Solvent-induced chirality inversion involving supramolecular helix transformation and color-tunable fluorescence of a C_6-symmetric hexakis(phenylethynyl)benzene derivative†

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A C_6-symmetric disk-like molecule, a hexakis(phenylethynyl)benzene derivative bearing chiral alanine parts, L-**1**, exhibited a solvent-induced supramolecular helix-sense inversion involving conformational changes followed by destruction of the supramolecular helical column. This phenomenon has been found by investigating the supramolecular assembly state of L-**1** in mixed solvents of various chloroform ($CHCl_3$)/*n*-hexane (Hx) ratios. L-**1** forms a stable helical columnar assembly *via* multiple noncovalent bonding interactions in nonpolar Hx, while the molecules in relatively polar $CHCl_3$ are in a molecularly dispersed state. Although one would expect disruption of the helical column with the addition of nonhelicogenic $CHCl_3$, an opposite-handed helical columnar structure was formed at 8–15 vol% of $CHCl_3$, and subsequently the inverted helical column was disassembled by a further increase of $CHCl_3$. In addition, this morphological transformation was accompanied by a significant change in fluorescent color, which varies over a wide visible range from orange in an original helical columnar state to light blue in a molecularly dispersed state through yellow in an inverted helical columnar state. These unprecedented behaviors are shown by the spectroscopic results, and the molecular conformations of L-**1** and the driving force for the helical sense inversion are discussed.

Introduction

Since the discovery of biological helices such as DNA and polypeptides that adopt regular one-handed helical structures composed of their homochiral components, significant attention has been paid to developing helical architectures[1] with controlled chirality that mimic the structures and functions of biological helices. Among such studies, chirality inversion is one of the highlighted topics.[1c,d,2] The majority of these studies involve polymers[3] and host–guest complexes.[4] There are, however, a few reports on supramolecular helical columns constructed using various types of noncovalent bonding interactions (such as π–π stacking, hydrogen-bonding and hydrophobic interactions) as utilized in biological systems.[5] Chirality inversion in supramolecular helical columnar assemblies are of great interest from fundamental and biological viewpoints, and such systems could have potential applications including liquid crystal, charge transport, luminescence and other combination properties.[1] Therefore, it is highly important to develop such materials and understand their behaviors. Recently, the solvent-induced helical sense inversion in supramolecular columnar assemblies has been demonstrated in detail for a DNA base derivative[5a] and a cholesterol-appended squaraine derivative.[5b] In both cases, the helical sense depends on the composition of binary solvent mixtures and only the transformation between two opposite helical regimes takes place. In addition, it is notable that solvent-induced helical sense inversion has been found for some helical polyacetylene derivatives bearing amino acid pendant groups.[3c,d]

From this background, we have investigated the influence of solvent composition for supramolecular assembly of a C_6-symmetric disk-like molecule, a hexakis(phenylethynyl)benzene derivative bearing chiral L-alanine parts, L-**1** (as shown in Fig. 1a), which forms a stable supramolecular helical columnar assembly in pure *n*-alkane and is molecularly dispersed in pure haloalkane as previously reported.[6] Fortunately, we have found the two-step transformation (three morphological states) in the binary solvent system using helicogenic *n*-alkane and nonhelicogenic haloalkane. Concretely, that is a solvent-induced supramolecular helix-sense inversion involving conformational changes followed by the destruction of the supramolecular columnar assembly. Moreover, these successive transitions are accompanied by a significant change in fluorescent color, which varies over a wide visible range. Here we report these unprecedented behaviors together with the results of UV-visible absorption, circular dichroism and fluorescence measurements, and discuss the molecular conformations of L-**1** and the driving force for the helical sense inversion.

Experimental

Experimental details are available in the Electronic Supplementary Information (ESI).†

Results and discussion

Supramolecular chirality inversion

We previously reported that a C_6-symmetric hexakis(phenylethynyl)benzene derivative bearing chiral L-alanine parts, L-**1**

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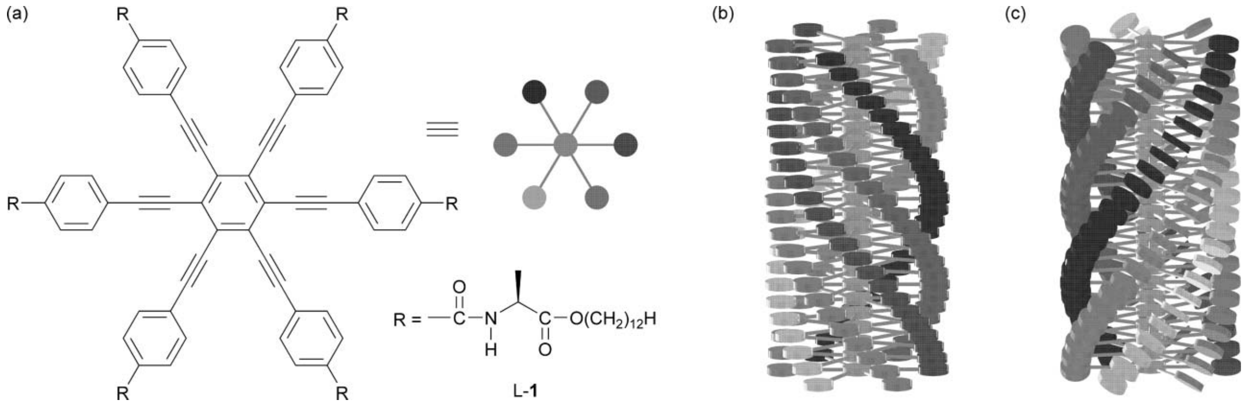

Fig. 1 (a) Molecular structure of L-**1**. Tentative schematic representation of (b) Pl-helical and (c) Pr-helical columnar assemblies.

(as shown in Fig. 1a), forms a stable helical columnar assembly *via* multiple noncovalent bonding interactions in nonpolar *n*-hexane (Hx), while the molecules in relatively polar chloroform ($CHCl_3$) are in a molecularly dispersed state.[6] In the present study, we investigated the supramolecular assembly state in the mixed solvents of various $CHCl_3$/Hx ratios (v/v). All samples were obtained as clear yellow homogeneous solutions, and then UV-visible absorption (UV-vis) and circular dichroism (CD) spectra of L-**1** (4.20×10^{-5} M) were measured at 25 °C. These are shown in Fig. 2a and b, respectively. At $CHCl_3$/Hx (6/94), L-**1** shows two major absorption bands at 361 nm ($\varepsilon = 1.30 \times 10^5$ M^{-1} cm^{-1}) and 299 nm ($\varepsilon = 6.25 \times 10^4$ M^{-1} cm^{-1}), and three main CD signals with a negative first Cotton effect ($\Delta\varepsilon_{1st} = -105$ M^{-1} cm^{-1} at 365 nm), a negative second Cotton effect ($\Delta\varepsilon_{2nd} = -272$ M^{-1} cm^{-1} at 305 nm) and a positive third Cotton effect ($\Delta\varepsilon_{3rd} = 94$ M^{-1} cm^{-1} at 292 nm). These spectra are essentially the same as those of the helical columnar assembly in pure Hx, *i.e.*, $CHCl_3$/Hx (0/100).[6] Hereinafter, we will refer to the helix giving this type of CD spectrum as a Pl-helix, because the central hexakis(phenylethynyl)benzene core adopts a nearly planar (Pl) conformation as described later in the section on molecular conformations.

When the $CHCl_3$ content was higher than $CHCl_3$/Hx (6/94), significant spectral changes were observed. At $CHCl_3$/Hx (8/92), the absorption bands at longer and shorter wavelengths shifted hypsochromically to 350 nm ($\varepsilon = 1.11 \times 10^5$ M^{-1} cm^{-1}) and 290 nm ($\varepsilon = 7.07 \times 10^4$ M^{-1} cm^{-1}), respectively. Concomitantly, the CD sign inversion occurred at around the wavelengths of the two absorption peaks, where the CD signals were observed with a positive first Cotton effect ($\Delta\varepsilon_{1st} = 279$ M^{-1} cm^{-1} at 355 nm), a positive third Cotton effect ($\Delta\varepsilon_{3rd} = 55$ M^{-1} cm^{-1} at 297 nm) and a negative fourth Cotton effect ($\Delta\varepsilon_{4th} = -55$ M^{-1} cm^{-1} at 276 nm), and an additional negative second Cotton effect ($\Delta\varepsilon_{2nd} = -133$ M^{-1} cm^{-1} at 336 nm) appeared. Almost the same CD spectrum was also obtained at $CHCl_3$/Hx (15/85), although the CD intensity decreased slightly ($\Delta\varepsilon_{1st} = 255$ M^{-1} cm^{-1}). Hereinafter, we will refer to the inverted helix giving this type of CD spectrum as a Pr-helix, because the central hexakis(phenylethynyl)benzene core adopts a propeller-like (Pr) conformation as described later in the section on molecular conformations.

It is noteworthy that these two types of CD spectra are not exact mirror images and that the positions and relative intensities are quite different, indicating a solvent-induced helical sense inversion

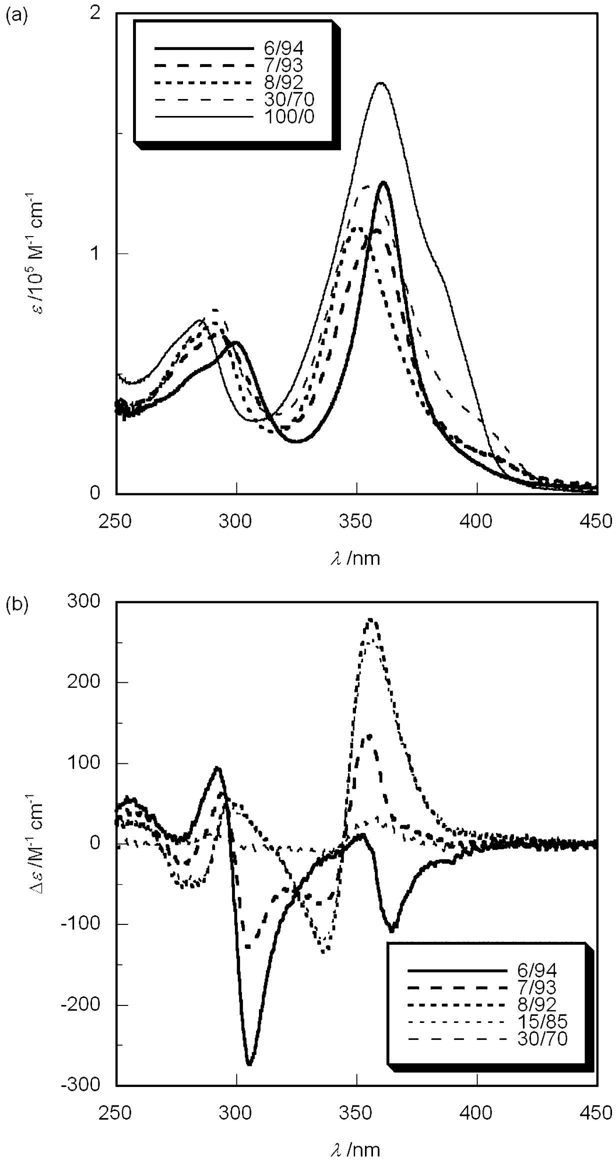

Fig. 2 (a) UV-vis and (b) CD spectra of L-**1** (4.20×10^{-5} M at 25 °C) measured in different solvent compositions ($CHCl_3$/Hx): (6/94), (7/93), (8/92), (15/85), (30/70) and (100/0).

(Pl-helix into Pr-helix) involving some structural change.[3d,e,s,t,5b] This result is surprising because one would expect that the addition of nonhelicogenic $CHCl_3$ disrupts a Pl-helical columnar assembly and monotonically decreases the CD intensity. However, the feature of being distorted from mirror image symmetry produces another interesting fluorescence property described in the next section.

The dependence of the supramolecular assembly on the $CHCl_3$/Hx ratio is more easily seen by examining the variations of the maximal absorption wavelength (λ_{max}) and the $\Delta\varepsilon_{1st}$ value. These are shown in Fig. 3. In the low $CHCl_3$ content, the most significant change was observed at $CHCl_3$/Hx (7/93), where the λ_{max} value was drastically blue-shifted and a sign inversion of the $\Delta\varepsilon_{1st}$ value occurred. These changes indicate the change of structure and helical sense, respectively. Consequently, this reveals that helical sense inversion involving some structural change takes place drastically at $CHCl_3$/Hx (7/93), and the CD spectral shape in Fig. 2b shows that almost equal amounts of the two opposite supramolecular helical species coexist at this solvent composition. Importantly, at 0–6 vol% of $CHCl_3$, where the Pl-helical assembly is formed, the values of λ_{max} and $\Delta\varepsilon_{1st}$ are almost independent of the nonhelicogenic $CHCl_3$ content. In addition, these values are also nearly constant in the range from 8 to about 15 vol% of $CHCl_3$, where the Pr-helical assembly is formed. This means that the supramolecular helical assemblies are not disrupted into smaller assemblies or free monomers in the range from 0 to about 15 vol% of the nonhelicogenic $CHCl_3$. When the $CHCl_3$ content was further increased to 30 vol%, $CHCl_3$/Hx (30/70), the CD intensity became significantly weaker ($\Delta\varepsilon_{1st} = 33\ M^{-1}\ cm^{-1}$) and the value of λ_{max} was red-shifted (355 nm) toward 359 nm as observed in the molecularly dispersed state in $CHCl_3$/Hx (100/0) as shown in Fig. 2 and 3. This result and a slight decrease in the $\Delta\varepsilon_{1st}$ value at $CHCl_3$/Hx (15/85) indicate that more than 15 vol% of the nonhelicogenic $CHCl_3$ is required to destabilize the supramolecular helical assemblies.

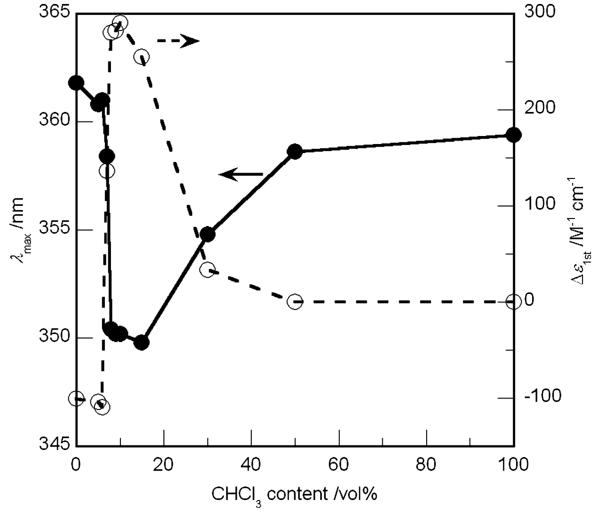

Fig. 3 Variations of the maximal absorption wavelength (λ_{max}) (closed circles) and the $\Delta\varepsilon_{1st}$ value (open circles) obtained from UV-vis and CD spectra of L-**1** (4.20×10^{-5} M at 25 °C), respectively, as a function of the $CHCl_3$ content in $CHCl_3$/Hx mixture.

The above-mentioned transition behavior was also observed in a more dilute (4.20×10^{-6} M) solution (see Fig. S1†), and the supramolecular chirality inversion occurred at $CHCl_3$/Hx (7.2/92.8), although no CD was detected at $CHCl_3$/Hx (30/70) owing to an overall decrease in intensity.

Intermolecular interactions and color-tunable fluorescence

To obtain information on intermolecular interactions (especially in the Pr-helical state found in this study), fluorescence (FL) spectra (4.20×10^{-6} M at 25 °C) were measured at an excitation of 360 nm.[7] These are shown in Fig. 4. At $CHCl_3$/Hx (5/95), where the Pl-helicity is formed, an orange emission at 605 nm (Stokes shift of 11 200 cm^{-1}) was observed. This spectrum is almost identical to that of the Pl-helical columnar state in pure Hx, *i.e.*, $CHCl_3$/Hx (0/100) reported previously.[6] On the other hand, the yellow emission at 550 nm (Stokes shift of 10 400 cm^{-1}) was observed at $CHCl_3$/Hx (10/90), where the Pr-helicity is formed. A similar spectrum was also obtained at $CHCl_3$/Hx (15/85) because of the Pr-helicity, and the maximum was observed at 547 nm (Stokes shift of 10 300 cm^{-1}). Here, it is noted that the Stokes shift in the Pr-helical state is comparable to that in the Pl-helical columnar state but is much larger than 5900 cm^{-1} in the molecularly dispersed state of $CHCl_3$/Hx (100/0), at which a light blue emission at 457 nm was observed. In addition to the large Stokes shift, the weak and broad spectral (excimer-like) features are commonly seen for both Pl- and Pr-helical states. These two facts suggest that the columnar structure is constructed by π–π stacking interactions between the large central cores in the Pr-helical state as well as the Pl-helical state.[6,8] This conclusion is also supported by a birefringent liquid crystal formation in concentrated solutions.[6,9] At over 15 vol% of $CHCl_3$, $CHCl_3$/Hx (15/85), the emission peak was gradually blue-shifted toward 457 nm (light blue) as observed in $CHCl_3$/Hx (100/0) and intensified because of the increase in the monomer ratio due to a reduction of the stacking interactions.

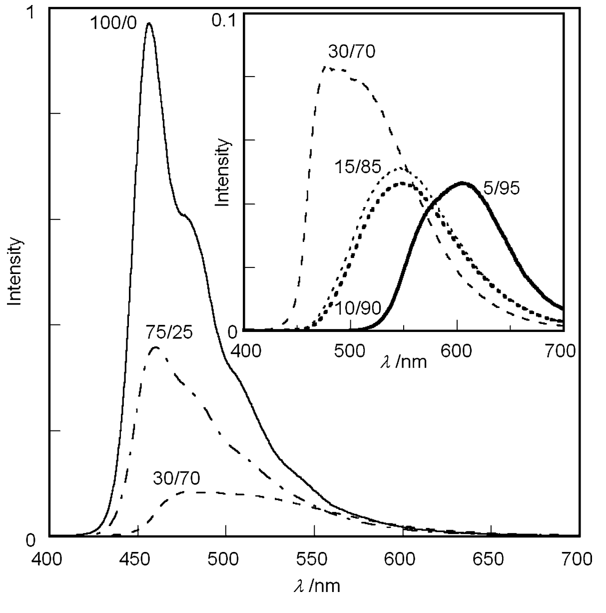

Fig. 4 FL spectra of L-**1** (4.20×10^{-6} M at 25 °C) measured in different solvent compositions ($CHCl_3$/Hx): (30/70), (75/25) and (100/0).[7] The inset shows an expanded view of FL spectra in (5/95), (10/90), (15/85) and (30/70). FL spectra ($\lambda_{ex} = 360$ nm) were normalized using the absorption values at 360 nm.

In this manner, it has been shown that a significant change in fluorescent color is observed with the successive transformations (orange in a Pl-helical columnar state to light blue in a molecularly dispersed state through yellow in a Pr-helical columnar state). Although there are some reports tuning fluorescent color by changing molecular conformations and packing,[10] the fluorescent color in our system can be controlled in a much wider visible range by adjusting the solvent composition and can be clearly seen by the naked eye (see Fig. S2†). At this point, these results could lead to a valuable design principle in developing new chiral functional materials.

Molecular conformations

According to previous semi-empirical calculations for a hexakis(phenylethynyl)benzene (HxPEBz), it was suggested that the value of λ_{max} greatly depends on the torsion angle β between the outer benzene rings and the central part of the molecule (see the inset of Fig. 5).[11] Experimentally, the λ_{max} value in aryleneethynylene molecules tends to decrease when the torsion angle around the ethynyl bond changes from 0° (planar conformation) to nearly 90°.[12] Hence, to gain insight into the molecular conformations of L-**1** in Pl- and Pr-helical states, the λ_{max} values for a model compound, HxPEBz, were calculated more precisely as a function of the β value using time-dependent density functional theory.[13] The calculated λ_{max} values are plotted against the β values in Fig. 5. A comparison of the calculated λ_{max} values with the measured λ_{max} values indicates that the central HxPEBz core adopts a nearly planar conformation (β = 0–10°) for Pl-helicity, whereas phenylethynyl groups are inclined by 30–35° from the central benzene plane for Pr-helicity, namely, the central core adopts a propeller-like conformation in the Pr-helical state.

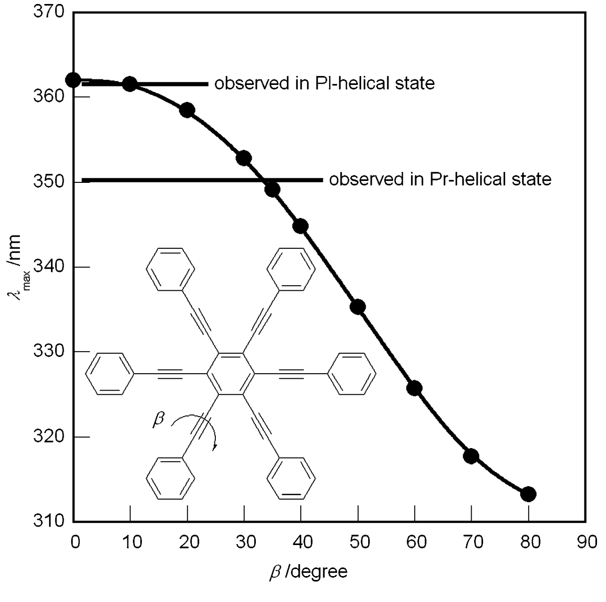

Fig. 5 Variation of the calculated λ_{max} value as a function of the torsion angle β for a hexakis(phenylethynyl)benzene (inset).

To get further information about the intermolecular hydrogen-bonding in these two helical columnar assemblies, infrared (IR) spectra (4.20 × 10^{-4} M) were measured. In a $CHCl_3$/Hx (8/92) solution of L-**1**, where the Pr-helicity is formed, the C=O stretching vibration of amide I was observed at 1637 cm^{-1}. This value is a slightly higher than 1634 cm^{-1} as observed in the Pl-helical columnar state, but much lower than 1655 cm^{-1} as observed in the molecularly dispersed state.[6] This result indicates that the Pr-helical columns are stabilized by hydrogen bonds between the large disk cores as well as between the Pl-helical columns, and the slight difference of the observed wavenumbers in both helices suggests that the Pl- and Pr-helical columnar assemblies are constructed by stacks of the L-**1** molecules adopting the different conformations. Although the slightly higher wavenumber in the Pr-helical columnar state might mean that the hydrogen-bonding within the Pr-helical columns is somewhat weakened in comparison with that within the Pl-helical columns, the combined results of FL and IR imply that close stacks reinforced by intermolecular hydrogen bonds are maintained in the Pr-helical columnar states.

In addition, the CD spectra in the Pl-helical state have a bisignate Cotton effect with the sign being negative at long wavelengths and positive at short wavelengths through zero near the absorption at around 300 nm as shown in Fig. 2. This profile (so-called negative coupling) suggests the presence of a left-handed helical arrangement of L-**1** molecules.[4b,c,5b] On the other hand, the CD spectra in the Pr-helical state have two positive couplings near the two absorptions at around 350 and 290 nm, which is suggestive of a right-handed helical arrangement of L-**1** molecules.

Therefore, it is proposed that the left-handed Pl-helical columnar assembly is constructed by stacks of the L-**1** molecules adopting a nearly planar central core as illustrated in Fig. 1b and the right-handed Pr-helical columnar assembly is constructed by stacks of the molecules adopting a propeller-like central core as illustrated in Fig. 1c, although their self-assembled structures may need some revision because the detailed self-assembled structures such as stacking mode and helical pitch have not yet been certain.[14]

Driving force for helix inversion

In a supramolecular system using an achiral ethane-bridged bis(zinc porphyrin) as the host and chiral amino acid ester ligands as the guests, it was reported that supramolecular chirality depends on the dielectric constant (ε_r) of the solvents, and that the sign of the induced CD in polar solvents is opposite to that in nonpolar solvents.[4c] Moreover, in some polyacetylene derivatives bearing amino acid pendants exhibiting a solvent-induced helical sense inversion, the value of ε_r is also considered to play a role in helix sense.[3c,d] These reports encouraged us to investigate the supramolecular assembly state of L-**1** in other binary solvent mixtures. Unfortunately, the poor solubility of L-**1** does not allow us to test various solvents,[15] but we could use the relatively polar 1,1,2,2-tetrachloroethane (TCE)/*n*-dodecane ($C_{12}H_{26}$) (v/v) as the binary solvent mixtures. These are nonhelicogenic and helicogenic solvents, respectively.[6] The ε_r value (2.01) of $C_{12}H_{26}$ is slightly higher than that (1.89) of Hx, whereas the ε_r value (8.50) of TCE is 1.77 times as high as that (4.81) of $CHCl_3$.[16] Fig. 6 shows the CD spectra of L-**1** in TCE/$C_{12}H_{26}$ (3/97) and TCE/$C_{12}H_{26}$ (5/95). At TCE/$C_{12}H_{26}$ (3/97), L-**1** shows three main CD signals with a negative first Cotton effect ($\Delta\varepsilon_{1st}$ = –90 M^{-1} cm^{-1} at 365 nm), a negative second Cotton effect ($\Delta\varepsilon_{2nd}$ = –229 M^{-1} cm^{-1} at 306 nm) and a positive third Cotton effect ($\Delta\varepsilon_{3rd}$ = 84 M^{-1} cm^{-1} at 292 nm). This spectrum is essentially the same as

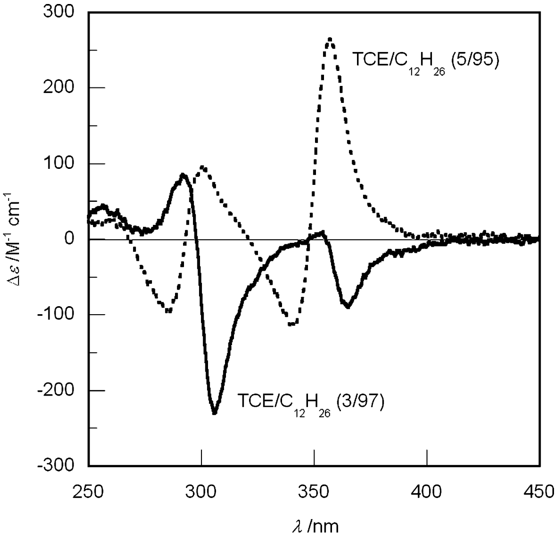

Fig. 6 CD spectra of L-**1** (4.20×10^{-5} M at 25 °C) measured in different solvent compositions (TCE/$C_{12}H_{26}$): (3/97) and (5/95).

that of the Pl-helical columnar assembly in $CHCl_3$/Hx (6/94), although the CD intensity is decreased slightly. At TCE/$C_{12}H_{26}$ (5/95), the CD signals were observed with a positive first Cotton effect ($\Delta\varepsilon_{1st}$ = 259 M^{-1} cm^{-1} at 356 nm), a negative second Cotton effect ($\Delta\varepsilon_{2nd}$ = −114 M^{-1} cm^{-1} at 342 nm), a positive third Cotton effect ($\Delta\varepsilon_{3rd}$ = 93 M^{-1} cm^{-1} at 300 nm) and a negative fourth Cotton effect ($\Delta\varepsilon_{4th}$ = −96 M^{-1} cm^{-1} at 284 nm). This profile is almost similar to that of the Pr-helical columnar assembly in $CHCl_3$/Hx (8/92), although an overall small red shift is observed in TCE/$C_{12}H_{26}$ (5/95) and the relative intensities are slightly changed. This difference could be due to a minor change in solvophobic interactions, which might result in a modified Pr-helical columnar structure with slight different conformation and packing fashion. Importantly, the helical sense inversion occurs at around 4 vol% of TCE, where the nonhelicogenic solvent content is lower than the case (7 vol% of $CHCl_3$) of the $CHCl_3$/Hx mixture. This clearly indicates that the higher ε_r value of TCE induces the helical sense inversion at lower content. These results clearly indicate that the helix sense of supramolecular columnar structure formed by the L-**1** molecules is much more sensitive to the ε_r value of the solvent than the stability of helix itself as can also be seen from the section on supramolecular chirality inversion. Moreover, considering that amino acid-based molecules have the potential to adopt several different conformations depending on the environment around the molecules,[3d,l,m,17] the helical sense inversion found in this study may originate from ε_r-triggered conformational changes of the peripheral alanine ester group,[4c,5a] which could influence the torsion angle β and packing fashion (helical arrangement) of the L-**1** molecules. This means that in our system the change in the ε_r value severely influences the stability of the conformational state.

Conclusions

We have shown by the spectroscopic studies that a C_6-symmetric disk-like molecule bearing chiral L-alanine parts, L-**1**, exhibits an unprecedented solvent-induced chirality inversion involving supramolecular helix transformation followed by the destruction of the supramolecular helical columnar assembly. The small increase (8–15 vol%) of nonhelicogenic $CHCl_3$ in a $CHCl_3$/Hx binary mixture gives rise to Pl- to Pr-helix transition without the collapse of helical columnar assembly, and subsequently the Pr-helical column is disassembled by a further increase of $CHCl_3$. In the relatively polar TCE/$C_{12}H_{26}$ mixture, a Pl-helical columnar structure is transformed into an opposite Pr-helical columnar structure at the lower nonhelicogenic TCE content (5 vol%). From these results, it is concluded that solvent polarity plays an important role in determining the helix sense of supramolecular columnar assembly constructed by stacks of the L-**1** molecules. In addition, this morphological transition is accompanied by a significant change in fluorescent color, and thus the color can be tuned over a wide visible range (orange in a Pl-helical columnar state to light blue in a molecularly dispersed state through yellow in a Pr-helical columnar state) by adjusting the solvent composition. Continued detailed investigations including preparations of the analogous compounds will be performed to further understand features of the supramolecular helicity.

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13 The computation method is described in the Electronic Supplementary Information.†.

14 The helical columnar assemblies as illustrated in Fig. 1b and c may need a minor revision because the λ_{max} values were calculated for a model compound without the amide substituents. For a more precise calculation, it is necessary to consider conformations of the substituents and the packing modes. It is, however, difficult because there are a lot of candidates adopting different conformations and packing structures. In addition, the calculation of such large molecules takes much time. Detailed helical columnar assembly state will also be investigated by the combination of several methods including atomic force microscopy and calculation of CD.

15 L-**1** is insoluble in many organic solvents, *e.g.*, dichloromethane, 1,2-dichloroethane, ethyl acetate, acetone, methanol and dimethyl sulfoxide. The analogous compounds with good solubility will enable more systematic studies using polar solvents. Their syntheses are in progress.

16 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC press, Boca Raton, 88th edn, 2007–2008, pp. 6–150 (chloroform and 1,1,2,2-tetrachloroethane), pp. 6–158 (hexane) and pp. 6–167 (dodecane). All dielectric constants (ε_r) described in the text are the values at 293.2 K (20.0 °C).

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