Supporting Information

ENCAPSULATION OF COFACIAL DIARYLACETYLENE DIMERS USING [c2]DAISY CHAIN ROTAXANE STRATEGY

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1. General comments

Permethylated α-cyclodextrin monotosylate (PM α-CD-OTs), Ethyl 4-(4-trimethylsilyl-ethynyl-phenoxy)butyrate and 4-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-3,5-dimethylaniline were prepared by the previous reported procedure. Other reagents were purchased from commercial sources and used without further purification. Commercially available dehydrated DMF was used without further distillation. Melting points were measured with a Stanford Research Systems Optimelt MPA100 melting point apparatus. ¹H NMR (400 MHz), ¹³C NMR (100 MHz) were recorded by a JEOL JNM-Alice 400 spectrometer. The ¹H NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protonated solvents (7.26 ppm) in CDCl₃ or (3.31 ppm) in CD₃OD. The ¹³C NMR chemical shifts were reported relative to ¹³CDCl₃ (77.0 ppm). Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) spectra were recorded on Bruker micrOTOF II-KE02 using sodium trifluoroacetate as cationization reagent. Absorption spectra were recorded by HITACHI U-1900 UV-Vis absorption spectrometer. Fluorescence spectra were recorded by HITACHI FL-7000.
2. Overview for synthetic routes (Scheme S1)

Scheme S1. Overview for synthetic routes of [c2]daisy chain rotaxanes 2a–d and stoppered monomers 3a–d.
3. Changes in the chemical shifts of the diarylacetylene protons (Table S1)

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( \Delta \delta (\text{ppm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1a ) (X = H)</td>
<td>(-0.24)  (-0.05^{[b]})  (-0.05^{[b]})  (+0.52)  (+0.19)</td>
</tr>
<tr>
<td>( 1b ) (X = OMe)</td>
<td>(-0.39)  (-0.04)  (-0.15)  (+0.54)  (+0.24)</td>
</tr>
<tr>
<td>( 1c ) (X = CN)</td>
<td>(-0.26)  (-0.01)  (-0.09)  (+0.58)  (+0.24)</td>
</tr>
<tr>
<td>( 1d ) (X = NO( _2 ))</td>
<td>(-0.26)  (+0.02)  (-0.26)  (+0.58)  (+0.23)</td>
</tr>
</tbody>
</table>

\[ [a] \text{Values were calculated by subtracting the chemical shifts of protons A–E in } \text{CDCl}_3 \text{ from those of the corresponding protons A’–E’ in } \text{CD}_3\text{OD}/\text{D}_2\text{O} (1/2). \[b] \text{Protons B (B’) and C (C’) are equivalent in monomer } 1a. \]
4. Maximum absorption wavelengths in UV-visible spectra (Table S2)

Table S2-1. Maximum absorption wavelengths of [2]daisy chain rotaxane 2a–d.

<table>
<thead>
<tr>
<th></th>
<th>2a (X = H)a)</th>
<th>2b (X = OMe)</th>
<th>2c (X = CN)</th>
<th>2d (X = NO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl3</td>
<td>297, 316</td>
<td>296</td>
<td>299</td>
<td>299</td>
</tr>
<tr>
<td>THF</td>
<td>296, 315</td>
<td>294</td>
<td>297</td>
<td>298</td>
</tr>
<tr>
<td>MeOH</td>
<td>296, 315</td>
<td>294</td>
<td>297</td>
<td>297</td>
</tr>
<tr>
<td>MeCN</td>
<td>296, 315</td>
<td>294</td>
<td>297</td>
<td>297</td>
</tr>
<tr>
<td>DMSO</td>
<td>297, 316</td>
<td>295</td>
<td>298</td>
<td>298</td>
</tr>
</tbody>
</table>

[2] = 1.3 × 10^{-5}–1.7 × 10^{-5} M. a) previous reported.[2]

Table S2-2. Maximum absorption wavelengths of stoppered monomer 3a–d.

<table>
<thead>
<tr>
<th></th>
<th>3a (X = H)a)</th>
<th>3b (X = OMe)</th>
<th>3c (X = CN)</th>
<th>3d (X = NO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl3</td>
<td>296, 315</td>
<td>299, 319</td>
<td>297</td>
<td>297, 314</td>
</tr>
<tr>
<td>THF</td>
<td>295, 314</td>
<td>296, 318</td>
<td>296</td>
<td>296, 314</td>
</tr>
<tr>
<td>MeOH</td>
<td>293, 311</td>
<td>292, 315</td>
<td>294</td>
<td>294, 311</td>
</tr>
<tr>
<td>MeCN</td>
<td>294, 313</td>
<td>295, 317</td>
<td>294</td>
<td>294, 312</td>
</tr>
<tr>
<td>DMSO</td>
<td>297, 316</td>
<td>302, 321</td>
<td>298</td>
<td>298, 315</td>
</tr>
</tbody>
</table>

[3] = 3.2 × 10^{-5}–4.0 × 10^{-5} M. a) previous reported.[2]
5. Maximum emission wavelengths in fluorescence spectra (Table S3)

![Diagram of rotaxane structure]

Table S3-1. Maximum emission wavelengths of [c2]daisy chain rotaxane 2a–d.

<table>
<thead>
<tr>
<th></th>
<th>2a (X = H)</th>
<th>2b (X = OMe)</th>
<th>2c (X = CN)</th>
<th>2d (X = NO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ_{flu} (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl₃</td>
<td>323, 335, 355</td>
<td>329, 343</td>
<td>370</td>
<td>327, 366</td>
</tr>
<tr>
<td>THF</td>
<td>322, 337, 357</td>
<td>326, 342</td>
<td>370</td>
<td>---</td>
</tr>
<tr>
<td>MeOH</td>
<td>322, 336, 358</td>
<td>328, 344</td>
<td>380</td>
<td>---</td>
</tr>
<tr>
<td>MeCN</td>
<td>322, 335, 360</td>
<td>328, 341</td>
<td>377</td>
<td>---</td>
</tr>
<tr>
<td>DMSO</td>
<td>323, 337, 361</td>
<td>328, 344</td>
<td>376</td>
<td>---</td>
</tr>
</tbody>
</table>

[2] = 2.6×10⁻⁷–8.0×10⁻⁷ M. a) previous reported.

![Diagram of stoppered monomer structure]

Table S3-2. Maximum emission wavelengths of stoppered monomer 3a–d.

<table>
<thead>
<tr>
<th></th>
<th>3a (X = H)</th>
<th>3b (X = OMe)</th>
<th>3c (X = CN)</th>
<th>3d (X = NO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>λ_{flu} (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHCl₃</td>
<td>323, 336, 344</td>
<td>329, 342</td>
<td>375</td>
<td>328, 363</td>
</tr>
<tr>
<td>THF</td>
<td>322, 334, 344</td>
<td>327, 342</td>
<td>372</td>
<td>---</td>
</tr>
<tr>
<td>MeOH</td>
<td>319, 333, 340</td>
<td>325, 339</td>
<td>390</td>
<td>---</td>
</tr>
<tr>
<td>MeCN</td>
<td>322, 333, 343</td>
<td>326, 341</td>
<td>387</td>
<td>---</td>
</tr>
<tr>
<td>DMSO</td>
<td>326, 338, 347</td>
<td>333, 346</td>
<td>388</td>
<td>---</td>
</tr>
</tbody>
</table>

[3] = 1.5×10⁻⁶–2.0×10⁻⁶ M. a) previous reported.
6. Synthetic procedures, and ¹H and ¹³C NMR spectra (Figure 1–19)

6-1. PM α-CD halide S1

**General procedure**

4-Bromo-2-cyanophenol (0.69 g, 3.5 mmol) and PM α-CD-OTs (4.0 g, 2.9 mmol) were dissolved in dry DMF (40 mL). Anhydrous K₂CO₃ (1.0 g, 7.2 mmol) was added to the solution and the mixture was stirred under nitrogen at 100 °C for 13 h and cooled to room temperature. The mixture was diluted with EtOAc and washed with saturated NaHCO₃aq. and brine. The organic layer was separated and dried over Na₂SO₄. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (EtOAc/toluene (1/1) and then EtOAc/MeOH (9/1)) to yield PM α-CD iodide S1c as a white formed solid (3.7 g, 92%).

**S1a**: 97%; This compound was previously reported. [⁶]¹H NMR spectrum was shown in Figure S1.

**S1b**: 93%; m.p.: 223-225 °C; ¹H NMR (400 MHz, CDCl₃, 22.4 °C): δ_H = 6.99-6.97 (m, 2H), 6.81 (d, J = 8.9 Hz, 1H), 5.11-5.00 (m, 6H), 4.39 (d, J = 10.4 Hz, 1H), 4.06 (dd, J = 5.0, 9.4 Hz, 1H), 3.98 (dd, J = 3.4, 10.8 Hz, 1H), 3.85-3.11 (m, 86H); ¹³C NMR (100 MHz, CDCl₃, 22.4 °C): δ_C = 150.05, 147.38, 122.70, 115.01, 114.74, 114.96, 99.69-99.61 (several peaks overlapped), 82.48, 81.98-81.60 (several peaks overlapped), 80.71, 77.19, 70.99-70.68 (several peaks overlapped), 70.28, 68.84, 61.34-61.25 (several peaks overlapped), 58.46-58.41 (several peaks overlapped), 58.30, 57.30-57.26 (several peaks overlapped), 55.41; ESI-TOF-HRMS: (m/z) 1417.5269 ([M·Na]+, C₆₀H₉₉BrO₃·Na, Calcd. 1417.5246)

**S1c**: 92%; m.p.: 233-235 °C; ¹H NMR (400 MHz, CDCl₃, 21.8 °C): δ_H = 7.68 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 2.5, 9.0 Hz, 1H), 6.95 (d, J = 9.0 Hz, 1H), 5.09-4.97 (m, 6H), 4.49 (d, J = 9.9 Hz, 1H), 4.43 (dd, J = 5.2, 10.3 Hz, 1H), 4.21 (dd, J = 4.8, 9.8 Hz, 1H), 4.02 (dd, J = 3.0, 11.0 Hz, 1H), 3.92-3.11 (m, 83H); ¹³C NMR (100 MHz, CDCl₃, 21.7 °C): δ_C = 159.48, 136.86, 135.52, 114.55, 114.30, 112.55, 103.87, 100.08, 99.98-99.95 (several peaks overlapped), 99.57, 82.65, 82.38, 82.20, 82.13-82.05 (several peaks overlapped), 81.90-81.85 (several peaks overlapped), 81.70, 81.11-81.06 (several peaks overlapped), 80.83, 77.20, 71.07-70.83 (several peaks overlapped), 70.10, 61.79, 61.73, 61.70,
61.62-61.58 (several peaks overlapped), 58.89-58.85 (several peaks overlapped), 58.79, 58.54, 57.77, 57.70, 57.64-57.58 (several peaks overlapped); ESI-TOF-HRMS: (m/z) 1412.5099 ([M·Na]^+, C_{60}H_{96}BrNO_{30}Na, Calcd. 1412.5093)

**S1d:** 90%; m.p.: 223-225 °C; ^1^H NMR (400 MHz, CDCl₃, 22.0 °C): δ_H = 7.95 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 2.5, 8.9 Hz, 1H), 7.06 (d, J = 8.9 Hz, 1H), 5.10-4.97 (m, 6H), 4.52 (dd, J = 5.2, 10.2 Hz, 1H), 4.44 (d, J = 9.7 Hz, 1H), 4.15 (m, 1H), 3.95-3.10 (m, 84H); ^1^C NMR (100 MHz, CDCl₃, 22.1 °C): δ_C = 151.06, 140.39, 136.39, 127.86, 116.65, 112.04, 100.06-99.98 (several peaks overlapped), 99.80, 99.52, 82.52, 82.38, 82.21, 82.12-82.04 (several peaks overlapped), 81.92-81.85 (several peaks overlapped), 81.75, 81.08-81.03 (several peaks overlapped), 80.83, 77.20, 71.16-70.95 (several peaks overlapped), 70.67, 70.34, 61.80, 61.73, 61.71, 61.66-61.62 (several peaks overlapped), 58.92-58.89 (several peaks overlapped), 58.81, 58.58, 57.75, 57.69-57.67 (several peaks overlapped), 57.63; ESI-TOF-HRMS: (m/z) 1432.5057 ([M·Na]^+, C_{59}H_{96}BrNO_{32}Na, Calcd. 1432.4991)
Figure S1. $^1$H NMR spectrum of PM α-CD Iodide S1a.
Figure S2. $^1$H and $^{13}$C NMR spectra of PM $\alpha$-CD bromide S1b.
Figure S3. $^1$H and $^{13}$C NMR spectra of PM $\alpha$-CD bromide S1c.
Figure S4. $^1$H and $^{13}$C NMR spectra of PM $\alpha$-CD bromide S1d.
6-2. PM α-CD ethyl ester S2

![Image of PM α-CD ethyl ester]

S2a: X = H
S2b: X = OMe
S2c: X = CN
S2d: X = NO₂

General Procedure

PM α-CD bromide S1c (1.0 g, 0.72 mmol), ethyl 4-(4-ethynylphenoxy)butyrate (0.86 g, 3.7 mmol), Pd(PPh₃)₄ (81 mg, 0.070 mmol), and CuI (6.6 mg, 0.035 mmol) were dissolved in i-Pr₂NH/THF (2/1) (30 mL) degassed with N₂ bubbling for 20 min. Under N₂ atmosphere, the mixture was stirred for 24 h. The mixture was diluted with EtOAc and washed with saturated NH₄Claq. and brine. The organic layer was separated and dried over Na₂SO₄. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (EtOAc/CHCl₃ (1/1) and then EtOAc/MeOH (95/5)) to yield PM α-CD ethyl ester S2c as a pale brown solid (1.0 g, 90%).

S2a: 89%; This compound was previously reported. \[^{[62]}\] H NMR spectrum was shown in Figure S5. S2b: the crude containing S2b was used to next reaction without purification. S2c: 90%; m.p.: 112-115 °C; \(^1\)H NMR (400 MHz, CDCl₃, 22.5 °C): \(\delta_H = 7.71\) (d, \(J = 2.1\) Hz, 1H), 7.65 (dd, \(J = 2.1, 8.8\) Hz, 1H), 7.41 (d, \(J = 8.8\) Hz, 2H), 7.01 (d, \(J = 8.8\) Hz, 1H), 6.86 (d, \(J = 8.8\) Hz, 2H), 5.10-4.97 (m, 6H), 4.56 (d, \(J = 10.0\) Hz, 1H), 4.42 (dd, \(J = 5.4, 10.1\) Hz, 1H), 4.24 (dd, \(J = 5.2, 9.8\) Hz, 1H), 4.15 (q, \(J = 7.2\) Hz, 2H), 4.09-4.01 (m, 3H), 3.94-3.12 (m, 83H), 2.52 (t, \(J = 7.3\) Hz, 2H), 2.12 (m, 2H), 1.26 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl₃, 22.5 °C): \(\delta_C = 172.90, 159.55, 159.05, 136.87, 136.09, 132.85, 117.06, 114.93, 114.45, 114.35, 112.96, 102.42, 100.11, 100.01, 99.95, 99.81, 99.52, 90.01, 85.17, 82.79, 82.34, 82.16-81.88 (several peaks overlapped), 81.72, 81.16-81.10 (several peaks overlapped), 80.88, 77.20, 71.10-70.90 (several peaks overlapped), 70.82, 70.13, 66.63, 61.81, 61.74, 61.70, 61.63-61.58 (several peaks overlapped), 60.29, 58.91, 58.87, 58.83, 58.78, 58.60, 57.82, 57.68, 57.62, 57.59, 30.50, 24.32, 14.05; ESI-TOF-HRMS: \((m/z)\) 1564.6937 ([M·Na]+, C₇₄H₁₁₁NO₃₃Na, Calcd. 1564.6931)

S2d: 96%; m.p.: 116-117 °C; \(^1\)H NMR (400 MHz, CDCl₃, 20.2 °C): \(\delta_H = 7.95\) (d, \(J = 2.1\) Hz, 1H),
7.64 (dd, $J = 2.1, 8.7$ Hz, 1H), 7.42 (d, $J = 8.3$ Hz, 2H), 7.11 (d, $J = 8.7$ Hz, 1H), 6.86 (d, $J = 8.3$ Hz, 1H), 5.12-4.98 (m, 6H), 4.54-4.48 (m, 2H), 4.20-4.12 (m, 3H), 4.03 (t, $J = 6.1$ Hz, 2H), 3.98 (dd, $J = 3.0, 10.9$ Hz, 1H), 3.92-3.11 (m, 83H), 2.52 (t, $J = 7.3$ Hz, 2H), 2.12 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$, 20.2 °C): $\delta_C = 173.01, 159.18, 151.27, 139.84, 136.36, 132.97, 127.95, 116.58, 115.01, 114.53, 114.32, 100.12-99.91$ (several peaks overlapped), 99.48, 90.33, 85.15, 82.57, 82.53, 82.25-81.94 (several peaks overlapped), 81.82, 81.22-81.11 (several peaks overlapped), 80.91, 77.20, 71.11-70.98 (several peaks overlapped), 70.82, 70.40, 66.71, 61.88, 61.80-61.69 (several peaks overlapped), 60.39, 58.95, 58.83, 58.70, 57.81, 57.78, 57.72-57.67 (several peaks overlapped), 30.58, 24.39, 14.13; ESI-TOF-HRMS: ($m/z$) 1584.6818 ([M·Na]$^+$, C$_{73}$H$_{111}$NO$_{35}$Na, Calcd. 1584.6829)
Figure S5. $^1$H NMR spectrum of PM $\alpha$-CD ethyl ester S2a.
Figure S6. $^1$H and $^{13}$C NMR spectra of PM $\alpha$-CD ethyl ester S2c.
Figure S7. $^1$H and $^{13}$C NMR spectra of PM $\alpha$-CD ethyl ester S2d.
6-3. Monomer 1

**General Procedure**

PM α-CD ethyl ester S2c (0.91 g, 0.59 mmol) was dissolved in mixture solvent of MeOH (30 mL) and 1 mol/L aqueous KOH (6.0 mL). The resulting mixture was stirred for 1 h at 60 °C under N₂ atmosphere. The mixture was cooled to room temperature, diluted with Chloroform and washed with 2 mol/L aqueous HCl and brine. The organic layer was separated and dried over MgSO₄. The solvent was removed in vacuo to yield monomer 1c as a pale yellow formed solid (0.89 g, quant.).

1a: 89%; This compound was previously reported. [S2] ¹H NMR spectrum was shown in Figure S8.

1b: After ester hydrolysis, the crude was purified by column chromatography on silica gel (EtOAc/MeOH (95/5)) to obtain monomer 1b in 35% yield in 2 steps from PM α-CD bromide S1b; m.p.: 121-123 °C; ¹H NMR (400 MHz, CDCl₃, 22.4 °C): δ_H = 7.42 (d, J = 8.9 Hz, 2H), 7.05 (dd, J = 1.8, 8.3 Hz, 1H), 7.01 (d, J = 1.8 Hz, 1H), 6.89 (d, J = 8.3 Hz, 1H), 6.84 (d, J = 8.9 Hz, 2H), 5.11-5.00 (m, 6H), 4.49 (d, J = 9.7 Hz, 1H), 4.31 (dd, J = 5.6, 10.5 Hz, 1H), 4.11-4.02 (m, 4H), 3.85-3.12 (m, 8H), 2.58 (t, J = 7.3 Hz, 2H), 2.13 (m, 2H). ¹³C NMR (100 MHz, CDCl₃, 20.6 °C): δ_C = 176.22, 158.47, 148.98, 148.49, 132.63, 124.17, 116.21, 115.26, 114.40, 114.24, 113.45, 99.95, 99.85-99.77 (several peaks overlapped), 87.79, 82.89, 82.11-81.76 (several peaks overlapped), 81.00, 77.20, 71.18-70.79 (several peaks overlapped), 70.55, 68.87, 66.40, 61.62-61.52 (several peaks overlapped), 58.75-58.67 (several peaks overlapped), 57.59-57.55 (several peaks overlapped), 55.47, 30.03, 24.15; ESI-TOF-HRMS: (m/z) 782.3329 ([M⋅2Na]⁺, C₇₂H₁₁₀O₄₄Na₂; Calcd. 782.3332)

1c: quant.; m.p.: 142-145 °C; ¹H NMR (400 MHz, CDCl₃, 19.3 °C): δ_H = 7.71 (d, J = 2.1 Hz, 1H), 7.65 (dd, J = 2.1, 8.8 Hz, 1H), 7.41 (d, J = 8.9 Hz, 1H), 7.02 (dd, J = 8.8 Hz, 1H), 6.86 (d, J = 8.9 Hz, 2H), 5.10-4.97 (m, 6H), 4.56 (dd, J = 9.9 Hz, 1H), 4.42 (dd, J = 5.5, 10.4 Hz, 1H), 4.25 (dd, J = 5.2, 9.9 Hz, 1H), 4.09-4.03 (m, 3H), 3.94-3.12 (m, 84H), 2.58 (t, J = 7.3 Hz, 2H), 2.13 (m, 2H); ¹³C NMR (100 MHz, CDCl₃, 20.1 °C): δ_C = 176.54, 159.52, 158.98, 136.89, 136.07, 132.84, 117.03, 114.94, 114.41, 114.37, 112.94, 102.36, 100.05, 99.94-99.89 (several peaks overlapped), 99.75, 99.47, 89.99, 85.17, 82.69, 82.27, 82.08-81.78 (several peaks overlapped), 81.63, 81.17-81.10 (several peaks overlapped), 80.88, 77.20, 71.07-70.78 (several peaks overlapped), 70.10-70.05 (several peaks overlapped).
overlapped), 66.49, 61.78, 61.72, 61.68, 61.60-61.55 (several peaks overlapped), 58.89, 58.86, 58.81, 58.76, 58.58, 57.82, 57.67, 57.61-57.57 (several peaks overlapped), 30.07, 24.15; ESI-TOF-HRMS: (m/z) 779.8272 ([M·2Na]^{2+}, C_{72}H_{107}NO_{33}Na_{2}, Calcd. 779.8255)

**1d**: 99%; m.p.: 149-152 °C; \(^1H\) NMR (400 MHz, CDCl\(_3\), 20.1 °C): \(\delta_H = 7.95 (d, J = 2.1 \text{ Hz}, 1\text{H}), 7.64 (dd, J = 2.1, 8.7 \text{ Hz}, 1\text{H}), 7.42 (d, J = 8.8 \text{ Hz}, 2\text{H}), 7.12 (d, J = 8.7 \text{ Hz}, 1\text{H}), 6.87 (d, J = 8.8 \text{ Hz}, 2\text{H}), 5.12-5.05 (m, 6\text{H}), 4.52 (m, 2\text{H}), 4.19 (m, 1\text{H}), 4.04 (t, J = 6.1 \text{ Hz}, 2\text{H}), 2.58 (t, J = 7.3 \text{ Hz}, 2\text{H}), 2.13 (m, 2\text{H}); \(^13C\) NMR (100 MHz, CDCl\(_3\), 20.0 °C): \(\delta_C = 177.27, 159.14, 151.31, 139.85, 136.41, 133.03, 128.00, 116.59, 115.03, 114.55, 114.45, 100.15-100.10 \text{ (several peaks overlapped)}, 100.01, 99.93, 99.52, 90.33, 85.23, 82.55, 82.26-82.17 \text{ (several peaks overlapped)}, 81.11, 81.96-81.94 \text{ (several peaks overlapped)}, 81.82, 81.28-81.16 \text{ (several peaks overlapped)}, 80.97, 77.20, 71.15-71.11 \text{ (several peaks overlapped)}, 71.02, 70.85, 70.40, 66.57, 61.92, 61.84-61.82 \text{ (several peaks overlapped)}, 61.74-61.72 \text{ (several peaks overlapped)}, 59.00-58.99 \text{ (several peaks overlapped)}, 58.87, 58.73, 57.85, 57.83, 57.76, 57.73, 57.71, 30.17, 24.23; ESI-TOF-HRMS: (m/z) 789.8195 ([M·2Na]^{2+}, C_{71}H_{107}NO_{32}Na_{2}, Calcd.789.8204)
Figure S8. $^1$H NMR spectrum of monomer 1a.
Figure S9. $^1$H and $^{13}$C NMR spectra of monomer 1b.
Figure S10. $^1$H and $^13$C NMR spectra of monomer 1c.
Figure S11. \(^1\)H and \(^{13}\)C NMR spectra of monomer 1d.
6-4. [c2]Daisy chain rotaxane 2

![Diagram of [c2]Daisy chain rotaxane 2]

**General Procedure**

Monomer 1c (107 mg, 0.070 mmol) and 4-[2-[2-(hydroxyethoxy)ethoxy]ethoxy]-3,5-dimethylaniline (113 mg, 0.42 mmol) were dissolved in MeOH/H$_2$O (1/2) (10 mL). After cooling the solution at below 2 °C, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (79.2 mg, 0.41 mmol) was added to the solution. The reaction mixture was stirred at below 2 °C for 2 h, and then stirred at room temperature for an additional 4 h. The reaction mixture was acidified with dilute HCl aq., diluted with EtOAc and washed with brine. The organic layer was separated and dried over MgSO$_4$. The solvent was removed in vacuo, and the residue was purified by column chromatography on silica gel (EtOAc/MeOH (4/1)) to yield [c2]daisy chain rotaxane 2c as a white formed solid (75.8 mg, 61%).

2a: 49%; This compound was previously reported. $^{[62]}$ $^1$H NMR spectrum was shown in Figure S12. 2b: 68%; m.p.: decomposition > 300 °C; $^1$H NMR (400 MHz, CDCl$_3$, 21.1 °C): $d_H = 7.98$ (d, $J = 8.6$ Hz, 4H), 7.14 (s, 4H), 7.05-6.98 (m, 8H), 6.84 (d, $J = 1.7$ Hz, 2H), 6.59 (d, $J = 8.4$ Hz 2H), 5.13-4.99 (m, 12H), 4.32-2.89 (m, 208H), 2.45 (t, $J = 7.4$ Hz, 4H), 2.34 (t, $J = 6.2$ Hz, 2H), 2.27 (s, 12H), 2.17 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$, 21.6 °C): $d_C = 169.76$, 159.35, 152.25, 150.50, 150.21, 134.41, 133.23, 131.44, 126.09, 120.24, 117.78, 116.25, 115.71, 114.14, 113.95, 100.50, 100.27-100.17 (several peaks overlapped), 99.82, 99.49, 88.69, 87.77, 82.52, 82.16-81.71 (several peaks overlapped), 81.46, 81.02, 80.84, 80.69-80.64 (several peaks overlapped), 77.20, 76.22, 72.41, 71.87, 71.59, 71.48-71.34 (several peaks overlapped), 71.15-70.94 (several peaks overlapped), 70.80, 70.57, 70.46, 70.41, 69.93, 66.71, 61.79, 61.70-61.69 (several peaks overlapped), 61.59, 61.50, 59.50, 59.14-59.12 (several peaks overlapped), 59.03, 58.86, 57.89-57.87 (several peaks overlapped), 57.78-57.74 (several peaks overlapped), 57.62, 33.41, 24.85, 16.29; ESI-TOF-HRMS: (m/z) 1202.8820 ([M·3Na]$^{3+}$, C$_{172}$H$_{262}$N$_{26}$O$_{74}$Na$_3$, Calcd. 1202.8826).

2c: 61%; m.p.: decomposition > 300 °C; $^1$H NMR (400 MHz, CDCl$_3$, 20.9 °C): $d_H = 8.01$ (d, $J = 8.5$ Hz, 4H), 7.64-7.62 (m, 4H), 7.14 (s, 4H), 7.05-7.02 (m, 6H), 6.76 (d, $J = 8.7$ Hz, 2H), 5.12-4.95 (m, 12H), 4.40-4.29 (m, 4H), 4.18-3.04 (m, 194H), 2.93-2.86 (m, 4H), 2.45 (t, $J = 7.3$ Hz, 4H), 2.35 (t, $J = 6.1$ Hz, 2H), 2.27 (s, 12H), 2.17 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$, 21.8 °C): $d_C = 169.71$, 160.18,
159.77, 152.18, 136.79, 134.51, 133.22, 131.37, 120.24-120.13 (several peaks overlapped), 116.94, 114.47, 114.11-114.02 (several peaks overlapped), 113.28, 103.52, 100.52-99.99 (several peaks overlapped), 99.85, 99.37, 99.23, 91.06, 85.39, 82.71, 82.56, 82.44, 82.31, 82.17-81.89 (several peaks overlapped), 81.69, 81.54, 81.26-81.22 (several peaks overlapped), 81.07, 80.67-80.47 (several peaks overlapped), 77.12, 72.64, 72.40, 71.94-71.86 (several peaks overlapped), 71.58-71.38 (several peaks overlapped), 71.16-71.10 (several peaks overlapped), 70.73-70.60 (several peaks overlapped), 70.40-70.32 (several peaks overlapped), 70.06, 66.76, 61.66-61.38 (several peaks overlapped), 59.46, 59.26, 59.07-58.98 (several peaks overlapped), 57.89-57.87 (several peaks overlapped), 57.76, 57.61, 57.55, 33.25, 24.74, 16.25; ESI-TOF-HRMS: (m/z) 1199.5365 ([M·3Na]^{3+}, C_{172}H_{256}N_{4}O_{72}Na_{3}, Calcd. 1199.5390).

2d: 10%; m.p.: decomposition > 300 °C; ^1H NMR (400 MHz, CDCl₃, 21.3 °C): δ_H = 8.01 (d, J = 8.7 Hz, 4H), 7.75 (d, J = 1.9 Hz, 2H), 7.68 (dd, J = 1.9, 8.6 Hz, 2H), 7.14 (s, 4H), 7.07-7.03 (m, 6H), 6.96 (d, J = 8.6 Hz, 2H), 5.15-4.96 (m, 12H), 4.49 (m, 2H), 4.25 (m, 2H), 4.17-3.03 (m, 194 H), 2.89-2.83 (m, 4H), 2.45 (t, J = 7.2 Hz, 4H), 2.30-2.27 (m, 14H), 2.17 (m, 4H); ^13C NMR (100 MHz, CDCl₃, 21.4 °C): δ_C = 169.70, 159.93, 152.27, 152.09, 140.64, 136.41, 134.63, 133.22, 131.46, 127.73, 120.23, 117.03, 116.50, 114.13, 113.07, 100.40, 100.32, 100.19, 99.97, 99.39, 91.33, 85.27, 82.71, 82.36, 82.20-82.02 (several peaks overlapped), 81.82, 81.71, 81.52, 81.37, 81.32, 81.18, 80.73, 80.65, 80.55, 77.20, 72.79, 72.42, 72.06, 71.63-71.37 (several peaks overlapped), 71.19, 70.89, 70.80, 70.46, 70.41, 70.15, 66.82, 61.73-61.61 (several peaks overlapped), 61.44, 59.53, 59.12-59.10 (several peaks overlapped), 58.95, 58.78, 57.93-57.84 (several peaks overlapped), 57.68, 57.63, 33.33, 24.79, 16.30; ESI-TOF-HRMS: (m/z) 1212.8654 ([M·3Na]^{3+}, C_{170}H_{256}N_{4}O_{70}Na_{3}, Calcd. 1212.8656).
Figure S12. $^1$H NMR spectrum of $[c2]$daisy chain rotaxane 2a.
Figure S13. $^1$H and $^{13}$C NMR spectra of [c2]daisy chain rotaxane 2b.
Figure S14. $^1$H and $^{13}$C NMR spectra of [c2]daisy chain rotaxane 2c.
Figure S15. $^1$H and $^{13}$C NMR spectra of [c2]daisy chain rotaxane 2d.
6-5. Stoppered monomer 3

![Diagram of monomer 3]

**General Procedure**

Monomer 1c (201 mg, 0.13 mmol) and 4-{2-[2-(hydroxyethoxy)ethoxy]ethoxy}-3,5-dimethylaniline (149 mg, 0.55 mmol) were dissolved in CH$_2$Cl$_2$ (3.0 mL). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (102 mg, 0.53 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 19 h. The reaction mixture was acidified with 2 mol/L HCl aq., diluted with EtOAc, and washed with brine. The organic layer was separated and dried over MgSO$_4$. The solvents were removed in vacuo, and the residue was purified by preparative GPC (Columns: JAIigel-1H and 2H, Eluent: CHCl$_3$). The fractions including desired stoppered monomer 3c was concentrated in vacuo to yield 3c as a white solid (150 mg, 64%).

3a: 46%; This compound was previously reported. [32] $^1$H NMR spectrum was shown in Figure S16. 3b: 50%; m.p.: 102-105 °C; $^1$H NMR (400 MHz, CDCl$_3$, 20.8 °C): $\delta_H = 7.42 (d, J = 8.8$ Hz, 2H), 7.11 (s, 2H), 7.06-7.04 (m, 2H), 7.01 (d, $J = 1.8$ Hz, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.12-5.01 (m, 6H), 4.50 (d, $J = 9.8$ Hz, 1H), 4.30 (dd, $J = 5.6, 10.6$ Hz, 1H), 4.12-3.12 (m, 102H), 2.55 (t, $J = 7.2$ Hz, 2H), 2.36 (brs, 1H), 2.26-2.20 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$, 20.4 °C): $\delta_C = 170.32, 158.60, 152.19, 149.12, 148.65, 133.23, 132.83, 131.39, 124.31, 120.37, 116.27, 115.50, 114.42, 113.49, 100.15, 100.05-99.97 (several peaks overlapped), 88.02, 87.85, 83.07, 82.33-81.95 (several peaks overlapped), 81.10-81.01 (several peaks overlapped), 77.20, 72.41, 71.39-70.95 (several peaks overlapped), 70.75, 70.68, 70.44, 70.37, 68.94, 66.77, 61.82-61.72 (several peaks overlapped), 61.65, 58.93-58.86 (several peaks overlapped), 57.75-57.69 (several peaks overlapped), 55.61, 33.58, 24.90, 16.25; ESI-TOF-HRMS: (m/z) 907.9068 ([M·2Na]$^{2+}$, C$_{86}$H$_{131}$NO$_{37}$Na$_2$, Calcd. 907.9092).

3c: 64%; m.p.: 104-106 °C; $^1$H NMR (400 MHz, CDCl$_3$, 20.5 °C): $\delta_H = 7.71 (d, J = 2.1$ Hz, 1H), 7.65 (dd, $J = 2.1, 8.8$ Hz, 1H), 7.42 (d, $J = 8.8$ Hz, 2H), 7.11 (s, 2H), 7.04-7.00 (m, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.10-4.97 (m, 6H), 4.56 (d, $J = 9.8$ Hz, 1H), 4.43 (dd, $J = 5.5, 10.1$ Hz, 1H), 4.25 (dd, $J = 5.5, 10.1$ Hz, 1H), 4.10-3.12 (m, 98H), 2.55 (t, $J = 7.0$ Hz, 2H), 2.38 (t, $J = 6.0$ Hz, 1H), 2.26-2.20 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$, 21.9 °C): $\delta_C = 170.25, 159.62, 159.07, 152.19, 136.95, 136.16, 133.21, 132.96, 131.37, 120.36, 117.07, 115.02, 114.53, 113.01, 102.46, 100.17, 100.06-100.01 (several peaks overlapped).
overlapped), 99.88, 99.60, 90.01, 85.30, 82.82, 82.23-82.09 (several peaks overlapped), 81.96-81.93 (several peaks overlapped), 81.77, 81.22-81.16 (several peaks overlapped), 80.93, 77.20, 72.38, 71.38, 71.16-70.89 (several peaks overlapped), 70.74, 70.42, 70.36, 70.14, 66.82, 61.89, 61.82, 61.78, 61.71-61.63 (several peaks overlapped), 58.97-58.91 (several peaks overlapped), 58.85, 58.68, 57.87, 57.76, 57.69-57.65 (several peaks overlapped), 33.46, 24.82, 16.23; ESI-TOF-HRMS: (m/z) 905.4071 ([M·2Na]^{2+}, C_{86}H_{128}N_{2}O_{36}Na_{2}, Calcd. 905.4016).

3d: 62%; m.p.: 107-110 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\), 23.6 °C): \(\delta_H = 7.95 (d, J = 2.1 \text{ Hz}, 1H), 7.63 (dd, J = 2.1, 8.7 \text{ Hz}, 1H), 7.42 (d, J = 8.8 \text{ Hz}, 2H), 7.12-7.10 (m, 3H), 7.03 (s, 1H), 6.87 (d, J = 8.8 \text{ Hz}, 2H), 5.11-4.97 (m, 6H), 4.51 (d, J = 3.0 \text{ Hz}, 2H), 4.19 (m, 1H), 4.08 (t, J = 5.9 \text{ Hz}, 2H), 3.99-3.11 (m, 96H), 2.55 (t, J = 7.0 \text{ Hz}, 2H), 2.35 (t, J = 6.2 \text{ Hz}, 1H), 2.26-2.20 (m, 8H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 19.7 °C): \(\delta_C = 170.25, 159.11, 152.15, 151.27, 139.76, 136.36, 133.21, 133.00, 131.36, 127.94, 120.35, 116.51, 114.97, 114.53-114.39 (several peaks overlapped), 100.06-99.87 (several peaks overlapped), 99.48, 90.22, 85.21, 82.52, 82.17-81.78 (several peaks overlapped), 81.13-80.89 (several peaks overlapped), 77.19, 72.37, 71.37, 71.07-70.96 (several peaks overlapped), 70.73, 70.41-70.35 (several peaks overlapped), 66.81, 61.88-61.59 (several peaks overlapped), 58.94-58.82 (several peaks overlapped), 58.69, 57.77-57.67 (several peaks overlapped), 33.46, 24.82, 16.23; ESI-TOF-HRMS: (m/z) 915.3995 ([M·2Na]^{2+}, C_{85}H_{128}N_{2}O_{36}Na_{2}, Calcd. 915.3965).
Figure S16. $^1$H NMR spectrum of stoppered monomer 3a.
Figure S17. $^1$H and $^{13}$C NMR spectra of stoppered monomer 3b.
Figure S18. $^1$H and $^{13}$C NMR spectra of stoppered monomer 3c.
Figure S19. $^1$H and $^{13}$C NMR spectra of stoppered monomer 3d.
7. References
