Supramolecular chiral sensing by supramolecular helical polymers
Supramolecular chiral sensing by supramolecular helical polymers†

Takehiro Hirao,‡a Sei Kishino‡a and Takeharu Haino*ab

A tetrakis(porphyrin) with branched side chains self-assembled to form supramolecular helical polymers both in solution and in the solid state. The helicity of the supramolecular polymers was determined by the chirality of solvent molecules, which permitted the polymer chains to be used in chiral sensing.

Molecular sensors consist of a broad and diverse subset of chromogenic and fluorogenic molecules.1–8 When they interact with analytes, their characteristic absorption and/or emission bands are changed. These spectral changes can be readout signals that are readable by using spectroscopic means as well as the naked eye. Among many target analytes, much research attention has been directed toward detecting chiral molecules, such as hydrocarbons, amines, amino alcohols, and amino acids.9,10 Electronic circular dichroism (ECD), X-ray crystallography, and nuclear magnetic resonance (NMR) are commonly used to determine the absolute chiralities of molecules. However, the above methods are often hampered when detecting absolute chiralities of chiral molecules with no appreciable absorption in the UV/vis region.11–14 Thus, due to their dynamic helicity, supramolecular polymers show promise as chiral sensors in which the chiral information of the analytes is outputted as the helix sense of the polymer chains.

Covalently linked tetrakis(porphyrin) 1, in which two bis(porphyrin) moieties are connected, forms helical supramolecular...
polymers by utilizing bis(porphyrin)-bis(porphyrin) self-complementary pairing interactions in an iterative fashion (Fig. 1). We envisioned that the helix sense of tetrakis(porphyrin) could be biased by the external chirality; this can be a chiral detection system in which the biased helix sense can be read by an ECD spectrometer due to the intense absorption of the porphyrin moieties. Here, we report the transference of the chirality within pure hydrocarbons to the helix comprised of 2.

We newly designed tetrakis(porphyrin) 2 with branched alkyl chains in the periphery to improve its solubility toward hydrocarbons (Fig. S1–S4, ESI†). Prior to studying the chiral detection capability, the self-assembly behavior of 2 was studied. 2 exhibited a characteristic absorption band at 420 nm that was assignable to the Soret band of porphyrins at 90 °C in toluene (Fig. 2a). Upon cooling the solution, a new band at approximately 435 nm was observed to grow while decreasing the absorption at 420 nm, which suggests the molecular association of 2 in the solution. The size of the assembled 2 was determined by evaluating diffusion coefficient (D) values at various concentrations (Fig. 2b and Fig. S5, ESI†). Diffusion-ordered 1H NMR spectroscopy (DOSY) provided D values of 2 at concentrations up to 30 mmol L⁻¹ in chloroform-d. The D value decreased upon concentrating the solution. An inversely proportional relation between D and the molecular size is described in the Stokes–Einstein equation; thus, the decrease in D values indicates that supramolecular polymers formed in solution.

Atomic force microscopy (AFM) and high-resolution mass spectrometry (HRMS) support that the supramolecular polymer poly-2 formed. Polymeric fibrous morphologies were visualized by the external chirality; this can be a chiral detection system in which the biased helix sense can be read by an ECD spectrometer due to the intense absorption of the porphyrin moieties. Here, we report the transference of the chirality within pure hydrocarbons to the helix comprised of 2.

Fig. 2  (a) Valuable temperature UV/vis absorption spectra of 2 in toluene at a concentration of 2.2 × 10⁻⁶ mol L⁻¹. The temperatures are (a–i) 90, 80, 70, 60, 50, 40, 30, 20, and 10 °C. The red and blue lines denote the spectra observed at 90 °C and 10 °C, respectively. (b) Plot of diffusion coefficient (D) values of 2 in chloroform-d. (c and d) AFM images of the cast films of 2 on HOPG prepared from its 1,2-dichloroethane solution.

Fig. 3  (a) ECD spectra of 2 (2.5 × 10⁻⁵ mol L⁻¹) in (red) (+)-limonene and (blue) (−)-limonene at room temperature. (b) Binding isotherm analysis corresponding to the formation of intermolecular bis(porphyrin)–bis(porphyrin) self-complementary pairs of 2 in an iterative fashion in (±)-limonene at 90 °C. The plotted extinction coefficient (ε) values are λ = 435 nm. The full spectra are shown in Fig. S7 (ESI†).
enantiomeric excess (ee) of α-pinene (Fig. S10, ESI†). A perfect linearity with the calculated $R^2$ values over 0.995 was clearly illustrated in the plot of ECD intensities of 2 at 422 nm and 437 nm against ee of α-pinene (Fig. 4b). The linear correlation can be used to precisely detect the ee of α-pinene. (+)- and (−)-α-pinenes were mixed in prechosen enantiomeric ratios and subjected to ECD measurements. The ee values of the specimens were estimated from their Δε values at 422 nm based on the linear formula (Fig. S11, ESI†) obtained from the plot shown in Fig. 4b. All estimated values were in good agreement with the actual values calculated from their compositions, in which the absolute error values were within ±4% (Table 1). The absolute error values are sufficiently small18,27 that poly-2 can be used as a chiral sensor.

To determine the limit of detection (LOD) of the poly-2 based sensing system, ECD spectra of 2 were monitored in (−)-α-pinene/toluene and (−)-α-pinene/chloroform mixtures. As can be seen in the ECD spectra (Fig. 5), monotonical decreases in the ECD intensity were observed upon diluting (−)-α-pinene by toluene and chloroform. Judging from the ECD intensities, at least 60% of α-pinene content in the organic media is required to sense the chirality of α-pinene.

In summary, we demonstrated the synthesis of tetrakis(porphyrin) 2, which contains branched alkyl chains in the periphery, and its self-assembling behaviors. 2 self-assembled to form linear supramolecular polymers both in solution and in the solid state, which is consistent with a previously reported tetrakis(porphyrin). The chiral information of limonene, α-pinene, and β-pinene was transferred to assembled 2 as its helical chirality, which can be read by an ECD spectrometer. Notably, linear correlation with the correlation coefficient $R^2 = 0.995$ was illustrated in the plot of the ECD intensities against the ee of α-pinene, providing promise in determining ee of the analyte. With the present approach, the ee values of α-pinene were detected within ±4% accuracy of their actual values. Supramolecular chiral sensors for pure hydrocarbons based on ECD probes have been limited so far; thus, the present work sets the stage for creating new molecular sensors that can detect the chirality of pure hydrocarbon molecules.

We are grateful to the Natural Science Center for Basic Research Development (N-BARD) and Hiroshima University for ECD and HRMS measurements. This work was supported by Grants-in-Aid for Young Scientists, JSPS KAKENHI (22K14727), Grants-in-Aid for Scientific Research (A), JSPS KAKENHI (21H04685), Grants-in-Aid for Transformative Research Areas (A), and JSPS KAKENHI (21H04941: Condensed Conjugation). Funding from the Research Foundation for Opto-Science and Technology, the Toshiaki Ogawara Memorial Foundation, Tobe Maki Scholarship Foundation, and the Urakami Scholarship Foundation is gratefully acknowledged.

Conflicts of interest

There are no conflicts to declare.

Notes and references


Table 1 Summary of the chiral sensing results for α-pinene and the absolute error values

<table>
<thead>
<tr>
<th>Entry</th>
<th>ee (%)</th>
<th>Estimated ee (%)</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>72.0</td>
<td>68.2</td>
<td>−3.8</td>
</tr>
<tr>
<td>2</td>
<td>44.0</td>
<td>45.2</td>
<td>1.2</td>
</tr>
<tr>
<td>3</td>
<td>18.3</td>
<td>15.7</td>
<td>−2.6</td>
</tr>
<tr>
<td>4</td>
<td>−12.0</td>
<td>−9.18</td>
<td>2.8</td>
</tr>
<tr>
<td>5</td>
<td>−44.3</td>
<td>−41.4</td>
<td>2.9</td>
</tr>
<tr>
<td>6</td>
<td>−70.8</td>
<td>−68.7</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* ee values calculated from the composition of (+)- and (−)-α-pinenes.
* Estimated ee values calculated from the observed ECD intensity by using the linear equation (Fig. S11, ESI†).