Supporting Information

Self-locked dipillar[5]arene-based pseudo[1]rotaxanes and bispseudo[1]rotaxanes with different lengths of bridging chains

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SUPPORTING INFORMATION

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1. Materials and methods

All reactions were performed in open atmosphere unless otherwise stated. All reagents, unless otherwise indicated, were obtained from commercial sources. Melting points (M.p.) were determined using a Focus X-4 apparatus and were not corrected. All yields were given as isolated yields. NMR spectra were recorded on a Bruker DPX 400 MHz or 600 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, and the chemical shifts (δ) were expressed in ppm and J values were given in Hz. 2D NOESY experiments were performed on a Bruker DPX 600 MHz spectrometer. High-resolution ionization mass spectra (HR-ESI-MS) were recorded on Trace DSQ XaMis LCMS equipped with an electrospray ionization (ESI) probe operating in positive-ion mode with direct infusion.

2. Experimental procedures

1. General procedure for the preparation of diamido-bridged bispillar[5]arenes 3a-3c: A mixture of pillar[5]arene oxyacetic acid (0.6 mmol), alkylenediamine (0.30 mmol), HOBt (0.60 mmol) and EDCl (0.60 mmol) in dry $CHCl_3$ (10.0 mL) was stirred at room temperature for 12 hours. The solvent was removed under reduced pressure. The residue was subjected to column chromatography with dichloromethane/methanol (V/V = 30:1~10:1) as eluent to give the pure product for analysis.

2. General procedure for the preparation of tetraamido-bridged bispillar[5]arenes 4a-4d:

A mixture of amido-functionalized pillar[5]arenes **2a**-**2d** (0.60 mmol), which were synthesized according to the reported methods [s1]and phenol-bridged diacid (0.30 mmol) in dry $CHCl_3$ (10.0 mL) was added HOBt (0.60 mmol) and EDCl (0.60 mmol) . The mixture was stirred at room temperature for 12 hours. The solvent was removed under reduced pressure. The residue was subjected to column chromatography with dichloromethane/methanol (V/V = 30:1~10:1) as eluent to give the pure product for analysis.

3. NOESY spectra of comp. 3b and 3c

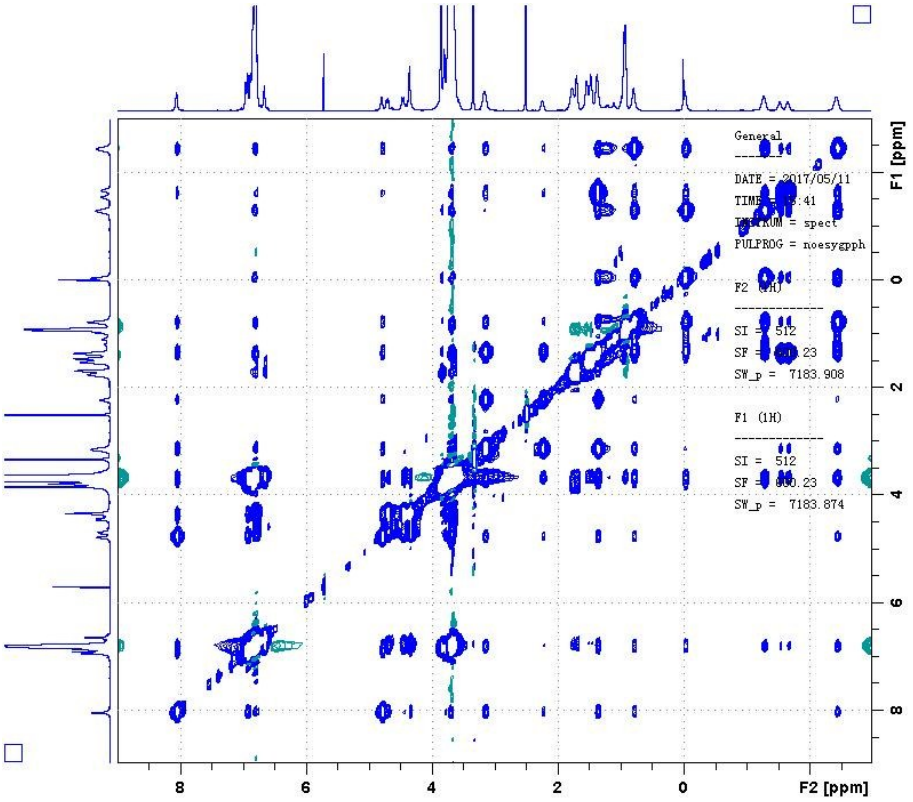

Fig. S1 NOESY spectrum of the compound **3b**

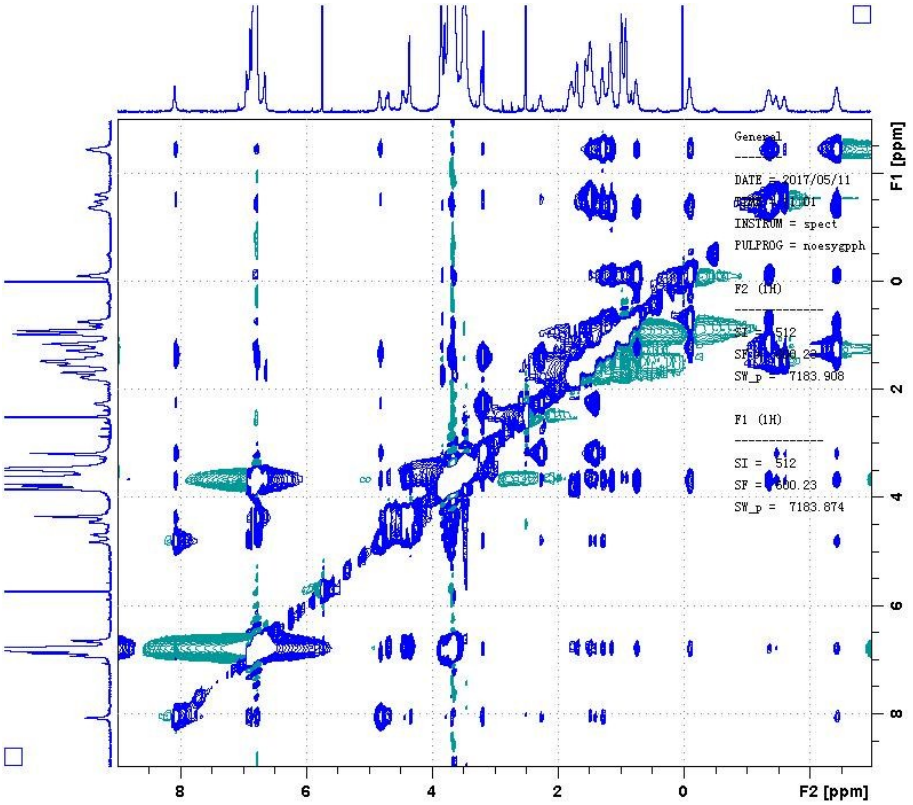

Fig. S2 NOESY spectrum of the compound **3c**

4. ^{1}H NMR and ^{13}C NMR spectra for new compounds

3a： White solid, 21%, M. p. 139-141℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96-6.69 (m, 20H, Ar*H*), 6.55 (brs, 1H, N*H*), 5.24 (brs, 1H, N*H*), 4.60 (s, 2H, CH_2), 4.38 (s, 2H, CH_2), 3.79 (s, 4H, CH_2), 3.77-3.68 (m, 68H, 10CH_2 , 16OCH_3), 2.66 (brs, 2H, CH_2), 1.72 (s, 6H, CH_2), 1.48 (s, 4H, CH_2), 0.94 (brs, 6H, CH_3), 0.41 (s, 2H, CH_2), (−1.06)- (−1.20) (m, 2H, CH_2), (−1.49)- (−1.56) (m, 2H, CH_2), −2.31 (brs, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.1, 151.3 (2C), 151.0, 150.8, 150.7, 150.6, 150.5, 149.7, 149.6, 148.3, 129.4, 129.2, 128.6, 128.4, 128.3, 128.2 (2C), 128.0, 127.8, 127.7, 126.4, 122.9, 115.6, 115.3, 114.9, 114.0, 113.9, 113.8 (2C), 113.5, 111.8, 108.8, 68.5, 68.3, 57.9, 56.4, 56.1, 56.0, 55.9, 55.8, 55.7 (2C), 31.7, 30.3, 29.7, 29.6, 25.9, 19.4, 13.9; IR (KBr) υ: 3414, 2940, 2836, 1681, 1609, 1503, 1460, 1400, 1306, 1211, 1045, 930, 876, 775, 709, 651cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{104}H_{124}N_2NaO_{22}$ ([M + Na]$^{+}$): 1775.8538, found: 1775.8539

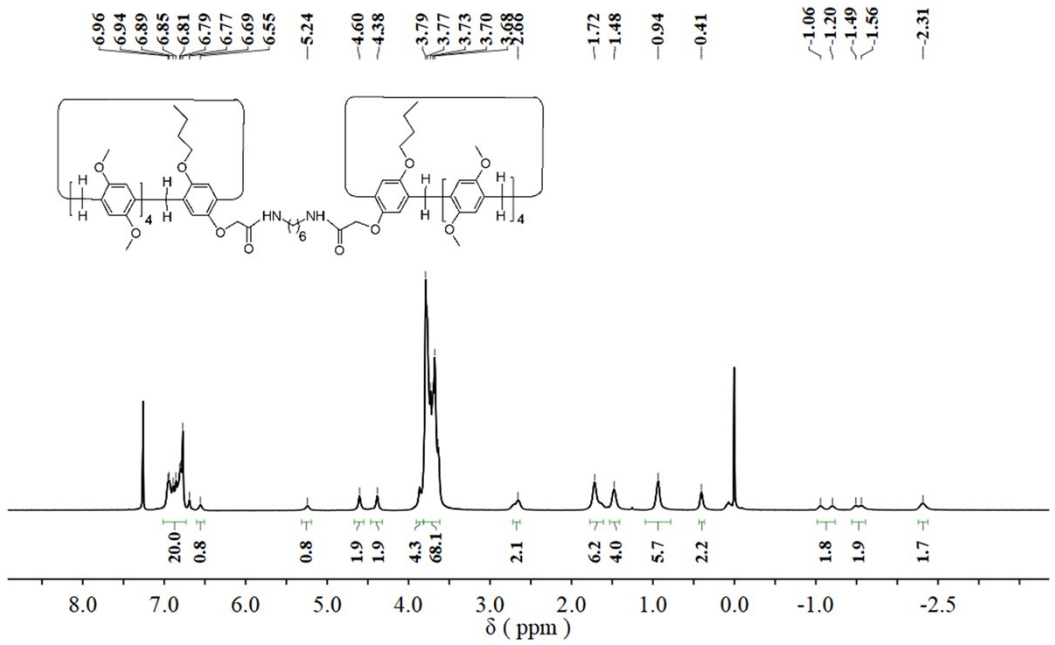

Fig. S3 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **3a**.

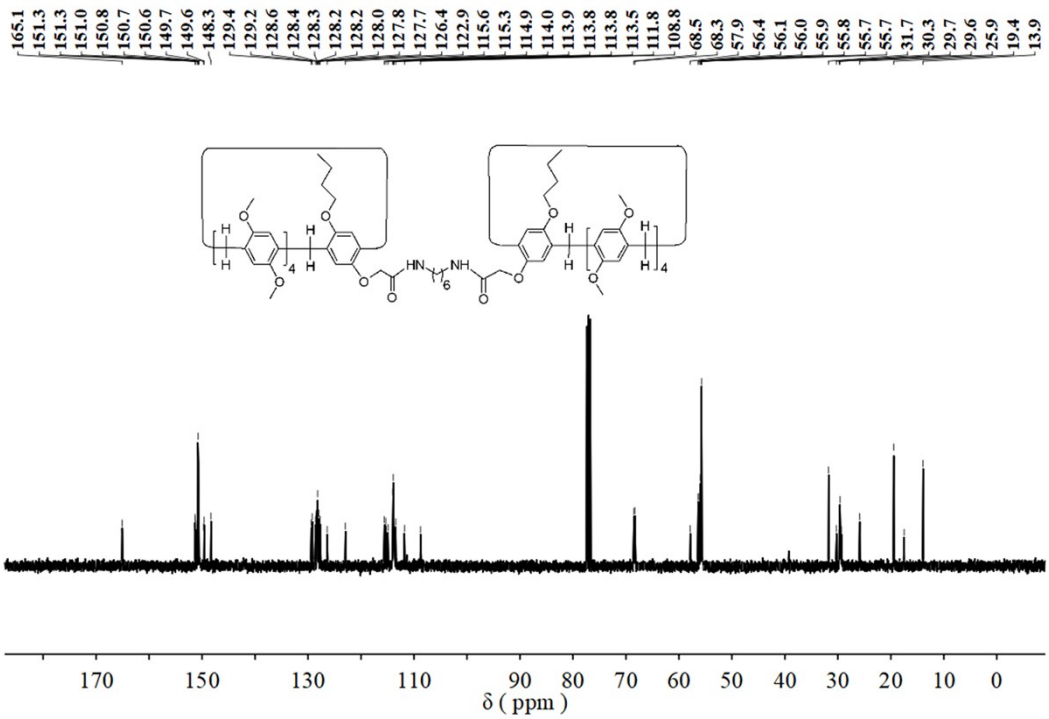

Fig. S4 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3a**.

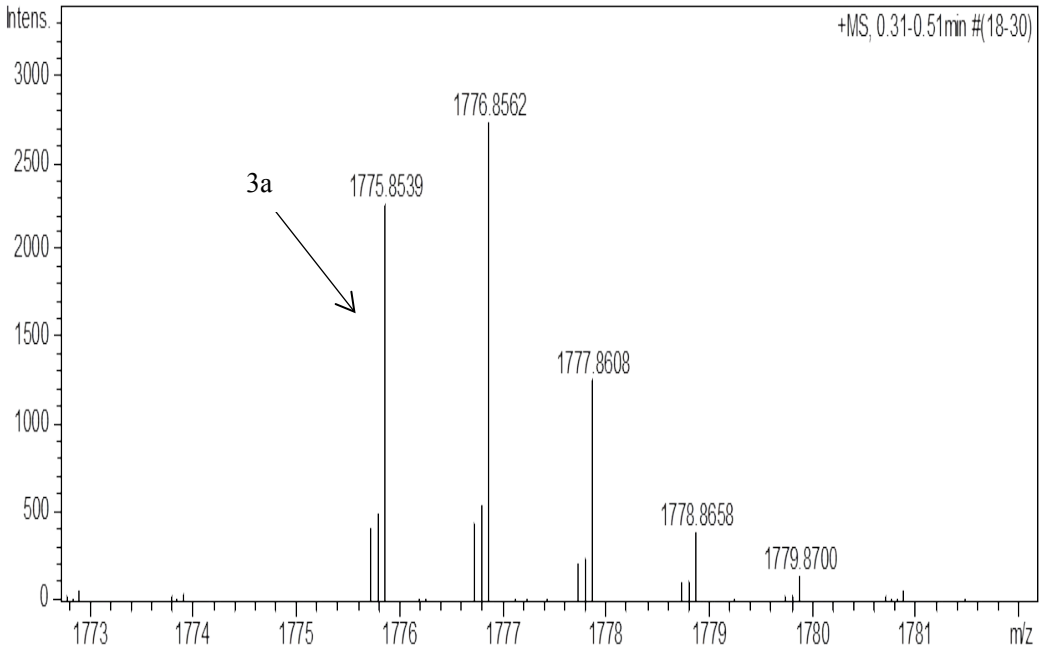

Fig. S5 HR-ESI-MS of **3a**.

Compound **3b**：White solid, 37%, M. p. 129-132℃; ^1H NMR (600 MHz, DMSO-d_6) δ: 8.03 (brs, 1H, N*H*), 6.94-6.80 (m, 20H, Ar*H*), 6.65 (brs, 1H, N*H*), 4.78-4.68 (m, 2H, CH_2), 4.46-4.34 (m, 2H, CH_2), 3.86-3.85 (m, 4H, CH_2), 3.84-3.68 (m, 68H, 10CH_2, 16OCH_3), 3.15 (brs, 2H, CH_2), 1.76-

1.69 (m, 4H, CH_2), 1.53-1.37 (m, 8H, CH_2), 0.91-0.79 (m, 6H, CH_3), 0.79 (brs, 2H, CH_2), -0.02 (brs, 2H, CH_2), −1.27 (brs, 2H, CH_2), (−1.54)- (−1.67) (m, 4H, CH_2), −2.43 (brs, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 151.3, 151.2, 151.1, 150.7 (3C), 150.6, 149.7, 149.6, 148.4, 129.4, 129.2, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.7, 126.4, 123.0, 122.9, 115.6, 114.0, 113.9, 113.7, 113.4, 111.8, 68.7, 68.6, 68.3, 57.7, 56.3, 56.2, 55.9 (2C), 55.8, 55.7 (2C), 31.8, 30.2, 29.7, 29.3, 28.8, 22.6, 19.4, 13.9; IR (KBr) υ: 3411, 2936, 2838, 2036, 1680, 1612, 1503, 1459, 1307, 1210, 1045, 930, 876, 772, 707cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{106}H_{128}N_2NaO_{22}$ ([M + Na]$^+$): 1803.8851, found: 1803.8881

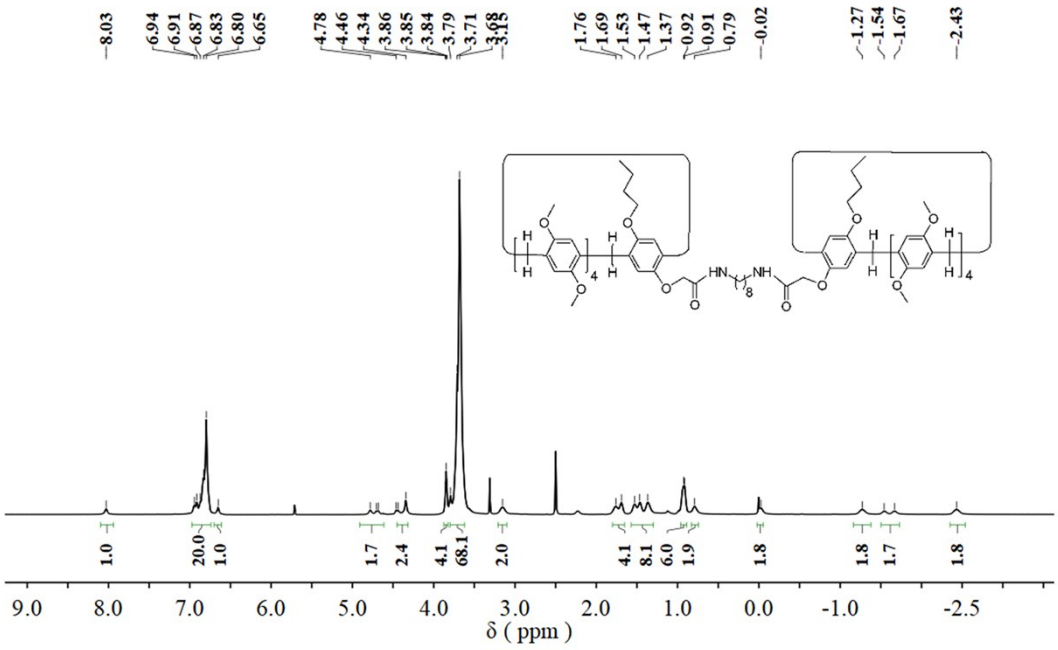

Fig. S6 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **3b**.

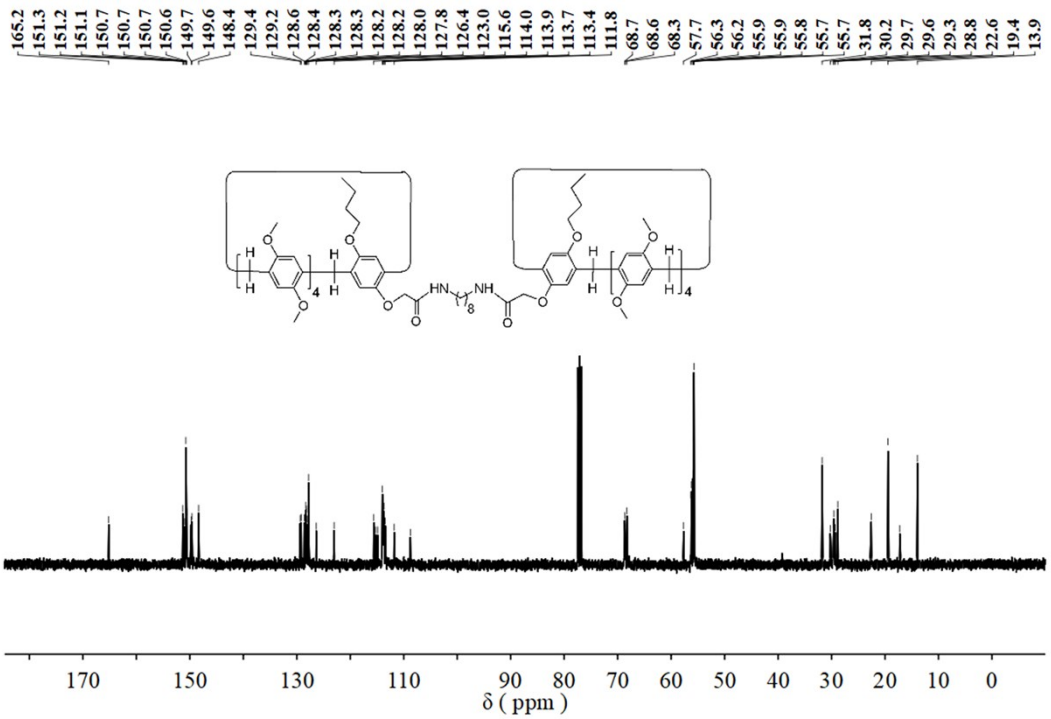

Fig. S7 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3b**.

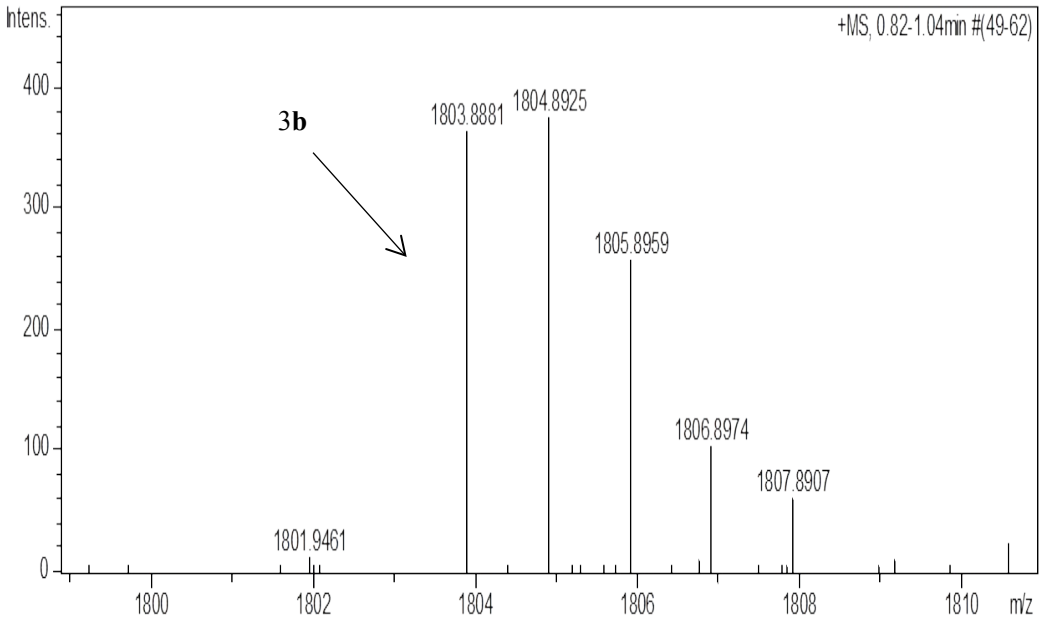

Fig. S8 HR-ESI-MS of **3b**.

Compound **3c**： White solid, 30%, M. p. 126-128℃; ^1H NMR (600 MHz, DMSO-d_6) δ: 8.06 (brs, 1H, N*H*), 6.94-6.65 (m, 20H, Ar*H*), 4.81-4.68 (m, 1H, N*H*), 4.46-4.35 (m, 2H, CH_2), 3.84-3.65 (m, 74H, 13CH_2 , 16OCH_3), 3.20-3.18 (m, 2H, CH_2), 1.69-1.54 (m, 4H, CH_2), 1.48-1.29 (m, 6H, CH_2),

1.15-1.12 (m, 6H, CH_2), 0.97-0.90 (m, 6H, CH_3), 0.75 (brs, 2H, CH_2), −0.09 (brs, 2H, CH_2), −1.34 (brs, 2H, CH_2), (−1.48)-(−1.61) (m, 2H, CH_2), −2.43 (brs, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.2, 151.3, 151.2, 150.7, 150.6 (2C), 149.6, 148.4, 129.4, 129.2 128.6, 128.4, 128.3 (2C), 128.2 (2C), 128.0, 127.8, 126.3, 115.6, 115.2, 114.9, 113.9 (2C), 113.8 (2C), 113.7, 113.5, 68.8, 68.6, 68.3, 57.8, 56.3, 56.2, 55.9 (2C), 31.8, 29.7, 29.6, 29.5, 29.0, 25.8, 19.4, 17.4, 13.9; IR (KBr) υ: 3410, 2934, 2857, 1681, 1609, 1503, 1460, 1400, 1305, 1211, 1045, 930, 876, 774, 708, 650cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{108}H_{133}N_2O_{22}$ ([M + H]$^+$): 1810.9305, found: 1810.9377

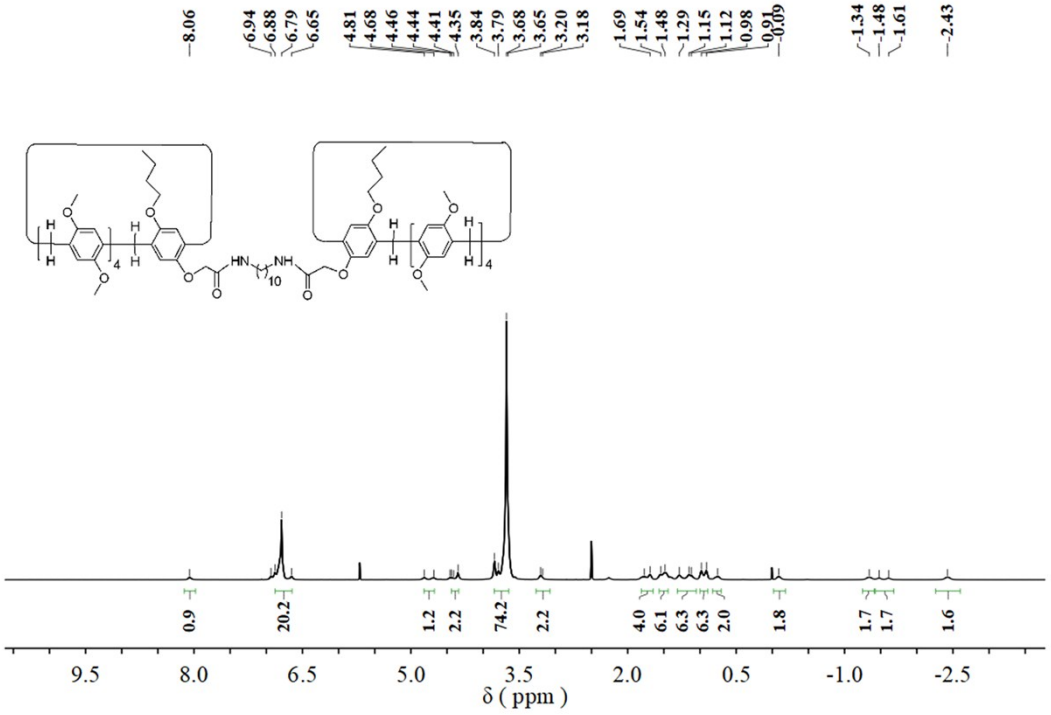

Fig. S9 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of **3c**.

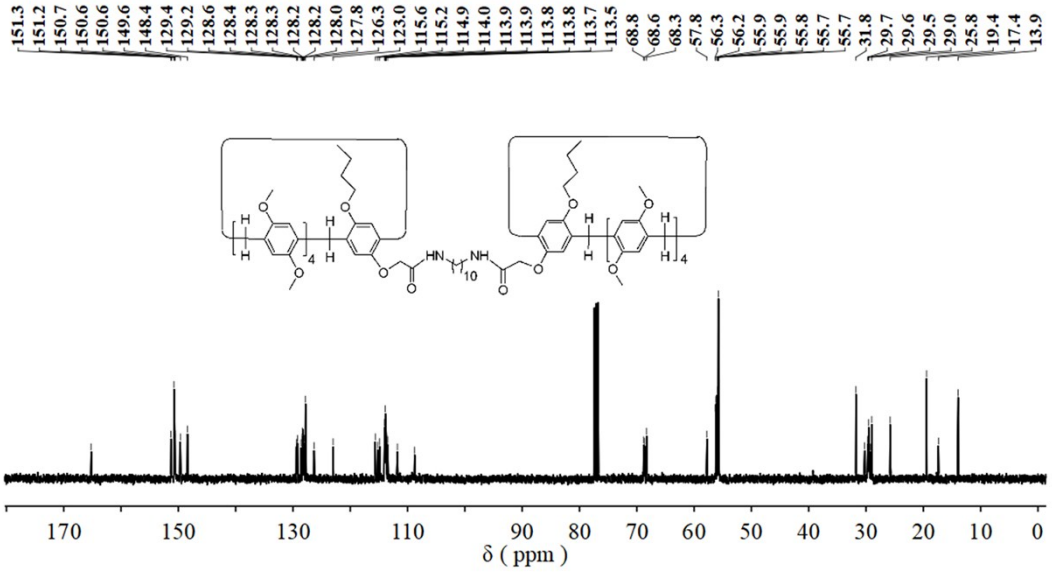

Fig. S10 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **3c**.

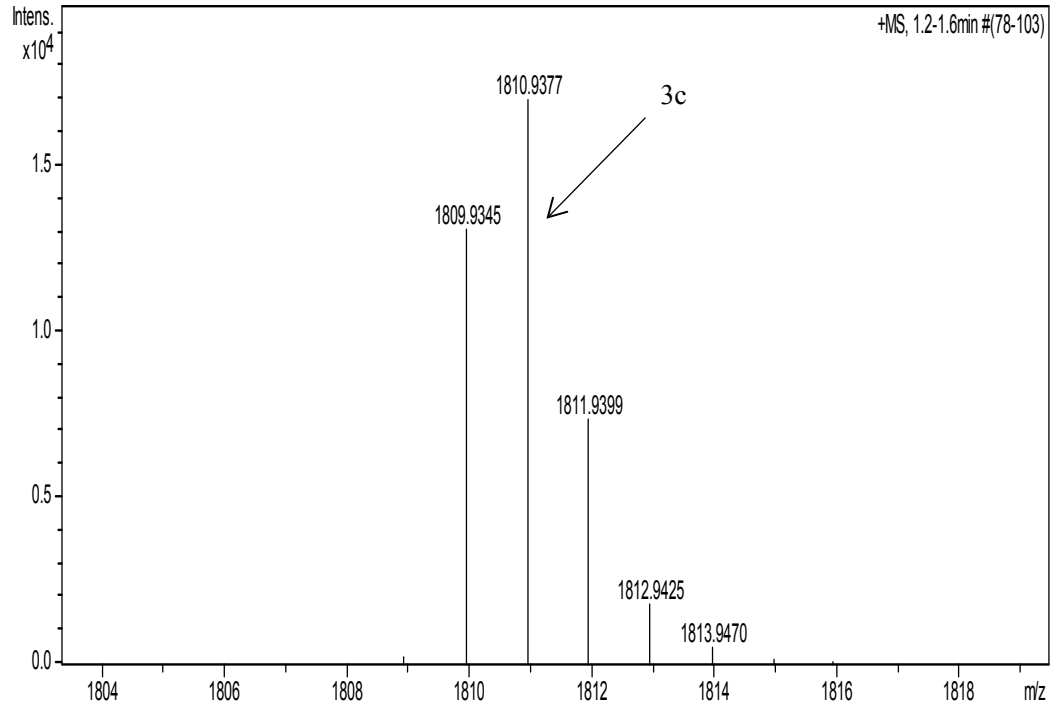

Fig. S11 HR-ESI-MS of **3c**.

Compound **4a**: White solid, 15%, M. p. 126-128℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20 (d, *J* = 8.0 Hz, 4H, Ar*H*), 6.99-6.77 (m, 24H, Ar*H*), 6.48 (brs, 2H, N*H*), 5.05 (brs, 2H, N*H*), 4.33 (s, 4H, CH_2), 3.90 (brs, 4H, CH_2), 3.86-3.57 (m, 78H, 15CH_2, 16OCH_3), 1.74-1.66 (m, 10H, 2CH_2, 2CH_3), 1.51-1.43 (m, 4H, CH_2), 1.25 (brs, 2H, CH_2), 0.95 (t, *J* = 7.2 Hz, 6H, CH_3); ^{13}C NMR (100

MHz, $CDCl_3$) δ: 166.8, 150.8, 150.7, 150.6, 150.5, 150.2, 148.8, 143.8, 128.8, 128.2, 127.7, 115.0, 114.3, 114.1 (2C), 114.0, 113.8, 112.9, 70.4, 66.7, 66.5, 61.3, 56.3, 56.0, 55.9, 55.7 (2C), 55.5, 55.4, 55.3, 52.8, 41.8, 31.8, 31.1, 29.6, 19.4, 14.0; IR (KBr) υ: 3554, 3402, 2938, 2839, 1680, 1614, 1506, 1457, 1399, 1303, 1211, 1044, 930, 873, 774, 652, 562 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{121}H_{141}N_4O_{26}$ ($[M + H]^+$): 2066.9789, found: 2066.9854

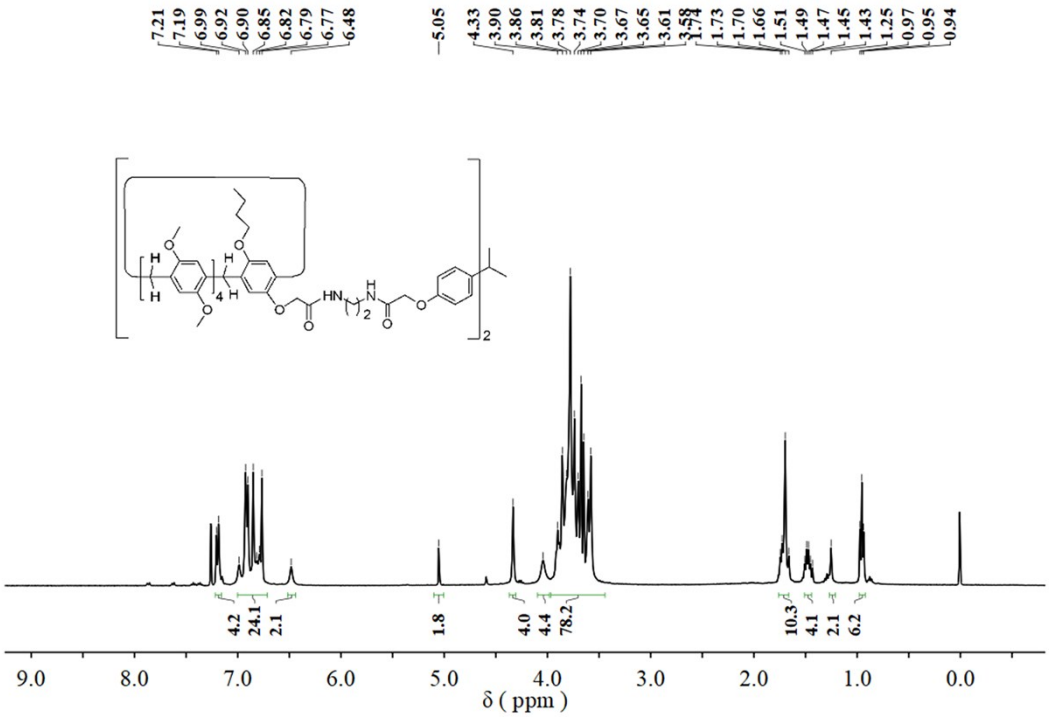

Fig. S12 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **4a**.

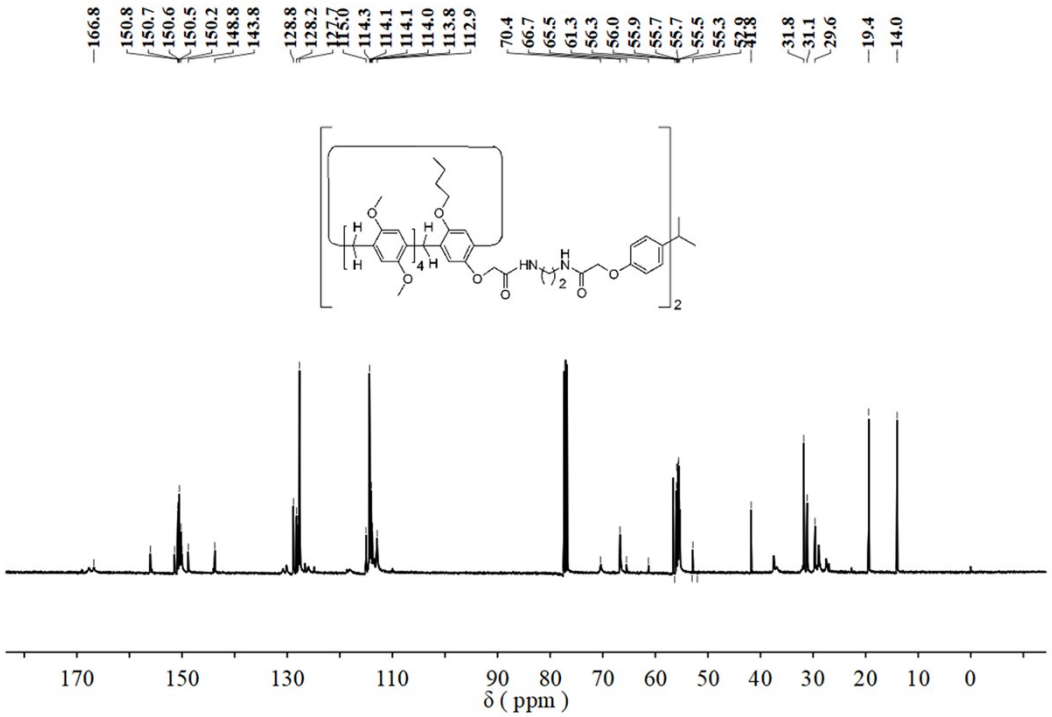

Fig. S13 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **4a**.

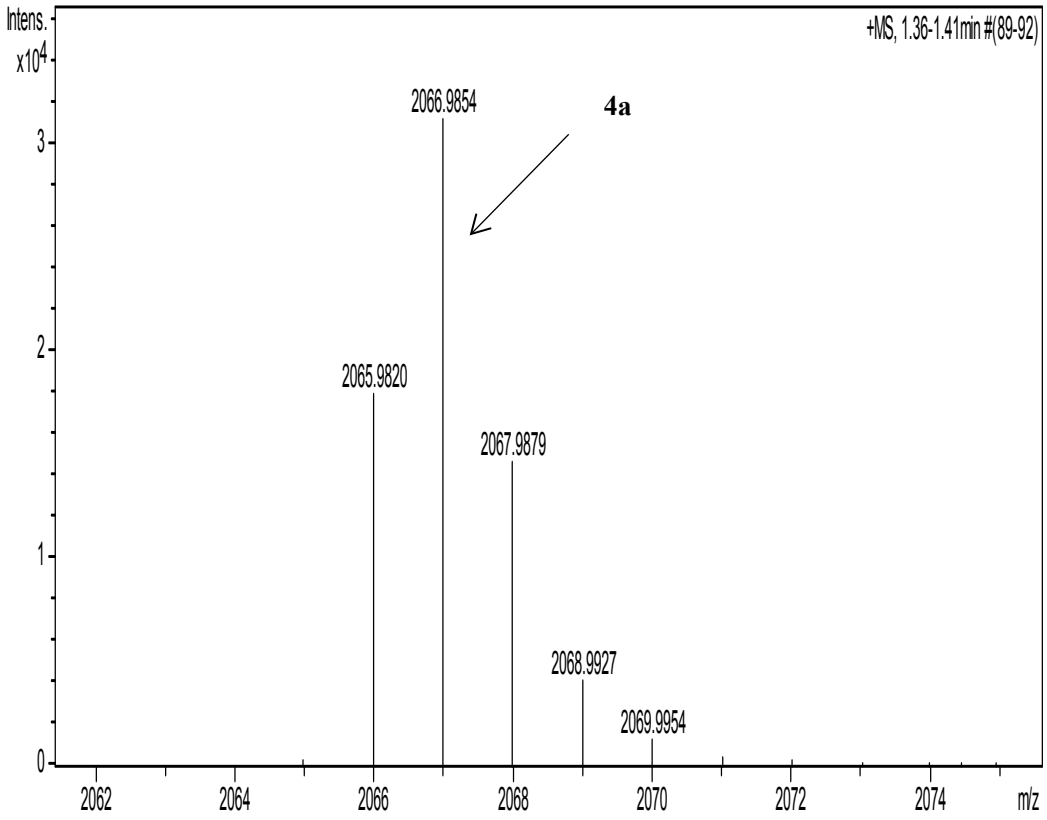

Fig. S14 HR-ESI-MS of **4a**.

Compound 4b: White solid, 19%, M. p. 129-131℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.23 (d, *J* =

8.4 Hz, 4H, Ar*H*), 7.01-6.80 (m, 24H, Ar*H*), 6.67 (brs, 2H, N*H*), 5.10 (brs, 1H, N*H*), 4.58 (brs, 1H, N*H*), 4.38 (s, 4H, CH_2), 4.30 (s, 4H, CH_2), 3.89-3.58 (m, 80H, 16CH_2, 16OCH_3), 1.69-1.66 (m, 10H, 2CH_2, 2CH_3), 1.48-1.42 (m, 4H, CH_2), 1.28-1.24 (m, 4H, CH_2), 0.91 (t, J = 7.6 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.1, 155.5, 150.7, 150.6, 150.5, 144.2, 128.7, 128.1, 128.0, 116.7, 114.7, 114.2, 113.7, 113.2, 69.3, 67.4, 66.6, 65.5, 61.3, 57.2, 55.8, 55.7, 55.6, 55.4, 41.9, 35.6, 34.9, 31.7, 31.0, 29.7, 29.6, 29.1, 27.4, 19.4, 14.1, 14.0; IR (KBr) υ: 3692, 3402, 2940, 2840, 1680, 1505, 1458, 1400, 1212, 1044, 929, 872, 775, 653cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{123}H_{145}N_4O_{26}$ ([M + H]$^+$): 2095.0102, found: 2095.0184

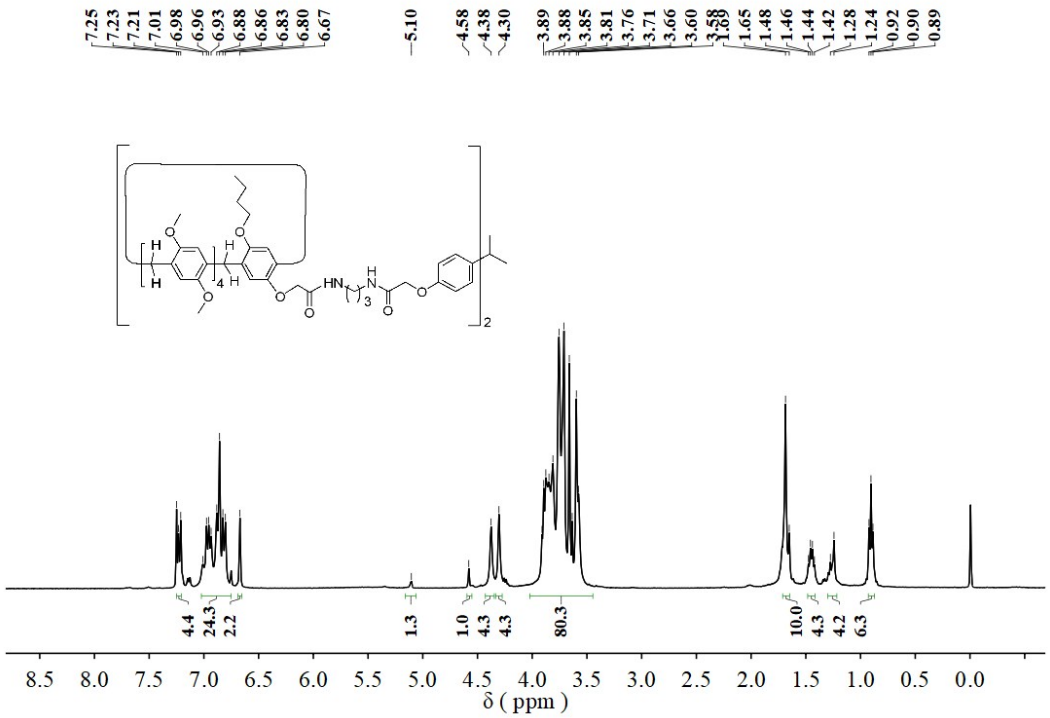

Fig. S15 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **4b**.

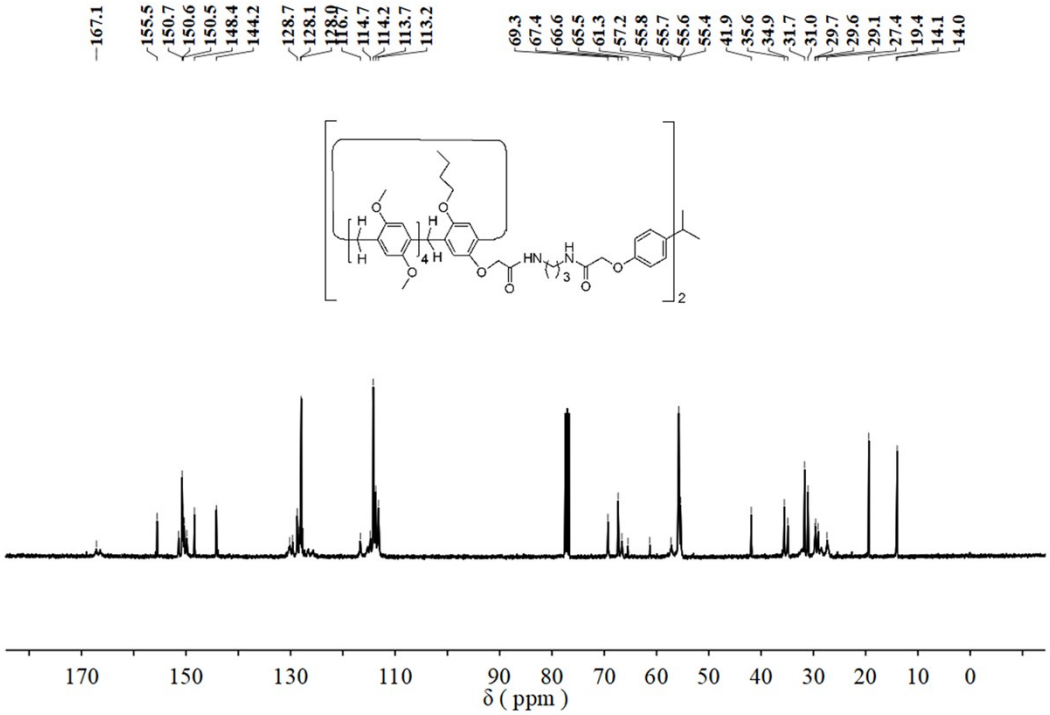

Fig. S16 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **4b**.

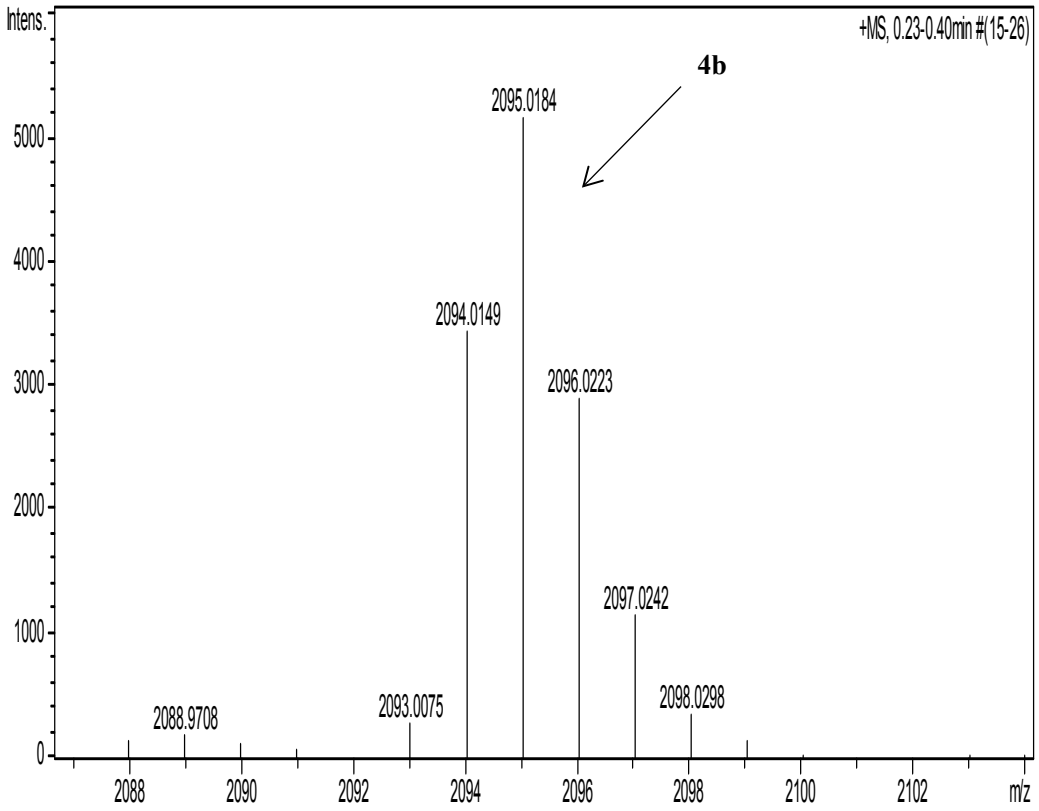

Fig. S17 HR-ESI-MS of **4b**.

Compound 4c: White solid, 25%, m.p. 135-137℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.25 (d, *J* =

8.0 Hz, 4H, Ar*H*), 7.03-6.79 (m, 24H, Ar*H*), 6.60 (brs, 2H, N*H*), 5.88 (brs, 2H, N*H*), 4.48 (d, *J* = 4.8 Hz, 4H, CH_2), 4.42 (s, 4H, CH_2), 3.85-3.66 (m, 72H, 12CH_2, 16OCH_3), 1.88-1.77 (m, 4H, CH_2), 1.69 (s, 6H, CH_3), 1.64-1.60 (m, 6H, CH_2), 1.41-1.24 (m, 4H, CH_2), 0.88 (t, *J* = 7.2 Hz, 6H, CH_3), 0.52 (brs, 2H, CH_2), -1.81 (brs, 4H, CH_2), -2.14 (brs, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0 (2C), 155.5, 151.5, 150.9, 150.4, 150.2, 150.1, 149.9, 148.3, 144.3, 129.9, 128.9, 128.8, 128.5, 128.3, 128.1, 127.9, 126.6, 117.1, 115.8, 114.6, 114.0, 113.9, 113.7, 113.3, 113.2, 112.9, 112.6, 69.9, 67.2, 66.1, 57.0, 56.3, 55.9, 55.7 (2C), 55.5, 55.2, 41.9, 38.9, 37.3, 31.8, 31.0, 29.7, 28.7, 23.2, 19.4, 14.0; IR (KBr) υ: 3555, 3407, 2939, 2838, 1679, 1616, 1504, 1457, 1398, 1301, 1210, 1043, 929, 875, 774, 710, 648, 559cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{125}H_{149}N_4O_{26}$ ([M + H]$^+$): 2123.0415, found: 2123.0517

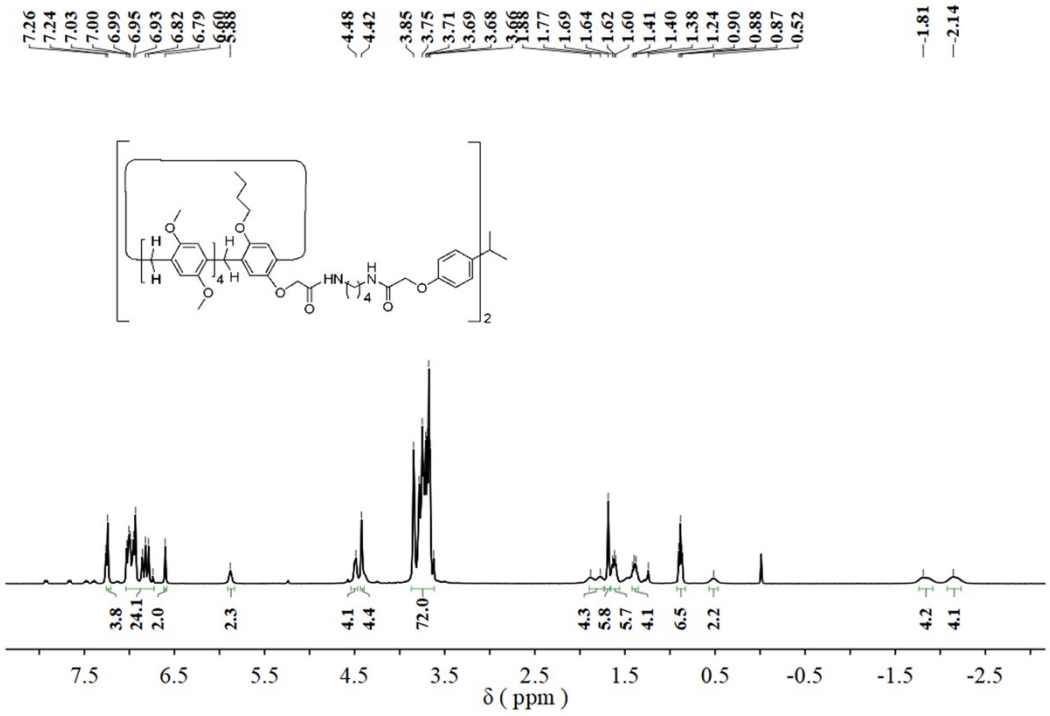

Fig. S18 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **4c**.

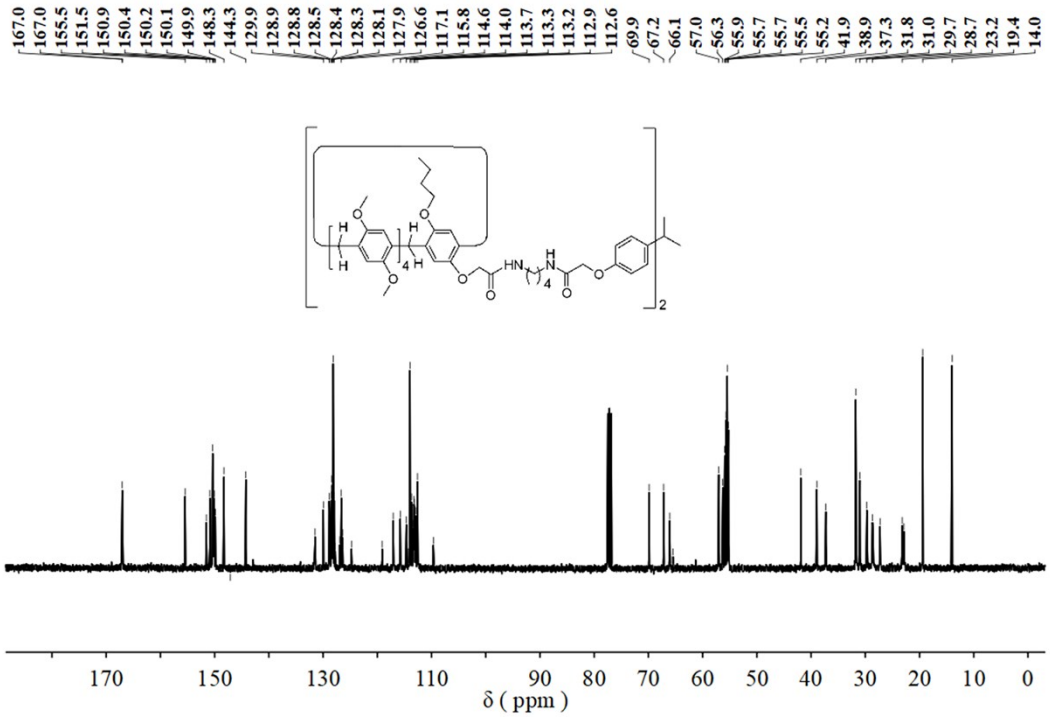

Fig. S19 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **4c**.

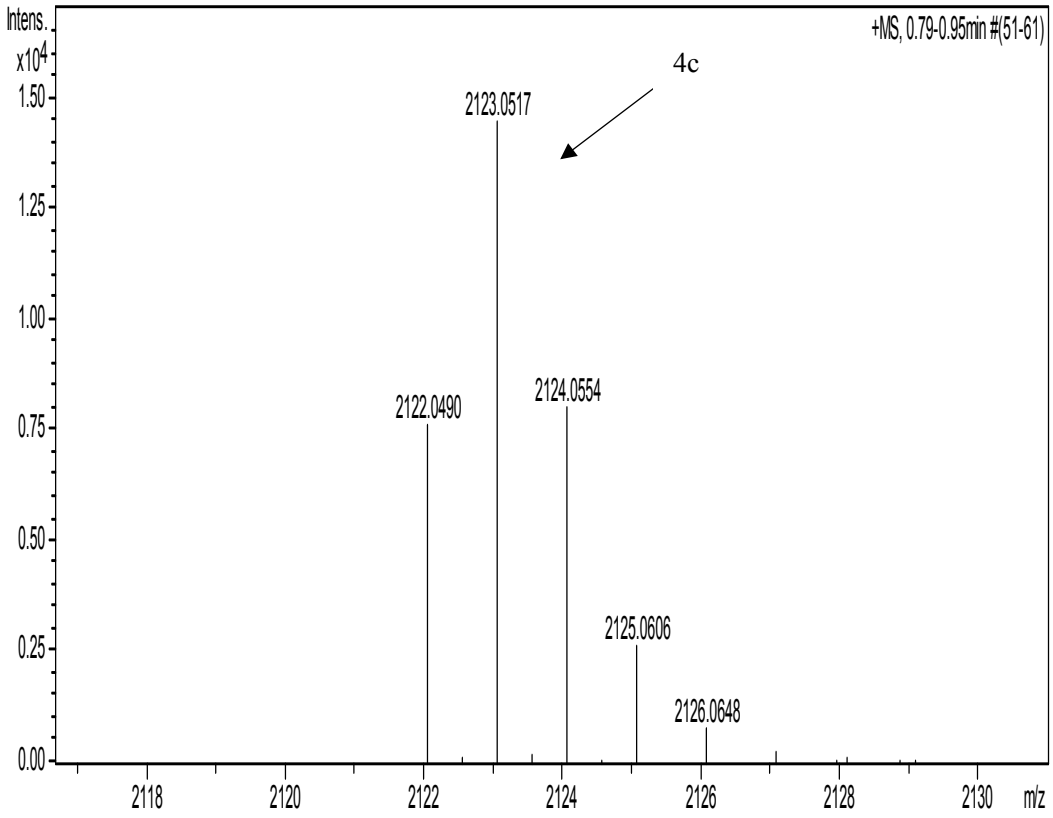

Fig. S20 HR-ESI-MS of **4c**.

Compound 4d: White solid, 9%, m.p. 139-142℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.24 (brs, 4H, Ar*H*), 6.96-6.78 (m, 24H, Ar*H*), 6.55 (brs, 2H, N*H*), 5.27 (brs, 2H, N*H*), 4.58 (s, 4H, CH_2), 4.47 (s,

4H, CH_2), 3.78-3.70 (m, 68H, 10CH_2, 16OCH_3), 2.71-2.48 (m, 8H, CH_2), 1.74-1.63 (m, 10H, 2CH_2, 2CH_3), 1.53-1.49 (m, 4H, CH_2), 1.26 (brs, 4H, CH_2), 0.92 (t, J = 7.2 Hz, 6H, CH_3), −0.09 (brs, 4H, CH_2), −0.96 (brs, 2H, CH_2), −1.09 (brs, 2H, CH_2), −1.61 (brs, 4H, CH_2), −2.29 (brs, 4H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.4, 167.2, 155.1, 150.8, 150.5 (2C), 150.3 (3C), 150.2, 150.1, 150.0, 147.0, 144.5, 129.6, 129.2, 128.4, 128.3, 128.2 (2C), 127.8, 127.0, 115.2, 114.7, 113.9 (2C), 113.8, 112.7, 112.2, 68.3, 67.4, 56.1, 55.8 (2C), 55.5, 55.4, 55.3, 55.1, 41.9, 39.2, 31.9, 31.0, 28.7, 19.6, 14.0; IR (KBr) υ: 3686, 3318, 2938, 2852, 1680, 1504, 1459, 1400, 1212, 1045, 929, 873, 775, 652cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{129}H_{157}N_4O_{26}$ ([M + H]$^+$): 2179.1041, found: 2179.1128.

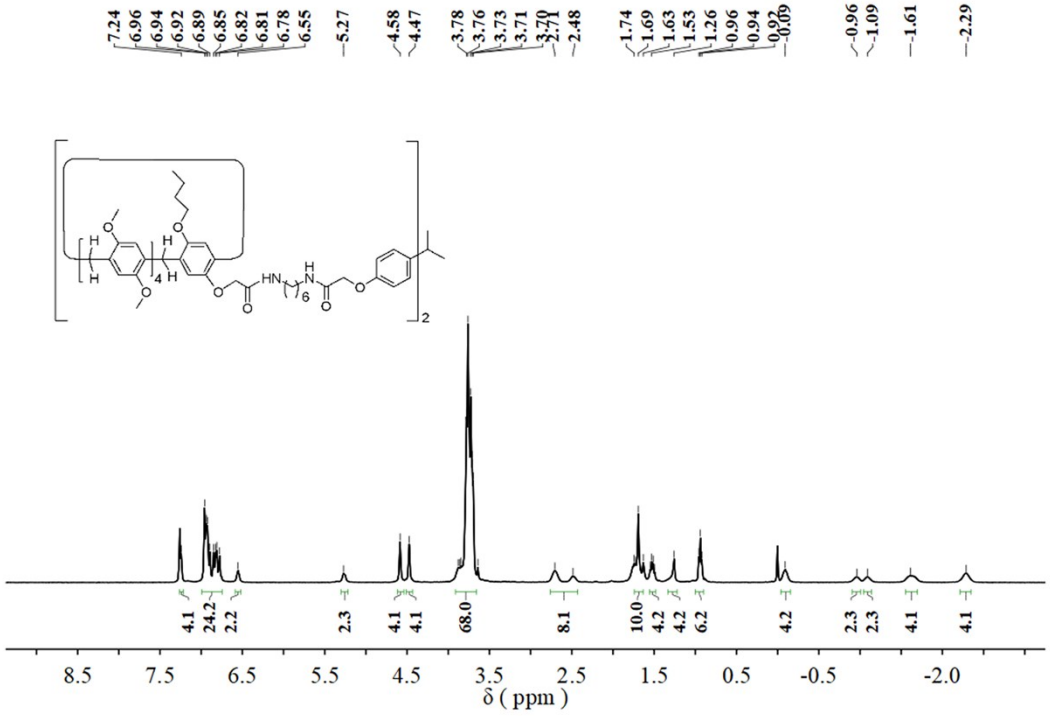

Fig. S21 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of **4d**.

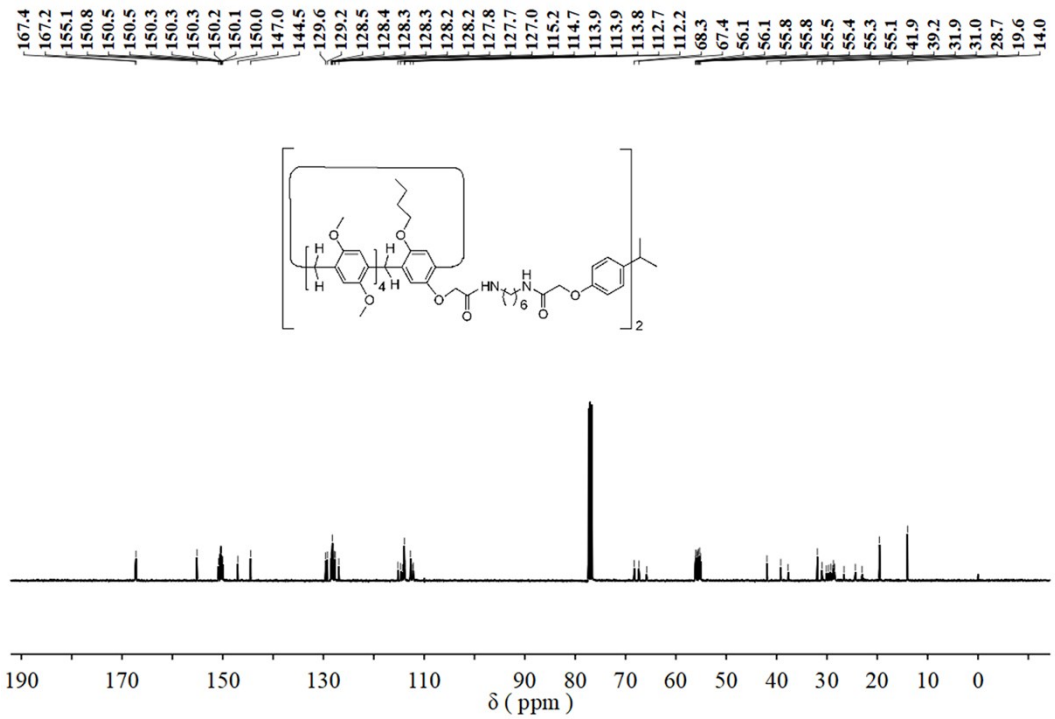

Fig. S22 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of **4d**.

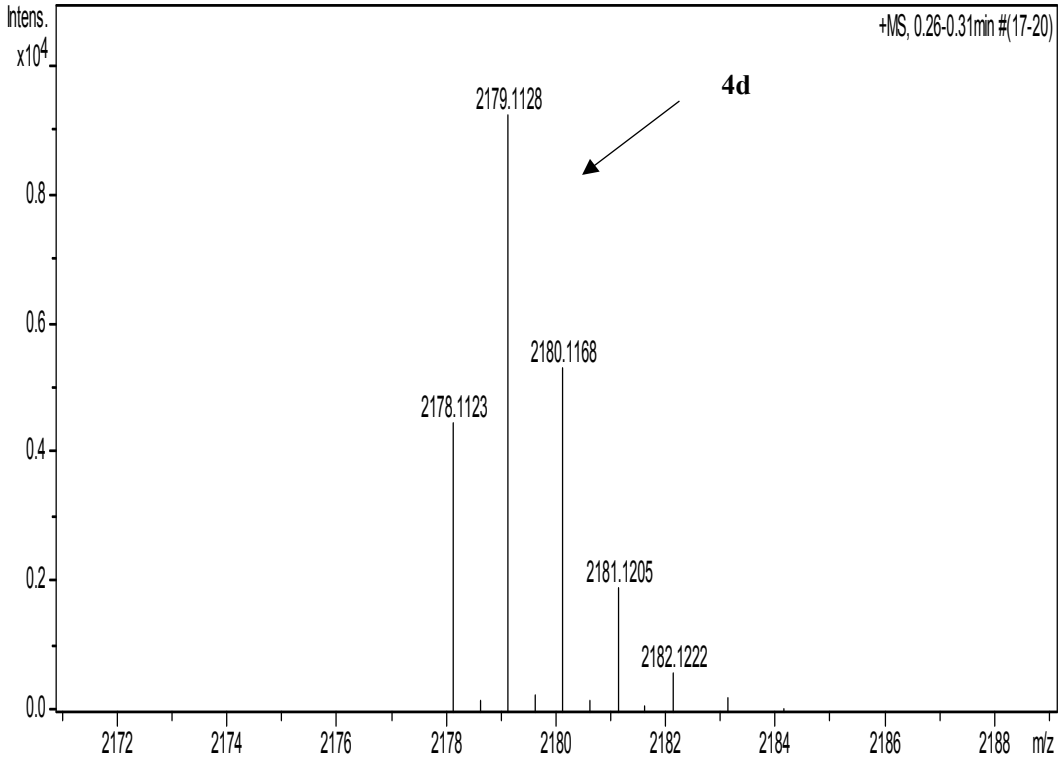

Fig. S23 HR-ESI-MS of **4d**.

5. X-Ray data for 3a and 4d

Table S1. Crystal data and structure refinement for **3a**

CCDC number	1565614
Empirical formula	$C_{104}H_{124}N_2O_{22}$
Formula weight	1754.04
Temperature	296 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P b P -1
a	12.413(2)
b	22.404(3)
c	22.568(3)
α	62.389(4)
β	77.747(4)
γ	81.705(4)
Volume	5426.9(14) $Å^3$
Z	2
Density (calculated)	1.073
Absorption coefficient	0.075
F(000)	1876
Crystal size	0.28 × 0.24 × 0.20 mm^3
Theta range for data collection	1.027 to 26.000°
Index ranges	-15<=h<=15, -27<=k<=27, -27<=l<=27
Reflections collected	94446
Independent reflections	20551
Completeness to theta = 24.71°	99.9 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on *F*2
Goodness-of-fit on *F*2	1.046
Final R indices [$I > 2\text{sigma}(I)$]	$R1 = 0.3110$, $wR2 = 0.4712$
R indices (all data)	$R1 = 0.2000$, $wR2 = 0.4349$
Largest diff. peak and hole	2.139 and -0.556 e·$Å^{-3}$

Table S2. Crystal data and structure refinement for **4d**

CCDC number	1583712
Empirical formula	$C_{129}H_{154}N_4O_{26}$
Formula weight	2176.55
Temperature	293 K

Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	P b c n
a	14.107(3)
b	23.359(4)
c	42.774(8)
α	90
β	90
γ	90
Volume	14095(5) $Å^3$
Z	4
Density (calculated)	1.026
Absorption coefficient	0.071
F(000)	4656
Crystal size	0.26 × 0.22 × 0.20 mm^3
Theta range for data collection	1.087 to 24.713°
Index ranges	-16<=h<=16, -27<=k<=27, -50<=l<=50
Reflections collected	175023
Independent reflections	12015
Completeness to theta = 24.71°	99.9 %
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on *F*2
Goodness-of-fit on *F*2	1.173
Final R indices [*I* > 2sigma(*I*)]	*R*1 = 0.3296, *wR*2 = 0.4790
R indices (all data)	*R*1 = 0.1801, *wR*2 = 0.4347
Largest diff. peak and hole	0.896 and -0.416 e·$Å^{-3}$

Reference:

[S1] Y. Han, G.-F. Huo, J. Sun, J. Xie, C.-G. Yan, Y. Zhao, X. Wu, C. Lin and L. Wang, *Sci. Rep.*, 2016, **6**, 28748.