Stable supramolecular helical structure of C_6-symmetric hydrogen-bonded hexakis(phenylethynyl)benzene derivatives with amino acid pendant groups and their unique fluorescence properties†

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A highly stable supramolecular helical structure was formed by the self-assembly of novel C_6-symmetric hydrogen-bonded discotic molecules, hexakis(phenylethynyl)benzene derivatives with chiral alanine parts, and exhibited orange excimer emission with a large Stokes shift.

Biological polymers, such as DNA and polypeptides, adopt regular one-handed helical structures composed of their homochiral components (D-sugars and L-amino acids), which further self-assemble into lyotropic liquid crystals because of their stiff helical backbones.[1] Since the discovery of biological helices and their liquid crystal properties, significant attention has been paid to developing helical architectures[2] with controlled helicity and liquid crystallinity that mimic the structures and functions of biological helices. In particular, supramolecular helical assemblies constructed using various types of noncovalent bonding interactions,[3] as utilized in biological systems, are of great interest from fundamental and biological viewpoints, and offer potential applications in chiral materials science.[2]

Among such supramolecular assemblies, most of the ordered structures have been obtained from disk-shaped molecules, which offers the possibility of forming highly ordered columns. To stabilize the π–π stacking among aromatic groups and enforce the intracolumnar stacking order, it is important to enlarge the disk size[4] and to introduce hydrogen bonds,[4d,5] respectively. The majority of studies on hydrogen-bonded helical columns have been performed on 1,3,5-benzene tricarboxamide derivatives, which are C_3-symmetric molecules consisting of a central benzene ring and three peripheral chiral segments connected *via* amide bonds.[3f,4e,f,6] The π–π interactions of the central benzene cores are enforced by 3-fold intermolecular hydrogen bonding. To enable efficient packing, the intermolecular hydrogen bonds rotate out of the plane, inducing a preferred one-handed helicity in the columns. Amino acid units are also widely used as effective structuring elements which set up hydrogen bonds in self-assembled architectures such as liquid crystalline dendritic peptides,[7a,b] functional cyclic peptides,[7c] and C_3-symmetric benzene and cyclohexane derived organogelators.[3g]

From this background, we have designed a new C_6-symmetric hydrogen-bonded discotic molecule, L-**1**, to enhance the stability of the supramolecular helix (Fig. 1). The L-**1** compound consists of a large hexakis(phenylethynyl)benzene central core, bearing chiral L-alanine parts contributing to the formation of hydrogen bonds and a one-handed helix, and peripheral hydrophobic dodecyl chains. L-**1** gives rise to viscous solutions when dissolved in *n*-alkane solvents. L-**1** gives a relatively low critical gelation concentration, 4.2×10^{-4} M (1.0 mg ml^{-1}), at a temperature of about 10 °C in *n*-dodecane and exhibits a lyotropic liquid crystalline gel over approximately 6 wt% in *n*-hexane.

To investigate the self-assembly of L-**1**, UV-visible absorption (UV-vis) and circular dichroism (CD) spectra were measured in several solvents (4.20×10^{-5} M). As shown in Fig. S1 and 2,† L-**1** shows two absorption bands at 285 ($\varepsilon = 7.23 \times 10^4$ M^{-1} cm^{-1}) and 359 nm ($\varepsilon = 1.71 \times 10^5$ M^{-1} cm^{-1}), at 25 °C in the relatively polar $CHCl_3$, and at 286 ($\varepsilon = 7.00 \times 10^4$ M^{-1} cm^{-1}) and 362 nm ($\varepsilon = 1.65 \times 10^5$ M^{-1} cm^{-1}) in 1,1,2,2-tetrachloroethane (TCE). On the other hand, the absorption bands at a shorter wavelength shifted bathochromically to 300 nm in both *n*-hexane ($\varepsilon = 6.30 \times 10^4$ M^{-1} cm^{-1}) and *n*-dodecane ($\varepsilon = 6.04 \times 10^4$ M^{-1} cm^{-1}), while the absorption bands at a longer wavelength were essentially unchanged at 362 ($\varepsilon = 1.28 \times 10^5$ M^{-1} cm^{-1}) and 361 nm ($\varepsilon = 1.24 \times 10^5$ M^{-1} cm^{-1}), respectively. The red shift observed for the shorter wavelength band in nonpolar solvents suggests that L-**1** stacks through π–π interactions between the large central cores.[8]

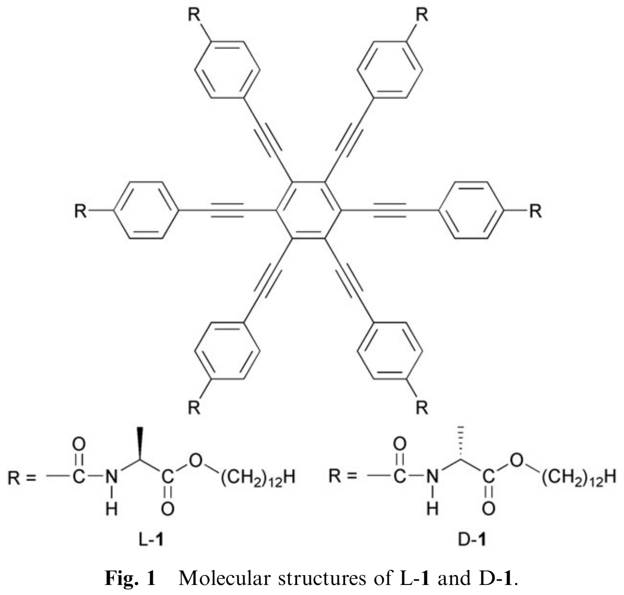

Fig. 1 Molecular structures of L-**1** and D-**1**.

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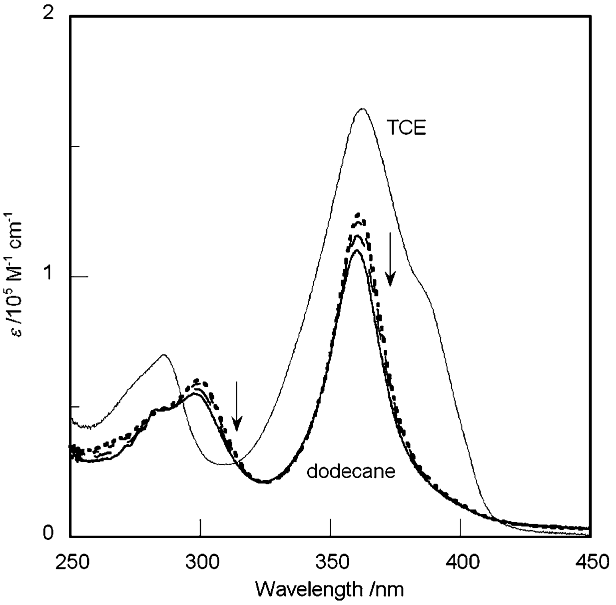

Fig. 2 Temperature dependent UV-vis spectra of L-**1** in *n*-dodecane (4.2×10^{-5} M) at 25, 40, 70 and 100 °C. Arrows indicate the change that occurs with increasing temperature. The UV-vis spectrum in TCE at 25 °C is also shown (thin solid line).

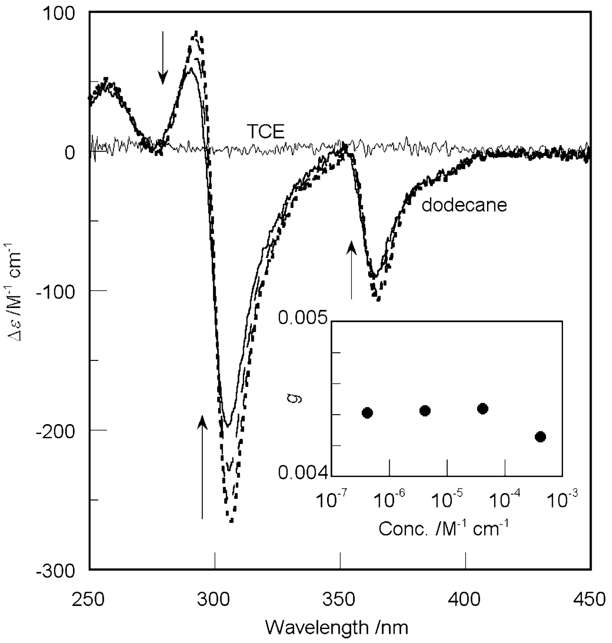

Fig. 3 Temperature dependent CD spectra of L-**1** in *n*-dodecane (4.2×10^{-5} M) at 25, 40, 70 and 100 °C. Arrows indicate the change that occurs with increasing temperature. The CD spectrum of L-**1** in TCE at 25 °C is also shown (thin solid line). The inset shows the concentration dependence of the chiral anisotropy *g* factor of D-**1** in *n*-dodecane at 25 °C.

In haloalkanes, L-**1** shows no CD in the UV-vis range (Fig. S2 and S3†). This indicates that the molecules do not form the predominantly preferred chiral structures. **L-1**, however, shows three major strong Cotton effects with a negative first Cotton effect ($\Delta\varepsilon = -100$ M^{-1} cm^{-1} at 364 nm), a negative second Cotton effect ($\Delta\varepsilon = -270$ M^{-1} cm^{-1} at 305 nm) and a positive third Cotton effect ($\Delta\varepsilon = 89$ M^{-1} cm^{-1} at 292 nm) at 25 °C in *n*-hexane, and similarly in *n*-dodecane (first: $\Delta\varepsilon = -108$ M^{-1} cm^{-1} at 365 nm; second: $\Delta\varepsilon = -266$ M^{-1} cm^{-1} at 307 nm; and third: $\Delta\varepsilon = 85$ M^{-1} cm^{-1} at 293 nm). The slight difference in the CD spectra in *n*-alkanes could be due to a minor change in solvophobic interactions. In addition, the CD spectrum of the other enantiomer, D-**1**, in *n*-dodecane was the mirror image of that of L-**1** as shown in Fig. S2.† These results indicate that **L-1** and **D-1** form opposite preferred-handed helical structures in nonpolar *n*-alkanes.

In a *n*-dodecane solution of L-**1** (4.20×10^{-4} M), an NH stretching vibration of amide A was observed at 3262 cm^{-1}; a similar wavenumber was observed for a solid film of **L-1** on KBr (3257 cm^{-1}), whereas a higher wavenumber was observed (3433 cm^{-1}) for a TCE solution of L-**1**. A similar trend was also observed for the C=O stretching vibration of amide I; 1634 cm^{-1} in *n*-dodecane, 1633 cm^{-1} in a solid film, and 1655 cm^{-1} in TCE. The combined results of the UV-vis, CD and IR indicate that **L-1** forms a rigid helical columnar assembly in nonpolar solvents, which is stabilized by strong hydrogen bonds among the large disk cores, while the molecules in haloalkanes are mostly in a molecularly dispersed state.

To investigate the stability of the helical structure, temperature and concentration dependent UV-vis and CD spectroscopy were performed from 25–100 °C (4.20×10^{-5} M) and from 4.20×10^{-4}–4.20×10^{-7} M (at 25 °C) in *n*-dodecane solutions of **1**. A gradual decrease in intensity was observed with increasing temperature along with a small blue shift of the absorption maximum from 300 to 298 nm (Fig. 2). Correspondingly, there was a gradual decrease in CD intensity with increasing temperature (Fig. 3), which may be attributed to a decrease in positional order of the molecules within the

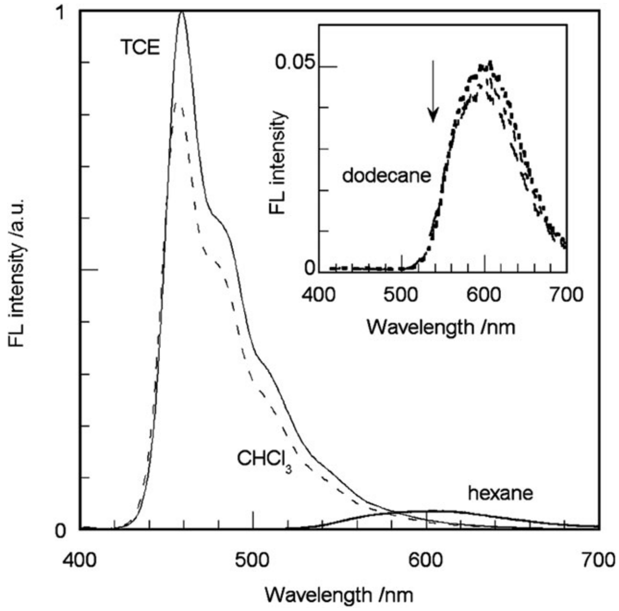

Fig. 4 FL spectra of L-**1** in $CHCl_3$, TCE and *n*-hexane (4.2×10^{-7} M) at 25 °C. The inset shows an expanded view of the temperature dependent FL spectra in *n*-dodecane at 25, 40 and 70 °C. The arrow indicates the change that occurs with increasing temperature. FL spectra ($\lambda_{ex} = 360$ nm) were normalized using the absorption values at 360 nm.

columns as a result of thermal motion. Importantly, the apparent CD spectrum at 100 °C reveals that the helical structure of **1** is exceptionally thermally stable. Subsequent cooling to 25 °C restored the original CD spectrum. In addition, the chiral anisotropy *g* factor ($\Delta\varepsilon_{307}/\varepsilon_{300} = 0.0044$) scarcely changes from low concentrations (4.20×10^{-7} M) to higher concentrations (4.20×10^{-4} M; Fig. 3, inset), suggesting strong association among the molecules.

To further investigate the differences in the intermolecular interactions, fluorescence (FL) spectra (4.20×10^{-7} M) were measured at an excitation of 360 nm (Fig. 4). Emission maxima in $CHCl_3$ and TCE solutions at 25 °C were observed at 457 nm (fluorescence quantum yield, $\phi = 0.26$) and 459 nm ($\phi = 0.32$), respectively. In contrast to the blue fluorescence observed for these nonhelicogenic solutions, the emission in helicogenic *n*-hexane and *n*-dodecane solutions was orange, and their maxima were observed at 604 ($\phi = 0.020$) and 607 nm ($\phi = 0.036$), respectively. For the helicogenic solutions, the broad peaks at around 605 nm are approximately 1/9–1/16 the intensity and are considerably red-shifted with respect to the emission peaks at around 458 nm for the nonhelicogenic solutions. This behavior also indicates that the molecules form columnar structures by strong π–π stacking in the helicogenic solvents.[9] In addition, close stacking of **1** in *n*-alkanes is also supported from the fact that the non-aggregated hexakis[4-(hexyloxycarbonyl)phenylethynyl]benzene, **2**, which does not include amide groups, shows no solvatochromism (Fig. S3†) and its UV-vis and FL spectra in *n*-hexane were essentially the same as those of L-**1** in nonhelicogenic solutions.[10] Consequently, the FL property is clearly dependent on the aggregation state of **1**, and the emission changes from blue in the molecularly dispersed state to orange in the helical columnar state. Here, the broad emission in the helical columnar state is shifted by approximately 5300 cm^{-1} to lower energy compared to that of monomer emission, considered to be excimer emission, because this energy difference is comparable to those of other excimers generated among the phenylethynyl units.[11] With heating, the excimer emission peak hypsochromically shifts by about 4 nm and the intensity gradually decreases; the monomer emission was not observed at all (Fig. 4, inset). This result also supports the strong association of **1** in *n*-alkane. The decrease in fluorescence intensity is probably due to several factors in combination: (1) a decrease in positional order of the molecules within the columns by thermal motion, (2) breaking of larger columnar stacks into smaller stacks but not monomers,[12a] and (3) thermally activated nonradiative processes occurring *via* the long chain alkyl group.[12b]

In summary, we have succeeded in the synthesis of a C_6-symmetric hydrogen-bonded discotic molecule. Stacking among large central cores of **1** is enforced by six intermolecular hydrogen bonds, resulting in a highly stable supramolecular helical structure, which exhibits excimer emission due to strong intermolecular interactions. In addition, the type of intermolecular association is dependent on the solvent, and the observed fluorescence changes from orange in a helical assembly state to blue in a molecularly dispersed state. Detailed investigations into aspects such as the fluorescence life-time, the self-assembled structure and the chiral amplification,[4e,f,5b,6a,b,9b] will be performed to further understand features of the supramolecular helicity.

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