Stereoregular Two-Dimensional Polymers Constructed by Topochemical Polymerization

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1. Reaction Schemes

1.1. Photoreaction

Scheme S1. Sunlight induced two-dimensional polymerization: it only shows the reaction of one monomer in the equation for simplicity. Part of the scheme was highlighted in blue for clarity.
1.2. Hydrolysis

Scheme S2. The hydrolysis of polymer IP: it only shows the hydrolysis of one unit in the above reaction for simplicity. Parts of the scheme was shown in blue or gray for clarity.
2. Spectra, Data, and Images

2.1. $^1$H and $^{13}$C NMR Spectra

Figure S1. $^1$H- (a) and $^{13}$C- (b) NMR spectra of monomer I in DMSO-$d_6$ at room temperature.
Figure S2. $^1$H- (a) and $^{13}$C- (b) NMR spectra of $\alpha$-truxillic acid 4 in DMSO-$d_6$ at room temperature.
$\alpha$-Truxillic acid derivative 5: 2-aminoethanaminium 2,4-diphenylcyclobutane-1,3-dicarboxylate

**Figure S2. Continued** $^1$H- (c) and $^{13}$C- (d) NMR spectra of $\alpha$-truxillic acid derivative 5 in D$_2$O at room temperature.
Figure S3. $^1$H- (a) and $^{13}$C- (b) NMR spectra of (2E,4E)-5-phenylpenta-2,4-dienoic acid 3 in DMSO-$d_6$ at room temperature.
Figure S4. $^1$H- (a) and $^{13}$C- (b) NMR spectra of monomer II in DMSO-$d_6$ at room temperature.
2.2. Solid State $^{13}$C NMR of Monomers and Polymers

(a) $^{13}$C CP/MAS 12.5 kHz rotation
Rotor 0371-50  ZMR-01

Monomer I

(b) $^{13}$C CP/MAS 12.5 kHz rotation
Rotor 0374-50  ZMR-02

Polymer IP

Figure S5. Solid state $^{13}$C NMR spectra of (a) monomer I and (b) 2D polymer IP.
Figure S6. Solid state $^{13}$C NMR spectra of (a) monomer II and (b) 2D polymer IIP.
2.3. **Crystal Image and Structure of Monomer I**

![Image](image1.png)

**Figure S7.** The crystals and crystal structures of monomer I: (a) The optical microscope image of crystals of monomer I; (b) The chemical structure of I; (c) The X-ray single crystal structure I.

2.4. **Crystal Images and Structures of α-Truxillic Acid 4 and its Derivative 5**

![Image](image2.png)

**Figure S8.** (a) The optical microscope image of single crystals of α-truxillic acid 4 from hydrolysis of the 2D polymer IP; (b) Crystal structure of the isolated α-truxillic acid 4 (A pair of α-truxillic acid showing the disordered relationship. Green and blue are two different disordered orientations and only one exists at a time with 50% probability. Carbon and Oxygen atoms are shown with same color for clarity); (c) ORTEP representation at 50% electron density of the α-truxillic acid crystal structure (*see a short movie in the supporting information for the 3D structure*); (d) The optical microscope image of single crystals of α-truxillic acid derivative 5 from hydrolysis of the 2D polymer IP and a sequential reaction with ethylenediamine; (e) Crystal structure of the α-truxillic acid 2-aminoethanaminium salt 5 (ORTEP at 50% electron density).
2.5. Truxillic Acid and its Five Possible Stereoisomers

Scheme S3. Truxillic acid: Chemical structures of α-truxillic acid 4, which was isolated as hydrolysis product of the 2D polymer IP, and the other four possible stereoisomers of truxillic acid, which were not observed in the hydrolysis.
### 2.6. Table S1. Crystal Data of the Monomers, α-Truxillic Acid and Salt.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Monomer I</th>
<th>Unreactive form of I</th>
<th>α-Truxillic acid 4</th>
<th>α-Truxillic acid aminium salt 5</th>
<th>Monomer II</th>
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<td>1033828</td>
<td>986274</td>
<td>1005428</td>
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<tr>
<td>Formula</td>
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<td>C₄₆H₃₈O₈</td>
<td>C₁₈H₁₄O₄</td>
<td>C₄₄H₆₈N₈O₁₀</td>
<td>C₅₄H₄₆O₈</td>
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<tr>
<td>FW</td>
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<td>718.76</td>
<td>294.29</td>
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<tr>
<td>Cryst. Size [mm]</td>
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<td>0.37, 0.34, 0.11</td>
<td>0.20, 0.25, 0.60</td>
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<td>Space Group</td>
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<td>C₂/c</td>
<td>P₂₁/n</td>
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<td>a (Å)</td>
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<tr>
<td>b (Å)</td>
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<td>9.2109(7)</td>
<td>5.6013(2)</td>
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<td>γ (°)</td>
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<td>Mo</td>
</tr>
<tr>
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<td>4256</td>
<td>63605</td>
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<td>No of independent refl.</td>
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<td>4019</td>
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<td>6064</td>
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<td>No of refl. (I ≥ 2σ)</td>
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<td>3475</td>
<td>1091</td>
<td>6544</td>
<td>5137</td>
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<tr>
<td>R1/wR2 (I ≥ 2σ) [%]</td>
<td>3.76/9.14</td>
<td>3.76/4.44</td>
<td>5.02/13.45</td>
<td>6.87/20.1</td>
<td>4.49/5.43</td>
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<td>R1/wR2 (all data) [%]</td>
<td>3.42/8.88</td>
<td>8.97/9.34</td>
<td>5.57/13.82</td>
<td>7.73/20.4</td>
<td>13.05/14.83</td>
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</table>
2.7. Ultraviolet Absorption of Monomer I

Figure S9. (a) The ultraviolet (UV) absorbance of monomer I in acetonitrile; (b) The UV transmittance of monomer I in the solid state.
2.8. X-ray Powder Diffraction of Monomer I

Figure S10. X-ray powder diffraction (XRD) of monomer I: The calculated powder pattern from single crystal structure of monomer I (top, red); Powder patterns of monomer I powder directly from synthesis without processing (middle, blue) and ground single crystals (bottom, black) showing they are nearly identical.

2.9. Thermogravimetric Analysis of Polymer IP

Figure S11. TGA of polymer IP operated under nitrogen (50.0 ml/min) with rate 20 °C/min.
2.10. Scanning Electron Microscope of Polymer IP

Figure S12. SEM images of polymer IP: The multiple layers of IP showed in (a) and (b); The extremely thin layers were obtained after exfoliation as shown (c) and (d).
2.11. Transmission Electron Microscopy of Polymer IP

Figure S13. The extremely thin sheets of polymer IP observed by TEM: (a) a folded sheet and (b) an opened thin sheet on copper grids with carbon film; (c) and (d) a thin sheet on a carbon film with holes.
2.12. Crystal Image and Structure of Monomer II

![Crystal Image and Structure](image_url)

Figure S14. (left) The optical microscope image of crystals of monomer II; (right) The chemical structure of monomer II.

2.13. Ultraviolet Absorption of Monomer II

![Ultraviolet Absorption](image_url)

Figure S15. The ultraviolet (UV) absorbance of monomer II in ethanol.
2.14. FT-IR Spectra of Monomer II and its Photopolymerization

![FT-IR Spectra](image)

**Figure S16.** FT-IR spectra showing the photopolymerization of monomer II by using UV irradiation.

2.15. X-ray Powder Diffraction of Monomer II and Polymer IIP

![X-ray Diffraction](image)

**Figure S17.** X-ray powder diffraction (XRD) of monomer II and 2D polymer IIP. The calculated powder pattern from single crystal structure of monomer II (top, red); Powder patterns of monomer II powder directly from synthesis without processing (middle, blue); Polymer powders after photoreaction (bottom, black).