**Supporting Information**

**Roles of Entropy in Supramolecular Photochirogenesis:** Enantiodifferentiating Photoisomerization of Cyclooctenes in Chiral Sensitizer-Immobilized MCM-41 Cavities

Ryo Maeda, a Takehiko Wada, a, b Atsushi Kusaka, a Tadashi Mori, a Masakazu Iwamoto, c and Yoshihisa Inoue a, b

a Department of Applied Chemistry Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan,
b Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1, Katahira, Aoba-
ku, Sendai 980-8577, Japan,
c Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

E-mail: inoue@chem.eng.osaka-u.ac.jp

1. Photosensitization

**Table S1.** Enantiodifferentiating photoisomerization of 1Z sensitized by 3b immobilized in MCM-41

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>Irrad. time/min</th>
<th>E/Z</th>
<th>Conv. %</th>
<th>Yield/% a</th>
<th>Amount of Sens*/10⁴ mol g⁻¹</th>
<th>% ee</th>
<th>% ee (obtained in pentane)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>5</td>
<td>0.036</td>
<td>5.6</td>
<td>3.4 (63.0)</td>
<td>2.24</td>
<td>+12.0</td>
<td>-3.0</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>0.122</td>
<td>16.0</td>
<td>10.3 (64.4)</td>
<td>2.08</td>
<td>+11.7</td>
<td>-3.0</td>
</tr>
<tr>
<td>-40</td>
<td>5</td>
<td>0.029</td>
<td>3.7</td>
<td>2.8 (75.7)</td>
<td>2.16</td>
<td>+11.9</td>
<td>-0.3</td>
</tr>
<tr>
<td>-60</td>
<td>10</td>
<td>0.068</td>
<td>9.8</td>
<td>6.1 (62.2)</td>
<td>2.21</td>
<td>+14.0</td>
<td>+8.0</td>
</tr>
<tr>
<td>-80</td>
<td>20</td>
<td>0.023</td>
<td>3.0</td>
<td>2.2 (73.3)</td>
<td>1.99</td>
<td>+12.2</td>
<td>+16.5</td>
</tr>
<tr>
<td>-110</td>
<td>20</td>
<td>0.011</td>
<td>c</td>
<td>1.97</td>
<td>+18.0</td>
<td>+48.4</td>
<td></td>
</tr>
</tbody>
</table>

[1Z] = 6.7 mM, [Sens*] = 1.3 mM. Photoisomerization was performed under argon atmosphere in a quartz cell, using a 500-W high-pressure mercury lamp. a) Yield based on 1Z used and consumed (in the parentheses). b) Reference data obtained without using the sensitizer-immobilized MCM-41 in homogeneous pentane solution at [1Z] = 5 mM and [Sens*] = 1 mM. c) Not determined.

**Table S2.** Enantiodifferentiating photoisomerization of 1Z sensitized by 3a immobilized in MCM-41

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>Irrad. time/min</th>
<th>E/Z</th>
<th>Conv. %</th>
<th>Yield/% a</th>
<th>Amount of Sens*/10⁴ mol g⁻¹</th>
<th>% ee</th>
<th>% ee (obtained in MCH)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>20</td>
<td>0.054</td>
<td>7.4</td>
<td>5.0 (67.6)</td>
<td>1.84</td>
<td>-7.6</td>
<td>-15.1</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>0.034</td>
<td>5.5</td>
<td>3.3 (60.0)</td>
<td>1.76</td>
<td>-5.7</td>
<td>-10.9</td>
</tr>
<tr>
<td>-40</td>
<td>20</td>
<td>0.019</td>
<td>c</td>
<td>c</td>
<td>1.77</td>
<td>-9.5</td>
<td>+6.4</td>
</tr>
<tr>
<td>-60</td>
<td>20</td>
<td>0.016</td>
<td>c</td>
<td>c</td>
<td>1.84</td>
<td>-13.6</td>
<td>+20.0</td>
</tr>
<tr>
<td>-80</td>
<td>20</td>
<td>0.010</td>
<td>1.4</td>
<td>1.0 (71.4)</td>
<td>1.96</td>
<td>-17.8</td>
<td>+33.6</td>
</tr>
</tbody>
</table>

[1Z] = 6.7 mM, [Sens*] = 1.3 mM. Photoisomerization was performed under argon atmosphere in a quartz cell, using a 500-W high-pressure mercury lamp. a) Yield based on 1Z used and consumed (in the parentheses). b) Reference data obtained without using the sensitizer-immobilized MCM-41 in homogeneous MCH solution at [1Z] = 5 mM and [Sens*] = 1 mM. c) Not determined.

**Table S3.** Enantiodifferentiating photoisomerization of 2ZZ sensitized by 3a immobilized in MCM-41

<table>
<thead>
<tr>
<th>Temp./°C</th>
<th>Irrad. time/min</th>
<th>E/Z</th>
<th>Conv. %</th>
<th>Yield/% a</th>
<th>Amount of Sens*/10⁴ mol g⁻¹</th>
<th>% ee</th>
<th>% ee (obtained in MCH)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>30</td>
<td>0.019</td>
<td>6.5</td>
<td>1.8 (27.7)</td>
<td>2.04</td>
<td>+5.4</td>
<td>-12.4</td>
</tr>
<tr>
<td>-40</td>
<td>40</td>
<td>0.029</td>
<td>17.7</td>
<td>2.4 (13.6)</td>
<td>1.89</td>
<td>+10.5</td>
<td>+14.0</td>
</tr>
<tr>
<td>-80</td>
<td>40</td>
<td>0.005</td>
<td>1.4</td>
<td>1.87</td>
<td>+12.2</td>
<td>+41.0</td>
<td></td>
</tr>
</tbody>
</table>

[2ZZ] = 6.7 mM, [Sens*] = 1.3 mM. Photoisomerization was performed under argon atmosphere in a quartz cell, using a 500-W high-pressure mercury lamp fitted with a UV-29 glass filter. a) Yield based on 2ZZ used and consumed (in the parentheses). b) Reference data obtained without using the sensitizer-immobilized MCM-41 in homogeneous MCH solution at [2ZZ] = 5 mM and [Sens*] = 1 mM. c) Not determined.
2. Immobilization of sensitizers in MCM-41

![UV spectral changes](image1)

*Figure S1.* UV spectral changes of the supernatant upon addition of MCM-41 to a MCH solution of 3a or 3b at room temperature.

3. IR spectra of sensitizer immobilized in MCM-41 (nujol mull)

![IR spectral changes](image2)

*Figure S2.* IR spectral changes upon immobilization of 3a in MCM-41.

![IR spectra](image3)

*Figure S3.* IR spectra of (−)-menthyl benzoate, phthalate, and pyromellitate sensitizers immobilized in MCM-41.