

Supporting Information

Weak intermolecular interactions directed assembly of calix[4]arene derivatives

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Contents

General synthetic procedure for calix[4]arene derivatives

Scheme S1 Syntheses of the seven compounds.

Supporting figure

Figure S1 The intermolecular C–H \cdots O and O \cdots π interactions in compound **16**.

Figure S2 The intermolecular C–H \cdots π interactions and $\pi\cdots\pi$ found in compound **17**.

Figure S3 C–H \cdots π interactions in compound **18**

Figure S4 One-dimensional wave structure was formed in compound **19**

Figure S5 Molecules staggered in compound **21**.

Figure S6 The intermolecular C–H \cdots Cl and O \cdots π interactions in compound **22**

Supporting table

Table S1 Dihedral angles of aromatic rings and reference molecular plane R of the seven compounds.

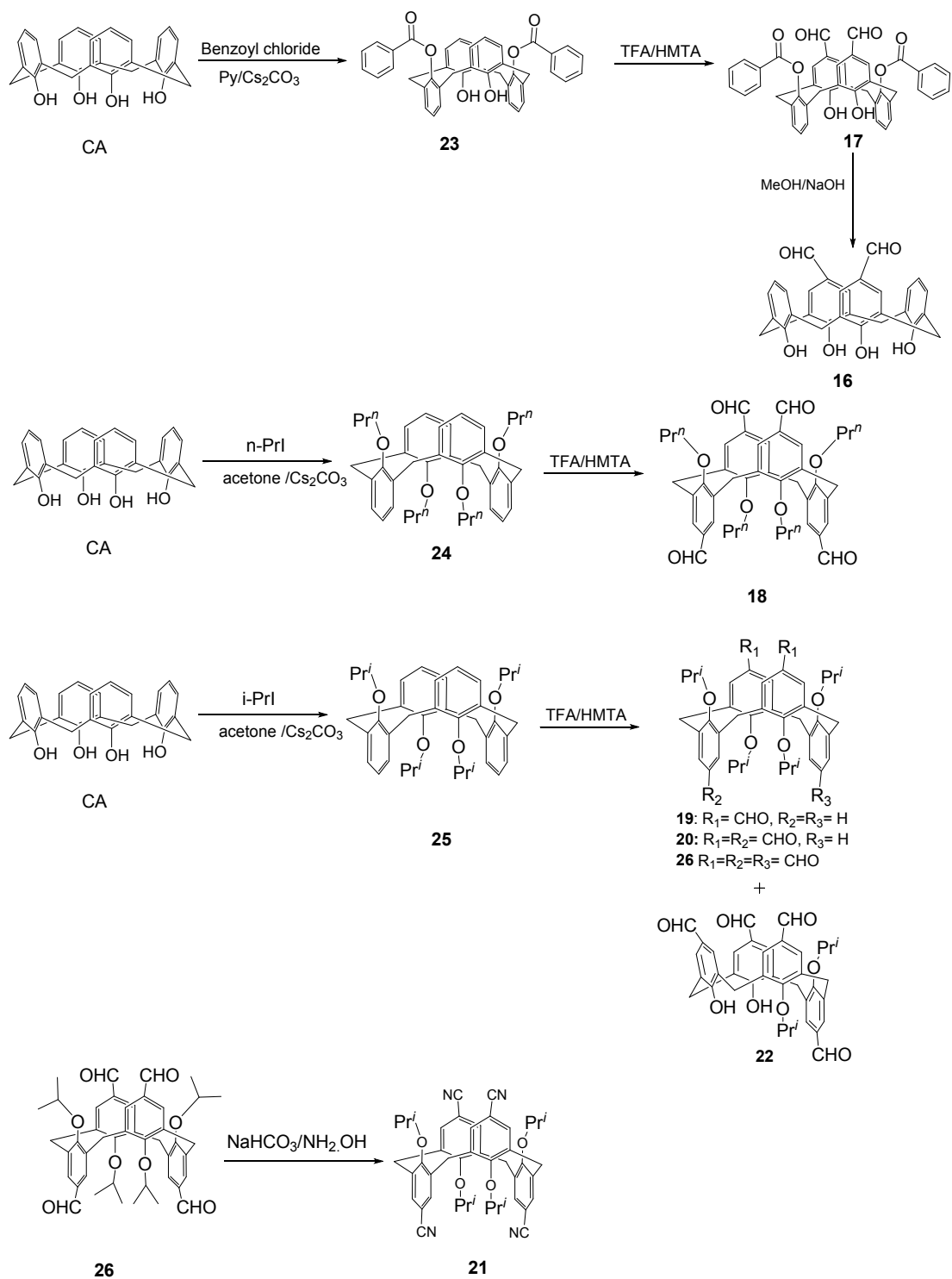
Table S2 Dihedral angles of the opposite aromatic rings of the seven compounds

Table S3 $\pi\cdots\pi$ interactions in compounds **16, 17** and **22**

Table S4 O \cdots π interactions in compounds **16, 17** and **22**

Table S5 Hydrogen bonds of five compounds

Table S6 C–H \cdots π interactions of five compounds



Scheme S1 Syntheses of the seven compounds.

Synthesis of 1,3-alternate calix[4]arene derivatives **23^a**, **24^b** and **25^b**

Compound CA (1.0 g, 2.35 mmol) in 40 mL of dry pyridine was treated with benzoyl chloride (0.56 mL, 24 mmol) in the presence of Cs₂CO₃ (15.34 g, 47.1 mmol). After reacting carried out at room temperature, the reaction system was evaporated to dryness under reduced pressure, and 40 mL of chloroform was added. Then 1 mol/L of HCl was slowly added and the pH was adjusted to neutral. The organic layer was washed with water and dried over MgSO₄ and the residue using petroleum ether / dichloromethane (100:1- 40:1) as a gradient eluent to give a white powder solid **23** (1.22 g, 83%).

Compound CA (1.0 g, 2.35 mmol) in 40 mL of dry acetone was treated with Iodo-n-propane (4.8 mL, 24 mmol) in the presence of Cs₂CO₃ (15.34 g, 47.1 mmol). After reacting carried out at reflux temperature. Other procedures of preparing **24** were similar to **23**. The residue was purified by column chromatography to give **24** (0.73 g, 50%).

The procedures of preparing **25** were similar to **24**. The yield of the obtained compound was 53%.

23: ¹H NMR (300 MHz, DMSO): δ (ppm) 3.48(d, 4H, $J = 12$ Hz, ArCH₂Ar), 3.94(d, 4H, $J = 12$ Hz, ArCH₂Ar), 6.77(t, 2H, $J = 7.2$ Hz, ArH), 6.81-6.97 (m, 6H, ArH), 7.09-7.42 (m, 6H, ArH), 8.33 (d, 4H, $J = 7.2$ Hz, ArH). ESI-MS: $m/z = 655$ [M+Na]⁺

24: ¹H NMR (300 MHz, CDCl₃): δ (ppm) 0.92(t, 12H, $J = 7.5$ Hz, CH₃), 1.59-1.70(m, 8H, CH₂CH₂CH₃), 3.53(t, 8H, $J = 7.2$ Hz, CH₂CH₂CH₃), 3.61 (s, 8H, ArCH₂Ar), 6.67 (t, 4H, $J = 7.5$ Hz, ArH). ESI-MS: $m/z = 591$ [M-H]⁻.

25: ¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.21(d, 24H, $J = 6.0$ Hz, CH₃), 3.61(s, 8H, ArCH₂Ar), 4.14(hept, 4H, $J = 6.0$ Hz, OCHMe₂), 6.61(t, 4H, $J = 7.2$ Hz, ArH), 7.01(d, 8H, $J = 7.2$ Hz, ArH). ESI-MS: $m/z = 591$ [M-H]⁻

Synthesis of 1,3-alternate calix[4]arene derivatives **17^c**, **18^b**, **19^d**, **20^b** and **22^b**

A mixture of calixarene **23** (0.47 g, 0.74 mmol), hexamethylenetetramine (3.84 g, 20.19 mmol), and trifluoroacetic acid (20 mL) was stirred at reflux for 48 h. Then the mixture was poured into 30 mL of ice-water and extracted with chloroform. The chloroform solution was washed with water and dried over MgSO₄, and then filtered and concentrated under vacuum. The residue was purified using petroleum ether /

dichloromethane (40:1-10:1) as a gradient eluent to give **17** (0.40 g, 80%)

The procedures of preparing **18-20** and **22** were similar to **17** except that the reaction time.

18 (reaction time: 48h, yield: 42%),

19 (reaction time: 24h, yield: 18%),

20 (reaction time: 24h, yield: 23%),

22 (reaction time: 96h, yield: 11%),

17: ^1H NMR (300 MHz, CDCl_3): δ (ppm) 9.68 (s, 2H, CHO), 8.26 (d, 4H, $J = 7.2$ Hz, ArH), 7.77 (t, 2H, $J = 6.9$ Hz, ArH), 7.59 (s, 4H, ArH), 7.55 (t, 4H, $J = 7.5$ Hz, ArH), 6.95-7.02 (m, 6H, ArH), 6.19 (s, 2H, ArOH), 4.01 (d, 4H, $J = 14.7$ Hz, ArCH_2Ar), 3.69 (d, 4H, $J = 14.7$ Hz, ArCH_2Ar). ESI-MS: m/z 687 $[\text{M}-\text{H}]^-$

18 : ^1H NMR (CDCl_3 , 300 MHz): 9.69 (s, 4H, CHO), 7.53 (s, 8H, ArH), 4.42 (hept, 4H, $J = 6.0$ Hz OCHMe₂), 3.74 (s, 8H, ArCH_2Ar), 1.33 (d, 24H, $J = 6.0$ Hz, CH₃).

^{13}C NMR (CDCl_3 , 75 MHz): δ 191.5 (CHO), 159.2, 134.3, 131.4, 130.5 (Ar), 74.9 (OCHMe₂), 35.7 (ArCH_2Ar), 22.5 (CH₃). ESI-MS m/z : 727 $[\text{M}+\text{Na}]^+$

19: ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 0.92-1.25 (m, 24H, CH₃), 3.65-3.75(m, 8H, $J = 12.7$ Hz, ArCH_2Ar), 4.21-4.40(m, 4H, OCHMe₂), 6.64(d, 4H, $J = 7.5$ Hz, ArH), 6.82(d, 2H, $J = 7.5$ Hz, ArH), 7.53(s, 4H, ArH), 9.80(s, 2H, CHO). ESI-MS: $m/z = 671$ $[\text{M}+\text{Na}]^+$

20: ^1H NMR (300MHz, CDCl_3): δ (ppm) 1.29-1.36(m, 24H, CH₃), 3.59(d, 2H, $J = 15.4$ Hz, ArCH_2Ar), 3.66 (d, 2H, $J = 15.4$ Hz, ArCH_2Ar), 3.69(s, 4H, ArCH_2Ar), 4.21-4.45(m, 4H, OCHMe₂), 6.54(t, 1H, $J = 7.5$ Hz, ArH), 6.97(d, 2H, $J = 7.5$ Hz, ArH), 7.51(s, 2H, ArH), 7.55(s, 2H, ArH), 7.59(s, 2H, ArH), 9.68(s, 2H, CHO), 9.83(s, 1H, CHO). ESI-MS: $m/z = 699$ $[\text{M}+\text{Na}]^+$

22: ^1H NMR (CDCl_3 , 300 MHz): δ 9.93 (s, 2H, CHO), 9.81 (s, 2H, CHO), 8.10 (s, 2H, ArOH), 7.73 (s, 4H, ArH), 7.64 (s, 2H, ArH), 7.61 (s, 2H, ArH), 4.40-4.52 (m, 2H, OCHMe₂), 4.14 (s, 2H, ArCH_2Ar), 4.07 (d, 2H, $J = 15.3$ Hz, ArCH_2Ar), 3.92 (d, 2H, $J = 15.3$ Hz, ArCH_2Ar), 3.83 (s, 2H, ArCH_2Ar), 0.97 (d, 6H, $J = 6.0$ Hz, CH₃), 0.92 (d, 6H, $J = 6.0$ Hz, CH₃).

^{13}C NMR (CDCl_3 , 75 MHz): δ 190.5, 190.3 (CHO), 157.0, 156.9, 134.5, 133.2, 132.0, 131.4, 130.3, 129.7, 128.1, 127.3 (Ar), 74.2 (OCHMe₂), 39.1, 34.9, 31.2 (ArCH_2Ar), 21.4, 20.8 (CH₃). ESI-MS m/z : 643 $[\text{M}+\text{Na}]^+$.

Synthesis calix[4]arene derivatives **16**^d

An aqueous solution of 0.1mmol compound **17**, 5 mL of NaOH (20%) was added to 20 mL of methanol and heated to reflux overnight. After the completion of the reaction, the solvent was distilled off under reduced pressure, and 1 mol/L HCl was added until no precipitate was formed. After filtration, the solid **17** was washed with

water, and the product was quantitatively obtained.

¹H NMR (300 MHz, CDCl₃): δ (ppm) 10.18 (s, 4H, ArOH), 9.74 (s, 2H, CHO), 7.61 (s, 4H, ArH), 7.14 (d, 4H, J = 7.2 Hz, ArH), 6.81 (t, 2H, J = 7.5 Hz, ArH), 3.51-4.40 (m, 8H, ArCH₂Ar). ESI-MS: m/z 479 [M-H]⁻.

Synthesis calix[4]arene derivatives **21**^{c,e}

0.2 g (0.28 mmol) compound **26** and 28 mmol NH₂OH were added to 20 mL acetonitrile. After reflux for 5 days, intermediate product extracted with dichloromethane and dried. The obtained solid was added to 5 mL acetic acid and refluxed for one night. After the reaction was completed, a large amount of water was added. Then the mixture was poured into 30 mL of ice-water and extracted with chloroform. The chloroform solution was washed with water and dried over MgSO₄, and then filtered and concentrated under vacuum. The residue was purified by column chromatography to give **21**(0.11g, 56%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.12(t, J = 7.4Hz, 6H, CH₃), 1.99(m, 4H, CH₂), 4.21(t, J = 6.6Hz, 4H, ArOCH₂), 6.65(t, J = 7.7Hz, 4H, ArH), 7.05 (d, J = 7.8Hz, 4H, ArH), 7.87(s, 4H, ArH), 8.43 (s, 2H, ArOH). ESI-MS: m/z = 629 [M-H]⁻

Ref:(a) Magrans J O, de Mendoza J, Pons M, et al. Are 1, 3-Di-O-benzoylcalix [4] arenes an Exception to the 13C-NMR Rule for Conformational Determination?[J]. The Journal of organic chemistry, 1997, 62(13): 4518-4520.

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(e) W. Wang, W. Yang, R. Guo and S. Gong, CrystEngComm, 2015, 17, 7663-7675

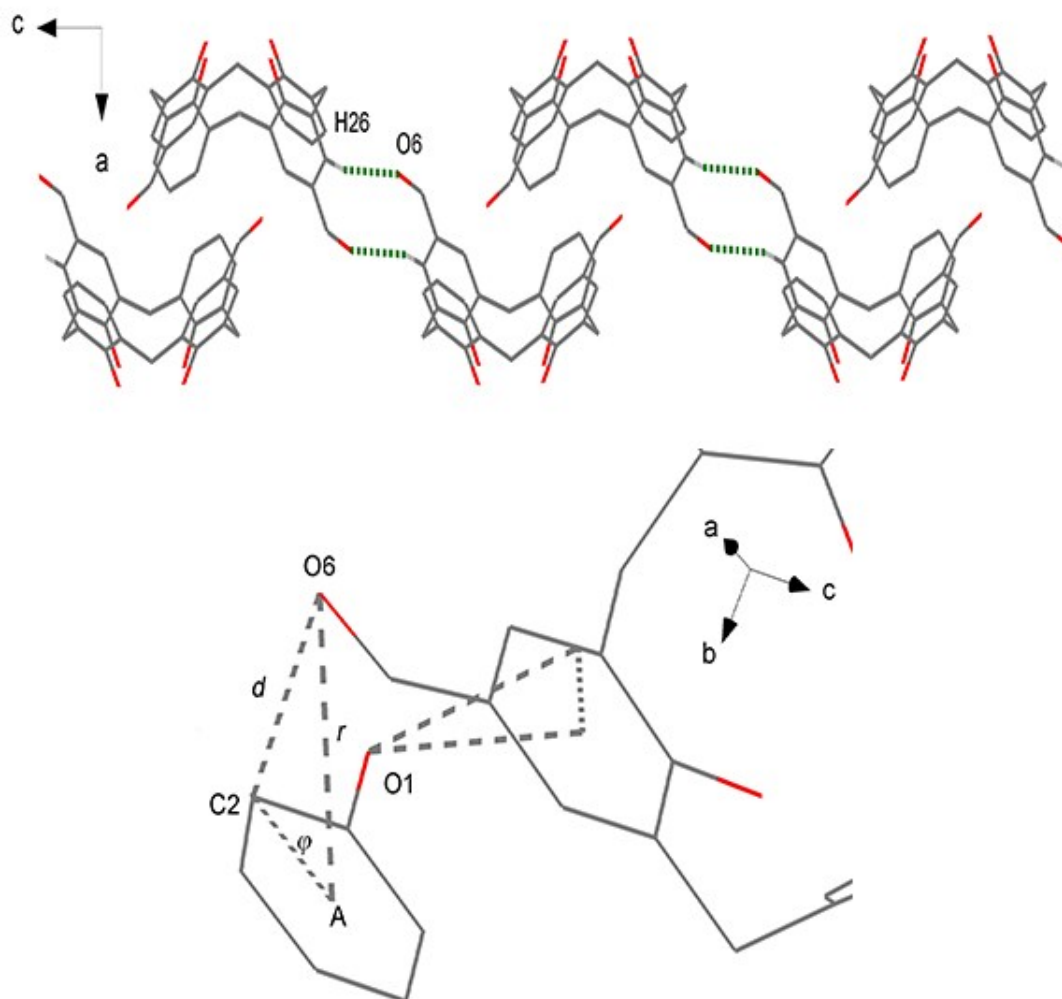
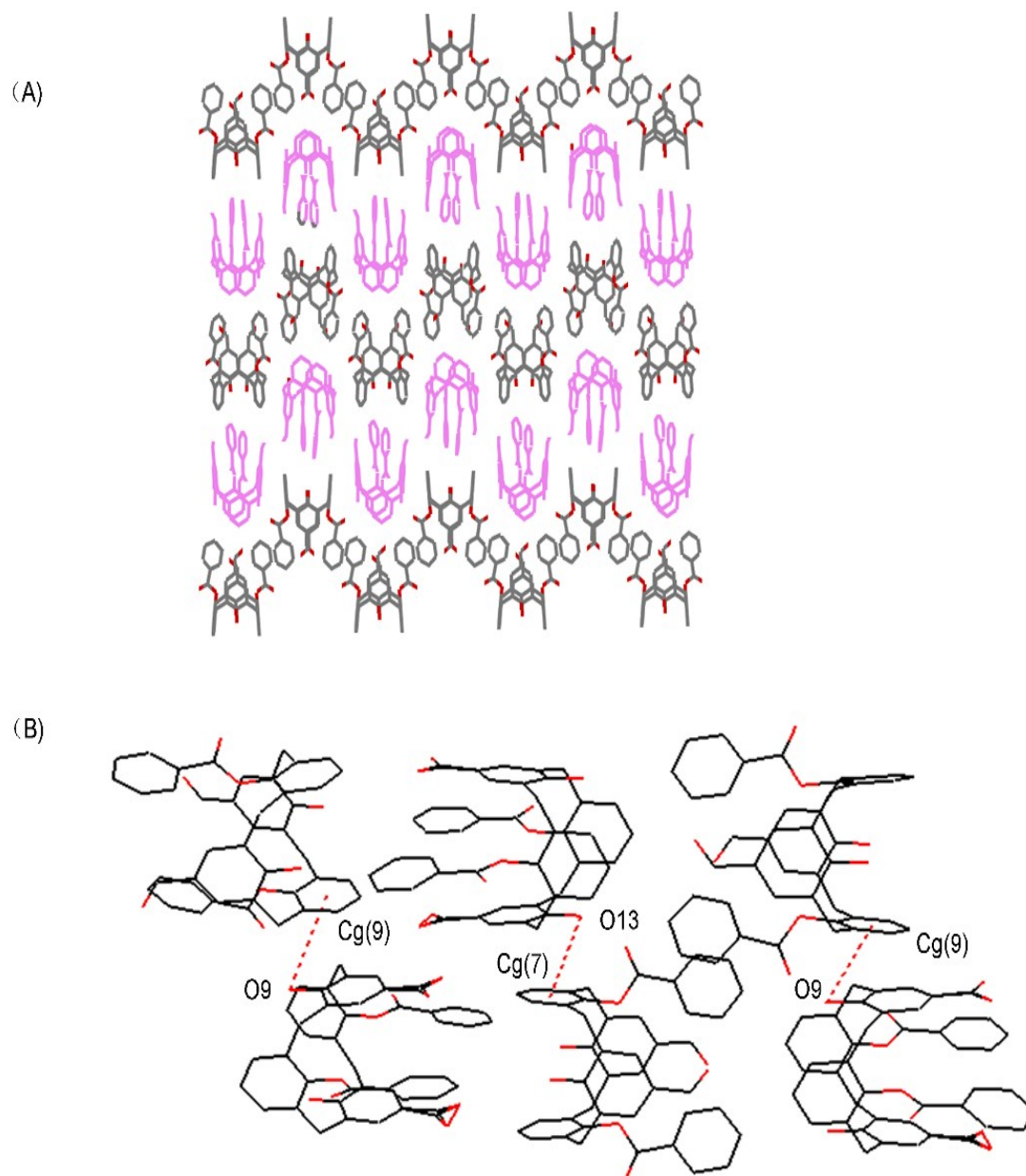


Figure S1 (A) $C-H \cdots O$ interactions was found in a wave structure of **16**. (B) The intermolecular $O \cdots \pi$ interactions was found in compound **16**. (The intermolecular $\pi \cdots \pi$, $C-H \cdots O$ and $O \cdots \pi$ interactions are red, green and grey dot lines, respectively).



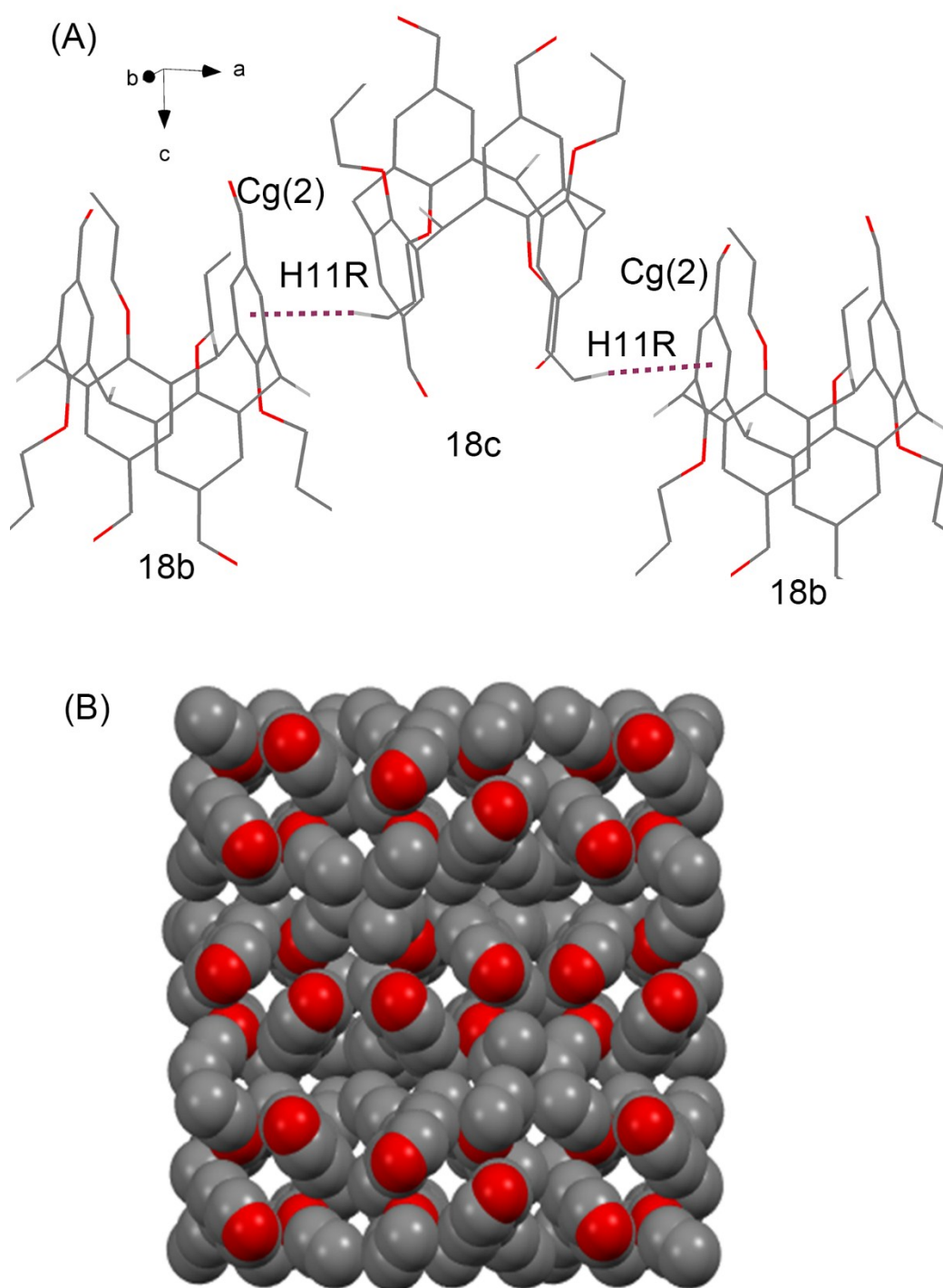


Figure S3 (A) The intermolecular C-H \cdots π interactions was observed in crystal **18**. (B) Space-filling representation of the extended structure was observed in compound **18** in the presence of weak bonds. (The intermolecular C-H \cdots π interactions is purple dot lines)

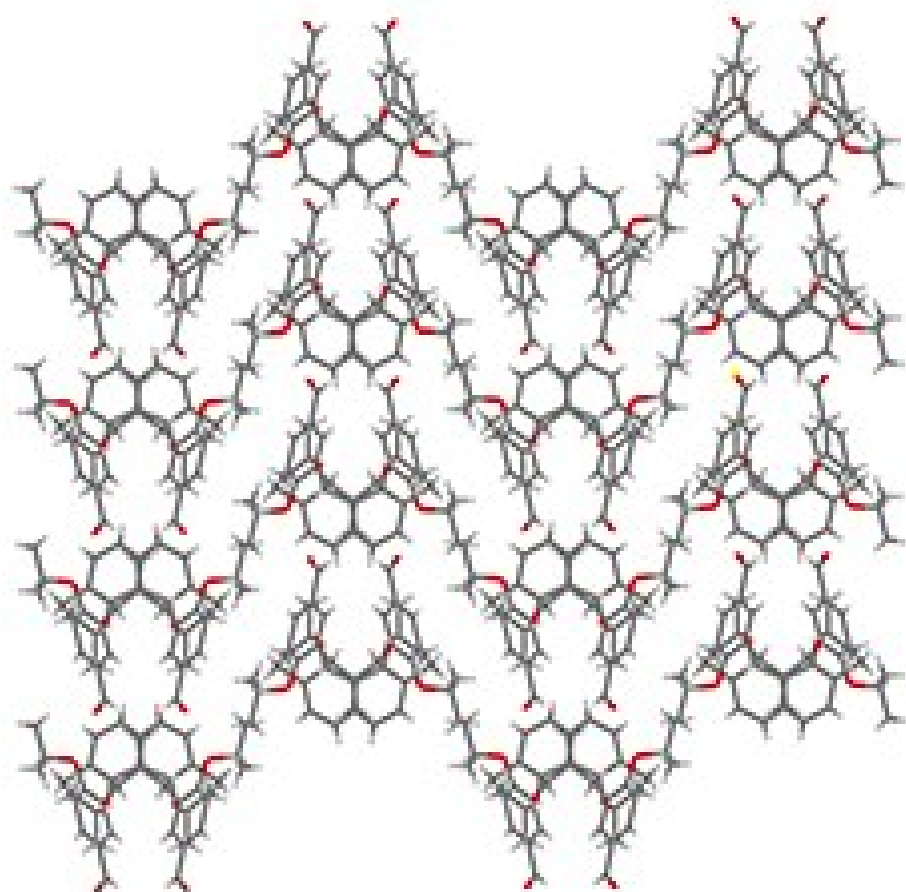


Figure S4 One-dimensional wave structure in compound **19**

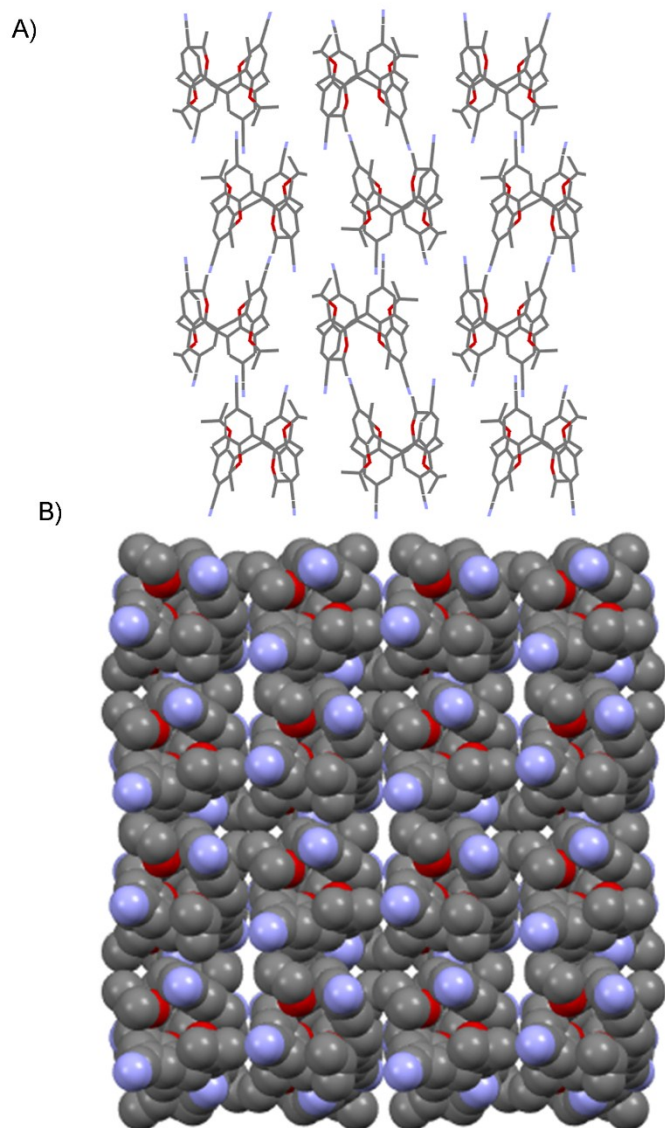


Figure S5 (A) Compounds **21** packs staggered in the crystal. (B) Space-filling representation of the extended structure in the compound **21** were formed by weak molecular forces.

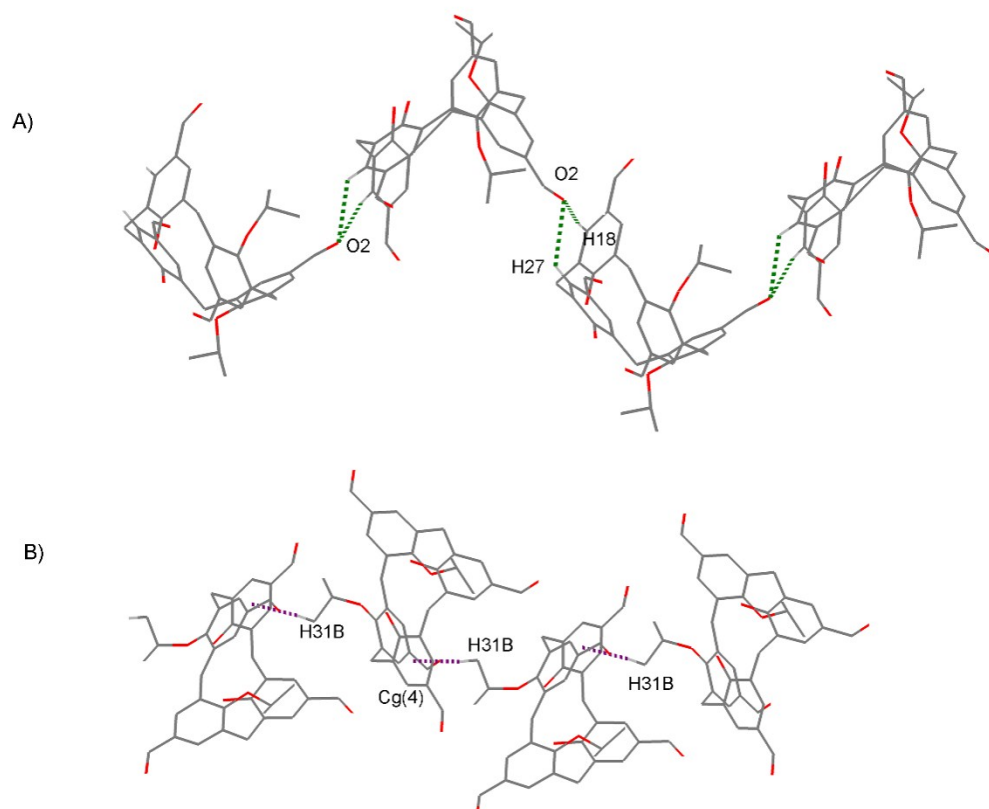


Figure S6 (A) One-dimensional wave structure of **22** was formed through C–H···O interactions. **(B)** The intermolecular C–H··· π interactions was observed in the single crystal structure of **22**. (The intermolecular C–H···O and C–H··· π interactions are green and violet dot lines)

Table S1 Dihedral angles of aromatic rings and reference molecular plane R of the seven compounds

Compound	Plane AR (°)	Plane BR (°)	Plane CR (°)	Plane DR (°)
16	125.88(3)	128.60(4)	125.54(8)	123.29(3)
17^a	93.82(2) (95.10(4))	75.80(3) (84.43(3))	95.68(6) (97.83(7))	78.91(5) (80.58(9))
18^b	88.05(2) ^a /88.29(4) ^b /89.29(2) ^c	82.61(3) ^b		
19	71.75(5)	77.64(2)		
20	71.81(4)	72.21(5)	76.65(3)	73.75(3)
21	100.31(3)	106.18(6)	104.79(5)	97.12(3)
22	110.71(3)	109.05(4)	111.87(4)	138.33(6)

a. There are two types of molecules in compound **17**.

b. There are three types of molecules in compound **18**.

Table S2 Dihedral angles of the opposite aromatic rings of the seven compounds

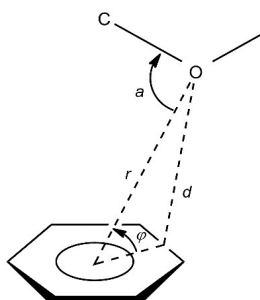
Compound	Plane AC (°)	Plane BD (°)
16	71.54(9)	71.80(6)
17^a	8.73(3) (14.61(5))	26.47(8) (13.09(3))
18^b	13.05(2) ^a /9.35(4) ^b /5.66(6) ^c	13.64(7) ^b
19	34.52(3)	29.81(5)
20	36.25(9)	29.44(9)
21	25.49(7)	23.30(4)
22	42.58(2)	29.73(7)

a There are two types of molecules in compound **17**.

b There are three types of molecules in compound **18**.

Table S3 $\pi \cdots \pi$ interactions for five compounds

Compound	Cg(I) \cdots Cg(J)	Symmetry	α	Cg \cdots Cg	Cg(J)Perp	Cg(J)Perp
16^a	Cg(1) \cdots Cg(4)	-1/4+Y,5/4-X,5/4-Z	2.25(7)	3.609(2)	-3.4969(14)	3.4632(16)
	Cg(2) \cdots Cg(3)	-1/4+Y,5/4-X,9/4-Z	2.93(4)	3.5850(19)	-3.3770(13)	3.3760(12)
17^b	Cg(1) \cdots Cg(9)	-1/2+X,1/2-Y,2-Z	11.94(9)	3.9560(18)	3.1353(12)	-3.5379(12)
	Cg(3) \cdots Cg(7)	1/2+X,1/2-Y,2-Z	10.60(6)	3.7971(17)	-3.2843(12)	3.5787(12)
	Cg(11) \cdots Cg(12)	1/2+X,Y,3/2-Z	0.29(8)	3.820(2)	3.5925(15)	3.5984(16)
a. 6-Membered Ring (Cg) Cg(1): C(1)- C(6), Cg(2): C(8)- C(13), Cg(3): C(15)- C(20) Cg(4): C(22)- C(27)						
b. 6-Membered Ring (Cg) Cg(1): C(45)- C(50), Cg(3): C(60)- C(65), Cg(7): C(1)- C(6) Cg(9): C(16)- C(21), Cg(11): C(32)- C(37), Cg(12): C(39)- C(44)						

Table S4 O \cdots π interactions in compounds **16**, **17** and **22**

Compound	C - O \cdots Cg	$r/\text{\AA}$		$d/\text{\AA}$	$\alpha(^{\circ})$	$\varphi(^{\circ})$
16^a	C(30)-O(5) \cdots Cg(2)	4.169(16)	C(13)	3.552(12)	60.89(7)	54.30(6)
	C(9)-O(2) \cdots Cg(3)	4.268(9)	C(15)-C(16)	3.666(7)	58.32(3)	52.82(8)
17^b	C(50)-O(9) \cdots Cg(9)	4.173(6)	C(20)	3.617(11)	66.53(4)	57.76(3)
	C(61)-O(13) \cdots Cg(7)	3.954(7)	C(1)	3.562(6)	68.30(4)	64.81(4)
22	C(32)-O(2) \cdots Cg(1)	3.771(15)	C(5)-C(6)	3.379(5)	89.06(5)	62.27(2)

a. 6-Membered Ring (Cg) Cg(2): C(8)- C(13), Cg(3): C(15)- C(20)

b. 6-Membered Ring (Cg) Cg(7): C(1)- C(6), Cg(9): C(16)- C(21)

c. 6-Membered Ring (Cg) Cg(1): C(1)- C(6)

Table S5 Hydrogen bonds of five compounds

Compound	D–H···A (Å)	H···A (Å)	D···A (Å)	<(D–H···A)(°)
16	O(1)–H(1A)···O(3) ^a	1.89(2)	2.669(4)	143(7)
	O(2)–H(2)···O(1) ^a	1.87(5)	2.672(4)	170(6)
	O(3)–H(3A)···O(4) ^a	1.88(3)	2.676(4)	163(8)
	O(4)–H(4)···O(2) ^a	1.85(5)	2.664(3)	176(1)
	C(16)–H(16)···O(5) ^b	2.54(3)	3.440(4)	164(3)
	C(18)–H(18)···O(6) ^b	2.60(2)	3.491(5)	166(5)
17	O(9)–H(9)···O(6) ^b	2.48(7)	3.070(3)	130(3)
	O(13)–H(13A)···O(2) ^b	2.35(6)	2.930(4)	129(6)
	C(5)–H(5)···O(10) ^b	2.58(6)	3.474(8)	162(5)
	C(5)–H(5)···O(10 ⁺) ^b	2.47(3)	3.331(8)	154(7)
	C(6)–H(6)···O(16) ^b	2.40(5)	3.282(4)	158(6)
	C(7)–H(7B)···O(16) ^b	2.60(2)	3.507(3)	156(3)
	C(18)–H(18)···O(14) ^b	2.39(4)	3.261(7)	155(5)
	C(42)–H(42)···O(9) ^b	2.52(3)	3.408(4)	161(8)
	C(58)–H(58)···O(6) ^b	2.54(9)	3.370(4)	148(4)
	C(67)–H(67A)···O(2) ^b	2.58(3)	3.424(4)	145(5)
	C(73)–H(73)···O(2) ^b	2.56(4)	3.352(4)	143(3)
	C(78)–H(78)···O(7) ^b	2.72(7)	3.558(4)	151(7)
18	C(1A)–H(1A)···O(1A) ^b	2.53(3)	3.430(9)	159(6)
	C(1B)–H(1B)···O(1C) ^b	2.56(2)	3.474(9)	162(9)
	C(1C)–H(1C)···O(1B) ^b	2.44(1)	3.313(8)	152(5)
	C(7D)–H(7DB)···O(1C) ^a	2.50(3)	3.443(8)	160(3)
	C(7B)–H(7BA)···O(1A) ^b	2.69(6)	3.531(7)	143(5)
	C(7D)–H(7DB)···O(1C) ^b	2.50(2)	3.637(2)	160(5)
	C(11B)–H(11E)···O(1B)	2.61(6)	3.452(2)	145(9)
	C(1D)–H(1D)···O(1D)	2.74(7)	3.267(8)	158(4)
21	C(2)–H(2)···N(3) ^b	2.69(5)	3.585(4)	163(7)
	C(13)–H(13)···N(1) ^b	2.69(3)	3.601(3)	166(2)
	C(26)–H(26)···N(1) ^b	2.62(5)	3.508(5)	160(5)
	C(37)–H(37)···N(3) ^b	2.83(5)	3.639(3)	146(4)
	C(39)–H(39)···N(2) ^b	2.70(8)	3.427(5)	158(4)
	C(15)–H(15)···N(4) ^b	2.58(4)	3.472(5)	160(7)
	C(24)–H(24)···N(4) ^b	2.50(5)	3.418(5)	170(6)
22	C(37)–O(6)···Cl(2) ^b		3.027(9)	145(6)
	C(35)–H(35B)···Cl(1) ^b	2.79(3)	3.693(5)	156(4)
	O(5)–H(5)···O(7) ^a	1.97(3)	2.756(5)	161(8)
	O(7)–H(7)···O(1) ^a	1.86(5)	2.657(4)	162(9)
	C(14)–H(14)···O(6) ^b	2.56(8)	3.416(7)	146(2)
	C(35)–H(35B)···O(5) ^b	2.79(6)	3.693(12)	156(3)
	C(39)–H(39A)···O(5) ^b	2.37(6)	3.212(18)	145(3)
	C(32)–H(32)···O(3) ^b	2.66(3)	3.570(2)	166(4)

C(27)–H(27)⋯O(2) ^b	2.72(8)	3.414(7)	133(2)
C(18)–H(18)⋯O(2) ^b	2.68(5)	3.595(8)	169(8)
C(28)–H(28)⋯O(6) ^b	2.62(5)	3.438(2)	142(3)

a represents intramolecular hydrogen bonding.

b represents intermolecular hydrogen bonding

Table S6 C–H⋯ π interactions for five compounds

Compound	Atoms involved C–H⋯Cg	Symmetry	H⋯Cg	C⋯Cg	<C–H⋯Cg
17^a	C(15)–H(15A)⋯Cg(10)	1/2–X, 1/2+Y, Z	3.14(9)	3.876(10)	134(3)
	C(71)–H(17)⋯Cg(8)	–X, 1–Y, 2–Z	3.41(7)	4.017(8)	125(5)
	C(52)–H(52A)⋯Cg(9)	1/2+X, Y, 5/2–Z	3.23(8)	3.80(6)	129(5)
18^b	C(11D)–H(11R)⋯Cg(2)	2–Y, X, –Z	2.91(6)	3.745(7)	144(7)
19^c	C(17)–H(17)⋯Cg(1)	1/2+X, 1/2+Y, Z	3.30(5)	4.07(11)	142(4)
20^d	C(7)–H(7A)⋯Cg(4)	1/2+X, 1/2–Y, –Z	3.15(3)	3.84(6)	133(3)
21^e	C(10)–H(10B)⋯Cg(4)	1/2–X, 1/2–Y, –Z	3.22(5)	4.03(9)	144(8)
22^f	C(21)–H(21B)⋯Cg(4)	1/2–X, 3/2–Y, –Z	2.82(6)	3.512(5)	129(3)
	C(31)–H(31B)⋯Cg(4)	1/2–X, 1/2+Y, 1/2–Z	2.85(8)	3.755(7)	158(2)

a. **6-Membered Ring (Cg)** Cg(8): C(8)–C(13), Cg(9): C(16)–C(21), Cg(10): C(23)–C(28),

b. **6-Membered Ring (Cg)** Cg(2): C(2C)–C(4C)

c. **6-Membered Ring (Cg)** Cg(1): C(1)–C(6)

d. **6-Membered Ring (Cg)** Cg(4): C(22)–C(27)

e. **6-Membered Ring (Cg)** Cg(4): C(34)–C(39)

f. **6-Membered Ring (Cg)** Cg(4): C(22)–C(27)