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Supporting Information

Assembly of calix[4]arene carboxylic acid derivatives by hydrogen bonding

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Author Contributions

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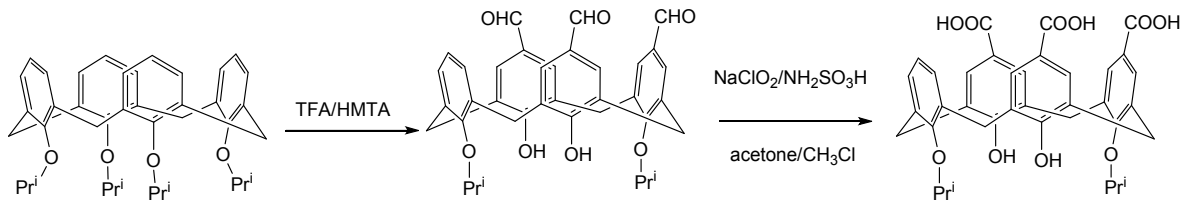
Experimental details



6

Preparation of **6**

Cone-tetra-O-isopropoxy-calix [4]arene(0.42g, 1 mmol), hexamethylenetetramine (3.84g, 20.19 mmol), and trifluoroacetic acid (20 mL) was stirred at 100 ° C for 24 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 by column chromatography to give *cone*-di-O-isopropoxy-*p*-tri-Formyl-calix [4]arene in a yield of 65%.

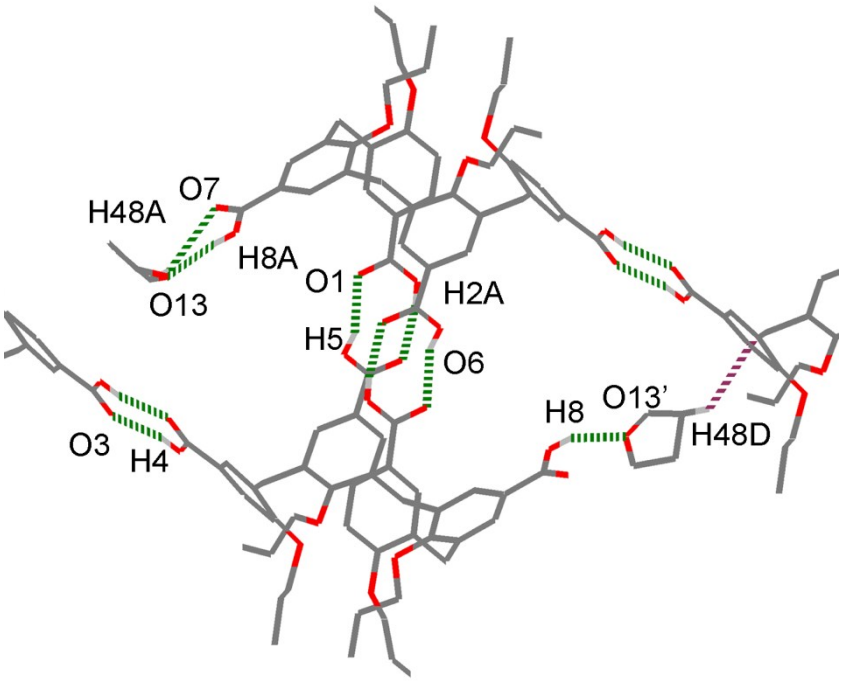
Cone-di-O-isopropoxy-*p*-tri-formyl-calix [4]arene (0.25g, 0.5 mmol) was dissolved in a mixed solvent of 15 mL of chloroform , 15 mL of acetone and 10 mL of DMSO. A freshly mixed solution of 5 mL of sulfamic acid (10 mmol) and sodium chlorite (10 mmol) was quickly added. The reaction was carried out at room temperature, and the reaction was stopped one day later. After washing and drying, almost quantitative compound **6** is obtained.

Synthesis of other compounds similar to compound **6**

Ref (a) R. T. Chester, R. De Marco, M. Mocerino, M. I. Ogden, B. W. Skelton and A. H. White, *Supramolecular Chemistry*, 2009, 21, 479-485.

(b) Yang W, Guo R, Wang W, et al. Tetrahedron Letters, 2012, 53(17): 2167-2170.

(A)



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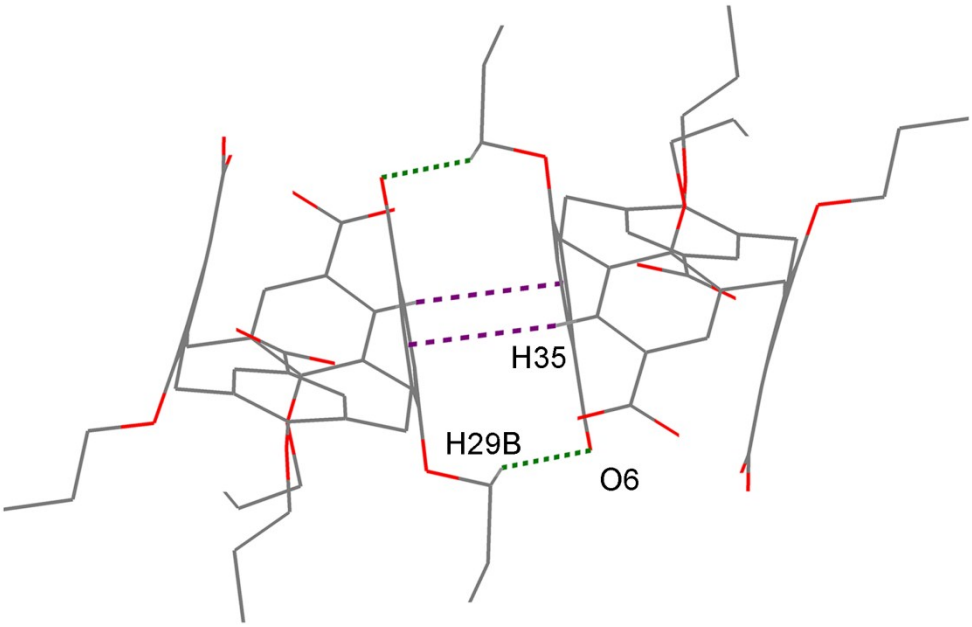
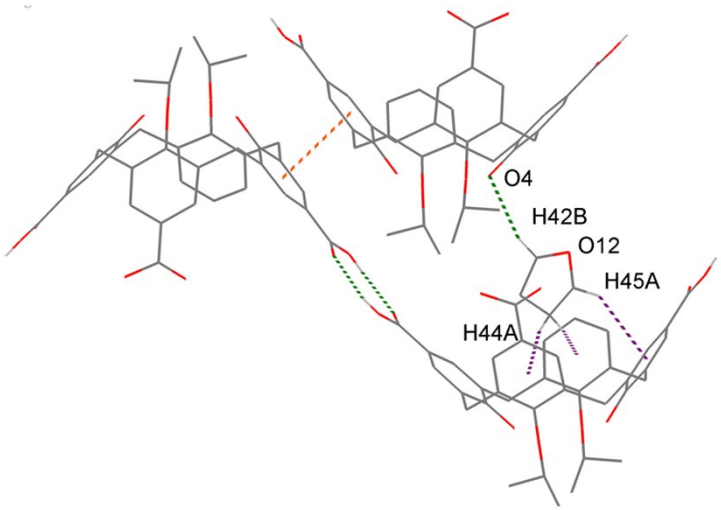


Figure S1 (A) The intermolecular O–H···O and C-H···π interactions in crystals of **1·THF**. (B) The intermolecular C–H···O and C-H···π interactions in the dimmer structure. Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity (The intermolecular O-H•••O, C-H•••O and C-H•••π interactions are green, green and violet).

A)



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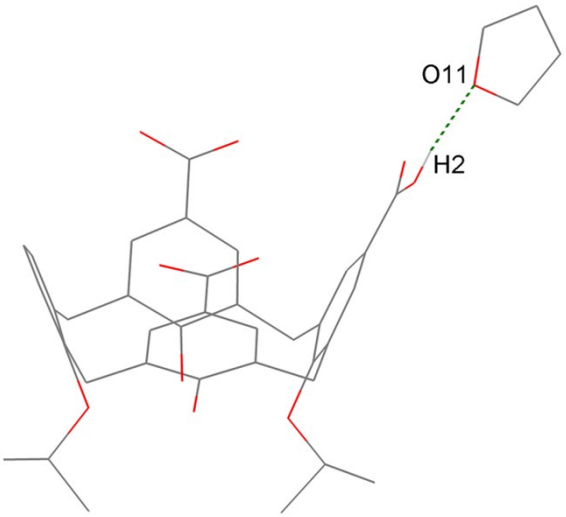

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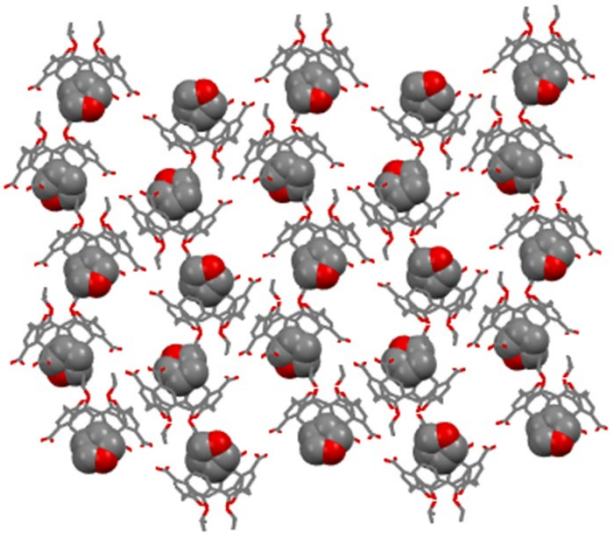
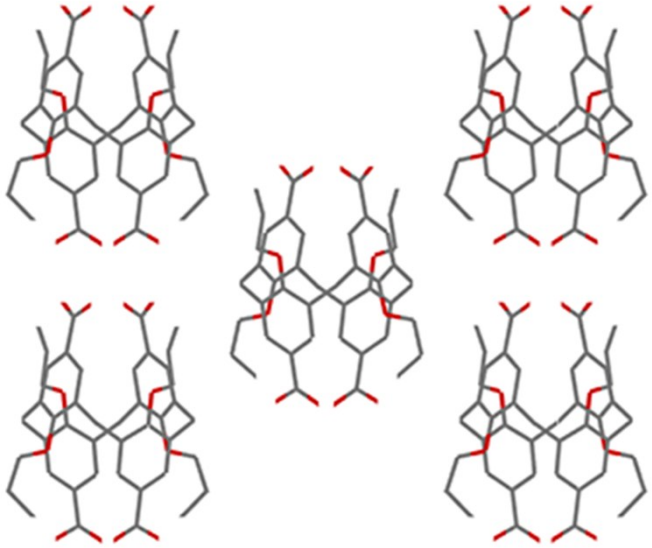


Figure S2

(A) The intermolecular C–H···O, C-H···π interactions and π···π in crystals of one-dimensional wave structures. (B) The O···HOCO hydrogen bond between THF [d] and compound **6. (C)** Tetrahydrofuran in the nanotube structure (CPK model). (The intermolecular O-H···O, C-H···π and π···π interactions are green, violet and red dot lines)

A)



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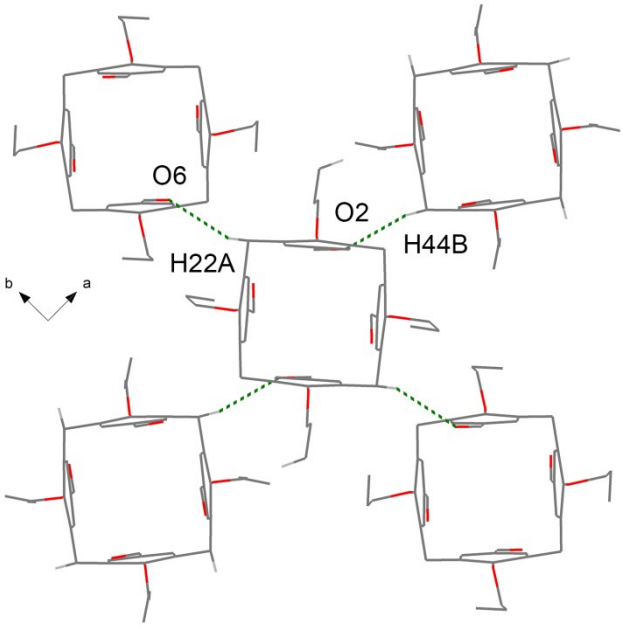


Figure S3 Pentameric structure is formed by the C–H···π interactions of **7.** (A) View along the crystallographic *a* axis, (B) View along the crystallographic c axis. (The intermolecular C-H···π interactions are green dot lines)

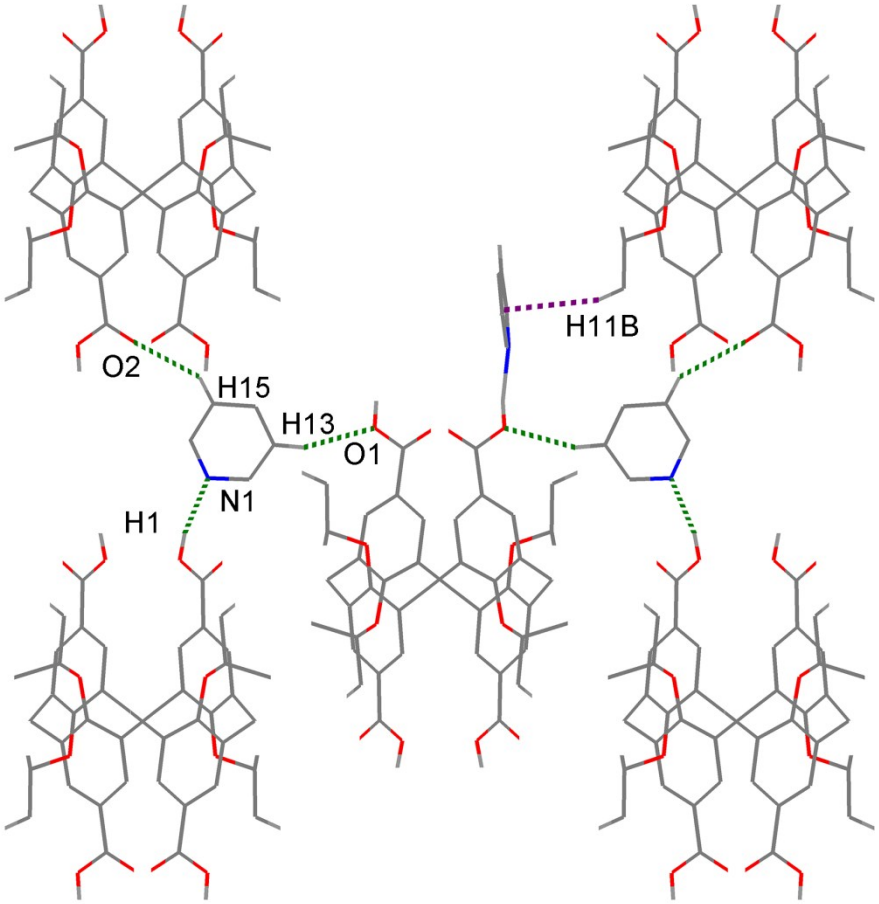


Figure S4 Pentameric structure is formed by the C–H···π interactions and O–H···N of **8·Py.** (The intermolecular C-H···O, O-H···N and C-H···π interactions are green, green and violet dot lines)

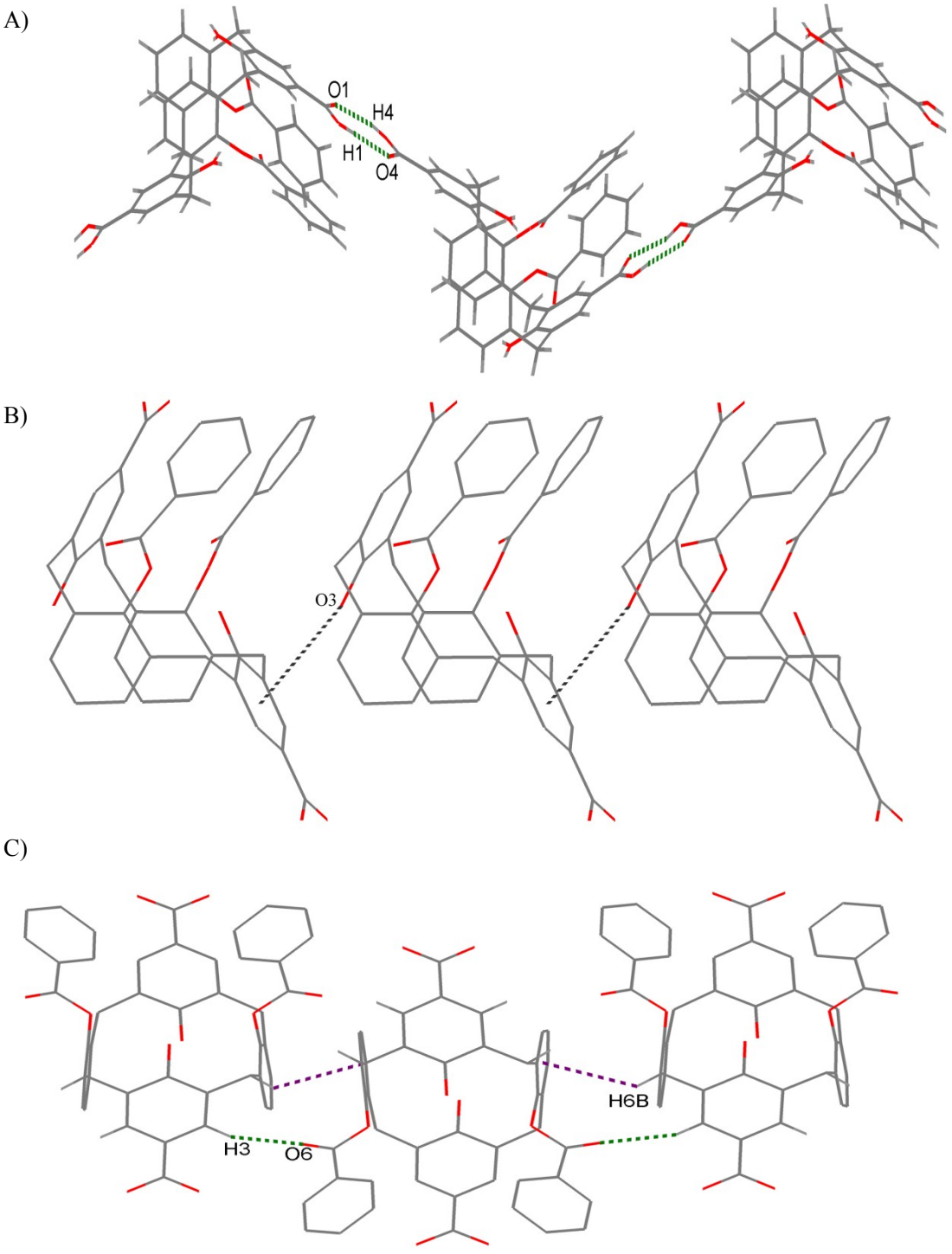


Figure S5

(A) One-dimensional wave structure formed by type **I** hydrogen bonds of carboxyl groups observed in the single crystal structure of **10.** (B) The intermolecular C- O···π interactions observed in the single crystal structure of **10**. (C) The intermolecular C–H···O, C-H···π interactions observed in the single crystal structure of **10**. (The intermolecular C–H···O, O-H···O, C- O···π and C-H···π interactions are green, green, gray and violet dot lines)

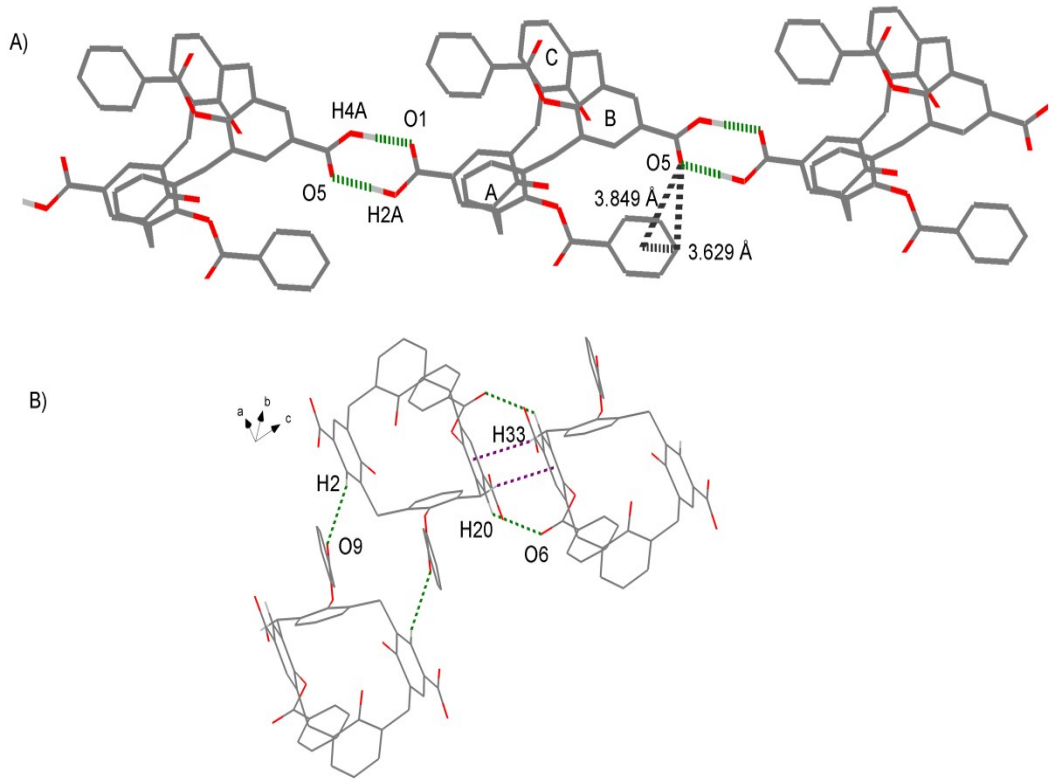


Figure S6

(A) One-dimensional wave structure is formed by type **I** hydrogen bonds of carboxyl groups observed in the single crystal structure of **11·MeOH.**

(B) C-H···O interactions and C-H···π interactions are observed in the single crystal structure of **11·MeOH.** (The intermolecular O-H···O, C-H···O C- O···π and C-H···π interactions are green, green, gray 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 (°)
1·THF	148.25	71.23	138.34	84.19
6·THF	112.44	130.39	114.50	133.87
6·THF·MeOH	112.19	128.53	116.34	130.82
7	77.65[a]/ 77.18[b]/ 76.69 [c] -77.25[c]			
3·Py	80.83	80.83	80.83	80.83
9·MeOH	83.71	83.25	83.71	83.25
10	94.88	88.41	94.88	144.58
11·MeOH	111.21	60.18	111.87	129.95

There are three types of molecules in compound 7.

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

Compound	Plane AC (°)	Plane BD (°)
1·THF	83.31	24.62
6·THF	46.94	84.82
6·THF·MeOH	48.53	79.35
7[A]	24.60[a]/ 25.51[b]/ 25.41 [c] -25.89[c]	
8·Py	18.26	
9·MeOH	12.59	13.51
10	9.81	52.98
11·MeOH	10.53	43.11

A. There are three types of molecules in compound 7.

Table S3 Hydrogen bonds of compound **1·THF**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(2) - H(2A)···O(6)	x,2-y,2-z	1.90	2.650(5)	152
O(4) - H(4)···O(3)	x,1-y,2-z	1.81	2.616(4))	166
O(5) - H(5)···O(1)	x,2-y,2-z	1.96	2.633(5)	139
O(8) - H(8)···O(13)	1-x,1/2+y,3/2-z	1.83	2.649(8)	172
O(8) - H(8)···O(13')	1-x,1/2+y,3/2-z	1.87	2.60(2)	147
C(11) - H(11B)···O(9)		2.40	2.866(5)	109
C(22) - H(22A)···O(11)		2.44	2.883(5)	108
C(29) - H(29B)···O(6)		2.44	3.481	147
C(33) - H(33B)···O(11)		2.46	2.875(5)	106
C(44) - H(44A)···O(9)		2.44	2.885(5)	108
C(48) - H(48A)···O(7)		2.60	3.245(4)	124

Table S4 Hydrogen bonds of compound **6·THF**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(2) - H(2)···O(11)	1+x,y,z	1.84	2.634(10)	163
O(4) - H(4)···O(1)	x,1-y,2-z	1.95	2.708(4)	154
O(5) - H(5A)···O(9)	1/2+x,1/2-y,1/2+z	1.84	2.631(5)	162
O(8) - H(8)···O(7)		1.98	2.708(4)	147
O(10) - H(10)···O(6)	1/2+x,1/2-y,-1/2+z	1.84	2.648(5)	169
C(5) - H(5)···O(2)		2.41	2.731(5)	100
C(11) – H11B)···O(1)		2.44	2.833(5)	104
C(19) - H(19A)···O(7)		2.53	2.934(5)	108
C(21)-H(21)···O(13)		2.60	3.447	161
C(29) - H(29A)···O(7)		2.46	2.846(5)	103
C(37) - H(37B)···O(1)		2.52	2.938(5)	106
C(37) - H(37B)···O(8)		2.41	2.752(5)	100
C(42) - H(42B)···O(4)	3/2-x,-1/2+y,1/2-z	2.48	3.413(13)	162

Table S5 Hydrogen bonds of compound **6·THF·MeOH**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(2) - H(2A)···O(13)	**1-x,1-y,1-z**	**1.81**	**2.604(8)**	**162**
O(4) - H(4)···O(1)		**1.95**	**2.686(3)**	**148**
O(5) - H(5A)···O(9)	**1/2+x,1/2-y,1/2+z**	**1.80**	**2.588(4)**	161
O(8) - H(8)···O(7)		**1.97**	**2.6704**	**144**
O(10) - H(10)···O(6)	**1/2+x,1/2-y,-1/2+z**	**1.82**	**2.634(4)**	**173**
O(14) - H(14A)···O(3)	**1-x,1-y,1-z**	**2.31**	**2.969(11)**	**125**
C(5) - H(5)···O(2)		**2.45**	**2.761(5)**	**100**
C(7) - H(7)···O(3)	**1-x,1-y,-z**	**2.59**	**3.325(5)**	**130**
C(11) – H(11B)···O(1)		**2.44**	**2.826(4)**	104
C(13) – H(13)···O(5)		**2.43**	**2.753(5)**	100
C(19) - H(19A)···O(4)		**2.42**	**2.757(4)**	100
C(19) - H(19A)···O(7)		**2.53**	**2. 9356)**	105
C(29) - H(29B)···O(7)		**2.46**	**2.8373**	103
C(37) - H(37A)···O(1)		**2.56**	**2.955(4)**	105
C(37) - H(37A)···O(8)		**2.41**	**2.7558**	100
C(44) - H(44B)···O(13)		**1.91**	**2.63(2)**	130
C(44) - H(44B)···O(3)	**1-x,1-y,1-z**	**2.37**	**3.02(3)**	125
C(44) - H(44C)···O(6)	**3/2-x,1/2+y,3/2-z**	**2.01**	**2.903(19)**	153

Table S6 Hydrogen bonds of compound **7**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(2) - H(2A)···O(1)	**y,x,1-z**	**1.71(3)**	**2.616(5)**	**168(5)**
O(4) - H(4)···O(8)	**x,y,-1+z**	**1.79(3)**	**2.631(4**	**175(7)**
O(7) - H(7)···O(5)	**2-x,1-y,1+z**	**1.86(3)**	**2.625(4)**	**156(5)**
O(10) - H(10)···O(11)	**y,1-x,1-z**	**1.76(3)**	**2.611(4)**	**172(5)**
C(4) -H(4A) ···O(1)		**2.42**	**2.72**	**100**

Table S7 Hydrogen bonds of compound **8·Py**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(1) - H(1)···N(1)	**1/2+x,y,3/2-z**	**1.898(19)**	**2.741(2)**	**165(3)**
C(13) – H(13)···O(1)	**1/4+y,5/4-x,5/4-z**	**2.44**	**2.686(3)**	**148**
C(15) – H(15)···O(2)	**1/4+y,5/4-x,1/4+z**	**2.43**	**3.225(3)**	**141**

Table S8 Hydrogen bonds of compound **9·MeOH**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(3) - H(3A)···O(2)	**7/4-x,-1/4-y,z**	**1.82**	**2.636(5)**	**172**
O(7) - H(7A)···O(4)		**1.81**	**2.731(9)**	**159**
C(5) – H(5A)···O(7)		**2.07**	**2.600**	**127**
C(5) – H(5)···O(2)		**2.47**	**2.780(6)**	**100**
C(8) – H(8A)···O(2)		**2.65**	**3.455**	**140**
C(15) – H(15)···O(5)		**2.36**	**2.725(7)**	**103**

Table S9 Hydrogen bonds of compound **10**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(1) - H(1)···O(4)	**1/2+x,y,3/2-z**	**1.83**	**2.626(14)**	**161**
O(2) - H(2)···O(5)		**2.17**	**2.988(9)**	**165**
O(4) - H(4)···O(1)	**1/2+x,y,3/2-z**	**1.81**	**2.626(14)**	**167**
C(3) – H(3)···O(6)	**1/2-x,-y,1/2+z**	**2.41**	**3.309(14)**	**160**
C(6) – H(6A)···O(5)		**2.37**	**2.830(14)**	**108**
C(12) – H(12A)···O(6)		**2.47**	**3.141(14)**	**125**

Table S10 Hydrogen bonds of compound **11·MeOH**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(2) - H(2A)···O(5)	**x,1+y,-1+z**	**1.62**	**2.638(4)**	**179**
O(3) - H(3)···O(10)		**1.88**	**2.707(4)**	**170**
O(4) - H(4A)···O(1)	**x,-1+y,1+z**	**1.56**	**2.589(4)**	**172**
O(10) - H(10A)···O(11)	**x,-1+y,z**	**1.87**	**2.693(5)**	**166**
O(11) - H(11A)···O(9)	**1+x,1+y,z**	**2.12**	**2.960(6)**	**145**
C(2) – H(2)···O(9)		**2.61**	**3.42**	**149**
C(8) – H(8A)···O(10)		**2.42**	**2.825(5)**	**104**
C(6) – H(6A)···O(5)		**2.52**	**2.942(4)**	**105**
C(12) – H(12A)···O(6)		**2.56**	**3.161(11)**	**119**
C(20) – H(20)···O(6)		**2.60**	**3.28**	**129**

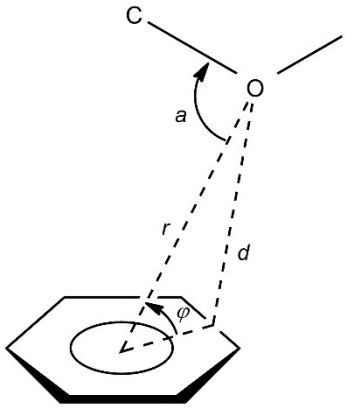
Table S11 π···π interactions for three compounds

Compound	Cg(I)···Cg(J)	Symmetry	α	Cg···Cg	Cg(I)Perp	Cg(J)Perp
6·THF	Cg(4)···Cg(4)	1-x,1-y,1-z	0	3.534(2)	3.5096(16)	3.5095(16)
6·THF·MeOH	Cg(4)···Cg(4)	2-X,1-Y,-Z	0	3.4720(19)	-3.4271(13)	-3.4271(13)
11· MeOH	Cg(2)···Cg(4)	x, y, -z	20	4.287(3)	3.1864(16)	-3.920(2)
	Cg(5)···Cg(4)	1+y,1-x-y ,-z	26	4.470(3)	2.9388(16)	4.121(2)

Table S12 C-H···π interactions for seven compounds

Compound	Atoms involved C--H···Cg	Symmetry	H···Cg	C···Cg	<C--H···Cg
1·THF	C(35) -H(35B)···Cg(3)	1-X, 2-Y, 2-Z	3.24	4.097	154
	C(48') -H(48D)···Cg(2)	1-X,1/2+Y,3/2-Z	2.71	3.47(3)	135
6·T HF	C(44) -H(44A)···Cg(1)	X,Y,Z	2.70	3.652	166
	C(44) -H(44B)···Cg(3)	X,Y,Z	2.88	3.74	149
	C(45) -H(45A)···Cg(4)	X,Y,Z	2.80	3.626(12)	143
6·THF·MeOH	C(42) -H(42F)···Cg(1)	3/2-X,1/2+Y,1/2-Z	2.88	3.65(2)	138
	C(39) -H(39B)···Cg(2)	X,Y,Z	3.06	3.87	141
7	C(28) -H(28B)···Cg(1)		3.143	3.695	110
	C(28) -H(28A)···Cg(1)		3.108	3.695	112
	C(29) -H(29A)···Cg(4)		3.253	4.170	157
	C(43) -H(43B)···Cg(4)		3.229	3.754	115
8·Py	C(16) -H(16)···Cg(18)	1/4+Y,7/4-X,7/4-Z	2.79	3.685(3)	158
	C(11) -H(11B)···Cg(5)	1.5-x, 1.5-y, 1.5-z	3.006	3.858	146
10	C(6) -H(6B)···Cg(2)	-x+1/2, -y, -z+1/2,	3.07	3.793	131
11·MeOH	C(30) -H(30A)···Cg(3)	X,-Y,1-Z	2.84	3.791(4)	161
	C(33) -H(33)···Cg(2)	1+X,Y,Z	2.81	3.504(5)	131

Table S13 O···π interactions in compounds **10** and **11**



Compound	C – O (C = O)···Cg	Symmetry	*r*/ Å	*d*/ Å		*α*(°)	*φ*(°)
10	C(14) -O(3)···Cg(1)	X,Y,-2+Z	3.471	C(5)	3.195	167	67.00º
11·MeOH	C(22) -O(5)···Cg(6)	X,Y,Z	3.596	C(19) - C(20)	3.849(4)	91.2(2)	60.56

Table S14 Related parameters of type **I** hydrogen bonds in seven compounds

Compound	The angle between carboxyl planes /°	The length of hydrogen bond / Å	The distance from the proximal carbon atom of the COOH groups / Å
1·THF	33.14	1.898, 1.960 (1.812)	3.639
6·THF	1.272	1.837, 1.841	-
6·THF·MeOH	14.71	1.798,1.819	-
7	-	1.712[a]/ 1.758[b]/ 1.785-1.864[c]	3.658[a]/ 3.598[b]/ 3.608-3.666[c]
8·Py	-	-	4.426
9·MeOH	10.66	1.822	4.460
10	3.15	1.810	-
11·MeOH	8.04	1.560，1.624	-