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A rodlike organogelator: fibrous aggregation of azobenzene derivatives with a *syn*-chiral carbonate moiety†

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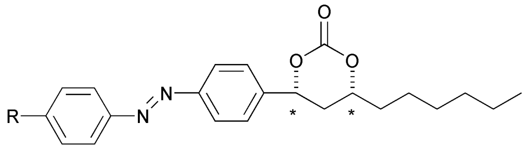
A chiral azobenzene derivative containing a cyclic *syn*-carbonate moiety functions as a gelator for various organic solvents; the dipole-dipole interaction drives the fibrous self-assembly of the rodlike gelator.

Self-assembly is a powerful tool to prepare functional molecular materials.[1,2] One example is fibrous molecular assembly in organic solvents, which leads to the formation of physical organogels.[3] In these materials, non-covalent interactions such as hydrogen bonding,[4–8] lipophilic,[9] and π–π interactions[10] drive such one-dimensional assembly of gelators. These gelators often have functional groups involved in molecular interactions positioned near to the chiral groups. For example, cyclohexane diamide and diurea derivatives having chiral centres at the amino groups are efficient gelators through the one-dimensional self-assembly by the formation of hydrogen bonding.[4,5] In the present study, we have found that an aromatic mesogenic rodlike molecule functions as a new type of organogelator. This azobenzene molecule of (*R*,*R*)-(+)-**1**[11] has a cyclic *syn*-carbonate moiety at the chiral position.

Table 1 shows the minimum gel concentrations (MGC, g L^{-1})‡ of (*R*,*R*)-(+)-**1**. Compound (*R*,*R*)-(+)-**1** acts as an excellent gelator for various organic solvents. In particular, it gelates alcohols, ethers, and hydrocarbons at low concentrations. These gels are stable for more than one year at room temperature. The gel and sol states are thermoreversible. The sol–gel phase transition temperatures of 2-propanol gels of (*R*,*R*)-(+)-**1** increase from 47 to 55 °C with an increase of the concentration from 8 to 20 g L^{-1}.



(*R*,*R*)-(+)-**1**; (±)-**1**: R = -OC_8H_{17} (*R*,*R*)-**2**: R = -OCH_3

Table 1 Minimum gel concentration (MGC) of (*R*,*R*)-(+)-**1** at 25 °C

Solvent	MGC/g L^{-1}	Solvent	MGC/g L^{-1}
Methanol	Cryst.[a]	Chloroform	Sol.[b]
Ethanol	8	Toluene	Sol.[b]
1-Propanol	12	Cyclohexane	6
2-Propanol	6	Hexane	6
Diethyl ether	17	Dodecane	11
Dibutyl ether	12	Hexafluorobenzene	25
Acetone	Sol.[b]	Perfluorohexane	Insol.[c]

[a] Cryst.: Crystallisation. [b] Sol.: Solution. [c] Insol.: Insoluble.

Scanning electron microscope (SEM) observation§ reveals that (*R*,*R*)-(+)-**1** forms fibrous aggregates (Fig. 1). The xerogel was prepared from (*R*,*R*)-(+)-**1**/2-propanol by slow evaporation of the solvent. The gelation ability of the compound is due to the formation of one-dimensional fibrous structures. Variable-temperature infrared (IR) measurements for (*R*,*R*)-(+)-**1** were carried out on both the dodecane gel and the sol state from 25 to 100 °C.§ The $\nu_{C=O}$ band of the carbonate group is observed at 1708 cm^{-1} in the gel states, while it is seen at 1720 cm^{-1} in the sol states. This result suggests that the C=O stretching is suppressed by intermolecular interactions between *syn*-chiral carbonate moieties in the gel state.

No gelation is observed for the corresponding racemate of **1** [(±)-**1**], which forms no fibrous aggregates. Thus, the chirality of the carbonate moiety may play a determining role in the fibre formation and the induction of the gelation ability. Compound (*R*,*R*)-(+)-**1** melts at 39 °C and shows a highly ordered smectic phase up to 118 °C.¶ The racemate of **1** also shows an ordered smectic phase from 61 to 118 °C on heating. However, the phase transition enthalpy from smectic to isotropic of (*R*,*R*)-(+)-**1** is 30 kJ mol^{-1}, which is twice as high as that of (±)-**1**.

For the gel state of 2-propanol with (*R*,*R*)-(+)-**1** (6 g L^{-1}) at 20 °C, weak diffraction peaks at 61.0, 31.3, 20.0 and 15.4 Å are observed by small-angle X-ray scattering (SAXS) measurements. These diffractions are attributed to the d_{100}, d_{200}, d_{300} and d_{400} lattices of the layer structure, respectively. On the other hand, the SAXS experiments of (*R*,*R*)-(+)-**1** on the liquid-crystalline (LC) state reveal that the layer spacing is 56.6 Å at 90 °C. The layer distance is slightly narrower than that in the 2-propanol gel state, suggesting that the self-assembled structures of both the gel and the LC states are basically the same.

The single-crystal X-ray analysis of an analogous compound of gelator (*R*,*R*)-(+)-**1** was carried out to examine the self-

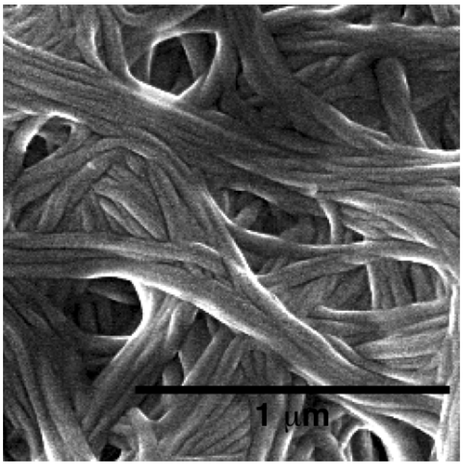


Fig. 1 SEM image of the self-assembled fibres prepared from the (*R*,*R*)-(+)-**1**/2-propanol gel. Scale bar: 1μm.

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† Electronic supplementary information (ESI) available: synthetic scheme for (*R*,*R*)-**2**; FT-IR and SAXS measurements of (*R*,*R*)-(+)-**1**. See http://www.rsc.org/suppdata/cc/b2/b205072b/

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assembled structure of (*R*,*R*)-(+)-**1**. Compound (*R*,*R*)-**2** with a short alkyl chain formed sharp needle-like single crystals from hexane solution by slow evaporation of the solvent at room temperature.‖ Fig. 2 shows a packing structure of (*R*,*R*)-**2** looking down the *a*- and *b*-axes [Fig. 2(a) and (b)] and a magnification view of the cyclic *syn*-carbonate moieties in the crystal structures [Fig. 2(c)]. The crystal has a layered structure through the ribbon-like aggregation of the carbonate moieties along the *b*-axis [Fig. 2(a)]. The dipole moment is compensated along the *a*-axis [Fig. 2(b)]. The stacking distances between the carbonate moieties along the *a*- and *b*-axes are 5.8 and 4.2 Å, respectively. The dipole–dipole interaction of the chiral carbonate moieties having a large dipole moment plays a key role in the formation of the ribbon-like structure, leading to the fibrous self-assembly. The large spontaneous polarisation[11] of (*R*,*R*)-(+)-**1** supports the existence of the large dipole moment.** The length of the *c*-axis is 40.7 Å, which is 15.9 Å shorter than the length of the smectic layer spacing of (*R*,*R*)-(+)-**1**. This difference corresponds to the difference in the alkyl chain length.

In summary, we have demonstrated that compound (*R*,*R*)-(+)-**1** shows excellent gelation properties for various organic solvents. The fibrous self-assembled structure is formed by the ribbon-like aggregation of (*R*,*R*)-(+)-**1** through dipole–dipole interactions of the chiral carbonate moieties. This new molecular design of gelators would lead to the development of novel molecular assemblies with high functionality. Further studies on photoresponsive sol-gel transition behaviour of (*R*,*R*)-(+)-**1** are now in progress.

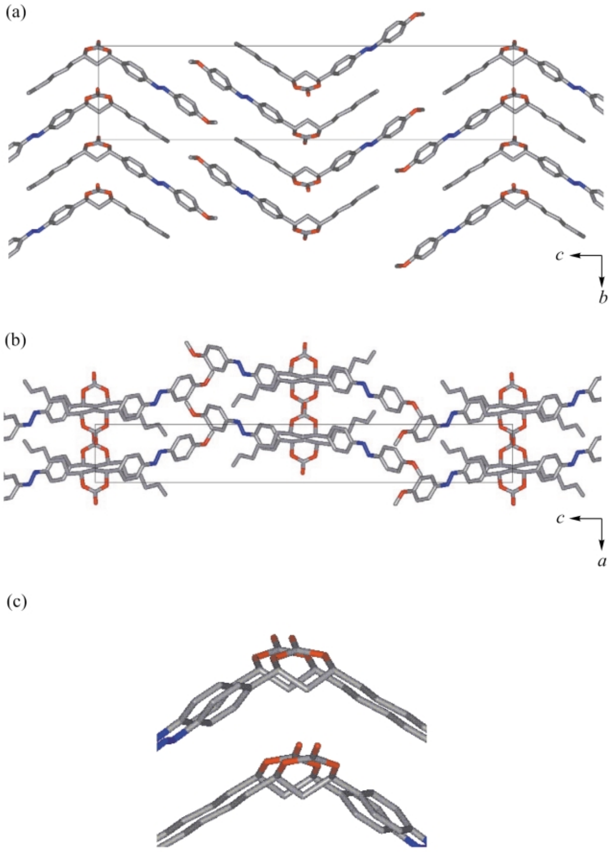

Fig. 2 X-Ray single crystal structure of (*R*,*R*)-**2**.

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Notes and references

‡ Gelation tests were carried out by mixing (*R*,*R*)-(+)-**1** and organic solvents in sealed test tubes. The mixtures were heated up to the isotropic liquid states, then cooled to appropriate temperatures. The minimum gel concentration was determined as described in ref. 12.

§ SEM observation was performed with a Hitachi S-900S. Variable-temperature FT-IR measurements were conducted on a JASCO Micro-20 spectrometer equipped with a Mettler FP-90 hot-stage. See ESI† for the IR spectra.

¶ SAXS measurements were carried out on a Rigaku RINT 2100 system with a temperature controller using Cu-Kα radiation. See ESI† for the SAXS profile of (*R*,*R*)-(+)-**1** in the liquid-crystalline state.

‖ *Crystal data* for (*R*,*R*)-**2**: $C_{23}H_{28}N_2O_4$, M = 396.487, crystal size 0.1 × 0.1 × 1.1 mm, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 5.8530(2), b = 9.3810(5), c = 40.728(3) Å, V = 2236.3(2) Å^3, T = 298 K, Z = 4, μ(Mo-Kα) = 0.087 mm^{-1}, 2073 reflections measured, 2050 unique, which were used in all calculations. The final R and $wR(F^2)$ were 0.095 and 0.126, respectively. All diagrams and calculations were carried out using maXus (Bruker Nonius, Delft & MacSciene, Japan). CCDC reference number 186620. See http://www.rsc.org/suppdata/cc/b2/b205072b/ for crystallographic data in CIF or other electronic format.

** Using CAChe software, the dipole moment of a single molecule of (*R*,*R*)-**2** under vacuum was calculated to be 12 Debye. The calculation was performed using the crystalline state conformation of (*R*,*R*)-**2**.

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