Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

# Rotaxane-Branched Dendrimers with Aggregation-Induced Emission Behavior

Xu-Qing Wang[1], Wei Wang[1], Wei-Jian Li[1], Yi Qin[1], Guang-Qiang Yin[1,2], Wei-Ling Jiang[1], Xiaopeng Li[2], Shuai Wu[3,*], Hai-Bo Yang[1,*]

[1] Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, Chang-Kung Chuang Institute, East China Normal University, Shanghai 200062, P. R. China.

[2] Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States.

[3] Department of Neurology, Zhongshan Hospital, Fudan University, Shanghai 200032, P. R. China.

To whom correspondence should be addressed; e-mail: Wushuai917777@hotmail.com; hbyang@chem.ecnu.edu.cn

# Table of Contents (23 Pages)

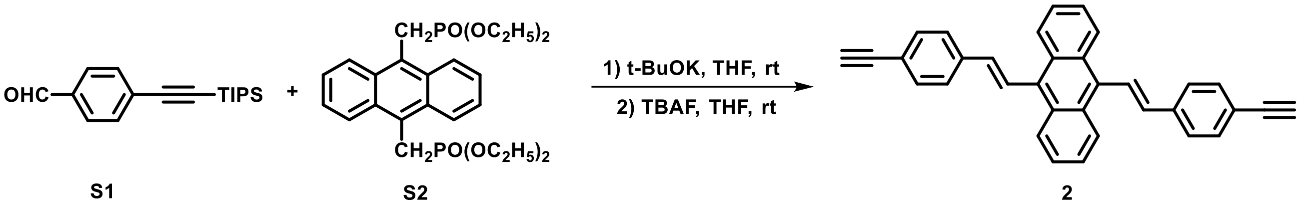
## *Section A. Materials and General Methods*

All reagents were commercially available and used as supplied without further purification, compounds **S1** and **1** were prepared according to the published procedures.[S1-S2] Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA).

All solvents were dried according to standard procedures and all of them were degassed under $N_2$ for 30 minutes before use. All air-sensitive reactions were carried out under inert $N_2$ atmosphere. $^1H$ NMR, $^{13}C$ NMR and $^{31}P$ NMR spectra were recorded on Bruker 300 MHz Spectrometer ($^1H$: 300 MHz; $^{31}P$: 122 MHz), Bruker 400 MHz Spectrometer ($^1H$: 400 MHz; $^{13}C$: 101 MHz, $^{31}P$: 162 MHz) and Bruker 500 MHz Spectrometer ($^1H$: 500 MHz; $^{13}C$: 126 MHz, $^{31}P$: 202 MHz) at 298 K. The $^1H$ and $^{13}C$ NMR chemical shifts are reported relative to residual solvent signals, and $^{31}P$ {$^1H$} NMR chemical shifts are referenced to an external unlocked sample of 85% $H_3PO_4$ ($\delta$ 0.0). 2D NMR spectra ($^1H$-$^1H$ COSY and DOSY) were recorded on Bruker 500 MHz Spectrometer ($^1H$: 500 MHz) at 298 K. The MALDI MS experiments were carried out on a Bruker UltrafleXtreme MALDI TOF/TOF Mass Spectrometer (Bruker Daltonics, Billerica, MA), equipped with smartbeam-II laser. All spectra were measured in positive reflectron or linear mode. UV-vis spectra were recorded in a quartz cell (light path 10 mm) on a Cary 50Bio UV-visible spectrophotometer. Fluorescence spectra were recorded in a conventional quartz cell (light path 2 mm) on a Cary Eclipse fluorescence spectrophotometer.

## *Section B. Synthesis and characterization of the rotaxane-branched dendrimers.*

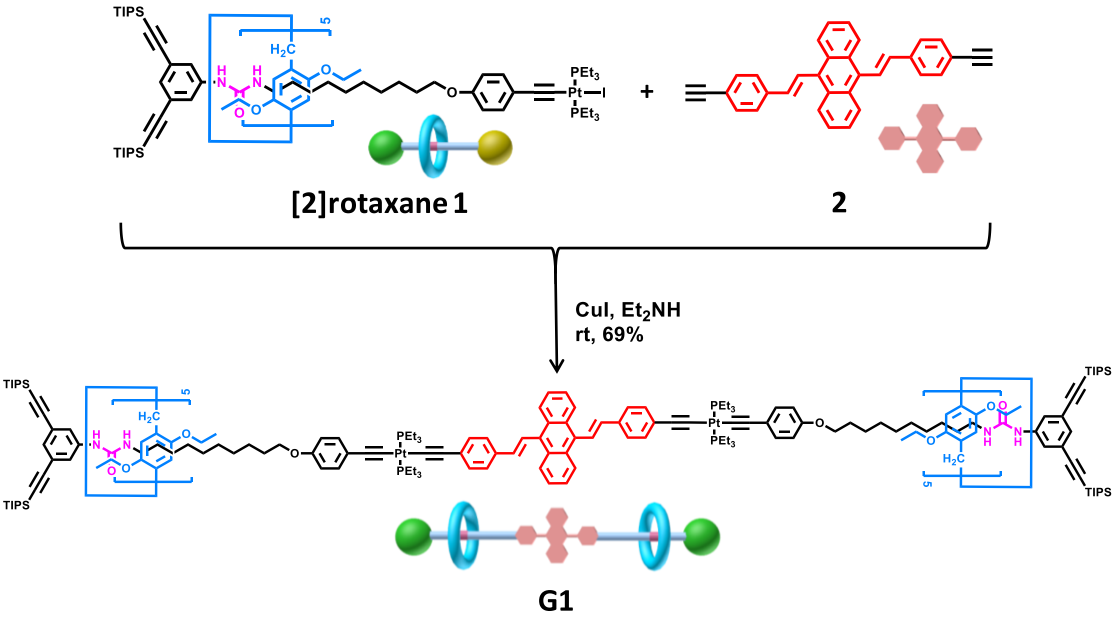
### 1. Synthesis of the core component 2.



**Synthesis of the core component 2:** Mixing compound **S1** (263 mg, 0.92 mmol) and commercially available 9, 10-Bis(diethylphosphonomethyl)anthracene **S2** (200 mg, 0.42 mmol) in THF, then *t*-BuOK (374 mg, 3.34 mmol) was added into the reaction flask, the reaction was stirred at room temperature. After 5h, adding MeOH into the reaction flask, then the reaction mixture was filtered and the filtrate was concentrated in vacuum, the residue was subsequently purified by column chromatography, a solution of $Bu_4NF$ (1.0 M, 89 mg) in THF was added dropwise into the reaction flask. The reaction mixture was stirred at room temperature for 4h. The obtained residue was washed by water, then dried with $Na_2SO_4$ and concentrated. The residue was further purified by column chromatography to afford an orange solid **2** (50 mg, 30%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.36-8.38 (m, 4H), 7.95-7.99 (d, $J$ = 16.0 Hz, 2H), 7.58-7.66 (m, 8H), 7.48-7.51 (m, 4H), 6.91-6.95 (d, $J$ = 16.0 Hz, 2H), 3.19 (s, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$): $\delta$ 137.63, 136.71, 132.60, 132.47, 129.49, 126.45, 126.40, 126.33, 125.42, 121.53, 83.66, 78.09, 29.69. HRMS (EI-MS): Calculated for Calculated for [**2**]$^+$: 430.1722; Found: 430.1727.

## 2. Synthesis of the first-generation rotaxane-branched dendrimer G1.

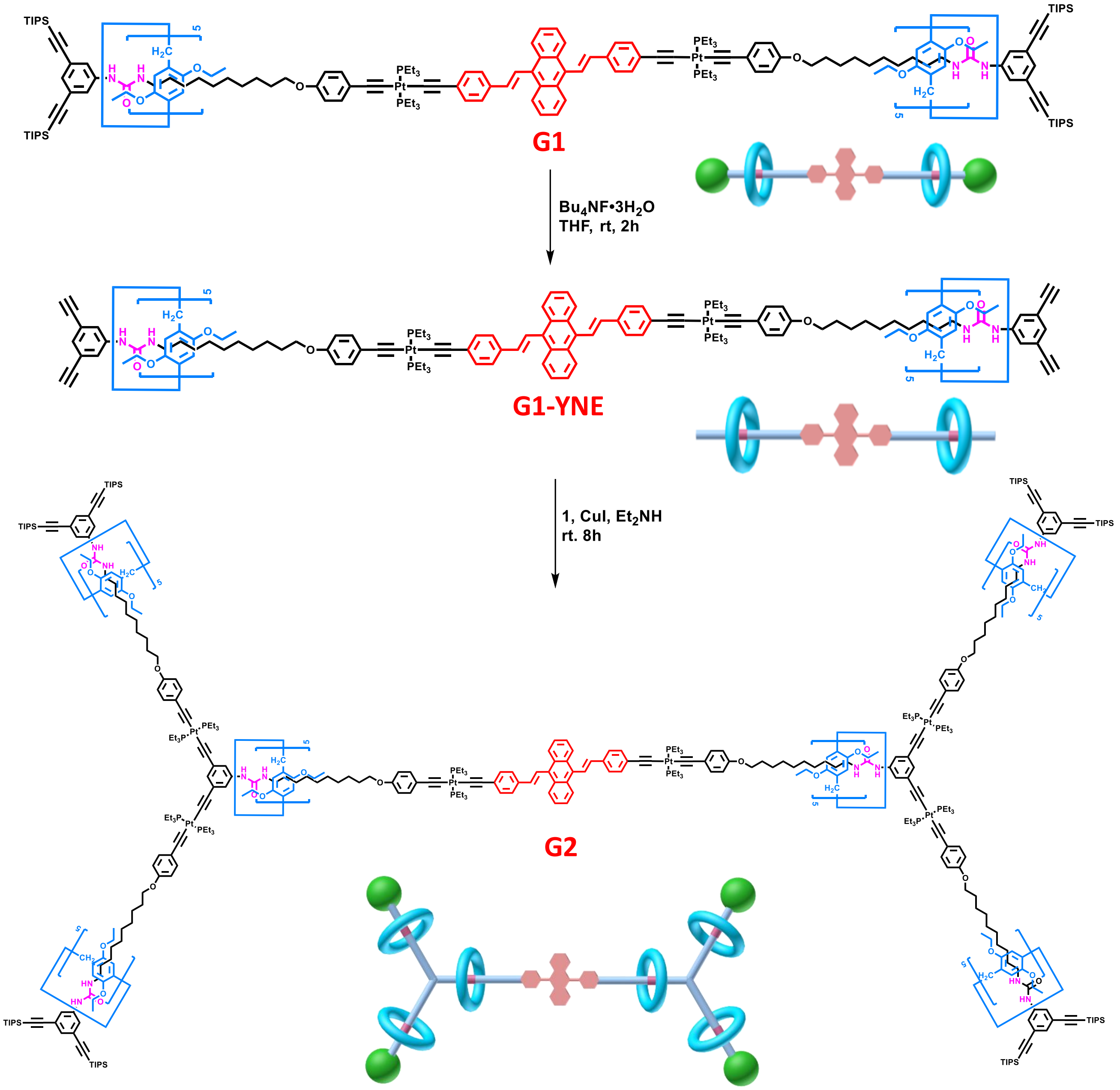
**Scheme S1:** Synthesis route of the first-generation rotaxane-branched dendrimer **G1**.



**Synthesis of the first-generation rotaxane-branched dendrimer G1:** A mixture of and [2]rotaxane **1** (200 mg, 0.091 mmol) and compound **2** (17.8 mg, 0.041 mmol) were added in a Schlenk flask, the Schlenk flask was then evacuated and back-filled with $N_2$ three times. Next, degassed diethylamine (10 mL) and a catalytic amount of CuI was added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography ($SiO_2$; PE/DCM) and preparative gel permeation chromatography (GPC) to yield an orange solid **G1** (130 mg, 69%). $^1$H NMR (300 MHz, THF-$d_8$): $\delta$ 8.40-8.43 (m, 4H), 7.94-7.99 (d, $J$ = 15.0 Hz, 2H), 7.71 (m, 2H), 7.65 (d, 4H), 7.56-7.59 (d, $J$ = 9.0 Hz, 4H), 7.44-7.47 (m, 4H), 7.29-7.31 (d, $J$ = 6.0 Hz, 4H), 7.19-7.22 (d, $J$ = 9.0 Hz, 4H), 7.10 (t, 2H), 6.86-6.94 (m, 22H), 6.73-6.76 (d, $J$ = 9.0 Hz, 4H), 4.91-4.95 (t, $J$ = 6.0 Hz, 2H), 3.73-4.09 (m, 60H), 2.94-3.01 (m, 4H), 2.52-2.57 (m, 4H), 2.20-2.29 (m, 24H), 1.38-1.50 (m, 60H), 1.24-1.35 (m, 36H), 1.16 (s, 84H), 0.68-0.83 (m, 16H), 0.12 (m, 2H), -0.01 (m, 2H), -0.78 (m, 2H), -1.26 (m, 2H). $^{31}$P NMR (202 MHz, THF-$d_8$): $\delta$ 12.50. $^{13}$C NMR (126 MHz, THF-$d_8$): $\delta$ 158.01, 154.95, 150.44, 150.35, 142.10, 138.32, 134.54, 133.52, 132.12, 131.59, 130.38, 130.12, 128.86, 128.85, 128.21, 127.09, 126.84, 125.68, 124.41, 122.17, 121.94, 114.62, 114.31, 107.62, 90.37, 69.10, 64.03, 64.01, 40.31, 32.67, 31.70, 31.53, 31.44, 31.27, 30.99, 30.79, 30.55, 30.43, 30.10, 29.82, 29.67, 29.42, 27.95, 26.18, 25.61, 24.19, 23.36, 18.89, 18.76, 17.32, 17.18, 17.04, 15.69, 15.66, 14.25, 12.27, 12.05, 11.82, 8.57, 1.17. ESI-MS: Calculated for $[\mathbf{G1} + 2H]^{2+}$ ($m/z$ = 2287.7271) and $[\mathbf{G1} + 3H]^{3+}$ ($m/z$ = 1526.1592); Found: $m/z$ = 2287.6082 and $m/z$ = 1526.2189.

## 3. Synthesis of the second-generation rotaxane-branched dendrimer G2.

**Scheme S2:** Synthesis route of the second-generation rotaxane-branched dendrimer **G2**.

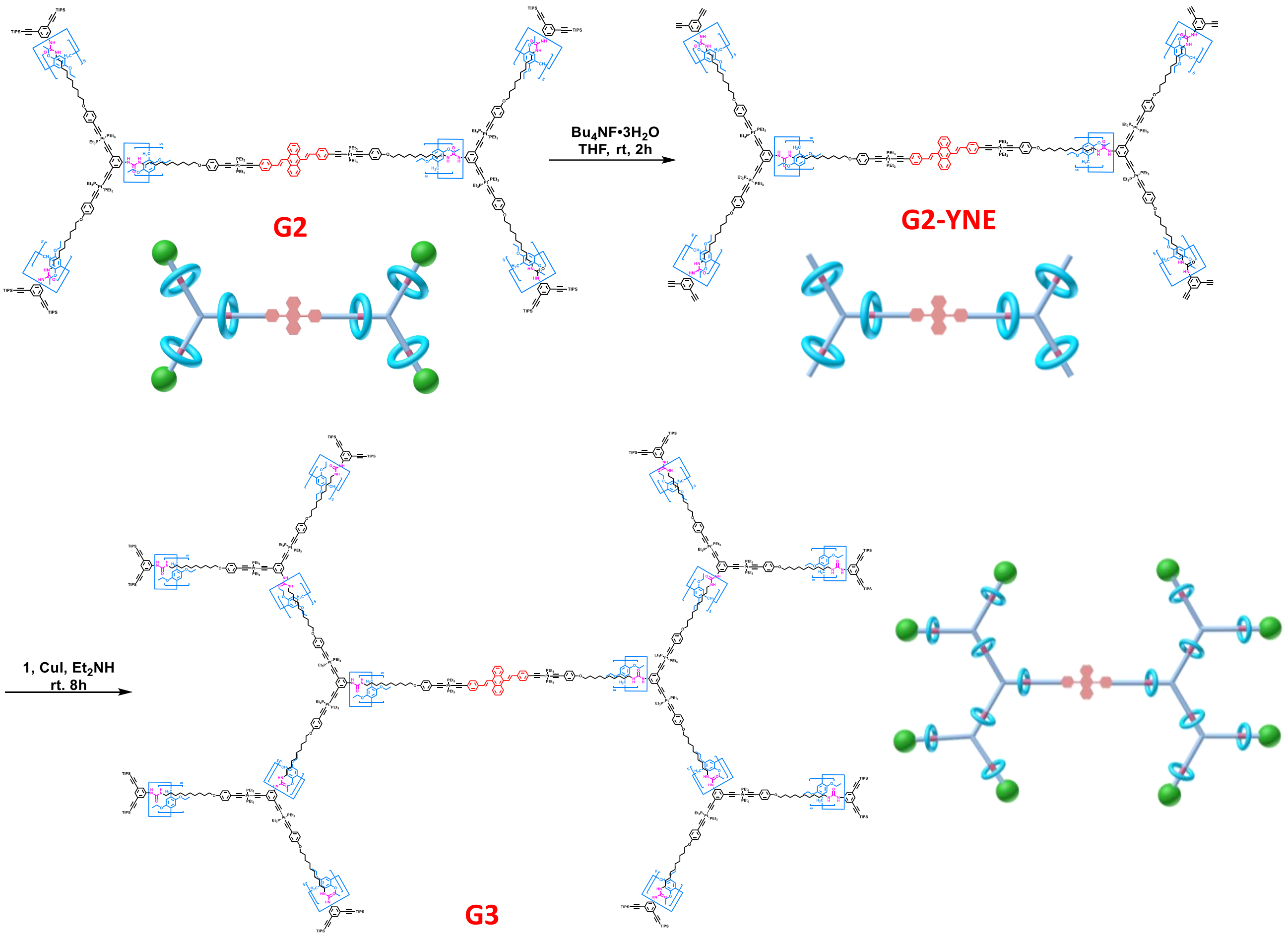


**Synthesis of the second-generation rotaxane-branched dendrimer G2:** A reaction flask was charged with a THF solution of **G1** (70 mg, 0.015 mmol) and then a solution of $Bu_4NF·3H_2O$ (39 mg, 0.122 mmol) in THF was added dropwise into the reaction flask. The reaction mixture was stirred at room temperature for 2h, the obtained residue was washed by water, then dried with $Na_2SO_4$ and concentrated. The residue was further purified by column chromatography ($SiO_2$; DCM) and preparative gel permeation chromatography (GPC) to afford an orange solid **G1-YNE**. Then the obtained **G1-YNE** (40 mg, 0.010 mmol) and [2]rotaxane **1** (98 mg, 0.044 mmol) were added in a

Schlenk flask, the Schlenk flask was then evacuated and back-filled with $N_2$ three times. Next, degassed diethylamine (10 mL) and a catalytic amount of CuI were added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography ($SiO_2$; DCM/EA) and preparative gel permeation chromatography (GPC) to yield an orange solid **G2** (100 mg, 54%). $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 8.40-8.42 (m, 4H), 7.94-7.98 (m, 2H), 7.46-7.65 (m, 20H), 7.29-7.31 (m, 4H), 7.10-7.20 (m, 24H), 6.87-6.95 (m, 62H), 6.73-6.77 (m, 12H), 4.70 (m, 6H), 3.73-4.09 (m, 180H), 3.01-3.06 (m, 12H), 2.40 (m, 12H), 2.22-2.26 (m, 72H), 1.16 (s, 168H), 1.25-1.52 (m, 288H), 0.55-0.78 (m, 60H), 0.19 (m, 12H), -0.65-(-0.74) (m, 12H), -1.09-(-1.19) (m, 12H). $^{31}$P NMR (202 MHz, THF-$d_8$): $\delta$ 12.50. $^{13}$C NMR (126 MHz, THF-$d_8$): $\delta$ 157.93, 155.30, 154.86, 150.45, 150.39, 150.35, 142.07, 140.76, 138.34, 133.54, 132.11, 131.59, 130.39, 129.77, 128.88, 128.85, 128.22, 126.84, 125.67, 124.42, 122.32, 121.98, 118.37, 114.65, 114.62, 114.29, 110.02, 109.30, 107.61, 90.39, 69.07, 68.03, 67.74, 64.07, 64.00, 40.30, 31.53, 31.46, 31.30, 30.82, 30.69, 30.44, 29.85, 29.67, 29.45, 27.91, 26.19, 25.62, 25.45, 25.29, 25.13, 24.97, 24.81, 24.28, 18.89, 18.76, 17.32, 17.18, 17.04, 15.76, 15.68, 15.65, 12.28, 12.06, 11.83, 8.61, 8.57, 1.17. ESI-MS: Calculated for [**G2** +4H]$^{4+}$ (*m/z* = 3057.0938) and [**G2** + 5H]$^{5+}$ (*m/z* = 2447.8875); Found: *m/z* = 3057.2095 and *m/z* = 2447.9238.

## 4. Synthesis of the third-generation rotaxane-branched dendrimer G3.

**Scheme S3:** Synthesis route of the third-generation rotaxane-branched dendrimer **G3**.



**Synthesis of the third-generation rotaxane-branched dendrimer G3:** A reaction flask was charged with a THF solution of **G2** (60 mg, 0.005 mmol) and then a THF solution of $Bu_4NF{\cdot}3H_2O$ (25 mg, 0.078 mmol) was added dropwise into the reaction flask, the reaction mixture was stirred at room temperature for 2h. The obtained residue was washed by water, then dried with $Na_2SO_4$ and concentrated. The residue was further purified by column chromatography ($SiO_2$; DCM) and preparative gel permeation chromatography (GPC) to afford an orange solid **G2-YNE**. Then the obtained **G2-YNE** (45 mg, 0.0041 mmol) and [2]rotaxane **1** (80 mg, 0.036 mmol) were added in a Schlenk flask, the Schlenk flask was then evacuated and back-filled with $N_2$ three times. Next, the mixture solvent of degassed $Et_2NH$ and $CH_2Cl_2$ (v/v, 5/5 mL) was added via syringe. Subsequently, a catalytic amount of CuI was added under an inert atmosphere. The reaction was stirred overnight at room temperature. The solvent was evaporated and the residue was purified by column chromatography ($SiO_2$; DCM/EA) and preparative gel permeation chromatography (GPC) to yield an orange solid **G3** (48 mg, 37%). $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 8.29-8.31 (m, 4H), 7.83-7.87 (m, 2H), 7.35-7.54 (m, 36H), 7.18-7.20 (m, 4H), 6.99-7.09 (m, 56H), 6.80-6.84 (m, 142H), 6.62-6.66 (m, 28H), 4.61 (m, 14H), 3.62-3.98 (m, 420H), 2.89-2.94 (m, 28H), 2.11-2.31 (m, 196H), 1.14-1.41 (m, 672H), 1.05 (s, 336H), 0.45-0.68 (m, 112H), 0.07 (m, 56H), -0.87-(-0.77) (m, 28H), -1.31-(-1.21) (m, 28H). $^{31}$P NMR (202 MHz, THF-$d_8$): $\delta$ 12.49. $^{13}$C NMR (126 MHz, THF-$d_8$): $\delta$ 157.93, 155.31, 154.88, 150.45, 150.38, 150.35, 142.08, 140.77, 138.33, 132.11, 131.59, 130.38, 129.77, 128.88, 128.85, 128.22, 127.65, 126.85, 125.68, 124.42, 122.32, 121.97, 118.37, 114.64, 114.62, 114.29, 110.02, 109.28, 107.61, 90.39, 69.07, 67.74, 64.06, 64.00, 40.31, 34.08, 31.53, 31.46, 31.29, 30.71, 30.44, 29.85, 29.67, 29.45, 27.92, 25.62, 24.26, 18.89, 17.32, 17.18, 17.04, 15.75, 15.68, 15.65, 12.06, 8.61, 8.57, 1.17. MALDI-TOF-MS: $m/z$ = 28001.6 and $m/z$ = 13924.5 were observed in the spectrum, which might be attributed to the **G3** molecule with encapsulated matrix molecules.

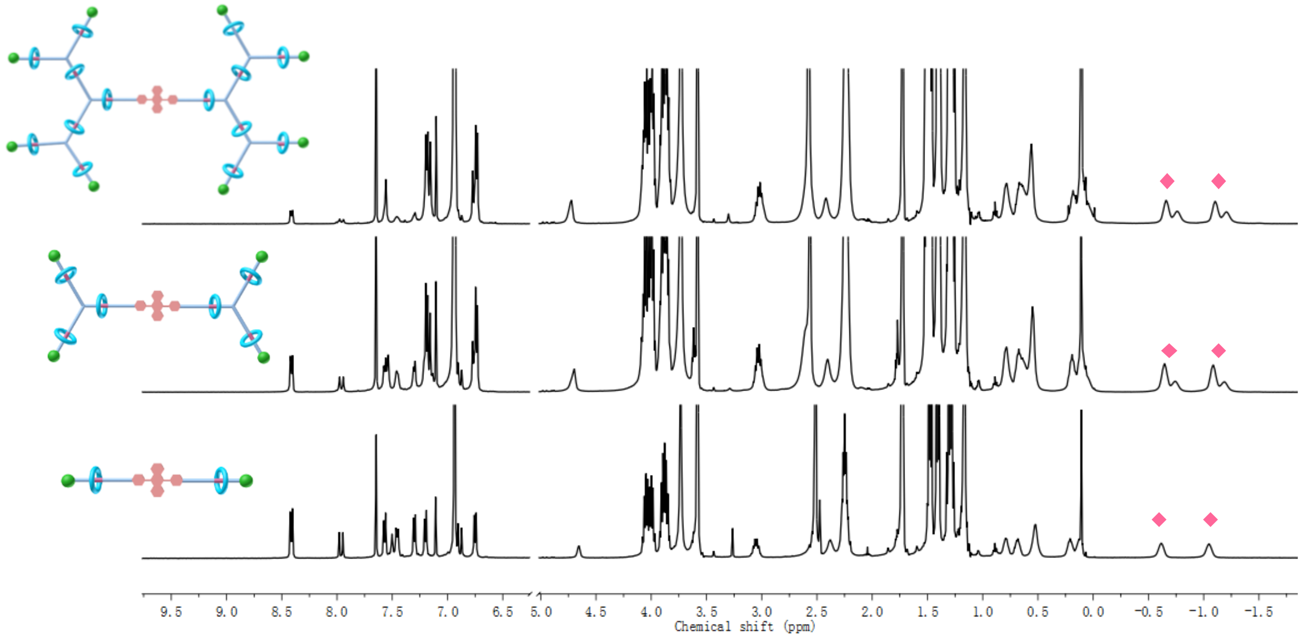


**Fig. S1** Partial $^{1}$H NMR (THF-$d_8$, 298 K, 500 MHz) spectra of rotaxane-branched dendrimer **G3** (*top*); rotaxane-branched dendrimer **G2** (*middle*); rotaxane-branched dendrimer **G1** (*bottom*);

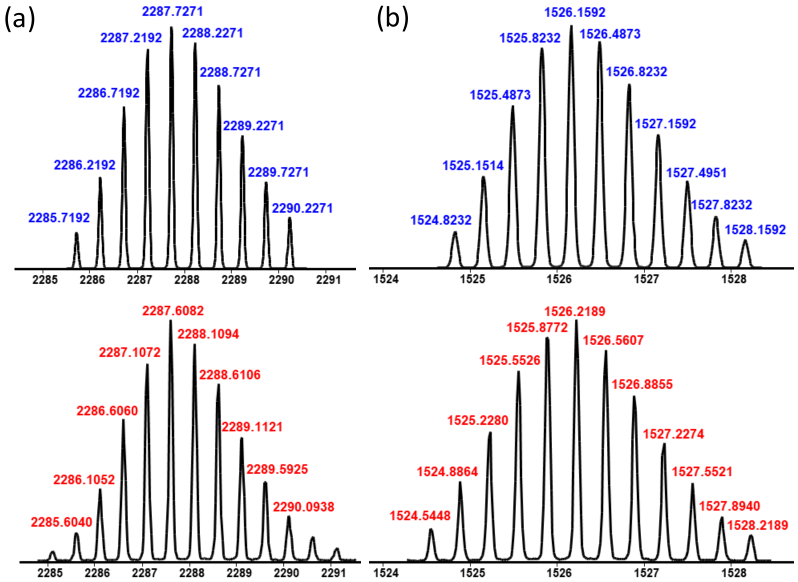


**Fig. S2** Calculated (*top*) and experimental (*bottom*) ESI-TOF-MS spectra of rotaxane-branched dendrimer **G1**: (a) [**G1** + 2H]$^{2+}$, (b) [**G1** + 3H]$^{3+}$.

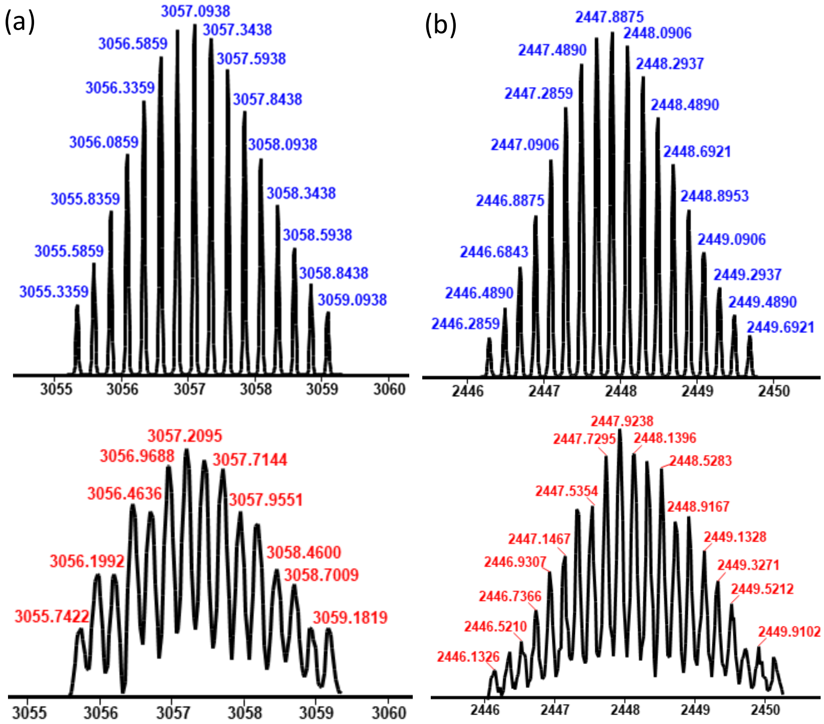


**Fig. S3** Calculated (*top*) and experimental (*bottom*) ESI-TOF-MS spectra of rotaxane-branched dendrimer **G2**: (a) [**G2** + 4H]$^{4+}$, (b) [**G2** + 5H]$^{5+}$.

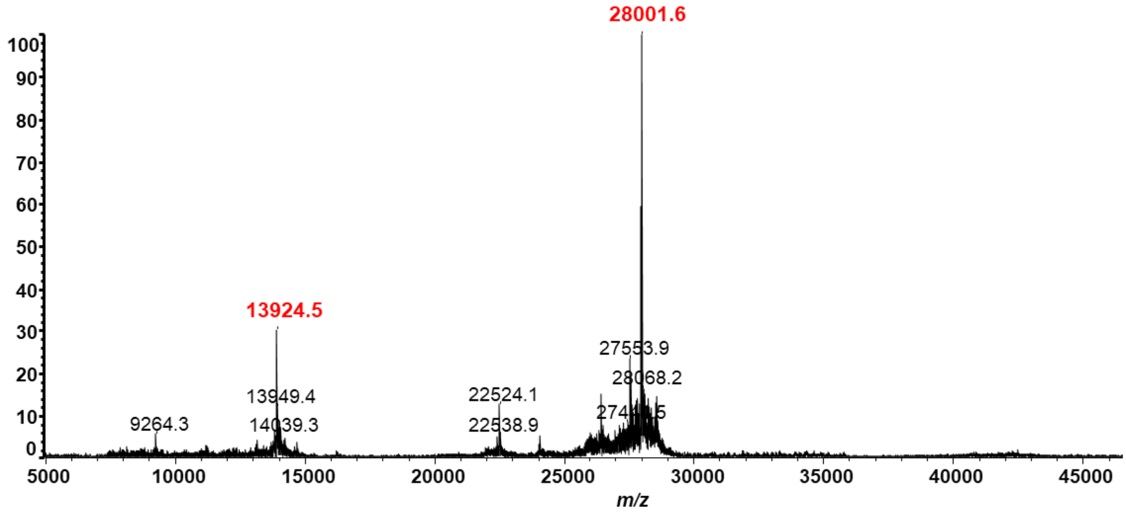


**Fig. S4** MALDI-TOF-MS spectrum of rotaxane-branched dendrimer **G3**.

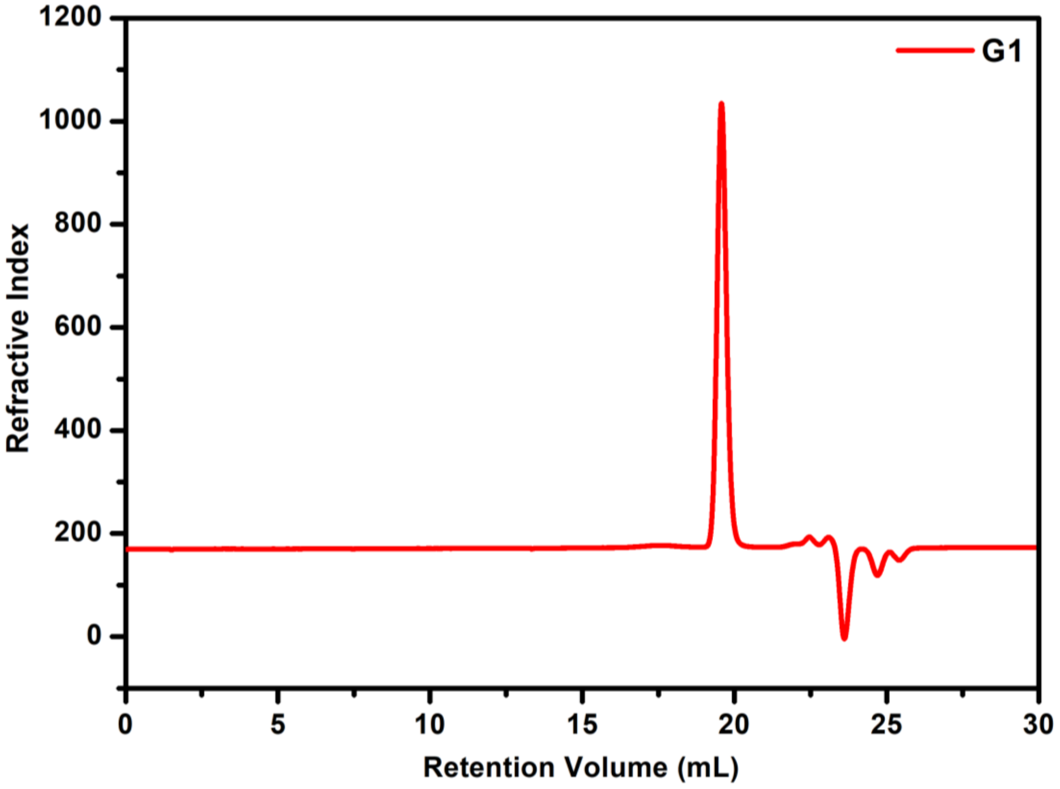


**Fig. S5** GPC spectrum of the rotaxane-branched dendrimer **G1**.

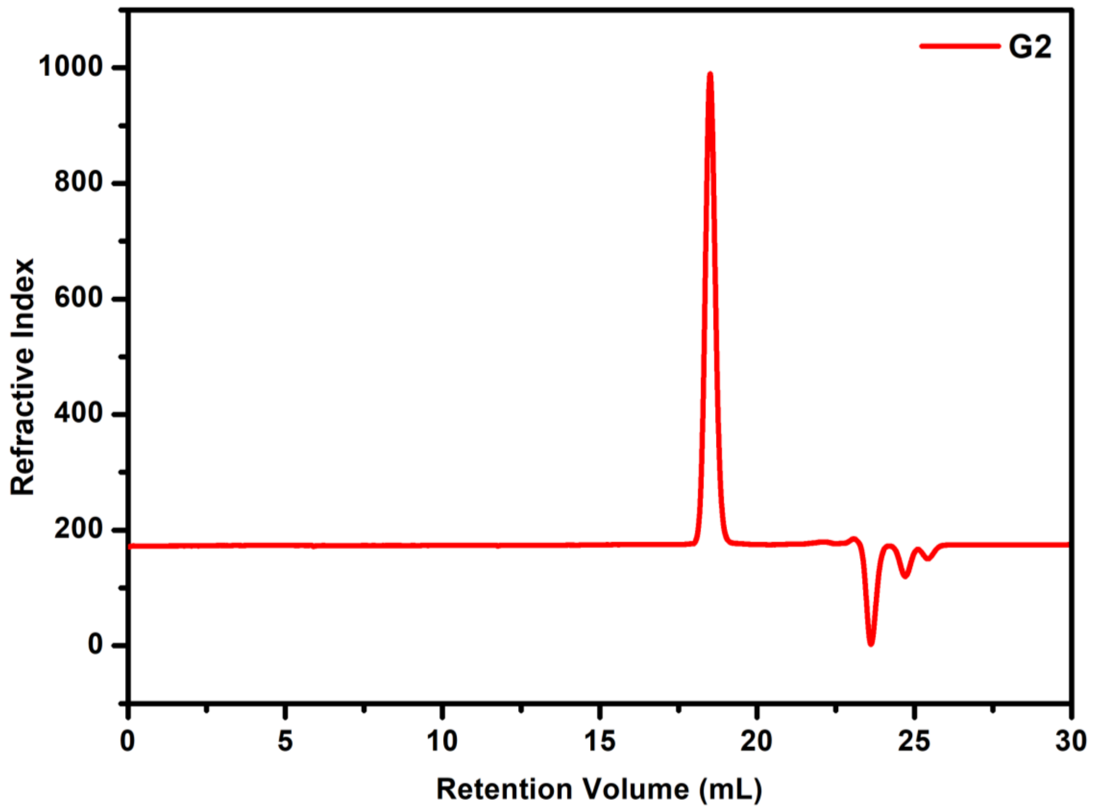


**Fig. S6** GPC spectrum of the rotaxane-branched dendrimer **G2**.

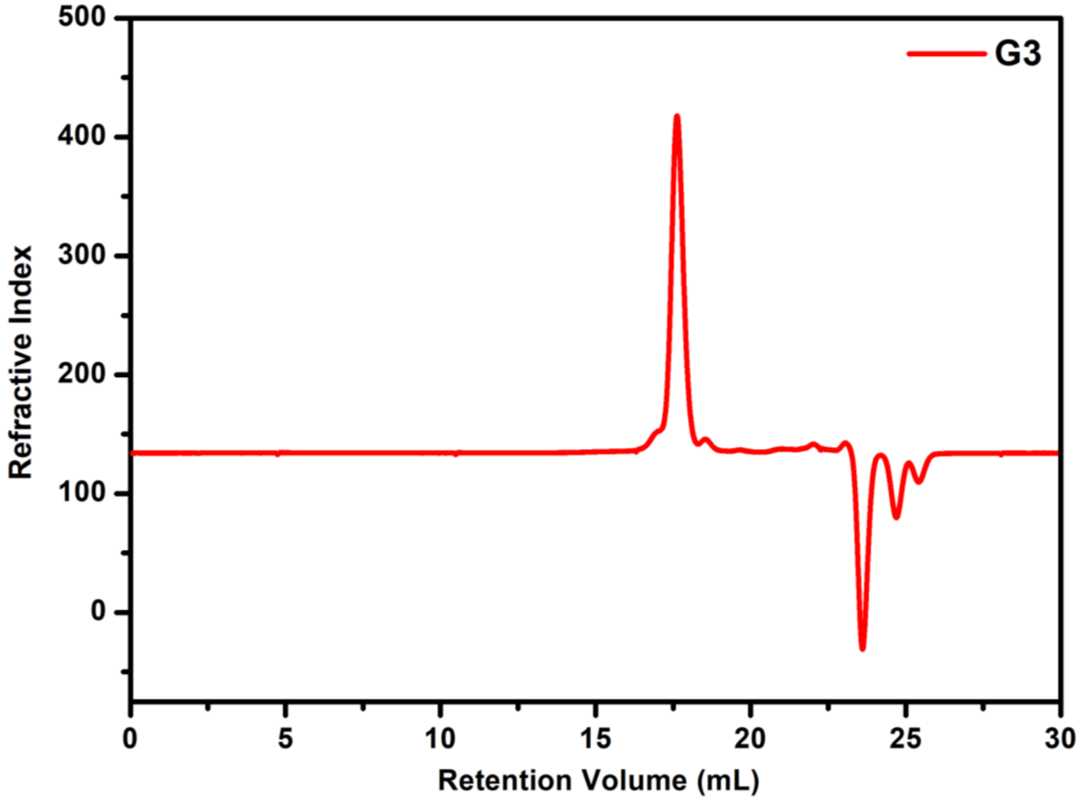


**Fig. S7** GPC spectrum of the rotaxane-branched dendrimer **G3**.

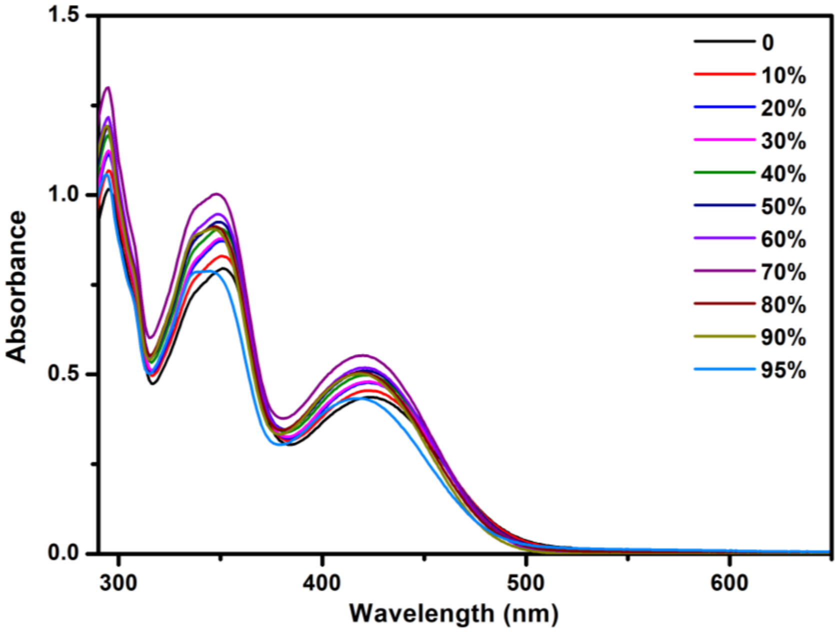


**Fig. S8** Absorption spectra (c = $10^{-5}$ M) of **G1** in $CH_2Cl_2$/n-hexane with various n-hexane fractions.

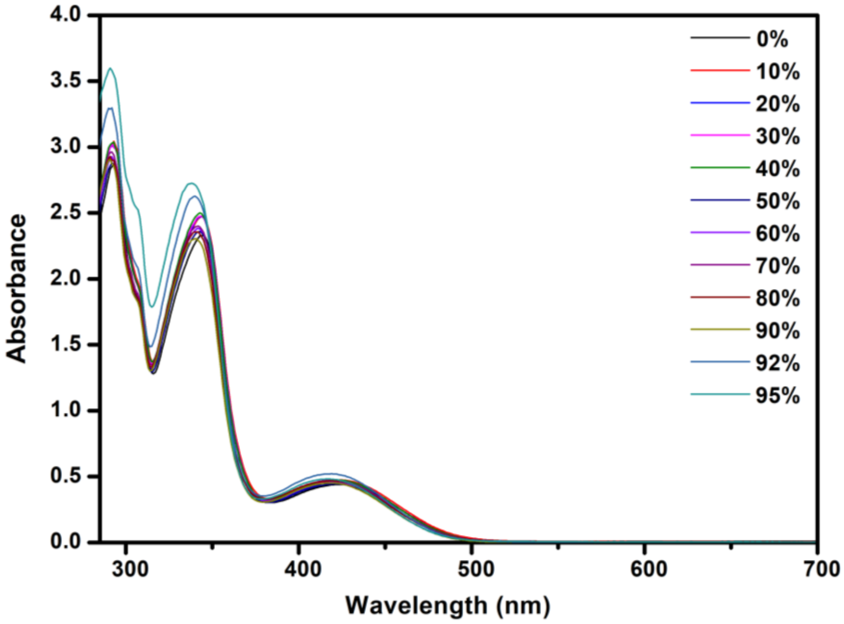


**Fig. S9** Absorption spectra (c = $10^{-5}$ M) of **G2** in $CH_2Cl_2$/n-hexane with various n-hexane fractions.

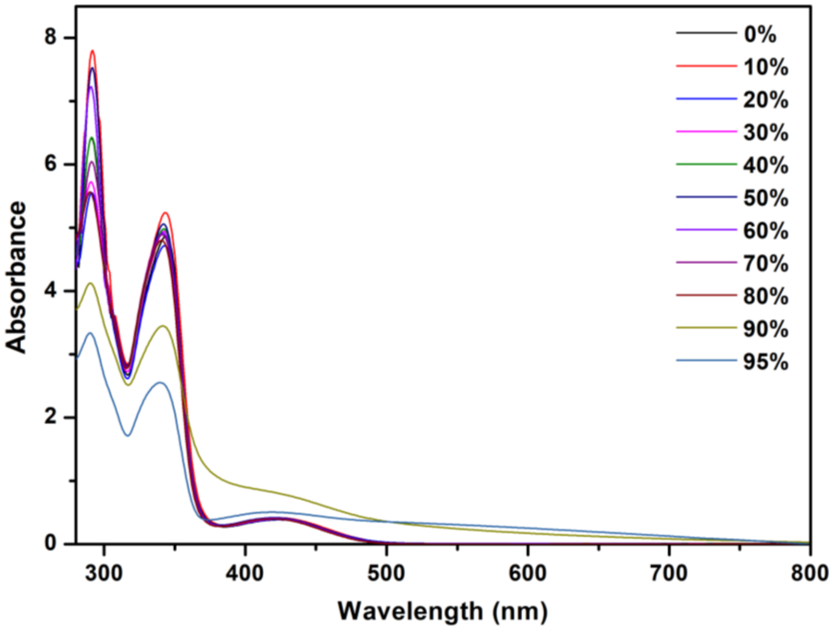


**Fig. S10** Absorption spectra (c = $10^{-5}$ M) of **G3** in $CH_2Cl_2$/n-hexane with various n-hexane fractions.

**Table S1**: Fluorescence quantum yields ($\Phi_F$) of **G1** in $CH_2Cl_2$/n-hexane with various n-hexane fractions ($f_h$).

| $f_h$ (%) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Phi_F$ (%) | 2.9 | 2.8 | 3.1 | 3.5 | 4.0 | 4.6 | 5.5 | 6.5 | 9.0 | 10.9 | 11.4 |

**Table S2**: Fluorescence quantum yields ($\Phi_F$) of **G2** in $CH_2Cl_2$/n-hexane with various n-hexane fractions ($f_h$).

| $f_h$ (%) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Phi_F$ (%) | 2.5 | 2.8 | 2.9 | 3.3 | 3.9 | 4.2 | 4.9 | 6.2 | 7.8 | 10.5 | 16.2 |

**Table S3**: Fluorescence quantum yields ($\Phi_F$) of **G3** in $CH_2Cl_2$/n-hexane with various n-hexane fractions ($f_h$).

| $f_h$ (%) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\Phi_F$ (%) | 2.6 | 2.8 | 2.9 | 3.3 | 3.8 | 4.2 | 4.9 | 6.2 | 7.5 | 11.8 | 17.9 |

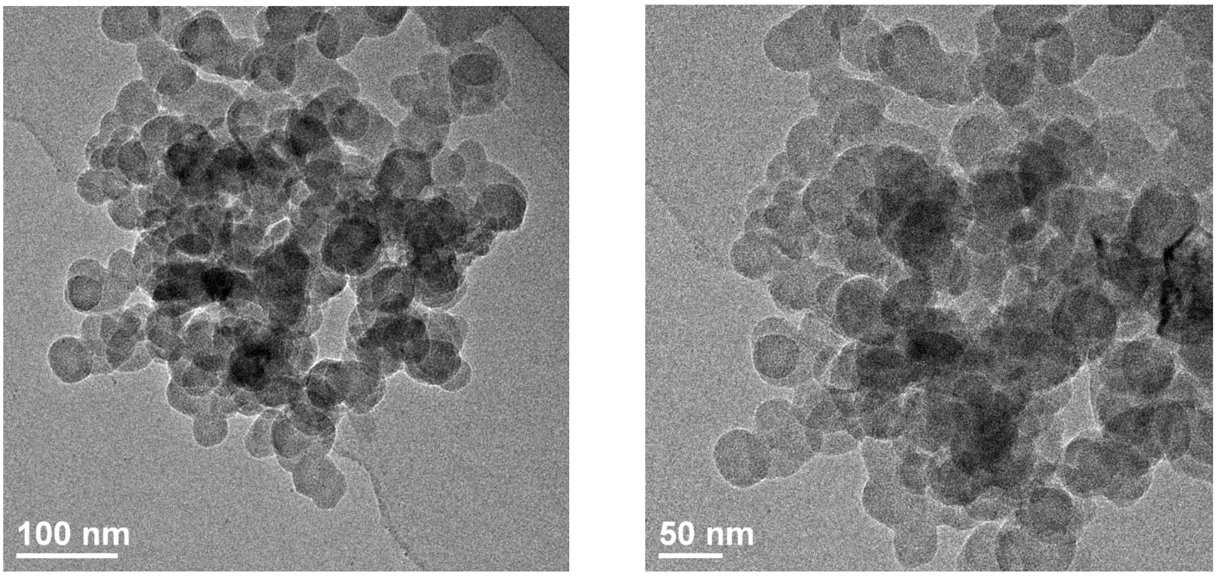


**Fig. S11** TEM images of the rotaxane-branched dendrimer **G1** in $CH_2Cl_2$/n-hexane with 90% n-hexane fractions.

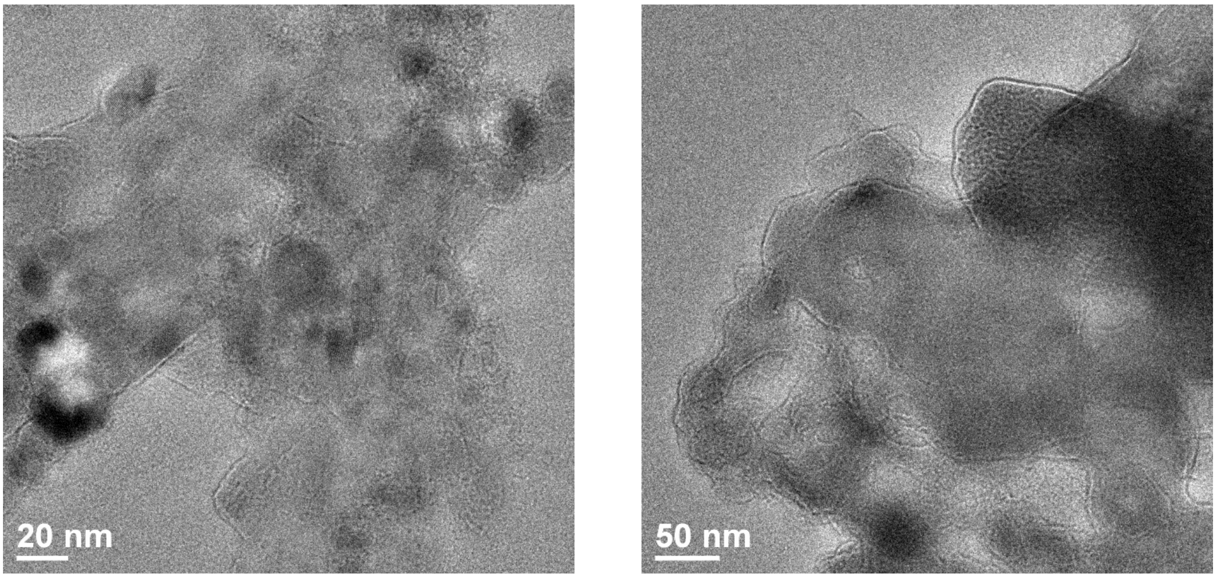


**Fig. S12** TEM images of the rotaxane-branched dendrimer **G2** in $CH_2Cl_2$/n-hexane with 90% n-hexane fractions.

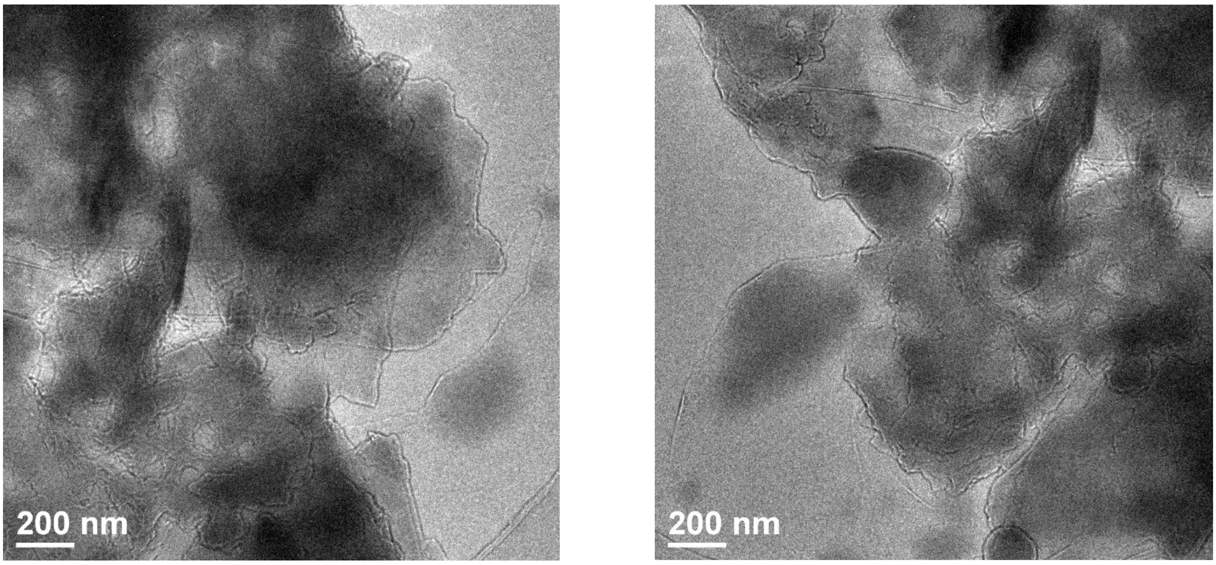


**Fig. S13** TEM images of the rotaxane-branched dendrimer **G3** in $CH_2Cl_2$/n-hexane with 90% n-hexane fractions.

## Section C. Supplementary data

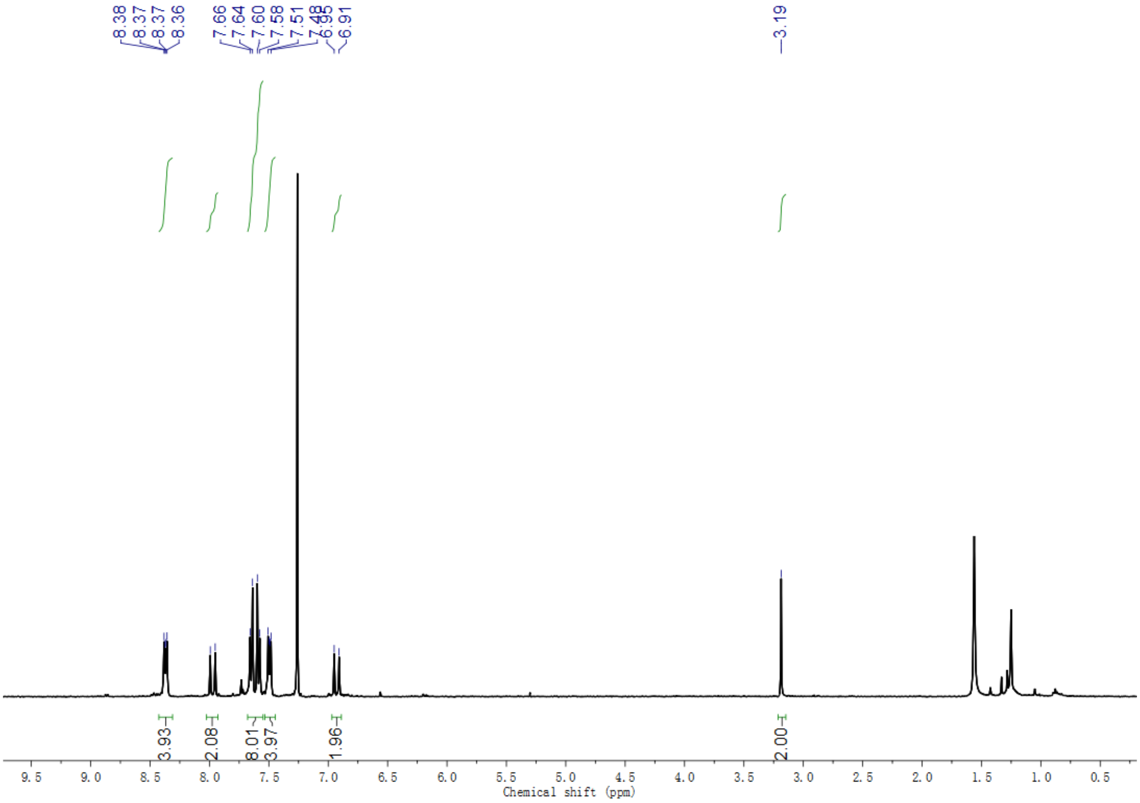


**Fig. S12** $^1$H NMR spectrum (CDCl$_3$, 298 K, 400 MHz) of compound **2**.

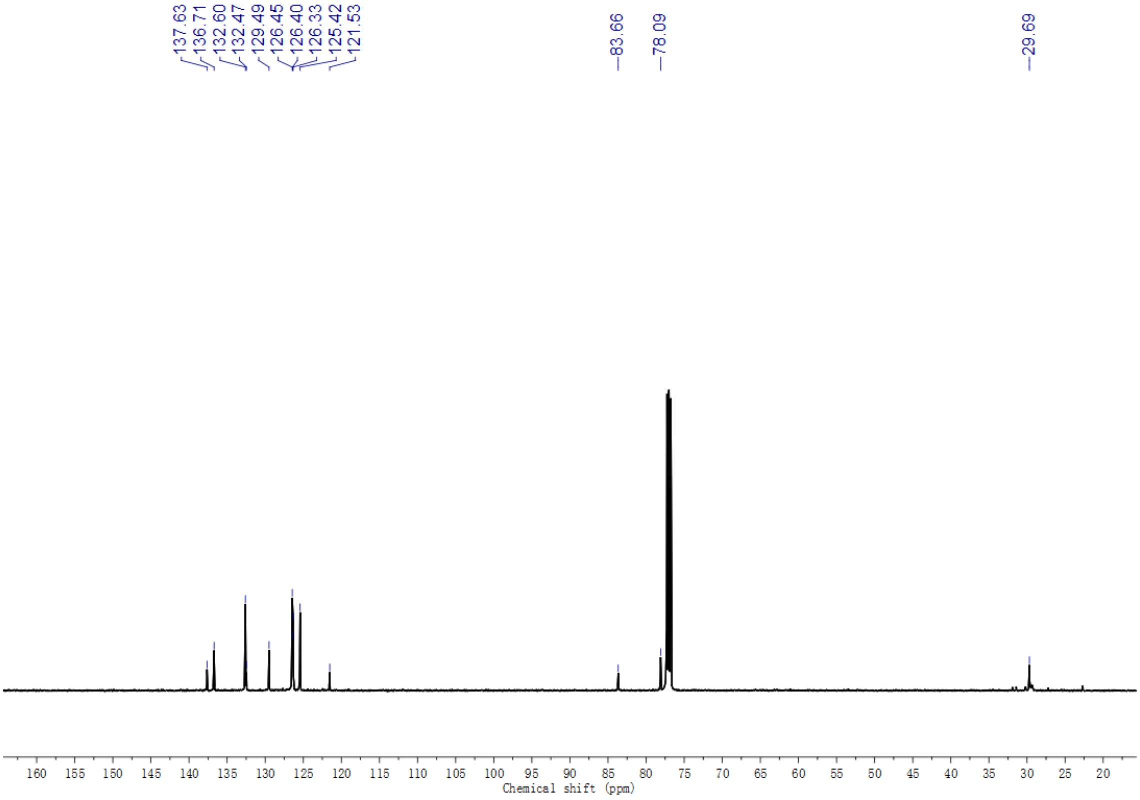
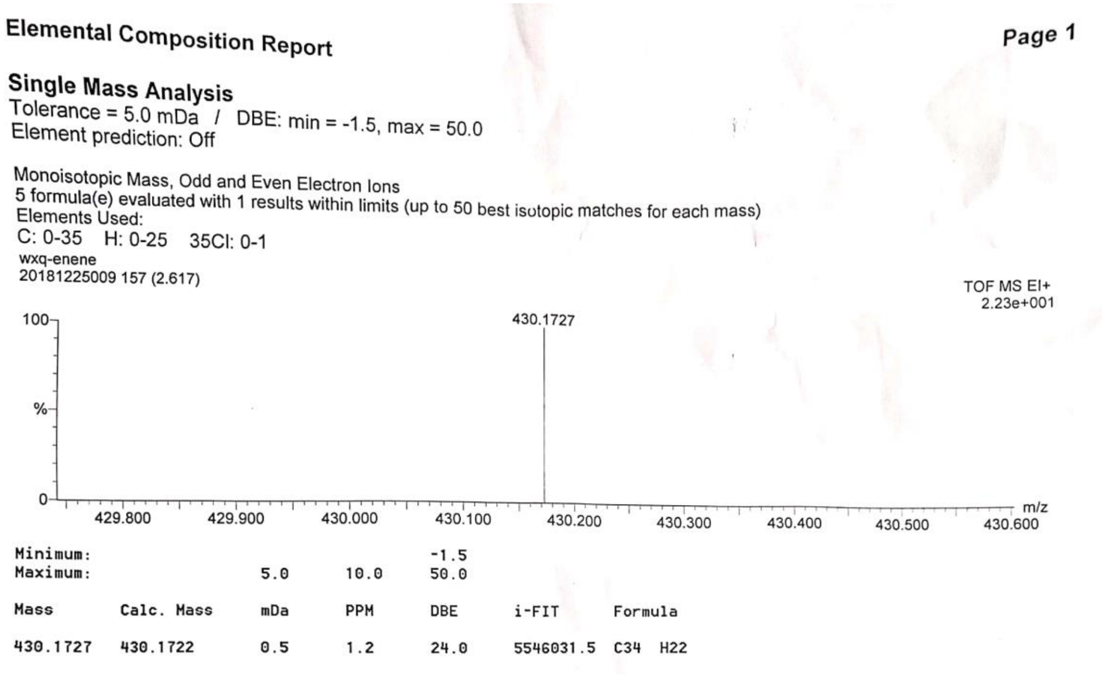


**Fig. S13** $^{13}$C NMR spectrum (CDCl$_3$, 298 K, 126 MHz) of compound **2**.



Elemental Composition Report

Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-35 H: 0-25 35Cl: 0-1
wxq-enene
20181225009 157 (2.617)

TOF MS EI+
2.23e+001

```
Minimum:                                  -1.5
Maximum:                 5.0     10.0     50.0

Mass       Calc. Mass    mDa     PPM      DBE      i-FIT        Formula

430.1727   430.1722      0.5     1.2      24.0     5546031.5    C34  H22
```

**Fig. S14** HRMS (EI-TOF) spectrum of compound **2**.

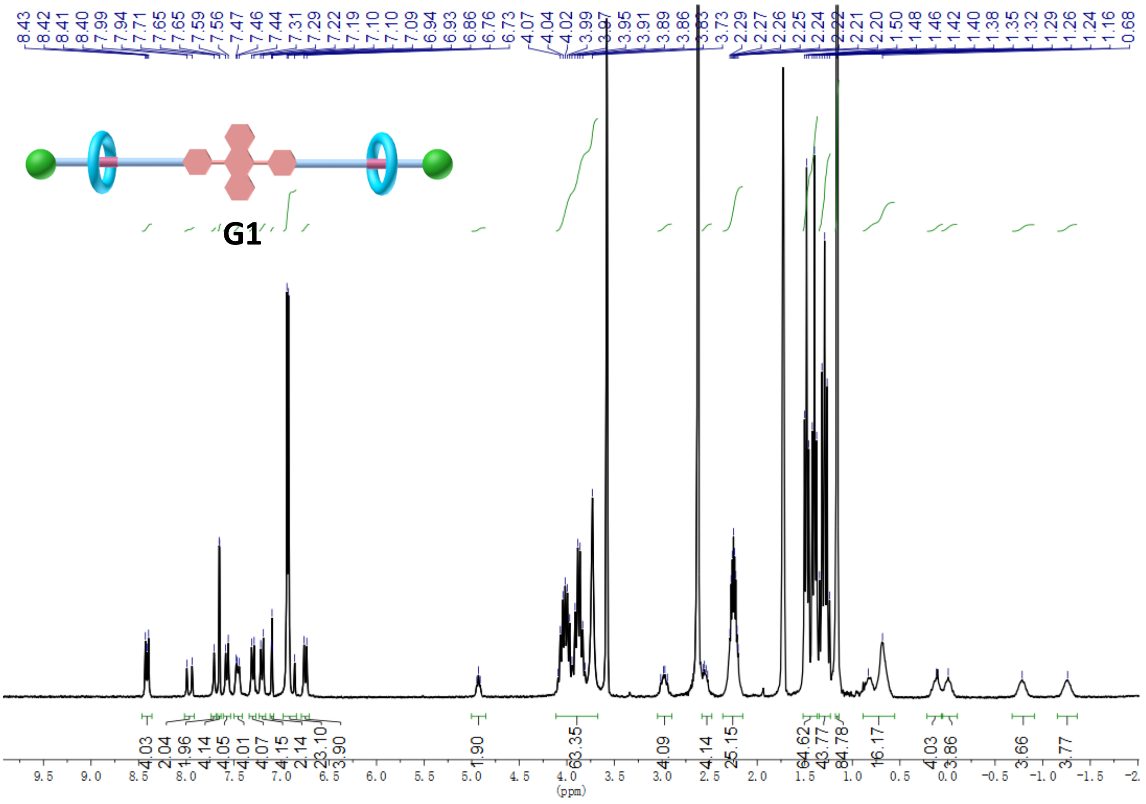


**Fig. S15** $^1$H NMR spectrum (THF-$d_8$, 298 K, 300 MHz) of rotaxane-branched dendrimer **G1**.

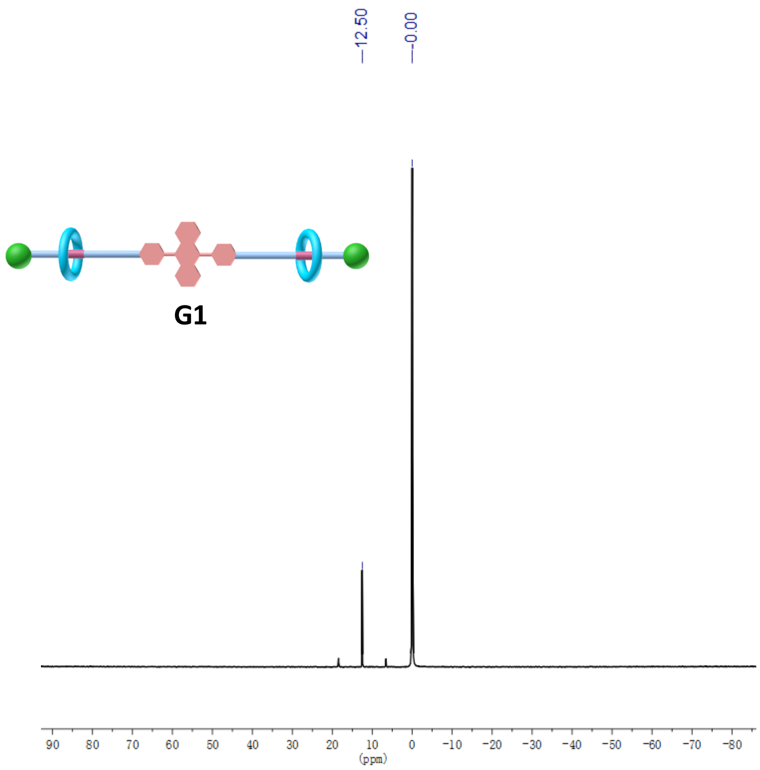


**Fig. S16** $^{31}$P NMR spectrum (THF-$d_8$, 298 K, 202 MHz) of rotaxane-branched dendrimer **G1**.

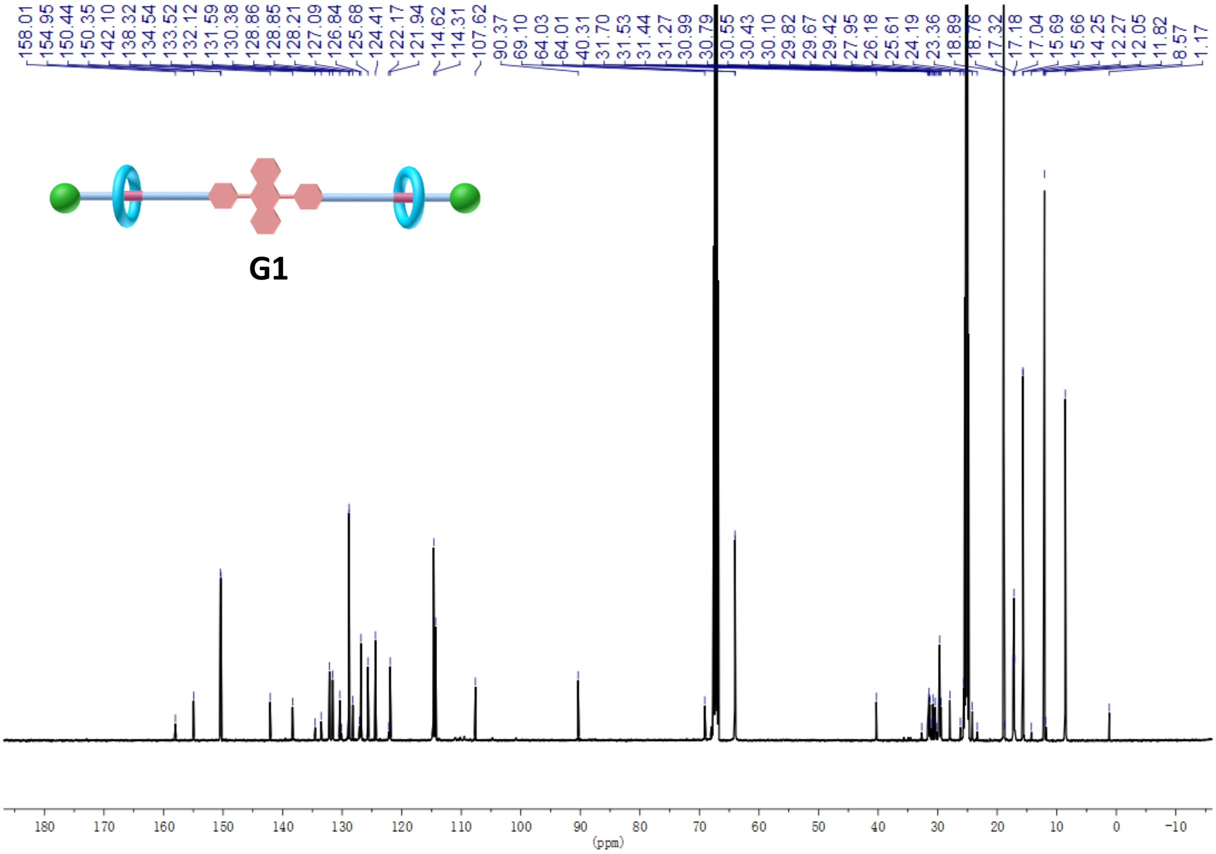


**Fig. S17** $^{13}$C NMR spectrum (THF-$d_8$, 298 K, 126 MHz) of rotaxane-branched dendrimer **G1**.

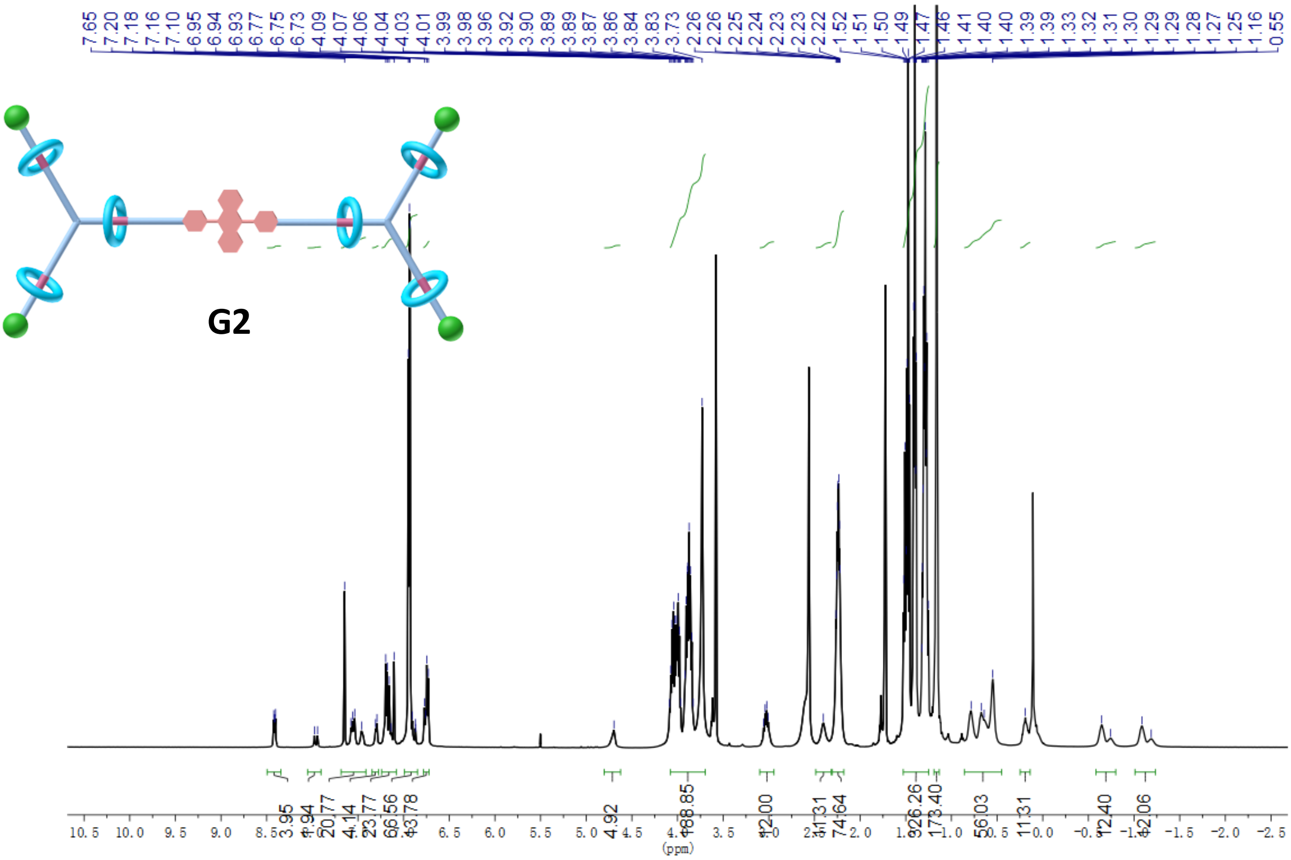


**Fig. S18** $^{1}H$ NMR spectrum (THF-$d_8$, 298 K, 500 MHz) of rotaxane-branched dendrimer **G2**.

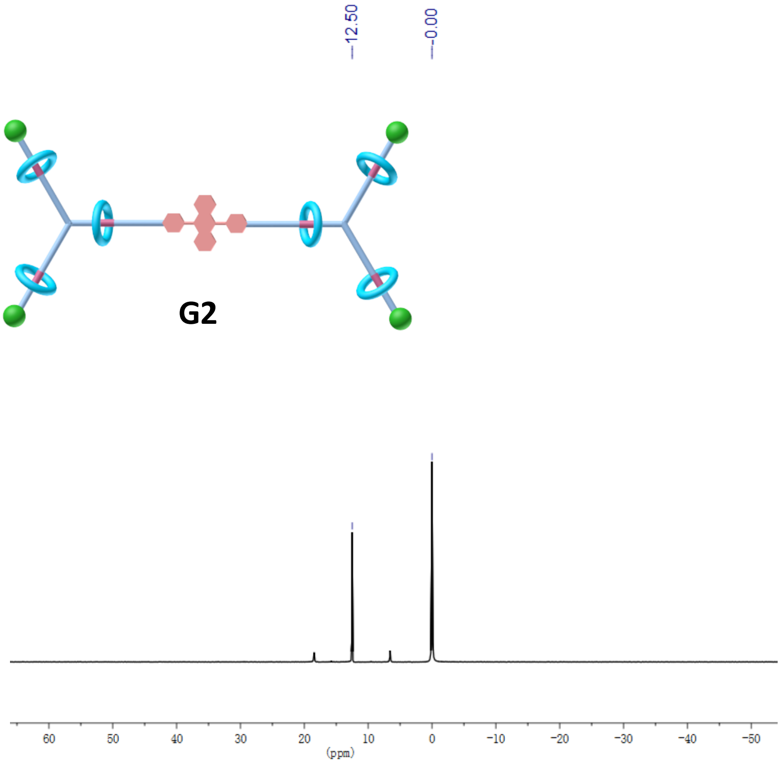


**Fig. S19** $^{31}P$ NMR spectrum (THF-$d_8$, 298 K, 202 MHz) of rotaxane-branched dendrimer **G2**.

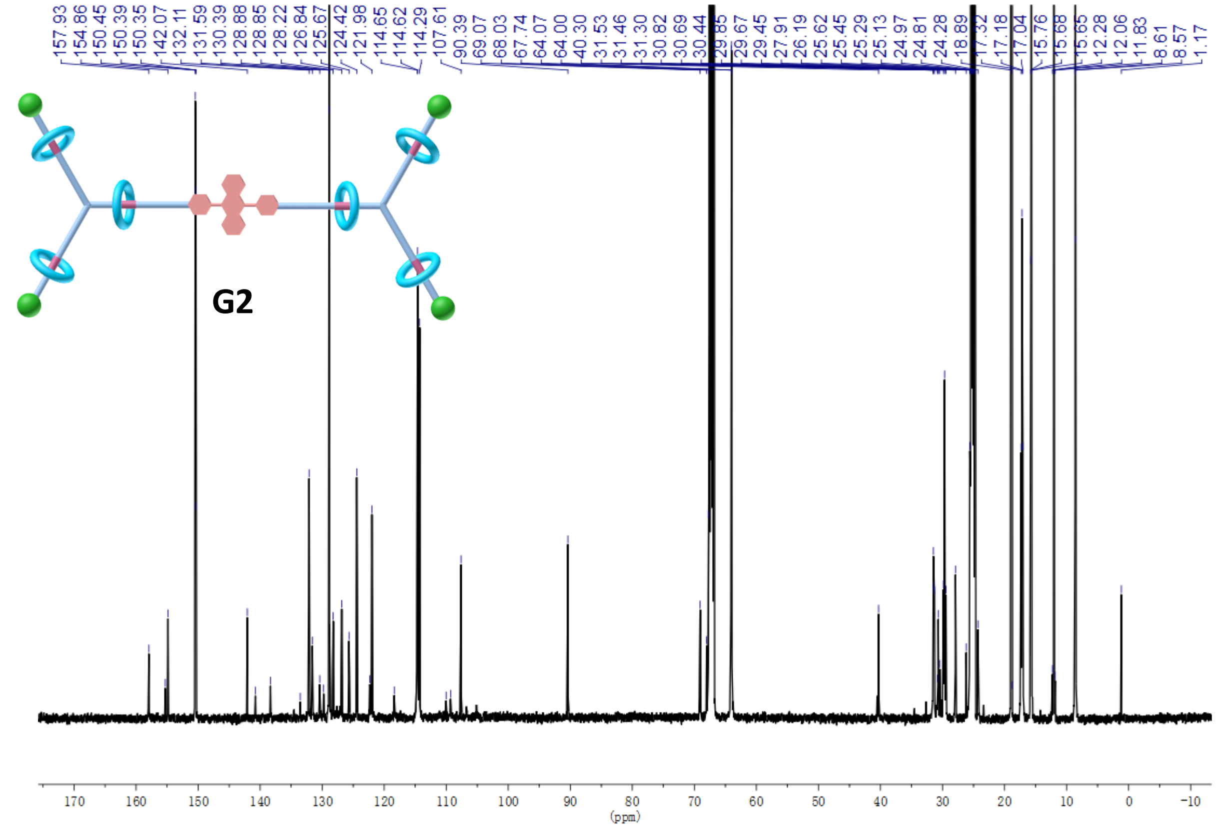


**Fig. S20** $^{13}$C NMR spectrum (THF-$d_8$, 298 K, 126 MHz) of rotaxane-branched dendrimer **G2**.

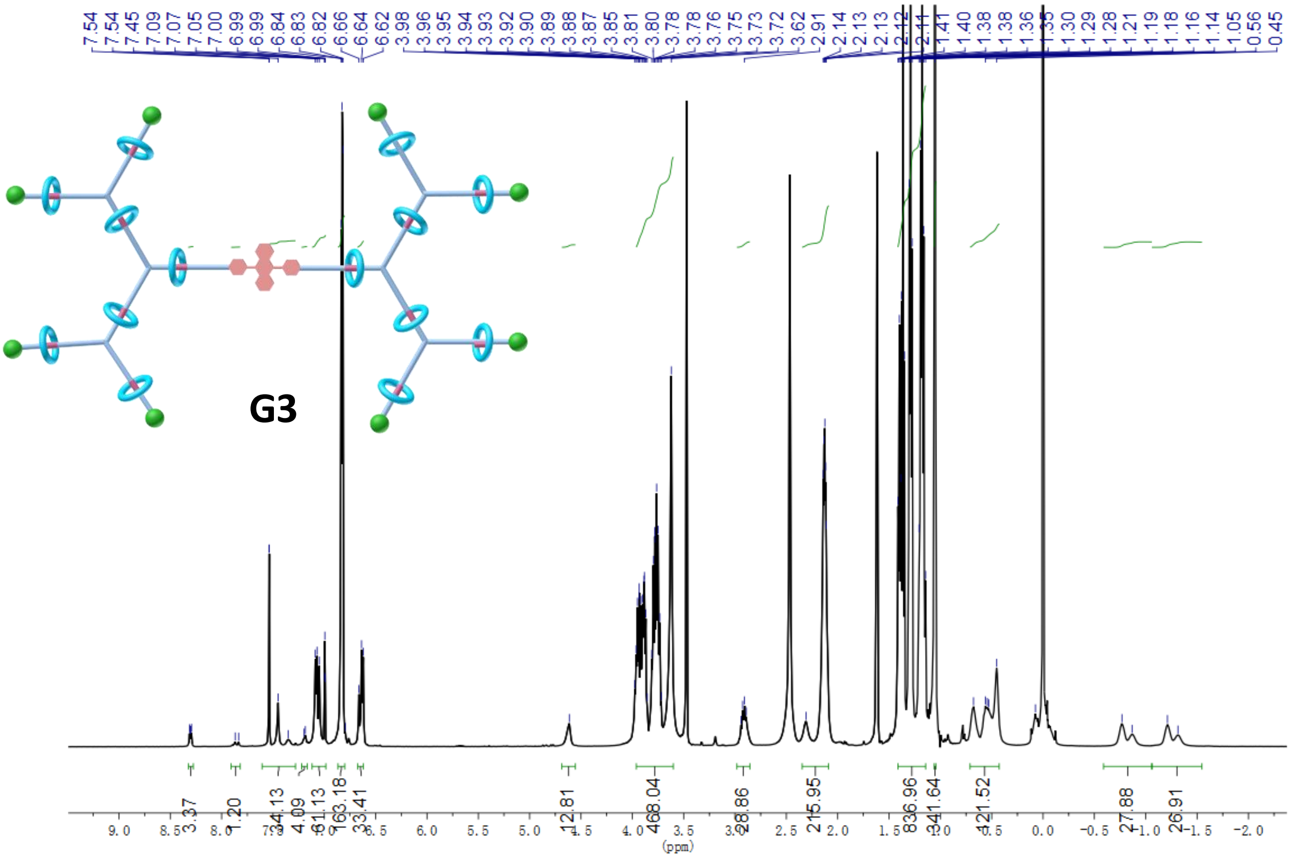


**Fig. S21** $^{1}$H NMR spectrum (THF-$d_8$, 298 K, 500 MHz) of rotaxane-branched dendrimer **G3**.

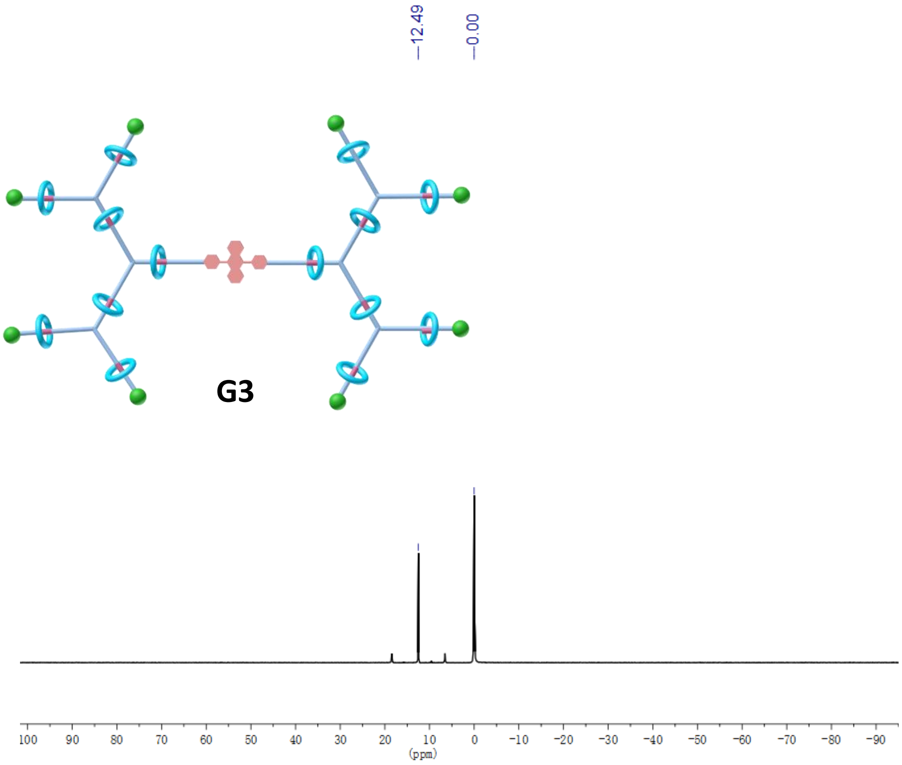


**Fig. S22** $^{31}$P NMR spectrum (THF-$d_8$, 298 K, 202 MHz) of rotaxane-branched dendrimer **G3**.

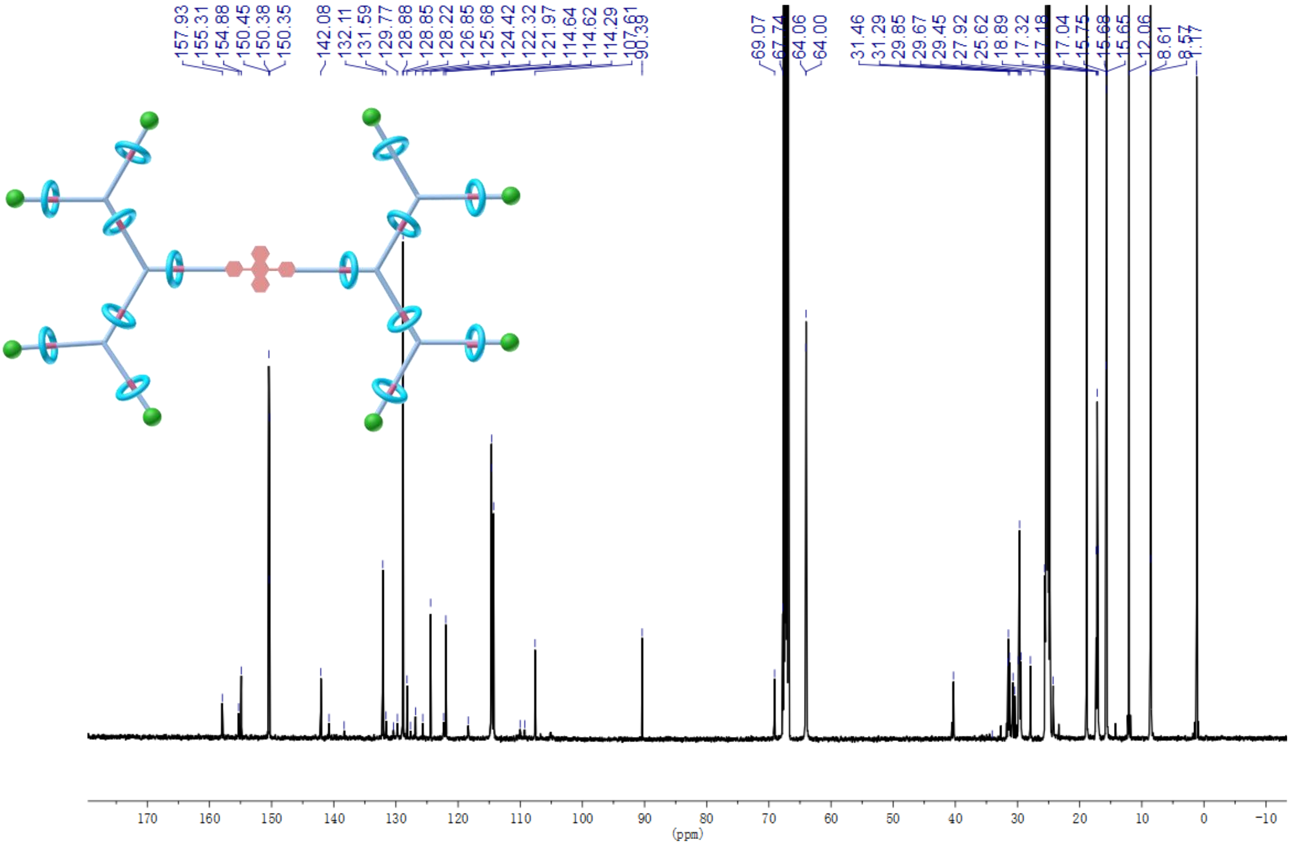


**Fig. S23** $^{13}$C NMR spectrum (THF-$d_8$, 298 K, 126 MHz) of rotaxane-branched dendrimer **G3**.

## *Section D. References*

1. H.-B. Yang et al. *Nat. Commun.*, **2018**, *9*, 3190.
2. F. Diederich et al. *Chem. Eur. J.*, **2017**, *23*, 14153.