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# Synthesis of a novel axially chiral amphiphile and study on its assembly behavior in two and three dimensions†

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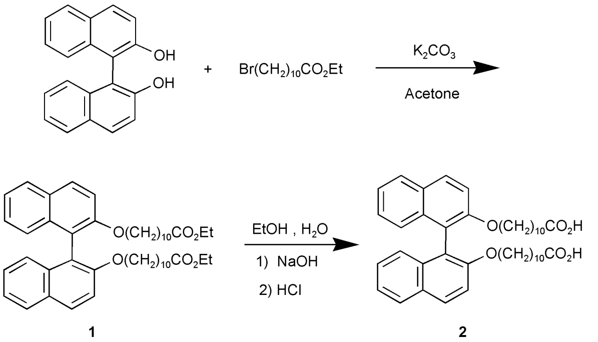
**An axially chiral amphiphile was synthesized and the single crystal of its racemate was characterized by X-ray crystallography. Its three dimensional assembly behaviors in crystallization process and two dimensional assembly behaviors at the air–water interface were investigated by X-ray crystallography and surface-area (π-A) isomers, respectively.**

Chirality is an important phenomena in many chemistry and biology processes, playing a key role in the assembly of supramolecular structures and recognition events between biomolecules. This field has received extensive attention, and in particular, 1,1′-binaphthyl derivatives are largely employed in chiral recognition processes, especially as auxiliaries in asymmetric organic synthesis.[1,2] Recently, the formation of thin ordered films of such compounds appears as an important issue, because the properties and application of axially chiral functional molecules are expanded in the film.[3]

Monolayer and Langmuir–Blodgett (LB) techniques are elegant methods to control molecular orientation and packing.[4,5] The introduction of molecular recognition sites, especially chiral sites, into LB assemblies is desired from the standpoint of designing an organized molecular assembly system capable of discriminating chiral substrates or biomaterials. Most of the work in this field has focused on molecules with one or more centrally chiral centers, especially *N*-acyl amino acid amphiphiles,[6] 1,2-dihexadecanonyl-*sn*-glycero-3-phosphocholine (DPPC),[7] phospholipids,[8] and aldonamides.[9] Moreover, a model for the assembly behavior in the monolayer of molecules with a single chiral center was given by Mao *et al*. by a simulation method.[10] However, to the best of our knowledge, there are limited reports on the study of the effects of axially chirality on three or two-dimensional assembly behavior. This study will better our understanding on the origin of self-assembly, which has great significance in the construction of three-dimensional ordered aggregations and fabrication of oriented ultra-thin films of the axially chiral functional molecules. Here we report the synthesis of a novel axially chiral amphiphilic molecule, 11,11′-[[1,1′-binaphthalene]-2,2′-diylbis(oxy)]bisundecanoic acid (**2**). The single crystal structure of its racemate was characterized by single crystal X-ray crystallography. Meanwhile, we also investigated the effect of chirality on the assembly behavior of *S*-enantiomeric and racemic molecules at the air–water interface by the π-A isotherm measurements.

The synthesis of (*R*)-, (*S*)-, and *rac*-**2** is divided into two steps: (Scheme 1) (1) Reaction of (*R*)-, (*S*)-, and *rac*-1,1′-bi (2-naphthol) with two equivalents of ethyl 11-bromoundecanoate in refluxed acetone in the presence of potassium carbonate results in the formation of (*R*)-, (*S*)-, and *rac*-**1,** respectively, as an oil in *ca.* 70% yield. (2) Hydrolysis of (*R*)-, (*S*)-, and *rac*-**1** in ethanol and water (v/v = 4 : 1) with sodium hydroxide as catalyst followed by acidification with hydrochloric acid give (*R*)-, (*S*)-, and *rac*-**2** respectively in *ca.* 90% yield.



**Scheme 1**

The details of synthesis and characterization of the compounds **1** and **2** are presented in the supplementary information.†

Colorless, block-shaped crystals of *rac*-**2** suitable for X-ray diffraction experiments were grown by slow evaporation of the solvent from an acetone–ethyl acetate solution.[11] The conformation of **2** (Fig. 1) is *trans*[12] because the dihedral angle between the two naphthyl planes [the torsion angle of C(10)–C(1)–C(11)–C(20) is 101.1(3)°] is greater than 90°. The conformation about the C(22)–C(23) bond is *trans* [C(21)–C(22)–C(23)–C(24) = 176.1(2)°], whereas the C(33)–C(34) conformer is *gauche* [C(32)–C(33)–C(34)–C(35) = 98.1(8)°]. The remainders of both chains are in all-*trans* conformations and are nearly parallel to each other.

In the crystal (Fig. 2a), dimers of two opposite enantiomers which are parallel to each other pack side-by-side to form quasi-two-dimensional layers. The angle between the orientations of the dimers of the neighboring layers is near the dihedral angle between the two naphthyl planes, while the orientation of dimer of every other layer is parallel. Meanwhile, we cannot observe the formation of dimers of mono-enantiomers. In short, the packing of the dimers of two opposite enantiomers makes the crystal. Formation of dimers is shown more clearly in Fig. 2b. As can be seen from the figure, the existence of H-bonding between O···O atoms (O(4)A···O(5′)B = 2.664(3) Å, O(3)A···O(6′)B = 2.619(3) Å, O(5)A···O(4′)B = 2.664(3) Å, O(6)A···O(3′)B = 2.619(3) Å) was suggested by the general criterion for inferring the presence of hydrogen bonds.[13] The result shows that the formation of the dimer may be ascribed to the H-bond between opposite enantiomers. Moreover, (*R*)- and (*S*)-**2** are oils, and cannot be crystallized in acetone–ethyl acetate solution. The difference can only be ascribed to the

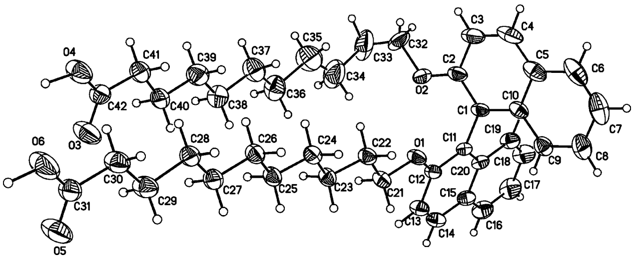


**Fig. 1** The conformation for the crystal structure for *rac*-**2**.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b302572a/

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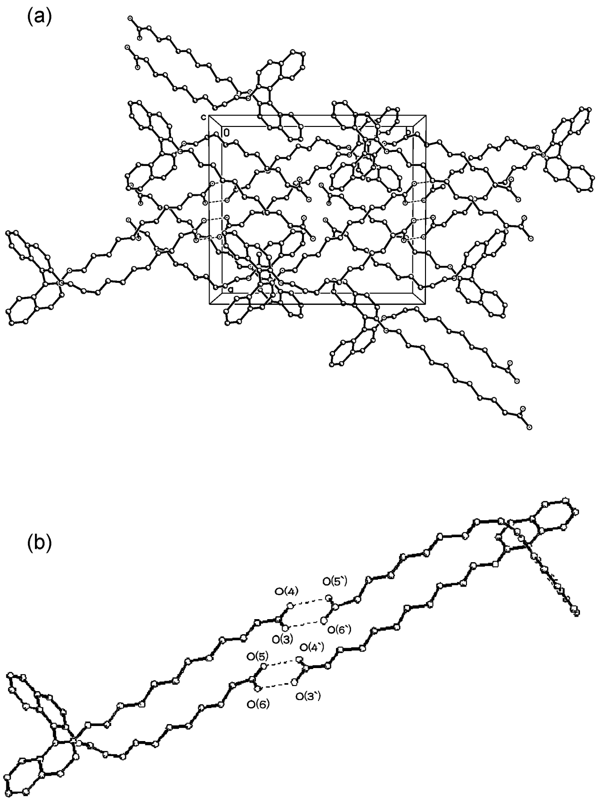

**Fig. 2** (a). Crystal packing for *rac*-**2**. (approximately *ab*-plane). (b). Formation of dimer by two molecules of **2** of opposite enantiomers. The dimer is stabilized by four hydrogen bonds.

formation of the dimer in racemate, which may be the main driving force for the formation of crystal. These observations indicate that the interaction in a sort of interlocking pattern between the (*S*)- and (*R*)-enantiomers may play an important role in the ordered three dimensional assemble of axially chiral molecules possessing long chains.

In order to understand the effect of chirality on the 2D-assembly behavior at the air–water interface, we measured the surface pressure *versus* the area per molecule (π-A) isotherms of **2** at the air–water interface[14] (Fig. 3). The appreciable difference in the π-A isomers between the racemic and the enantiomeric films can be observed, while the curves of the two enantiomeric film are identical, (not shown) which is consistent with the previous report.[6,15–17] The limiting mean molecular area of the racemate is 0.65 nm$^2$ molecule$^{-1}$, much smaller than that of (*S*)-**2** (1.18 nm$^2$ molecule$^{-1}$). The phenomenon may be attributed to the coexistence of monolayer and part bilayer in the more condensed racemic film. This may arise from the possibility that the *S*- and *R*-enantiomers could interact in a sort of interlocking pattern during the compression. That is to say, the difference in the isomer could be assigned to the preferential heterochiral interaction.[17] The long alkyl chains can be stabilized by the formation of dimer by hydrogen bonding of carboxylic acid groups in the ends of the long chains in 3-D racemate crystals. But in the floating 2-D crystals formed at the air–water interface, the carboxylic moiety of molecules of **2** is attracted to water while the long chains and binaphthyl moiety are hydrophobic and effectively repel water.[15] As a result, the molecules tend to orient with the polar headgroups in contact with the water and the long chains and the binaphthyl moiety protruding to the plane of the water surface. Therefore, the formation of dimer of *rac*-**2** in the 2-D crystal is hindered by the orientation of the molecule. However, the interlocking interactions between opposite enantiomers still play a key role in the 2-D assembly of axially chiral molecules at the air–water interface though they do not form hydrogen bonds as in 3-D assembly.

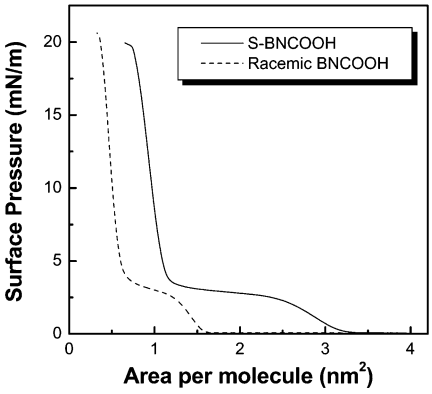

**Fig. 3** The surface pressure *vs.* molecular area (π-A) isotherms of *S*- and racemic BINA at the air–water interface at 20 °C.

In summary, the results above indicate that for the amphiphile molecule studied, the interlocking interactions between opposite enantiomers may be the main reason for the origin of the difference between enantiomer and racemate in both the three dimensional ordered assemble in crystal and the two dimensional ordered assemble at the air–water interface.

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