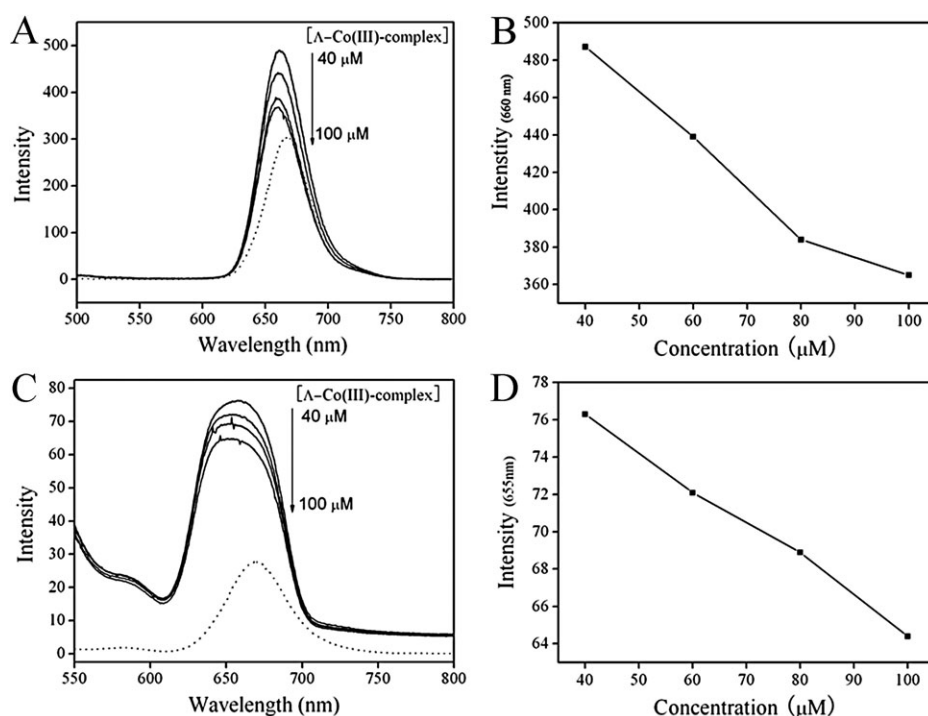
Fig. 5 Fluorescence spectra of the H$_2$TPPS J-aggregates induced by the Λ-Co(III) complex with different concentration. A: λ_{ex} = 434 nm; B: Fluorescence intensity decrease (λ_{ex} = 434 nm) versus Λ-Co(III) complex concentration; C: λ_{ex} = 491 nm; D: Fluorescence intensity decrease (λ_{ex} = 491 nm) versus Λ-Co(III) complex concentration (dashed curve: H$_2$TPPS solution without Co(III) complex). The emission of the H$_2$TPPS monomer shows a red-shift with the addition of the Co(III) complex, and the intensity decreases with increasing concentration of the Co(III) complex.

absence of the Co(III) complex shows a peak at 668 nm. However, the addition of the Co(III) complex to the H$_2$TPPS resulted in the hypsochromic shift of the main fluorescence peak to about 660 nm. It was also observed that the intensity of the peak at 660 nm decreased with increasing molar ratio of the Co(III) complex and H$_2$TPPS. This is consistent with the trend demonstrated in the absorbance spectra.

While being excited at the wavelength of 491 nm (Fig. 5B), the main peak of the fluorescence emission spectra was shifted to 655 nm. Interestingly, the linear relationship between the fluorescence intensity (excited at 491 nm) and the concentration of the Co(III) complexes shows the aggregation process is substantially enantiospecific. However, excitation at 491 nm, directly at the J-band, yields no fluorescence at 715 nm, which

was attributed to the emission of J-aggregates. It is expected that quenching occurred in the emission spectra of the formed H$_2$TPPS J-aggregates.

The titration with a small amount of Co(III), whose concentration is below 40 μM, does not cause the aggregation of porphyrin under the same experimental condition. The UV-vis spectra, ICD spectra, and fluorescence were almost the same as the monomer H$_2$TPPS (data not shown).

3. Chiral memory in H$_2$TPPS J-aggregates

In this paper, the porphyrin aggregates induced by the Λ-Co(III) complex were further modified by the addition of the Δ-Co(III) complex. As shown in Fig. 6A and B, the UV absorption at the Soret band (434 nm) gradually decreased
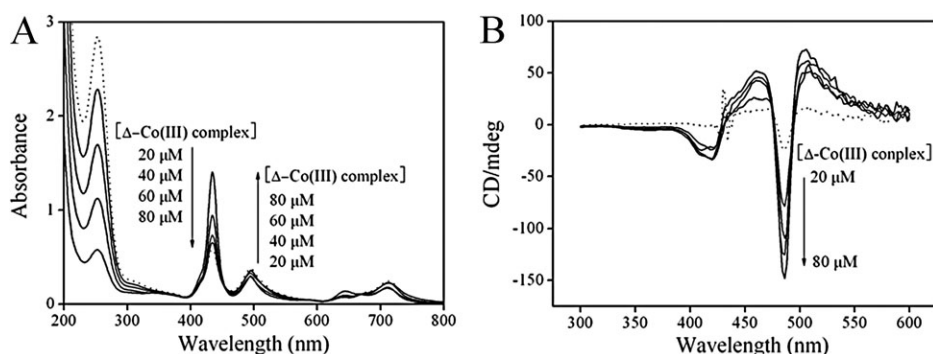
Fig. 6 A: UV-absorption and B: ICD spectra of the H$_2$TPPS (10 μM) in the presence of Λ-Co(III) complex (dashed curve) and after the addition of Δ-Co(III) complex with different concentrations.

upon the addition of the chiral Δ-Co(III) complex inducer, and interestingly, the induced CD signal of the porphyrin aggregates increase (rather than inverting) after the addition of excess Δ-Co(III) complex. It is suggested that while the H$_2$TPPS J-aggregates induced by the Λ-Co(III) complex were formed, their chirality was able to be kept and memorized despite excess opposite enantiomer Δ-Co(III) complex being added.

There also were similar effects when the porphyrin aggregates induced by the Δ-Co(III) complex was further modified by the addition of the Λ-Co(III) complex (data not shown).

These results might be caused by the formation of the "chiral seed".[12] The porphyrin heteroaggregates initially "borrow" chirality from the chiral inducer, and then themselves become intrinsically chiral. The addition of the opposite configurational enantiomers could act only as an accelerator for the formation of the aggregates based on the previously formed "chiral seeds".

4. Chiral amplification in H$_2$TPPS J-aggregates

The inherently chiral H$_2$TPPS aggregates induced by the Ru(III) complex have been considered as a template for the amplification of their own structures.[14] In the current work, the inherently chiral H$_2$TPPS aggregates induced by the Δ- and Λ-Co(III) complexes were also tested as chiral templates.

By adding the H$_2$TPPS monomer to the chiral H$_2$TPPS aggregates the Λ- and Δ-Co(III) complexes were removed by centrifugal separation. As shown in Fig. 7A, the absorbance at 434 nm increased with increasing monomer concentration, and the peak at 491 nm of the J-aggregates also increased. This can also be confirmed by the ICD spectra (Fig. 7B), in which the ICD signal at 484 nm shows an increase upon the addition of more TPPS monomers.

To see if the trace amount of the Co(III) complex (not removed from the H$_2$TPPS aggregate supernatant) was a chiral inducer to initiate the re-aggregation of the H$_2$TPPS monomers, the opposite chiral Co(III) complex was added to the solution. The results indicated that the chirality of H$_2$TPPS aggregates remained the same and that the CD signal increased (data not shown). Combined with the above chiral memory in H$_2$TPPS J-aggregates, this demonstrates that the
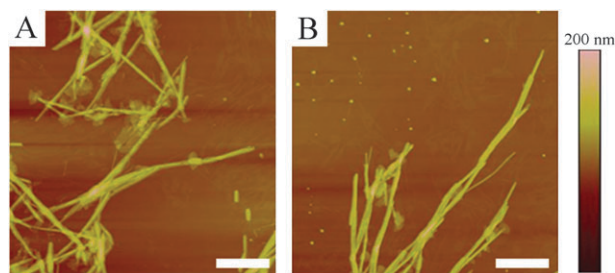
Fig. 8 AFM images of the H$_2$TPPS J-aggregates induced by the chiral Co(III) complex. A: with low magnification; B: with high magnification. Scale bar = 200 μm.

aggregation of the H$_2$TPPS could be continued using the chiral TPPS J-aggregates themselves as templates. Accordingly, it was observed that the amount of the aggregates increased with the addition of the TPPS monomer. Thus we suggest that the amplification of chirality is due to the increasing concentration of the aggregates.

5. AFM images of chiral H$_2$TPPS J-aggregates

To visually investigate the morphological shape of the chiral aggregates, AFM was used to determine the morphology of the chiral TPPS J-aggregates. As shown in Fig. 8, the chiral TPPS J-aggregate induced with chiral Co(III) complexes shows a twisted ribbon-like morphology, though no helicity is directly observed. This result may be explained by the chirality of the aggregate, which is oriented according to the inner structures of the molecules.[45]

6. Possible mechanism of the interactions of porphyrins with cationic Co(III) complexes

The mechanism of interactions of the porphyrin with chiral Co(III) complexes is under investigation in our laboratory. The preliminary results indicated that the cationic Co(III) complex induced the formation of chiral aggregation of H$_2$TPPS; however, the anionic Co(III) complex did not cause the aggregation. Thus, we speculate that the interaction between the chiral Co(III) complex and the porphyrin aggregates may be based on electrostatic interactions.
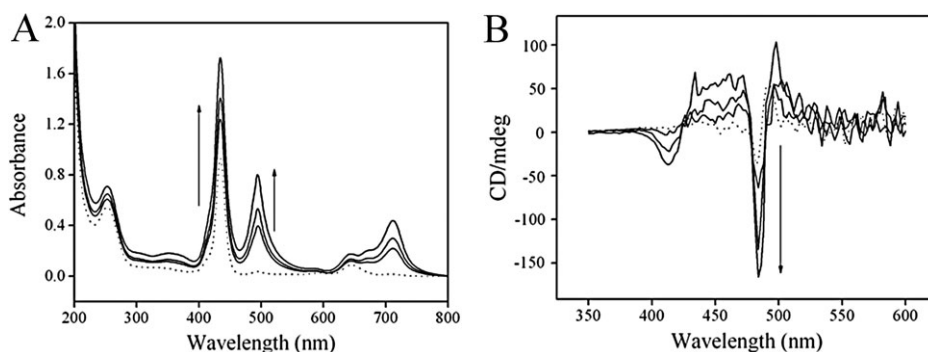
Fig. 7 A: UV absorption and B: CD spectra of the Λ-Co(III) complex induced aggregates before (dashed curve) and after (other curves) three additions of the individual porphyrin aliquots. Arrows indicate increasing TPPS concentration (2.5 μM to 7.5 μM). With the increasing monomer H$_2$TPPS concentration, both the absorption of the Soret band (at 434 nm) and the absorption at 491 nm increase, as does the peak at 484 nm in the ICD spectra.

Conclusions

In summary, an enantiomeric excess was spontaneously obtained *via* the absolute asymmetric synthesis of chiral Λ- and Δ-Co(III) complexes. The chirality could be transferred from the chiral Co(III) complexes to the achiral H_2TPPS to form mirror-image J-aggregates. By the addition of excess opposite configurational complexes to the previously formed chiral aggregates, the chirality of the aggregates could not only be memorized, but also amplified. Once the chiral J-aggregates were formed, the opposite-handed Co(III) complexes could play an accelerator role by using the chiral J-aggregates as "reactant seeds", and the formed chiral J-aggregates could also be used as a chiral template in the process of assembly.

Acknowledgements

References

1 R. Breslow and Z. L. Cheng, *Proc. Natl. Acad. Sci. U. S. A.*, 2009, **106**, 9144.
2 L. Q. Keszthelyi, *Q. Rev. Biophys.*, 1995, **28**, 473.
3 K. J. Koch, F. C. Gozzo, S. C. Nanita, Z. Takats, M. N. Eberlin and R. G. Cooks, *Angew. Chem., Int. Ed.*, 2002, **41**, 1721.
4 J. Podlech, *Angew. Chem., Int. Ed.*, 1999, **38**, 477.
5 C. Bolm, F. Bienewald and A. Seger, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1657.
6 V. Avetisov and V. P. Goldanskii, *Proc. Natl. Acad. Sci. U. S. A.*, 1996, **93**, 11435.
7 D. G. Blackmond, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 5732.
8 A. Saghatelian, Y. Yokobayashi, K. Soltani and M. R. Ghadiri, *Nature*, 2001, **409**, 797.
9 K. Asakura, K. Kobayashi, Y. Mizusawa, T. Ozawa, S. Osanai and S. Yoshikawa, *Phys. D*, 1995, **84**, 72.
10 K. Asakura, S. Osanai and D. K. Kondepudi, *Chirality*, 2001, **13**, 435.
11 D. K. Kondepudi and K. Asakura, *Acc. Chem. Res.*, 2001, **34**, 946.
12 R. Randazzo, A. Mammana, A. D'Urso, R. Lauceri and R. Purrello, *Angew. Chem., Int. Ed.*, 2008, **47**, 9879.
13 R. Randazzo, R. Lauceri, A. Mammana, A. D'Urso and R. Purrello, *Chirality*, 2009, **21**, 92.
14 L. Rosaria, A. D'Urso, A. Mammana and R. Purrello, *Chirality*, 2008, **20**, 411.
15 E. Castiglioni, S. Abbate, G. Longhi, R. Gangemi, R. Lauceri and R. Purrello, *Chirality*, 2007, **19**, 642.
16 B. Kokona, A. M. Kim, R. C. Roden, J. P. Daniels, B. J. Pepe-Mooney, B. C. Kovaric, J. C. de Paula, K. A. Johnson and R. Fairman, *Biomacromolecules*, 2009, **10**, 1454.
17 Z. El-Hachemi, C. Escudero, O. Arteaga, A. Canillas, J. Crusats, G. Mancini, R. Purrello, A. Sorrenti, A. D'Urso and J. M. Ribo, *Chirality*, 2009, **21**, 408.
18 Y. Egawa, R. Hayashida and J. I. Anzai, *Langmuir*, 2007, **23**, 13146.
19 D. Kuciauskas and G. A. Caputo, *J. Phys. Chem. B*, 2009, **113**, 14439.
20 L. G. Marzilli, P. Gabor, L. Mengfen, K. Min Sook and D. W. Dixon, *J. Am. Chem. Soc.*, 1992, **114**, 7575.
21 R. F. Pasternack, A. Giannetto, P. Pagano and E. J. Gibbs, *J. Am. Chem. Soc.*, 1991, **113**, 7799.
22 S. Ikeda, T. Nezu and G. Ebert, *Biopolymers*, 1991, **31**, 1257.
23 E. Bellacchio, R. Lauceri, S. Gurrieri, L. M. Scolaro, A. Romeo and R. Purrello, *J. Am. Chem. Soc.*, 1998, **120**, 12353.
24 R. Purrello, A. Raudino, L. M. Scolaro, A. Loisi, E. Bellacchio and R. Lauceri, *J. Phys. Chem. B*, 2000, **104**, 10900.
25 R. Lauceri, A. Raudino, L. M. Scolaro, N. Micali and R. Purrello, *J. Am. Chem. Soc.*, 2002, **124**, 894.
26 A. S. R. Koti and N. Periasamy, *Chem. Mater.*, 2003, **15**, 369.
27 C. Escudero, J. Crusats, I. Diez-Perez, Z. El-Hachemi and J. M. Ribo, *Angew. Chem., Int. Ed.*, 2006, **45**, 8032.
28 P. A. J. de Witte, M. Castriciano, J. J. L. M. L. Cornelissen, M. Scolaro, R. J. M. Nolte and A. E. Rowan, *Chem.–Eur. J.*, 2003, **9**, 1775.
29 R. Lauceri, M. De Napoli, A. Mammana, S. Nardis, A. Romeo and R. Purrello, *Synth. Met.*, 2004, **147**, 49.
30 T. Hasegawa, T. Fujisawa, M. Numata, C. Li, A.-H. Bae, S. Haraguchi, K. Sakurai and S. Shinkai, *Chem. Lett.*, 2005, **34**, 1118.
31 R. Lauceri and R. Purrello, *Supramol. Chem.*, 2005, **17**, 61.
32 T. Kawauchi, J. Kumaki, A. Kitaura, K. Okoshi, H. Kusanagi, K. Kobayashi, T. Sugai, H. Shinohara and E. Yashima, *Angew. Chem., Int. Ed.*, 2008, **47**, 515.
33 R. Lauceri, G. F. Fasciglione, A. D'Urso, S. Marini, R. Purrello and M. Coletta, *J. Am. Chem. Soc.*, 2008, **130**, 10476.
34 A. Mammana, A. D'Urso, R. Lauceri and R. Purrello, *J. Am. Chem. Soc.*, 2007, **129**, 8062.
35 H. Onouchi, T. Miyagawa, K. Morino and E. Yashima, *Angew. Chem., Int. Ed.*, 2006, **45**, 2381.
36 M. Ishikawa, K. Maeda, Y. Mitsutsuji and E. Yashima, *J. Am. Chem. Soc.*, 2004, **126**, 732.
37 K. Toyofuku, M. A. Alam, A. Tsuda, N. Fujita, S. Sakamoto, K. Yamaguchi and T. Aida, *Angew. Chem., Int. Ed.*, 2007, **46**, 6476.
38 P. L. Chen, X. G. Ma, P. F. Duan and M. H. Liu, *ChemPhysChem*, 2006, **7**, 2419.
39 D. Monti, M. Venanzi, M. Stefanelli, A. Sorrenti, G. Mancini, C. Di Natale and R. Paolesse, *J. Am. Chem. Soc.*, 2007, **129**, 6688.
40 L. Liu, Y. G. Li and M. H. Liu, *J. Phys. Chem. C*, 2008, **112**, 4861.
41 B. Liao, R. G. Liu and Y. Huang, *Polym. J.*, 2007, **39**, 1071.
42 V. V. Borovkov, G. A. Hembury and Y. Inoue, *Angew. Chem., Int. Ed.*, 2003, **42**, 5310.
43 M. L. Tobe, Martin, F. Dean, A. A. Thelen, L. Hilo, G. Glover and John P. Fackler Jr, *Inorg. Synth.*, 1966, **8**, 198.
44 H. Zhang, X. Wang, L. Chen, X. Fang, J. Gao and Z. Xu, *Acta Phys.–Chim. Sin.*, 2006, **22**, 608.
45 L. X. Zeng, Y. J. He, Z. F. Dai, J. Wang, Q. Cao and Y. L. Zhang, *ChemPhysChem*, 2009, **10**, 954.
46 L. Zhang, J. Yuan and M. H. Liu, *J. Phys. Chem. B*, 2003, **107**, 12768.
47 L. Z. Zhao, X. Wang, Y. Li, R. J. Ma, Y. L. An and L. Q. Shi, *Macromolecules*, 2009, **42**, 6253.
48 L. Z. Zhao, R. J. Ma, J. B. Li, Y. Li, Y. L. An and L. Q. Shi, *Biomacromolecules*, 2008, **9**, 2601.
49 A. Synytsya, A. Synytsya, P. Blafkova, J. Ederova, J. Spevacek, P. Slepicka, V. Kral and K. Volka, *Biomacromolecules*, 2009, **10**, 1067.
50 V. V. Borovkov, N. Yamamoto, J. M. Lintuluoto, T. Tanaka and Y. Inoue, *Chirality*, 2001, **13**, 329.
51 H. L. Ma and W. J. Jin, *Spectrochim. Acta, Part A*, 2008, **71**, 153.
52 J. B. Li, Y. L. An, X. Chen, D. A. Xiong, Y. Li, N. Huang and L. Q. Shi, *Macromol. Rapid Commun.*, 2008, **29**, 214.
53 J. Valanciunaite, S. Bagdonas, G. Streckyte and R. Rotomskis, *Photochem. Photobiol. Sci.*, 2006, **5**, 381.