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Chirality induction to achiral molecules by silica-coated chiral molecular assemblies

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Abstract

Hybrid silica-organic nanohelices are used to organize a large variety of non-chiral small organic molecules or inorganic anions to nanometer-sized assemblies. Such chiral organization of achiral molecules induces chiroptical properties as detected by vibrational or electronic circular dichroism (CD), as well as from circularly polarized luminescence (CPL).

KEYWORDS

circular dichroism, circularly polarized luminescence, excimer emission, induced chirality, silica nanohelice

1 | INTRODUCTION

Chiral ions or ionic molecules are attractive owing to their asymmetric catalytic activity,^{1–4} enantioselectivity,⁵ or

their chiroptical properties.^{6,7} Chiral co-crystallization,⁸ chiral molecular assemblies,^{9–15} or confinement of achiral ions in chiral cyclodextrins¹⁶ can be used to induce chiroptical properties to achiral ions or molecules and/or enhancing chiral signals with promising advantages such as (1) tunability of the chiral properties, (2) versatility of

choices of chromophores (molecules, ions particles, etc.), and (3) transparency of solutions in the UV-vis region due to the nanometric size of the assemblies. However, addition of guest chromophores to molecular host assemblies can disturb or destroy their chiral organization, giving a significant limitation to this method.

Recently, we reported the formation of hybrid silica-coated chiral crystalline molecular assemblies with controlled handedness (right vs. left) for the induction of circular dichroism (CD) signals to the achiral monoatomic anions, methyl orange, and anthracene carboxylate.^{17–19} The hybrid system used to organize these achiral molecules is based on self-assemblies of gemini surfactants with enantiomeric tartrate counterions, *N,N'*-dihexadecyl-*N,N,N',N'*-tetramethylethylene diammonium L- or D-tartrate (hereafter, abbreviated as 16-2-16 L- or D-tartrate, (Scheme 1)).^{17,20} Depending on the enantiomer of the tartrate counterion, the self-assemblies form right-handed (RH-) or left-handed (LH-) twisted and helical ribbon-like and tubular self-assemblies with a double bilayer in water and some organic solvents.^{21,22} These chiral nanostructures, following transcription into a silica matrix using TEOS, form hybrid organic-inorganic composites.^{17–19} Once the organic assemblies are coated with silica shells, the tartrate anions can be replaced by small or large achiral anionic molecules through ion exchange without destroying the helical morphology of the molecular assemblies (Figure S1). These newly introduced anions are then organized in a chiral environment.

In this study, we extend this approach to a number of different anions in order to demonstrate the generality of this methodology. We also investigate how the confinement of the anions can affect their electronic properties and lead to the emergence of chiroptical properties even with small inorganic anions such as nitrate. We also show how these anions influence the organization of the surrounding molecular assemblies. We show that this approach can be used for luminescent molecules such as pyrene, perylene, and porphyrin (**TPPS**)¹⁶ derivatives in order to induce circularly polarized luminescence from the confined achiral anionic fluorophores, in particular through excimer formation in some cases.

2 | MATERIALS AND METHODS

2.1 | Materials

All reagent grade solvents and chemicals for the synthesis of 16-2-16 gemini tartrate were received from Merck and used without further purification. All external molecules for the integration in the hybrid structures were received from TCI and used without further purification.

2.2 | Synthesis of PTCTK

The synthesis of perylene-3,4,9,10-tetracarboxylic acid tetra potassium salt (**PTCTK**) was performed as previously reported,^{23,24} starting from commercial perylene-3,4,9,10-tetracarboxylic dianhydride. Typically, 5 g were poured into 150 ml of ultrapure water containing 6 g of potassium hydroxide then headed to reflux and reacted for 14 h before precipitation in a mixture of isopropanol: acetone.

2.3 | Synthesis of 16-2-16 gemini tartrate and organic

The synthesis of 16-2-16 gemini tartrate was performed as previously reported^{16,19} starting from *N,N,N',N'*-tetramethylethylenediamine and 1-bromohexadecane then exchanging the bromide counterion to acetate using silver acetate then to enantiopure tartrate using tartaric acid. The powder of 16-2-16 gemini tartrate was dissolved into water at 70°C (1 mM) then aged for 4 days at 20°C typical used quantities are 20 mg of powder for 28 ml of ultrapure water. The powder containing L-tartrate enantiomer forms a suspension of right-handed nanohelices, whereas the one with D-tartrate forms a suspension of left-handed structures. The good formation of the structures is confirmed using TEM.

2.4 | Preparation of hybrid

A silica shell is formed around the organic helices through polycondensation of tetraethylorthosilicate (TEOS). To do so, TEOS need first to be hydrolyzed in an acidic medium. One and a half milliliters of TEOS were typically dispersed in 30 ml of 10 mM L or D tartaric acid solution for 7 h. Then, TEOS solution was added in the suspension of organic helices. After overnight reaction, hybrid helices are washed by water at 4°C using centrifugation (12 min/3893 g). Afterward, tip sonication (130 W/10 s) was performed in order to have well-dispersed suspensions.

2.5 | Ion exchange with inorganic or dye molecules

The suspensions of Hyb-helix-tart (0.20 mg ml⁻¹) were washed 8–10 times by 100-mM solution of the potassium or sodium salt of targeted inorganic molecular anions (NO₃⁻, SCN⁻, WO₄²⁻, CrO₄²⁻, and MnO₄⁻) using centrifugation (12 min/3893 g) at 4°C. It was followed by 8–10

Self-assembling molecule: Cationic gemini surfactant with chiral counterion

Achiral anionic guests (1): Inorganic molecular anions

Achiral anionic guests (2): Anionic polyaromatic chromophores

SCHEME 1 Molecular structure of 16-2-16 tartrate, achiral inorganic molecular anions, and achiral anionic or acidic polyaromatic chromophores used in this study

FIGURE 1 Transmission electron microscopy (TEM) image of hybrid nanohelices and schematic representation of these structures

washings by ultrapure water (4°C) to remove the excess of molecule. In order to insert chromophore in the structure, the counterions of Hyb-helix-tart were first replaced by chloride ions, by washing with 100-mM KCl, until no tartrate was detected using CD followed by washing with ultrapure water (4°C) five times. The concentration of Hyb-helix-Cl was then adjusted to the desired value (0.238 or 0.095 mg ml⁻¹) by addition of ultrapure water and various quantity of a dyes were added to obtain a concentration of 20–200 µM. This solution was then kept for 2 h on roller mixer at 6°C.

2.6 | IR and VCD spectral

In order to avoid the intense absorption peaks of H₂O in the 1500–1800 cm⁻¹ and the 3000–4000 cm⁻¹ regions, D₂O was used as a solvent for all infrared (IR) and vibrational circular dichroism (VCD) spectral measurements. L- and D-helix-tart as well as L- and D-helix-NO₃ aqueous solutions (2.0 mg ml⁻¹) were washed with D₂O at 4°C using centrifuge (3893g, 12 min). The concentration of these samples was adjusted to 20 mg ml⁻¹. IR spectra were recorded with a Thermo-Nicolet Nexus 670 FTIR spectrometer, at a resolution of 4 cm⁻¹, by coadding 50 scans. Samples were held in a demountable CaF₂ cell with fixed path length of 55 µm (Biotools™, Biotools). All IR spectra were shown with subtraction of solvent background. VCD measurements were performed using a ThermoNicolet Nexus 670 FTIR spectrometer equipped with a VCD optical bench. In this optical bench, the light beam was focused on the sample by a BaF₂ lens (191-mm focal length), passing an optical filter, a BaF₂ wire grid polarizer (Specac), and a ZnSe photoelastic modulator (Hinds Instruments, Type II/ZS50). The light was then focused by a ZnSe lens (38.1-mm focal length) onto a 1 × 1 mm² HgCdTe (ThermoNicolet, MCTA* E6032) detector. VCD spectra were recorded at a

resolution of 4 cm⁻¹, by coadding 24,000 scans (8-h acquisition time). Baseline corrections of the VCD spectra were performed by subtracting the raw VCD spectra of a D₂O solvent. The photoelastic modulator was adjusted for a maximum efficiency in the mid-IR region at 1400 cm⁻¹. Calculations were performed via the standard ThermoNicolet software, using Happ and Genzel apodization, de-Haseth phase-correction and a zero-filling factor of one.

2.7 | CD spectral measurements

JASCO J-815 instrument was used for CD spectral measurements. The hybrid suspensions were put in a quartz cell. All the data discussed in this work has linear dichroism (LD) less than 0.001 (delta OD) and high tension (HT) less than 600 V to ensure the identity of the CD signal. The detail measurement condition for all inorganic anions (NO₃⁻, SCN⁻, WO₄²⁻, CrO₄²⁻, and MnO₄⁻) and some organic anions (**Py**, **IC**, and **CR**) are as follows. Scan speed: 200 nm min⁻¹; bandwidth: 1 nm, digital integration time: 0.5 s; temperature: 20°C. The measurement conditions for other organic anions (1-pyreneacetic acid [**PAA**], 1-pyrenesulfonic acid [**PSA**], **PTCTK**, **TPPS**, and corrole [**SiCor**]) are as follows. Scan speed: 100 nm min⁻¹; bandwidth: 2 nm, digital integration time: 1 s; temperature: 4°C.

2.8 | Circularly polarized luminescence spectral measurements

Various hybrid suspensions were put in a quartz cell with 10-mm path length. The measurements were conducted with the scan speed at 100 nm min⁻¹, with a data integration time of 4 s. Circularly polarized

luminescence (CPL) spectral measurement was performed at 4°C using a JASCO CPL-300. Excitation and emission bandwidths and high tension of the detector were adapted for each sample as follows: for **PSA**, both band widths are set to 10 nm with a high tension of 680 V; for **PTCTK**, both band widths are set to 15 nm with a high tension of 930 V; and for **TPPS**, the slit width were set at 3000 μm with a high tension of 600 V.

For the chirality induction from gemini to anions, it is crucial that the chiral organization of gemini molecules are maintained inside the hybrid structures. This organization is closely related to the temperature of phase transition which is, around 35°C.^{17,19} As we wanted to keep the chiral organization of gemini during the introduction of achiral anions, we chose to measure the CD and CPL at the temperature farthest as possible from the transition temperature in order to maintain the stability of gemini organization in the hybrid structure, which is, 4°C.

3 | RESULTS AND DISCUSSION

We selected two types of achiral anionic guests: (1) inorganic molecular anions with different shapes such as trigonal planar nitrate (NO_3^-), linear thiocyanate (SCN^-), tetrahedral orthotungstate (VI) (WO_4^{2-}), chromate (VI) (CrO_4^{2-}), and permanganate (VII) (MnO_4^-); and (2) anionic polyaromatic chromophores (Scheme 1).

The method for ion exchange is detailed in the experimental section below. Briefly, self-assembled nanohelices of 16-2-16 L- or D-tartrate were coated with a thin layer of silica via sol-gel transcription (denoted as Hyb-helix-tart).¹⁷⁻¹⁹ Unreacted TEOS was removed by repeated centrifugation and washing with water at 4°C. The choice of the solvent and temperature is of high importance to keep the organic self-assembly inside the silica shell. The structures obtained are denoted Hyb-helix-tart (0.20 mg ml^{-1}). Subsequently, the inorganic anions were inserted directly in Hyb-helix-tart by ion exchange: 100-mM solution of the corresponding potassium or sodium salt was added to the sample, followed by washing 8–10 times using 4°C water. This allows tartrate to be exchanged by inorganic anions, leading to the formation of Hyb-helix- NO_3^- and so on. For the insertion of organic dyes, a preliminary step is needed to replace tartrate by chloride in order to facilitate the introduction of the dye: Hyb-helix-Cl are first formed via ion exchange.¹⁹ The Hyb-helix-Cl (0–0.25 mg ml^{-1}) are then mixed with the chromophores having concentrations adjusted to reach the desired gemini/dye ratio. All of the dye is incorporated, and no further washing is necessary.

As shown in Figure 2, induced CD (ICD) signals were observed from all of the inorganic anions at wavelengths maxima of their UV-vis absorption spectrum. As expected, inversion of the helical chirality of the silica template (RH vs. LH) provides mirror-image ICD signals. These results indicate that the silica-coated molecular assembled nanohelix can induce chiroptical properties to various achiral inorganic anions.

In the case of the Hyb-helix- NO_3^- system, we also performed detailed IR spectroscopic studies along with VCD. Exchanging tartrate anions by nitrate anions results in the disappearance of the IR absorption bands at 1611 cm^{-1} ($\nu_a\text{CO}_2^-$), 1383 cm^{-1} ($\nu_s\text{CO}_2^-$), and 1340 cm^{-1} ($\delta\text{C}^*\text{H}$), characteristic of tartrate. This is accompanied by the appearance of a broad intense band around 1360 cm^{-1} that is characteristic of the ν_3 vibration of the nitrate anion, thereby confirming the exchange of tartrate by NO_3^- . The VCD band in the 1400–1300 cm^{-1} region of Hyb-helix- NO_3^- in D_2O (Figure 3B, top) confirms the induced chirality in the NO_3^- anions due to their chiral organization inside the silica nanohelices.

The 3000–2800 and 1520–1450 cm^{-1} regions of the IR spectra group provide vibrational information from the hydrocarbon chains of the gemini surfactant (Figure 3). From this, we can extract information pertaining to the packing of 16-2-16 surfactants. In the case of Hyb-helix-tart, the bending modes of the methylene groups (δCH_2) at 1471 and 1466 cm^{-1} are split. This is a signature of the highly ordered orthorhombic packing of the hydrocarbon chains of the gemini surfactant, which exhibits a two-fold axis symmetry (C_2) parallel to the membrane plane and perpendicular to the ribbon axis.^{20,25} These absorption bands merge into one peak at 1469 cm^{-1} for the Hyb-helix- NO_3^- system, indicating a transition to a less-ordered hexagonal packing which is accompanied by a small shift of $\delta_a\text{CH}_3$ peak from 1497 to 1494 cm^{-1} (Figure 3B, bottom). On the other hand, no significant change was observed for the asymmetric ($\nu_a\text{CH}_2$) and symmetric ($\nu_s\text{CH}_2$) stretching vibrations of the alkyl chain of 16-2-16 surfactant at 2919 and 2850 cm^{-1} , respectively (Figure S2). The VCD signals for the gemini surfactant in the 1520–1450 cm^{-1} region showed a ca. 50% reduction of intensity, confirming the reduction of the chiral organization of the gemini surfactant as seen from the IR band during NO_3^- inclusion.

Encouraged by results showing that the Hyb-helix-X systems are capable of inducing chiroptical properties in achiral anions, we then investigated anionic dyes such as pyrene derivatives **PAA** and **PSA**, **PTCTK** as well as **TPPS** and **SiCor** derivatives (Scheme 1). These were selected based on their ability to be emissive both in solution and in the solid-state and their strong propensity

FIGURE 2 Circular dichroism (CD) (top) and UV-vis absorption (bottom) spectra of RH- (red lines) and LH- (blue lines) Hyb-helix in water (0.20 mg ml^{-1}) obtained by washing with (A) water, (B) KNO_3 aq., (C) KSCN aq., (D) Na_2WO_4 aq., (E) K_2CrO_4 aq., and (F) KMnO_4 aq. Dotted black lines represent water (A) and $50 \mu\text{M}$ -inorganic salts (KNO_3 , (B); KSCN , (C); Na_2WO_4 , (D); K_2CrO_4 , (E); KMnO_4 , (F)) aqueous solutions, respectively. All samples were measured at 20°C

towards self-aggregation leading to the efficient induction of chirality in an analogous system as we have shown previously.²⁶

For all the organic chromophores, mirrored ICD signals were observed with the use of RH- versus LH- hybrid helices (Figure 4). The dissymmetry factor g , is defined as

$$g = \frac{\Delta\epsilon}{\epsilon} = \frac{\theta}{32,982A}$$

where ϵ is molar extinction coefficient and θ is molar ellipticity (milli degrees), and $\Delta\epsilon$ are the difference of ϵ for left circularly polarized light and right circularly polarized light, and A the absorbance allows a direct comparison of the chiroptical activity of the samples and are presented in Table 1.

We investigated the effect of the dye concentration of **PAA**, **PSA**, and **PTCTK** for the ICD signal. Varying the dye concentrations from 0.02 to 0.2 mM did not result in a significant change in the g factor, which instead

FIGURE 3 Vibrational circular dichroism (VCD) (top) and infrared (IR) absorption (bottom) spectra of (A) Hyb-helix-tart and (B) Hyb-helix-NO₃ in D₂O. Red and blue lines represent RH- and LH- silica-coated molecular assembled nanohelices. The peaks indicated by green arrows are attributed to the gemini surfactant

remained constant ($\sim 5 \times 10^{-4}$). This is in stark contrast with our previous observation for dye molecules covalently grafted onto the silica nanohelices, which showed an exponential relationship between g and the concentration of dyes.²⁶ We interpret this difference as being due to the different mechanism for chirality induction in the two systems. In the case of dyes grafted onto the silica nanohelices without the presence of the gemini surfactants, the origin of the ICD lies in the interdy interactions and their chiral arrangement. For such ICD to be observed, the dye molecules need to be closely packed, giving an exponential growth of the signal versus surface concentration of the dye. This is also confirmed by the recent results reported by us and others on the chiral aggregation of porphyrin-based systems, which feature sensibly larger g values, that scales with the dimensions of the aggregates.^{27–29} In contrast, when the dyes are incorporated inside the surfactant assembly, the chiral organization of the dyes is induced by the chiral environment of the surfactant.¹⁹ Therefore, the chirality induced on each dye molecule should be independent of its concentration, as seen herein for the g factor that remains

almost constant with increasing dye concentration. Globally, larger g factors were observed for **PSA** than for **PAA** that is attributed to the stronger interaction between the less basic sulfonate (**PSA**) with the quaternary ammonium cation of the gemini surfactant as compared with the carboxylate group in **PAA**.^{30,31} The ion exchange process followed over 4 days showed faster kinetics for **PSA** (Figure S8).

The absorbed organic chromophores are emissive and the fluorescence signals originating from the bound dyes can also provide information on their local environment and chirality. ICD signals were observed for all the bound dyes, confirming the chiral induction from the macroscopic host. In contrast, induced circularly polarized luminescence was observed only for **PSA**, **TPPS**, and **PTCTK** (Figure 5). In the case of **PSA**, when the dye is mixed with hybrid helices, a broad fluorescence peak that is assigned to an emissive excimer appears at approximately 460 nm. This suggests that **PSA** inside the surfactant assembly can form stacked dimers. Induced CPL (ICPL) originating from these excimers is clearly distinguished from the contribution of the monomer

FIGURE 4 Circular dichroism (CD) (top) and UV-vis absorption (bottom) spectra of (A) **PAA** aq., (B) **PSA** aq., (C) **Py** aq., (D) **TPPS** aq., (E) **SiCor** aq., (F) **PTCTK** aq., (G) **IC** aq., and (H) **CR** aq. without (black dotted lines) and with RH- (red lines) and LH- (blue lines) Hyb-helices, respectively. The molar ratio between gemini surfactant and dye molecules ($[gemini]/[dye]$) are (A) 1/1, (B) 1/1, (C) 1/1, (D) 1/0.1, (E) 1/0.1, (F) 1/1, (G) 1/0.8, and (H) 1/1.6

TABLE 1 g_{CD} values of various achiral organic chromophores mixed with RH- and LH- Hyb-helices

Dye	Conc of dye (mM)	Conc of Hyb-helix (mg ml ⁻¹)	$g_{CD} \times 10^4$ RH- Hyb-helix	$g_{CD} \times 10^4$ LH-Hyb-helix	Wavelength λ_{abs} (nm)
PAA	0.20	0.095	3.2	-4.8	283.0
	0.20	0.238	4.0	-6.3	283.0
	0.10	0.238	5.0	-6.0	283.0
	0.05	0.238	3.0	-4.1	283.0
	0.02	0.238	1.7	-2.9	283.0
PSA	0.20	0.095	4.4	-3.7	283.4
	0.20	0.238	6.3	-6.2	283.4
	0.10	0.238	8.0	-8.0	283.4
	0.05	0.238	7.2	-7.4	283.2
	0.02	0.238	4.4	-6.0	283.0
PTCTK	0.20	0.238	2.0	-2.7	484.6
	0.10	0.238	3.1	-4.0	484.4
	0.05	0.238	2.4	-3.0	484.0
	0.02	0.238	3.5	-3.1	483.8
Py	0.02	0.050	-9.3	6.8	409.5
TPPS	0.01	0.125	7.2	-7.0	420.0
SiCor	0.01	0.125	6.4	-6.7	401.5
			-5.2	5.2	409.0
IC	0.04	0.060	-1.8	1.8	624.0
CR	0.04	0.060	5.4	-5.6	494.5

FIGURE 5 CPL and fluorescence spectra of (A) **PSA** (ex 340 nm), (B) **PTCTK** (ex 430 nm), and (C) **TPPS** (ex 410 nm) in the presence of RH- (red line) or LH- (blue line) handed hybrid helices. The molar ratios between gemini surfactant and dye molecules ($[gemini]/[dye]$) are (A) 1/0.2, (B) 1/2, and (C) 1/0.1

TABLE 2 g_{lum} values of **PSA** (ex 340 nm), **PTCTK** (ex 430 nm), and **TPPS** (ex 410 nm) mixed with RH- and LH- Hyb-helices

Dye	Conc of dye (mM)	Conc of Hyb-helix (mg mL ⁻¹)	$g_{lum} \times 10^4$ RH-Hyb-helix	$g_{lum} \times 10^4$ LH- Hyb-helix	Wavelength λ_{em} (nm)
PSA	0.05	0.600	13.0	−13.0	470
PTCTK	0.20	0.238	−2.9	2.8	479
TPPS	0.01	0.125	2.3	−3.2	671

(Figure 5A), making this system one of the rare showing CPL from intermolecular excimers based on nonchiral chromophores.^{32–34} For **PTCTK**, we can clearly see two peaks, one at 486 nm and the other around 525 nm. The first peak may be attributed to chirality induction from the chiral supramolecular organization of the gemini molecules to the **PTCTK** monomer, whereas the second emission peak may originate from **PTCTK** *J*-aggregates or excimers. In the case of **TPPS**^{4−} incorporated into the RH- and LH- hybrid helices containing Cl[−] as the anion yield positive and negative CPL signals with $g_{lum} = 2.4$ and 1.6×10^{-4} , respectively.

The dissymmetry factors g_{lum} of the three dyes exhibiting ICPL are collected in Table 2. Globally, they are between 10^{-4} and 10^{-3} , and similar to the values of g_{abs} values shown in Table 1. Although not particularly large compared with those observed from fluid solutions of inherently chiral molecules, it is important to note that the dissymmetry observed here reflects the induction of chirality from a chiral macroscopic object to a molecular dye. Thus, the method described in this study is versatile in that silica-coated molecular assembled nanohelices are capable of inducing chiral signals from a broad panel of anionic nonchiral chromophores and fluorophores.

4 | CONCLUSION

We report that CD and CPL signals from various families of achiral anionic inorganic or dye molecules can be obtained by co-organizing them with chirally crystallized cationic gemini surfactant molecules in the chiral nanospace within silica nanohelices. In spite of very different molecular structures, all these molecules showed ICD after simply being dissolved in the suspension of silica-coated molecular assembled nanohelices. Some of these luminescent molecules with no chiral auxiliary on chromophore such as **TPPS**, **PSA**, and **PTCTK** also showed ICPL and, in the case of **PSA**, the ICPL was observed from intermolecular excimer which is a rare observation to date for achiral molecules.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article which can be found in the online version of this article at the publisher's website.

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