Manipulating the nanostructure of organogels generated from molecules with a 3-dimensional truxene core

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Supplementary Information

Materials and methods:
All the starting materials were purchased from commercial sources and used without further purification. Solvents for chemical synthesis were purified by distillation. All chemical reactions were carried out under an argon or nitrogen atmosphere. 1H and 13C NMR spectra of compounds were collected on a 400 MHz spectrometer at room temperature. IR data was obtained from a Perkin Elmer Spectrum 2000 FT-IR spectrometer.

Synthesis:

Scheme S1

1 We thank Dr. Tsung-Han Lin for the Powder X-ray diffraction experiments and technical assistant of Technology Commons, College of Life Science and Precision Instrumentation Center, NTU with CLSM and TEM analysis.
Synthesis of 1b. A mixture of 1a (2.31g, 2.58 mmol), ethyl bromoacetate (5mL, 41.88 mmol), potassium carbonate (10g, 72.36 mmol) and potassium iodide (4g, 24 mmol) was added to a solution of acetonitrile (120 mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over MgSO4. After removal of solvent under vacuum, the crude product was filtered off and washed with n-hexane, compound 1b as a white powder was obtained. (3.3g, 91.6%). mp:183-184°C; IR (KBr) ν 3044, 2982, 2908, 1887, 1758, 1582, 1507, 1441, 1377, 1299, 1210, 1081, 1011, 835, 737, 628, 593, 519 cm⁻¹; ¹H NMR (Acetone-d₆, 400 MHz) δ 7.52 (d, J = 8.8 Hz, 12H), 7.36 (d, J = 7.6Hz, 3H), 7.20 (d, J = 7.6 Hz, 3H), 7.00 (t, J = 8 Hz, 3H), 6.82-6.77 (m, 15H), 4.61 (s, 12H), 4.13 (q, J = 7.2 Hz, 12H), 1.17 (t, J = 7.2 Hz, 18H); ¹³C NMR (DMSO-d₆, 500 MHz) δ 168.552, 156.178, 155.795,146.791, 139.143, 135.539, 132.634, 129.439, 127.515, 126.235, 125.279, 124.531, 114.143, 64.554, 63.216, 60.503, 13.909; HRMS (m/z, FAB⁺) Calcd. for C₈₇H₇₉O₁₈ 1411.54, found 1411.5273.

Synthesis of 2b. A mixture of 2a (2.31g, 2.58 mmol), ethyl bromoacetate (5mL, 41.88 mmol), potassium carbonate (10g, 72.36 mmol) and potassium iodide (4g, 24 mmol) was added to a solution of acetonitrile (120 mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over MgSO4. After removal of solvent under vacuum, the crude product was filtered
off and washed with n-hexane, compound 2b as a white powder was obtained. (3.2g, 88.8%) mp:109-111°C; IR (KBr) ν 3067, 2981, 2934, 1757, 1596, 1486, 1439, 1377, 1205, 1081, 1026, 940, 855, 782, 751, 701, 632 cm⁻¹; ¹H NMR (Acetone- d₆, 400 MHz) δ 7.41 (d, J = 7.8 Hz, 3H), 7.29 (s, 6H), 7.24 (d, J = 7.8, 3H), 7.19-7.13 (m, 12H), 7.06 (t, J = 7.2 Hz, 3H), 6.88 (t, J = 7.2 Hz, 3H), 6.50 (dt, J = 7.2, 2.2, 12H), 4.51 (s, 12H), 4.12-4.06 (m, 12H), 1.14 (t, J = 7.6 Hz, 18H); ¹³C NMR (DMSO- d₆, 500 MHz) δ 168.44, 127.28, 154.78, 146.22, 141.50, 139.48, 135.67, 129.31, 127.72, 126.09, 125.65, 124.70, 121.26, 115.23, 112.89, 64.66, 64.33, 60.54, 13.87; HRMS (m/z, FAB⁺) Calcd. for C₈₇H₇₉O₁₈ 1411.54, found 1411.5259. 146.9, 139.1, 136.0, 132.5, 129.4, 126.8, 126.6, 125.0, 123.9, 113.0, 63.9, 55.3; MS (m/z, FAB⁺) 978 (43); HRMS (m/z, FAB⁺) Calcd. for C₆₉H₅₄O₆ 978.3943, found 978.3932.

Synthesis of 1c. To a stirred mixture of 1b (3.6g, 2.58 mmol) in THF (100mL) was added lithium hydroxide monohydrate (2g, 0.25mol) then slowly added distilled water (100mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over MgSO₄. After removal of solvent under vacuum, the crude product was purified through re-precipitation from EtOAc and hexane. The product 1c was obtained as a white solid (2.5g, 86%). mp:182-183°C; IR (KBr) ν 3531, 3066, 2918, 2756, 2542, 2088, 1915, 1736, 1605, 1506, 1469, 1373, 1294, 1220, 1183, 1076, 1010, 832, 813, 755, 687, 629, 592, 565 cm⁻¹; ¹H NMR (DMSO- d₆, 400 MHz) δ 7.43 (d, J = 7.6 Hz, 12H), 7.37 (d, J = 7.6 Hz, 3H), 7.08 (d, J = 7.6 Hz, 3H), 7.00 (t, J = 7.6 Hz, 3H), 6.82-6.77 (m, J = 8.4 Hz, 15H), 4.670 (s, 12H); ¹³C NMR (DMSO- d₆, 400 MHz) δ 170.92, 156.31, 156.00, 146.31, 139.25, 135.62, 132.54, 129.53, 127.59, 126.35, 125.39, 124.64, 114.15, 64.43, 63.26; HRMS (m/z, ESI⁺) Calcd. for C₇₅H₅₄O₁₈ 1242.33, found 1242.32.
Synthesis of 2c. To a stirred mixture of 2b (3.6 g, 2.58 mmol) in THF (100 mL) was added lithium hydroxide monohydrate (2 g, 0.25 mol) then slowly added distilled water (100 mL). After refluxing for 24 hours, the reaction mixture was cooled down to room temp, extracted with EtOAc and dried over MgSO₄. After removal of solvent under vacuum, the crude product was purified through re-precipitation from EtOAc and hexane. The product 2c was obtained as a white solid (2.7 g, 85.3%). mp: >200°C; IR (KBr) \(\nu\) 3521, 3068, 2921, 2548, 1941, 1585, 1485, 1438, 1221, 1082, 881, 808, 755, 702, 579 cm⁻¹; \(^1\)H NMR (DMSO-\(d_6\), 400 MHz) \(\delta\) 7.40 (d, \(J = 8\) Hz, 3H), 7.22 (s, 6H), 7.140 (t, \(J = 8\) Hz, 6H), 7.08 (d, \(J = 8\) Hz, 3H), 7.05-6.99 (m, 9H), 6.834 (t, \(J = 8\) Hz, 3H), 6.72 (dd, \(J = 8\) Hz, 6H), 4.52 (s, 12H); \(^{13}\)C NMR ((DMSO-\(d_6\), 500 MHz) \(\delta\) 169.94, 157.40, 154.90, 146.24, 141.4, 139.503, 135.65, 129.34, 127.74, 126.10, 125.67, 124.62, 121.05, 115.49, 112.60, 64.58, 64.25, 21.01; HRMS (m/z, ESI⁺) Calcd. for C\(_{75}\)H\(_{54}\)O\(_{18}\) 1242.33, found 1242.32.

Synthesis of TPDA. (500 mg, 0.407 mmol) was stirred in thionyl chloride (25 ml) reflux for 2 hr. After concentration in vacuo, the residue was rediluted in CH\(_2\)Cl\(_2\) and concentrated again. This was redissolved in dry CH\(_2\)Cl\(_2\) (30 mL), cooled to 0 °C, and NEt\(_3\) (10 mL, excess) and \(n\)-decyl amine (0.82 mL, 4.07 mmol) were added. The reaction mixture was stirred for 16 h then extracted with EtOAc and dried over MgSO₄. After removal of solvent under vacuum, the crude product was purified
through re-precipitation from EtOAc and hexane. The product TPDA was obtained as a white solid (750 mg, 88.6%). mp: 110-111°C; IR (KBr) ν 3302, 3069, 2924, 2853, 1663, 1606, 1540, 1506, 1467, 1245, 1182, 1060, 812, 738, 593, 521. 1H NMR (Acetone-d$_6$, 400 MHz) δ 7.54 (d, J = 9.2 Hz, 12H), 7.42 (t, J = 6 Hz, 6H), 7.36 (d, J = 7.8 Hz, 3H), 7.21 (d, J = 7.8 Hz, 3H), 7.01 (t, J = 7 Hz, 3H), 6.84-6.78 (m, 15H), 4.37 (s, 12H), 3.2 (q, J = 7.2 Hz, 12H), 1.47-1.45 (m, 12H), 1.27 (s, 84H), 0.87 (t, J = 6.8 Hz, 18H). 13C NMR (DMSO-d$_6$, 500 MHz) δ 167.135, 156.307, 155.830, 146.821, 139.148, 135.574, 132.623, 129.389, 127.411, 126.235, 125.272, 124.498, 114.312, 66.929, 63.245, 52.007, 31.245, 28.916, 28.642, 26.257, 22.033, 13.858, 7.135; HRMS (m/z, FAB$^+$) Calcd. for C$_{135}$H$_{180}$O$_{12}$N$_6$ 2077.3659, found 2077.3657.

**Synthesis of TMDA.** 2c (500 mg, 0.407 mmol) was stirred in thionyl chloride (25 ml) reflux for 2 hr. After concentration in vacuo, the residue was rediluted in CH$_2$Cl$_2$ and concentrated again. This was redissolved in dry CH$_2$Cl$_2$ (30 mL), cooled to 0°C, and NEt$_3$ (10 mL, excess) and n-decyl amine (0.82 mL, 4.07 mmol) were added. The reaction mixture was stirred for 16 h then extracted with EtOAc and dried over MgSO$_4$. After removal of solvent under vacuum, the crude product was purified through re-precipitation from EtOAc and hexane. The product TMDA was obtained as a brown solid (600 mg, 71%). mp: 112-113°C; IR (KBr) ν 3313, 3072, 2924, 2853, 1663, 1595, 1538, 1486, 1437, 1374, 1226, 1166, 1068, 851, 748, 702, 580. 1H NMR (Acetone-d$_6$, 400 MHz) δ 7.50 (t, J = 5.8 Hz, 6H), 7.39 (d, J = 7.6 Hz, 3H), 7.31 (s, 6H), 7.25-7.19 (m, 12H), 7.04 (t, J = 7.5 Hz, 3H), 6.87 (d, J = 7.5 Hz, 3H), 6.79-6.76 (m, 6H), 4.28-4.19 (m, 12H), 3.20-3.12 (m, 12H), 1.45-1.43 (m, 12H), 1.27 (s, 78H), 0.87 (t, J = 6.8 Hz, 18H); 13C NMR (DMSO-d$_6$, 500 MHz) δ 167.149, 157.343, 154.902, 146.289, 141.476, 139.429, 135.669, 129.279, 127.615, 126.131, 125.593, 124.570, 121.057, 115.382, 113.152, 66.984, 64.343, 31.232, 29.013, 28.943, 28.915, 28.686, 28.639, 26.324, 22.025, 13.847; HRMS (m/z, FAB$^+$) Calcd. for C$_{135}$H$_{180}$O$_{12}$N$_6$ 2077.3659, found 2077.3635.
Instruments and Experimental Techniques

Optical Measurements:
UV-visible absorption spectra were recorded on a spectrophotometer (HITACHI U2800A). PL spectra were measured with a fluorescence spectrophotometer (HITACHI F9500).

Field Emission-Scanning Electron Microscope (FE-SEM):
Samples were prepared by dropcasting a cyclohexane solution of TPDA or TMDA onto a flat SiO₂/Si substrate as described above. The samples were imaged using a FEI Nova NanoSEM 200 in low-vacuum mode with no conductive overcoat. The chamber pressure was maintained at 0.45 Torr water using a differential pumping system. An immersion lens was employed and the secondary electrons amplified by gas vapor and collected by an electrode mounted on the pole piece.

Transmission Electron Microscope (TEM):
Samples were dropcast onto a 200 mesh copper grid coated with formvar film stabilized with vacuum-evaporated carbon and dried under air. The samples were examined in electron microscopes operating at 75 kv (Hitachi H-7650).

Confocal Laser Scanning Microscope (CLSM):
Confocal laser scanning microscope (CLSM) images were taken with Leica laser scanning confocal microscope (Leica TCS SP5 Spectral Confocal) equipped with 50 mW diode Laser / 100 mW Ar blue Laser / 10 mW Green DPSS Laser / 10 mW He-Ne Red Laser. The sample was air-dried on a glass slide and the excitation wavelength for images is 405 nm using 50 mW diode Laser.

Power X-ray diffraction:
Powder X-ray diffraction (XRD) patterns were recorded using a PANalytical X’pert Pro diffractometer with Cu Kα radiation operated at 40 mA and 45 kV.

Solid-State NMR:
All NMR experiments were carried out at ¹³C and ¹H frequencies of 100.6 and 400.0 MHz, respectively, on a Bruker Avance III NMR spectrometer equipped with a commercial 3.2-mm probe. The measurements were carried out at ambient temperature. The sample was confined to the middle one-third of the rotor volume using Teflon spacers. Chemical shifts were externally referenced to tetramethylsilane (TMS) for ¹³C and ¹H. Unless stated otherwise, the ¹³C{¹H} cross-polarization magic-angle spinning (CPMAS) spectra were measured at a spin rate of 17 kHz with a
variation limited to ±3 Hz using a commercial pneumatic control unit (Bruker, MAS II). During the CP period, the $^1$H rf field was set to 50 kHz and that of $^{31}$P was linearly ramped through the zero-quantum Hartmann–Hahn matching condition. The rf field of TPPM proton decoupling was set to 90 kHz during the acquisition period. Recycle delay was set to 4 s. For the variable contact-time experiments, the CP period was varied from 0.3 to 10 ms.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>TPDA</th>
<th>TMDA</th>
</tr>
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<tbody>
<tr>
<td>Cyclohexane</td>
<td>G(5.0)</td>
<td>G(5.0)</td>
</tr>
<tr>
<td>Methyl cyclohexane</td>
<td>G(4.8)</td>
<td>G(5.2)</td>
</tr>
<tr>
<td>Toluene</td>
<td>PG</td>
<td>PG</td>
</tr>
<tr>
<td>Benzene</td>
<td>PG</td>
<td>PG</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>THF</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Acetone</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Hexane</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Dodecane</td>
<td>PG</td>
<td>PG</td>
</tr>
<tr>
<td>MeOH</td>
<td>P</td>
<td>P</td>
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<tr>
<td>EtOH</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>DMF</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>DMSO</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>

$^a$ G = gel, PG = partial gel, P = precipitation, S = solution. The values in parentheses are the critical gelation concentration (CGC) wt %.

Table S1 Organic solvents tested for gelation for two isomeric organogelators.$^a$
Fig. S1 Normalized absorption/emission spectra of TPDA (a) and TMDA (b).

Table S2 Optical Properties of TPDA and TMDA in different phases.

<table>
<thead>
<tr>
<th></th>
<th>TPDA</th>
<th>TMDA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{abs}$/nm</td>
<td>$\lambda_{PL}$/nm</td>
</tr>
<tr>
<td>DCM</td>
<td>315 (3.6)$^a$</td>
<td>382</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>316 (1.6)</td>
<td>382</td>
</tr>
<tr>
<td>Gel</td>
<td>318</td>
<td>383</td>
</tr>
</tbody>
</table>

$^a$ The values in parentheses are the extinction coefficients ($\varepsilon$ = number $\times 10^4$ / M$^{-1}$ cm$^{-1}$).
**Fig. S2** SEM images of gels (5 wt% in cyclohexane) of TPDA (a, b) and TMDA (c). The hollow sphere was characterized by TEM (d).

**Fig. S3** TEM images of TMDA fibers (a, b) indicate the twisting and interlacing features.
Fig. S4 SXRD and WXRD measurements of TPDA (a, b) and TMDA (c, d).
Fig. S5 FT-IR spectra of (a) TPDA in CH₂Cl₂ and in gel phase, (b) TMDA in CH₂Cl₂ and in gel phase.
Temperature-dependent $^1$H NMR analysis of TPDA and TMDA.

(a)

353 K
343 K
333 K
323 K
313 K
303 K
293 K

(b)

353 K
343 K
333 K
323 K
313 K
303 K
293 K
Fig. S6 Temperature-dependent $^1$H NMR spectra of aliphatic and aromatic signals for TPDA (a, b) verse aliphatic and aromatic signals for TMDA (c, d) in cyclohexane-$d_{12}$, respectively.
Solid-state NMR results.

Fig. S7 shows the $^{13}$C$\{^1$H}$^1$ CPMAS spectra obtained for the model compounds $1c$ and $2c$. It is intriguing to find that the spectral features of these two isomers are quite different. In particular, the linewidths of $2c$ are so narrow that some spectral fine structures are observed in the carbonyl (170–180 ppm), peripheral arene (150–160 ppm, 110–120 ppm), and truxene core (120–150 ppm) regions. Additional measurements of the variable contact-time experiments show that $1c$ and $2c$ have somewhat different CP dynamics for the peaks in the truxene core region (Table S3). Therefore, the observation of these fine structures indicates that $2c$ has a higher degree of molecular ordering than $1c$. One may also infer that the motional dynamics of the peripheral arene and truxene core of $1c$ have a correlation time comparable to the NMR time scale, leading to a broadening of the corresponding $^{13}$C NMR peaks. Because alkyl chains usually have considerable motional dynamics. As such, the relatively narrow linewidths of the aliphatic carbons are due to the effects of motional narrowing. The main difference between the $^{13}$C spectra of TMDA and TPDA are in the linewidths of the aromatic signals (Fig. S8). Accordingly, TMDA shows a higher structural order than TPDA.

![Fig. S7 $^{13}$C$\{^1$H}$^1$ CPMAS spectrum measured for $1c$ (top) and $2c$ (bottom). The contact time was set to 3 ms.](image-url)
The $^{13}\text{C}\{^1\text{H}\}$ CPMAS spectra of $1\text{c}$ and $2\text{c}$ measured at 10 kHz, where the signals of the sp$^2$ carbons exhibit sizable spinning sidebands, are shown in Fig. S9. The sideband intensities can provide a sensitive measurement of the chemical shift anisotropy (CSA), which in turn depends on the electronic environment of the resonating nuclei. Although the spectral resolution and the limited number of sidebands do not allow us to quantify the CSA accurately, we can infer from the sideband intensities that there is no significant variation in the electronic environment of the aromatic carbons for $1\text{c}$ and $2\text{c}$. From the $^{13}\text{C}\{^1\text{H}\}$ CPMAS spectra of TMDA and TPDA in Fig. S10, we find that the sideband intensities of the aromatic carbons are again very similar. Consequently, we conclude that the molecular geometry of the truxene region is not significantly perturbed by the alkylation when $1\text{c}$ or $2\text{c}$ is transformed to TPDA or TMDA. Apparently, the fibrillar structure of TMDA has a higher structural order, whereas the globular structure of TPDA has considerable motional dynamics in the truxene region.

**Fig. S8** $^{13}\text{C}\{^1\text{H}\}$ CPMAS spectrum measured for TPDA (top) and TMDA (bottom). The contact time was set to 3 ms.
Fig. S9 $^{13}$C{$^1$H}CPMAS spectra measured for 1c (top) and 2c (bottom) at a MAS frequency of 10 kHz. The contact time was set to 1.5 ms. The asterisks represent the spinning sidebands.
**Fig. S10** $^{13}$C{$^1$H}CPMAS spectra measured for TPDA and TMDA under 5 kHz spinning. The contact time was set to 1.5 ms. The asterisks represent the spinning sidebands.

**Summary of the variable contact-time data**

The data of the variable contact-time experiments were analyzed by the following equation:

$$M(t) = M_0 \left(1 - \exp\left(-t/\tau_{CP}\right)\right) \exp\left(-t/T_{1H}^{cp}\right)$$

where the parameters of $\tau_{CP}$ and $T_{1H}^{cp}$ can characterize the rate of polarization transfer from $^1$H to $^{13}$C and the dipolar coupling among the proton spins, respectively. The results are summarized in Tables 1 and 2.
Table S3 Summary of the chemical shift data and the parameters characterizing the $^{13}$C{¹H} CP dynamics of 1c and 2c.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assignment</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\tau_{CP}$ (ms)</th>
<th>$T_{1/2}$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1c</td>
<td>C</td>
<td>179–171</td>
<td>0.30 ± 0.01</td>
<td>6.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>156</td>
<td>0.39 ± 0.05</td>
<td>10.4 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>146</td>
<td>1.3 ± 0.4</td>
<td>11.3 ± 3.5</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>141–136</td>
<td>0.72 ± 0.15</td>
<td>12.9 ± 3.2</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>129</td>
<td>&lt; 0.1</td>
<td>10.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>125.9–121.5</td>
<td>&lt; 0.1</td>
<td>11.0 ± 0.5</td>
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<tr>
<td></td>
<td>P</td>
<td>110.0–107</td>
<td>&lt; 0.1</td>
<td>9.7 ± 0.7</td>
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<tr>
<td></td>
<td>B</td>
<td>65.0</td>
<td>0.43 ± 0.08</td>
<td>11.3 ± 2.4</td>
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<tr>
<td>2c</td>
<td>C</td>
<td>172.9</td>
<td>0.56 ± 0.10</td>
<td>6.0 ± 0.9</td>
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<tr>
<td></td>
<td>P</td>
<td>156.7</td>
<td>0.38 ± 0.05</td>
<td>6.7 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>148.7</td>
<td>2.1 ± 0.8</td>
<td>5.3 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>136.4</td>
<td>0.36 ± 0.05</td>
<td>8.1 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>130.7</td>
<td>&lt; 0.1</td>
<td>4.6 ± 0.4</td>
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<tr>
<td></td>
<td>T</td>
<td>126.0</td>
<td>&lt; 0.1</td>
<td>6.2 ± 0.3</td>
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<tr>
<td></td>
<td>P</td>
<td>114.7</td>
<td>&lt; 0.1</td>
<td>2.7 ± 0.4</td>
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<tr>
<td></td>
<td>B</td>
<td>64.8</td>
<td>0.15 ± 0.03</td>
<td>7.2 ± 0.6</td>
</tr>
</tbody>
</table>

$^a$ C = carbonyl, P = peripheral arene, T = truxene core, TC = Truxene sp$^3$ carbon, B = peripheral benzylic carbon, A = alkyl chain.
Table S4 Summary of the NMR data and the parameters characterizing the $^{13}$C{$^1$H} CP dynamics of TMDA and TPDA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Assignment$^a$</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\tau_{CP}$ (ms)</th>
<th>$\tau_{1H}$ (ms)</th>
<th>$T_1$ (s)</th>
</tr>
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<tbody>
<tr>
<td>TMDA</td>
<td>C</td>
<td>168.7</td>
<td>0.25 ± 0.02</td>
<td>8.4 ± 0.4</td>
<td>47.4 ± 6.6</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>157.2</td>
<td>0.38 ± 0.05</td>
<td>11.8 ± 1.8</td>
<td>175 ± 19</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>146.8</td>
<td>1.12 ± 0.25</td>
<td>13.0 ± 3.6</td>
<td>n.d.</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>141.6</td>
<td>0.79 ± 0.17</td>
<td>13.8 ± 3.9</td>
<td>28.6 ± 2.5</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>137.2</td>
<td>0.64 ± 0.12</td>
<td>12.5 ± 2.9</td>
<td>n.d.</td>
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<tr>
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<td>&lt; 0.1</td>
<td>13.7 ± 0.8</td>
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</tr>
<tr>
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<td>T</td>
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<td>&lt; 0.1</td>
<td>12.1 ± 0.6</td>
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</tr>
<tr>
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<td>T</td>
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<td>&lt; 0.1</td>
<td>13.6 ± 0.4</td>
<td>n.d.</td>
</tr>
<tr>
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<td>P</td>
<td>115.5</td>
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<td>8.4 ± 0.4</td>
<td>7.3 ± 0.5</td>
</tr>
<tr>
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<td>T</td>
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</tr>
<tr>
<td>TC</td>
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<td>69.6</td>
<td>&lt; 0.1</td>
<td>7.3 ± 1.6</td>
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</tr>
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<td>n.d.</td>
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<td>0.64 ± 0.05</td>
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<tr>
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<td>A</td>
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<td>0.55 ± 0.12</td>
<td>21.2 ± 8.1</td>
<td>0.45 ± 0.02</td>
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<td>A</td>
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<td>0.23 ± 0.03</td>
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<td>0.34 ± 0.01</td>
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<tr>
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<td>A</td>
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<td>n.d.</td>
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<td>0.63 ± 0.04</td>
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<td>13.2 ± 0.1</td>
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<tr>
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<td>n.d.</td>
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<td>4.1 ± 0.4</td>
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<td>n.d.</td>
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<td>0.87 ± 0.05</td>
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<tr>
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<td>0.41 ± 0.01</td>
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<tr>
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<td>A</td>
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<td>6.0 ± 0.4</td>
<td>n.d.</td>
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<td>20.1 ± 6.7</td>
<td>1.07 ± 0.06</td>
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<td>A</td>
<td>14.4</td>
<td>1.21 ± 0.14</td>
<td>&gt;50</td>
<td>1.21 ± 0.06</td>
</tr>
</tbody>
</table>

$^a$ C = carbonyl, P = peripheral arene, T = truxene core, TC = Truxene sp$^3$ carbon, B = peripheral benzylic carbon, A = alkyl chain.
References


1b, $X_1 = OCH_2CO_2Et$, $X_2 = H$
1b, $X_1 = \text{OCH}_2\text{CO}_2\text{Et}$, $X_2 = \text{H}$
2b, $X_1 = H$, $X_2 = OCH_2CO_2Et$
Current Data Parameters

NAME     wongkt-kmc-090504-tmet  
EXPNO               400  
PROCNO                1  

F2 - Acquisition Parameters

Date_          20090504  
Time              18.26  
INSTRUM           spect  
PROBHD   5 mm TBO BB-1H  
PULPROG          zgpg30  
TD                65536  
SOLVENT            DMSO  
NS                 1534DS                    4SWH           35211.270 HzFIDRES         0.537281 HzAQ            0.9306612 secRG                16384DW               14.200 usec  
DE                30.00 usec  
TE                300.2 K  
D1           2.00000000 sec  
d11          0.03000000 secDELTA        1.89999998 secTD0                 100

2b, X₁ = H, X₂ = OCH₂CO₂Et
1c, $X_1 = \text{OCH}_2\text{CO}_2\text{H}$, $X_2 = \text{H}$
2c, $X_1 = H$, $X_2 = OCH_2CO_2H$
Current Data Parameters

NAME     wongkt-kmc-090504-tmac
EXPNO               400
PROCNO                1

F2 - Acquisition Parameters
Date_          20090504
Time              21.23
INSTRUM           spectPROBHD   5 mm TBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                 3072
DS                    4
SWH           35211.270 Hz
FIDRES         0.537281 Hz
AQ            0.9306612 sec
RG                16384
DW               14.200 usec
DE                30.00 usec
TE                300.5 K
D1           2.00000000 sec
D11          0.03000000 sec
DELTA        1.89999998 sec

TD0                   3

======== CHANNEL f1 ========
NUC1                13C
P1                10.30 usec
PL1                3.00 dBSFO

125.7728299 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                1.00 dB
PL12              20.80 dB
PL13              20.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7578528 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.00

2c, X₁ = H, X₂ = OCH₂CO₂H
TPDA, $X_1 = \text{OR}$, $X_2 = \text{H}$
Current Data Parameters

NAME     wongkt-kmc-090504-tpda-4
EXPNO               400
PROCNO                1

F2 - Acquisition Parameters
Date_          20090505
Time               6.01
INSTRUM           spect
PROBHD   5 mm TBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT            DMSO
NS                 3072
DS                    4
SWH           35211.270 Hz
FIDRES         0.537281 Hz
AQ            0.9306612 sec
RG                16384
DW               14.200 usec
DE                30.00 usec
TE                301.0 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   3

======== CHANNEL f1 ========
NUC1                13C
P1                10.30 usec
PL1                3.00 dB
SFO1        125.7728299 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2                1.00 dB
PL12              20.80 dB
PL13              20.00 dB
SFO2        500.1320005 MHz

F2 - Processing parameters
SI                32768
SF          125.7578539 MHz
WDW                  EM
SSB                   0
LB                 2.00 Hz
GB                    0
PC                 1.00

R = \begin{array}{c}
\text{O} \\
\text{N}
\end{array}

TPDA, X_1 = OR, X_2 = H
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