Electronic Supplementary Material (ESI) for RSC Advances.

Pillar[5]arene derivatives containing two dinitrophenyl rings: Syntheses, conformations and the tubular self assembly in the solid state

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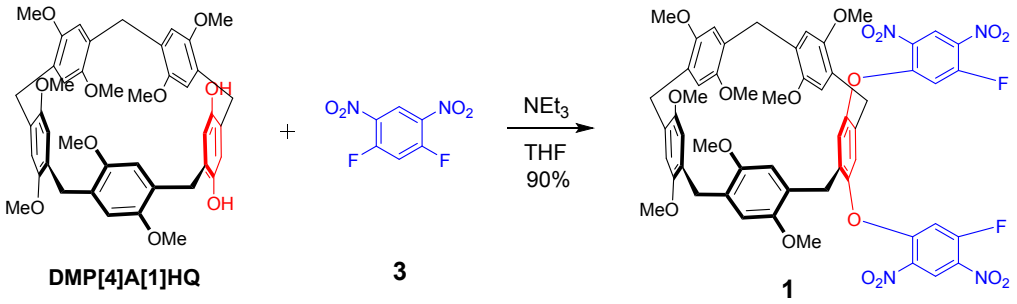
Electronic Supplementary Information

1. Materials and Methods:

DMP[4]A[1]HQ was synthesized according to literature procedures.[S1] All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Advance Ⅱ DMX 400 spectrophotometer with use of the deuterated solvent as the lock and TMS as the internal reference. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer or with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). The melting points were collected on a SHPSIC WRS-2 automatic melting point apparatus.

*2. Synthesis of **1***



Scheme S1. Synthesis of **1**.

To a solution of 1,5-difluoro-2,4-dinitrobenzene **3** (0.174 g, 0.855 mmol) in THF (20 mL) was added dropwise a mixture of **DMP[4]A[1]HQ** (0.206 g, 0.285 mmol) and NEt_3 (0.0870 g ,0.855 mmol) in THF (10 mL). The reaction mixture was stirred for 10 h under nitrogen atmosphere, and then concentrated and chromatographed on a silica gel column to give pure **1** (90%) as a yellow solid.

1 M.p. 153.2-153.5 °C. The ^{1}H NMR spectrum of **1** is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ (ppm): 3.40 (d, J = 5.32 Hz, 2H, C**H**$_3$), 3.48 (s, 6H, C**H**$_3$), 3.60 (s, 6H, C**H**$_3$), 3.65 (s, 2H, C**H**$_3$), 3.74 (d, J = 17.89 Hz, 8H, C**H**$_3$), 3.77 (s, 8H, ArC**H**$_2$), 3.82 (s, 1H, ArC**H**$_2$), 3.85 (s, 1H, ArC**H**$_2$), 6.35 (d, J = 11.52 Hz, 2H, Ar**H**), 6.60 (s, 2H, Ar**H**), 6.74 (d, J = 11.80 Hz, 4H, Ar**H**), 6.93 (s, 2H, Ar**H**),

7.21 (s, 2H, Ar**H**), 8.90 (d, J = 7.40 Hz, 2H, Ar**H**). The ^{13}C NMR spectrum of **1** is shown in Figure S2. ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ (ppm): 28.0, 28.3, 28.5, 29.3, 48.1, 54.2, 54.4, 54.6, 4.7, 106.2, 106.4, 112.0, 112.2, 112.7, 112.9, 123.1, 123.6, 123.8, 126.5, 127.1, 127.6, 129.1, 129.4, 129.4, 133.1, 134.0, 147.3, 149.3, 149.4, 149.5, 149.7, 155.8, 156.0, 156.1, 158.6. MS (ESI): *m/z* calcd [M+H$^+$] $C_{55}H_{48}F_2N_4O_{18}H^+$: 1091.3; Found: 1091.3. LRESIMS: *m/z* calcd. for [M + Na]$^+$ $C_{55}H_{48}F_2N_4O_{18}Na$, 1113.2829, found 1113.2806, error 2.1 ppm.

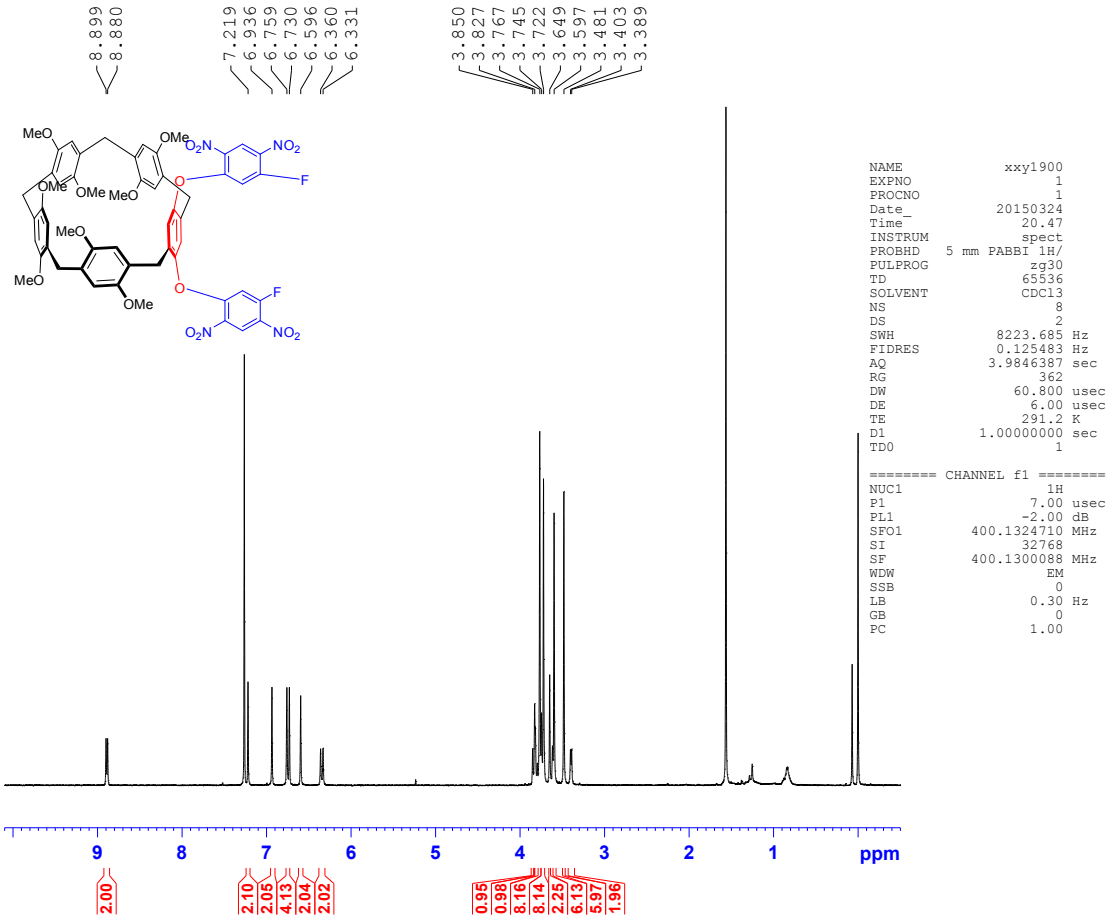


Fig. S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **1**.

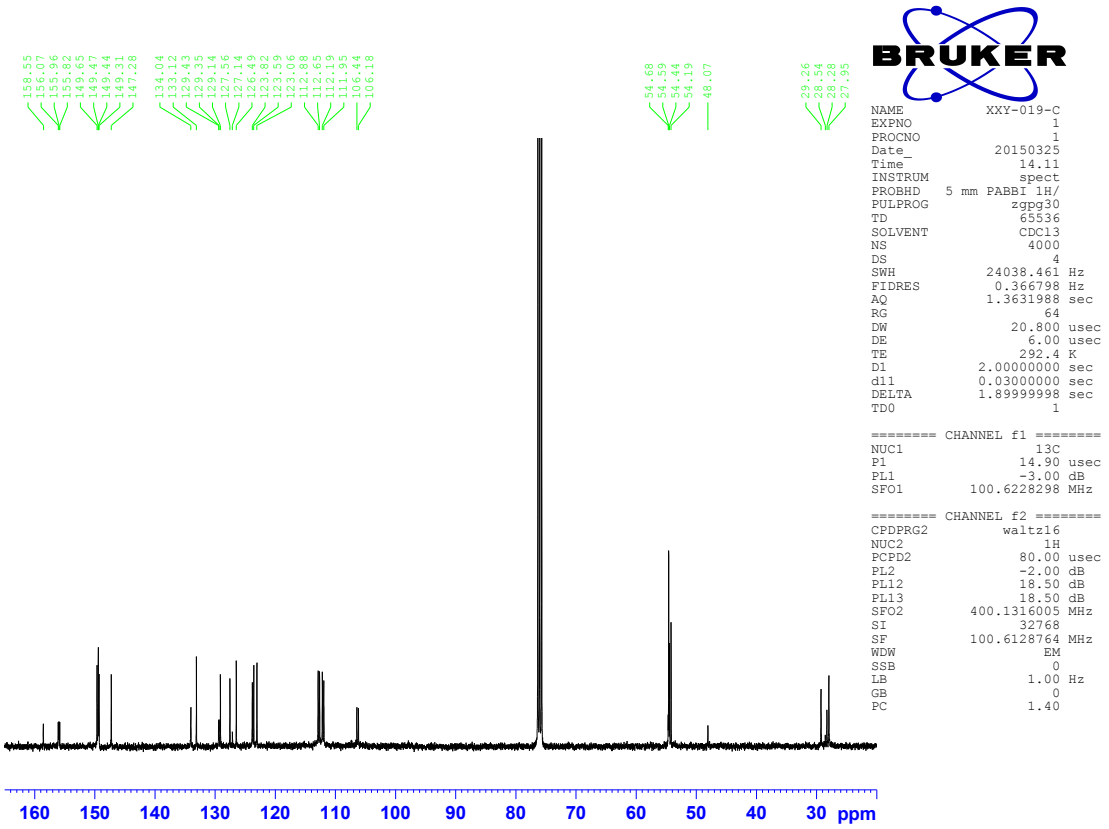
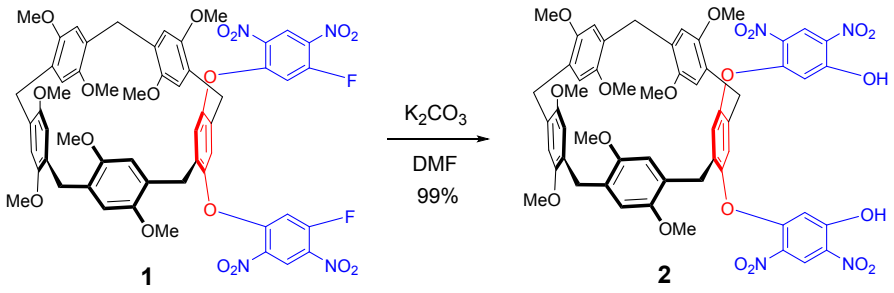


Fig. S2. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, room temperature) of **1**.

*3. Synthesis of **2***



Scheme S2. Synthesis of **2**.

To a solution of **1** (235 mg, 0.215 mmol) in DMF (10 mL) was added K_2CO_3 (178 mg, 1.29 mmol) before heating the suspension at 90℃ for three days. The suspension was then cooled to room temperature. The solvent was removed by evaporation under reduced pressure. The obtained solid was purified on a silica gel column (100%-50% ethyl acetate/acetone) to give the pure product (231 mg, 99%).

2 M.p. > 300 °C. The ^1H NMR spectrum of **2** is shown in Figure S3. ^1H NMR (400

MHz, DMSO-d_6, room temperature) δ (ppm): 3.67 (s, 3H, C**H**$_3$) 3.74 (d, J = 6.12 Hz, 21H, C**H**$_3$), 3.82 (s, 10H, ArC**H**$_2$), 5.97 (s, 2H, O**H**), 6.61 (s, 2H, Ar**H**), 6.69 (s, 3H, Ar**H**), 6.74 (s, 3H, Ar**H**), 6.92 (s, 2H, Ar**H**), 7.18 (s, 2H, Ar**H**), 8.94 (s, 2H, Ar**H**). MALDI TOF-MS: *m/s* calcd [M+H$^+$] $C_{55}H_{50}N_4O_{20}H^+$: 1087.0, Found: 1087.0; [M+Na$^+$] $C_{55}H_{50}N_4O_{20}Na^+$: 1110.0, Found: 1110.0. LRESIMS: *m/z* calcd. for [M] $C_{55}H_{50}N_4O_{20}$, 1186.3018, found 1186.2988, error 2.5 ppm.

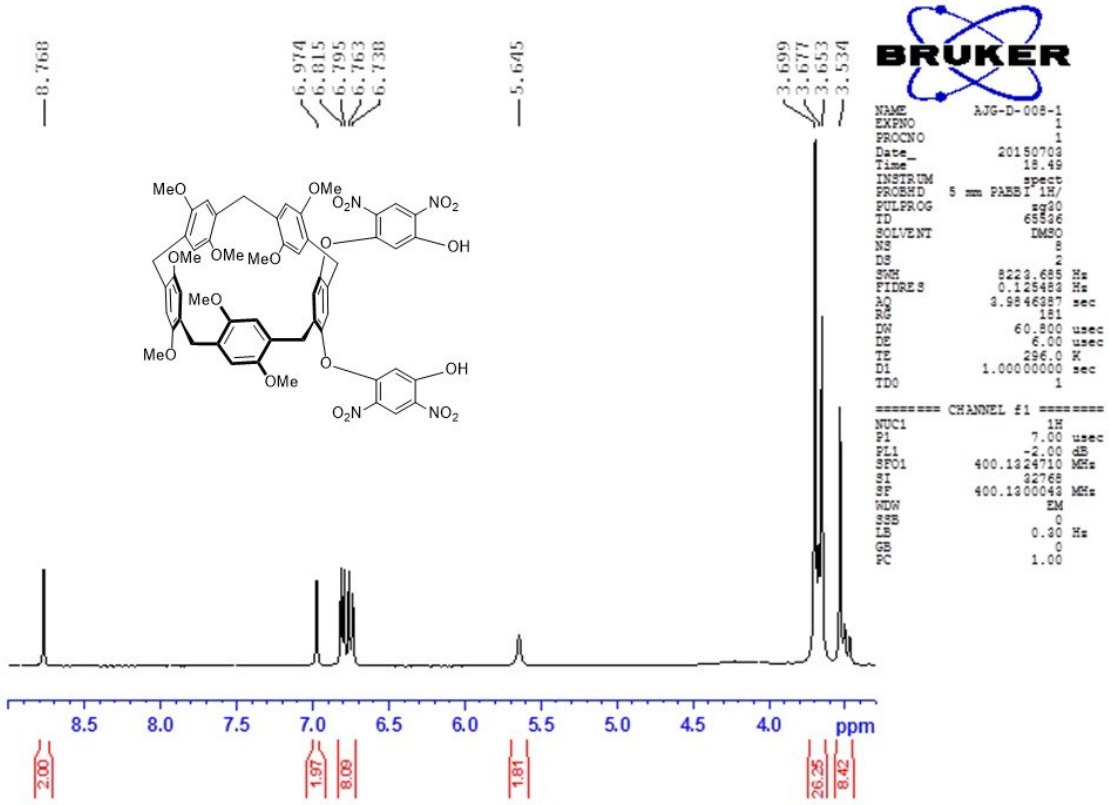


Fig. S3. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, room temperature) of **2**.

*4. X-ray crystal data of **1** and **2***

Crystal data of ***1***: yellow, $C_{55}H_{48}F_2N_4O_{18}$, *FW* 1260.83, monoclinic, space group *P1 21/c 1*, a = 10.9412(5) Å, b = 15.9438(6) Å, c = 37.9153(15) Å, α = 90.00°, β = 102.511(4) °, γ = 90.00°, V = 6457.1(5) Å^3, Z = 4, D_c = 1.297 g cm^{-3}, T = 170(2) K, μ = 0.258 mm^{-1}, 29158 measured reflections, 11789 independent reflections, 774 parameters, 0 restraints, F(000) = 2608, R_1 = 0.0906, wR_2 = 0.1875 (all data), R_1 = 0.0695, wR_2 = 0.2005 [$I > 2\sigma(I)$], max residual density 0.555 e•Å^{-3}, and goodness-of-fit (F^2) =1.105. CCDC number: 1444303.

Crystal data of ***2***: yellow, $C_{55}H_{50}N_4O_{20}$, *FW* 1397.79, orthorhombic, space group *C 1 2/c 1*, a = 24.236(3) Å, b = 15.7969(10) Å, c = 20.4001(19) Å, α = 90.00°, β = 122.480(14) °, γ = 90.00°, V = 6588.5(10) Å^3, Z = 4, D_c = 1.409 g cm^{-3}, T = 170(2) K, μ = 0.337 mm^{-1}, 13475 measured reflections, 6014 independent reflections, 467

parameters, 78 restraints, $F(000) = 2880$, $R_1 = 0.0948$, $wR_2 = 0.1596$ (all data), $R_1 = 0.0603$, $wR_2 = 0.1856$ [$I > 2\sigma(I)$], max residual density 0.376 e•Å^{-3}, and goodness-of-fit (F^2) = 1.034. CCDC number: 1444304.

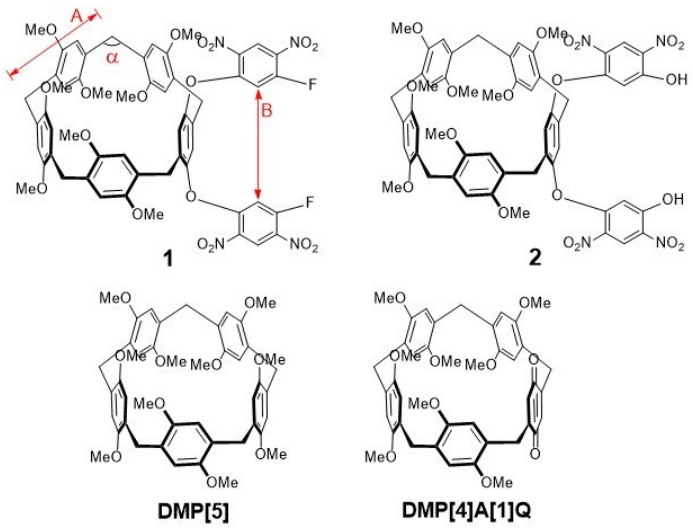


Fig. S4. Structures of **1**, **2**, **DMP[5]** and **DMP[4]A[1]Q** and the representation of *A, B and α.*

Table S1. Crystal data of **1**, **2**, **DMP[5]** and **DMP[4]A[1]Q**

Compounds	A (Å)	α (°)	B (Å)
1	5.85	107.9	5.410
2	5.85	107.8	5.461
DMP[5]	5.84	107.9	–
DMP[4]A[1]Q	5.85	107.9	–

*5. Crystal structure of **2***

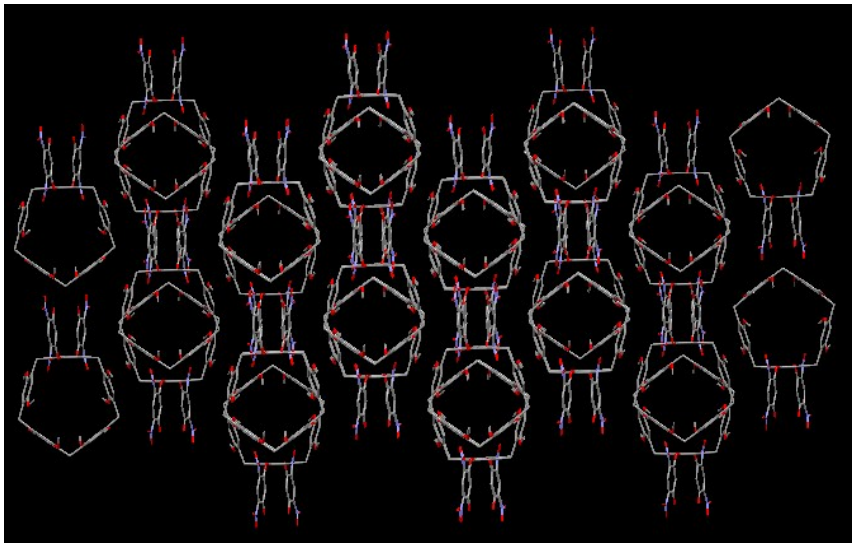


Fig. S5. Crystal packing of **2**. Solvent molecules and hydrogen atoms are omitted for clarity. C, black; H, white; O, red; N, blue.

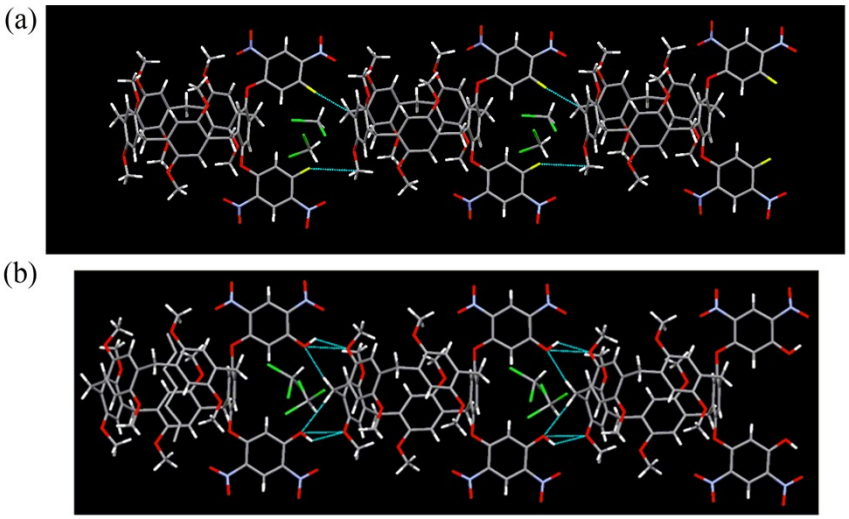


Fig. S6. Hydrogen bonds provided by F atoms in molecules **1** (a) and OH groups in molecules **2** (b) in the solid state.

References:

S1. C. Xie, W. Hu, W. Hu, Y. A. Liu, J. Huo, J. Li, B. Jiang and K. Wen, *Chin. J. Chem.*, 2015, **33**, 379–383.