Supporting Information

'Honeycomb' nanotube assembly based on thiacalix[4]arene derivatives by weak interactions

Wei Wang[a], Weiping Yang[a,b], Rong Guo[a] and Shuling Gong[a,*]

[a] *College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, PR China*

[b] *Key Laboratory of Tobacco Flavor Basic Research, Zhengzhou Tobacco Research Institute of CNTC, No. 2, Fengyang Street, High-Tech Zone, 450001 Zhengzhou, China*

[*] *Corresponding Author: E-mail: gongsl@whu.edu.cn; Fax: +86 27 68754067; Tel: +86 27 68752701.*

Contents

Suppupporting figure

Suppupporting table

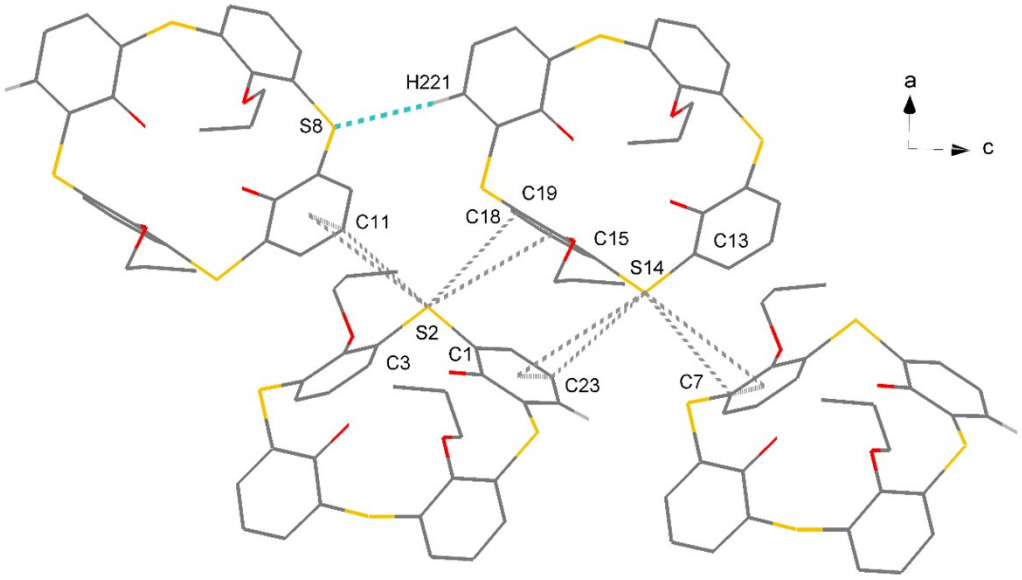


Figure S1 The intermolecular C–H···S and S···π interactions in crystals of **2**. C-H···S and S···π interactions are aqua and gray dot lines, respectively. Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity.

Atoms involved D-H···A	Symmetry	H···A	D···A	<(DHA)
C(22) - H(221)···S(8)	x, y, z+1	3.02(4)	3.795(3)	139(3)

Compound	Type	S···Cg	Symmetry	*r*/ Å	*d*/ Å		*α*/ *α*'(°)	*φ*(°)
2	III	S(2)···Cg(2)	1/3+x-y, 1/3+x, 2/3-z	4.194	C(11)	3.463	177.33//74.41	49.14
		S(2)···Cg(3)	1/3+x-y, 1/3+x, 5/3-z	4.104	C(18)-C(19)	3.650	72.62/157.94	59.95
	III	S(14)···Cg(1)	1/3+y, 2/3-x+y, 2/3-z	4.250	C(7)	3.727	75.15/156.22	58.92
		S(14)···Cg(4)	1/3+y, 2/3-x+y, 5/3-z	4.241	C(23)	3.546	172.37/69.70	51.49

The parameter values of *r*, *d*, α, α', and *φ* lie in the allowable range of S···π interactions.[S1]

Reference

S1 C. –Q. Wan, J. Han and C. W. M. Thomas, *New J. Chem*., 2009, **33**, 707–712

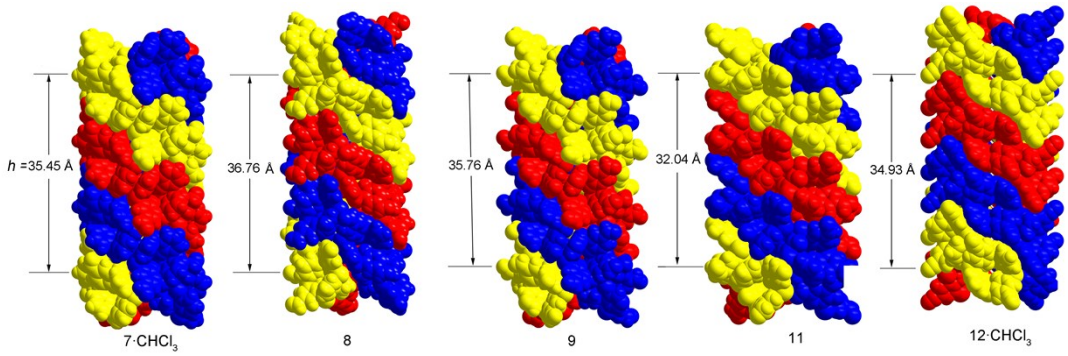


Figure S2

Space filling view of the triply helical nanotube motif are found in the crystal structure of five compounds. Side view showing helical nature of strands coloured yellow, red and blue. Other molecular components omitted for clarity.

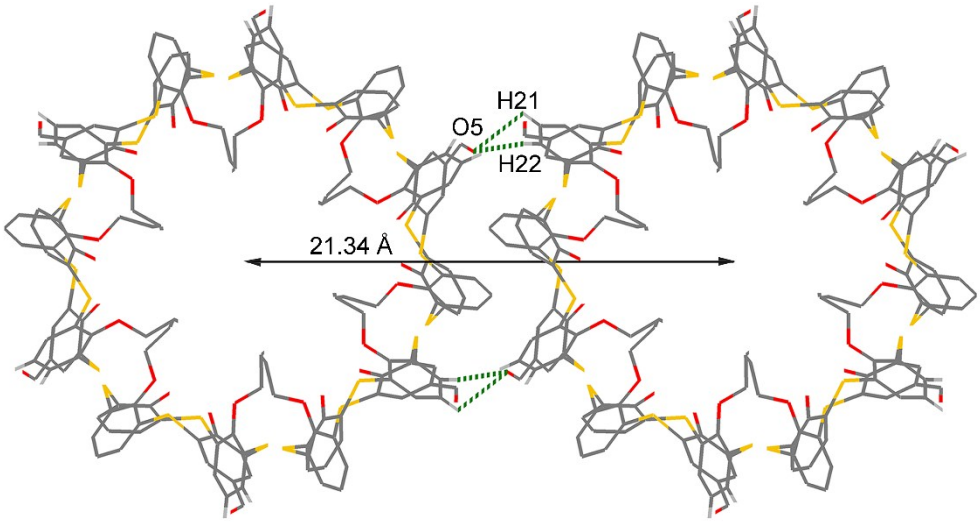


Figure S3 The C-H···O interactions are found in the packing between neighbouring hexameric discs of **7·CHCl$_3$**. The green dotted lines represent C-H···O interactions. Hydrogen atoms (except for those involved in hydrogen bonding) and $CHCl_3$ molecules not involved in omitted for clarity.

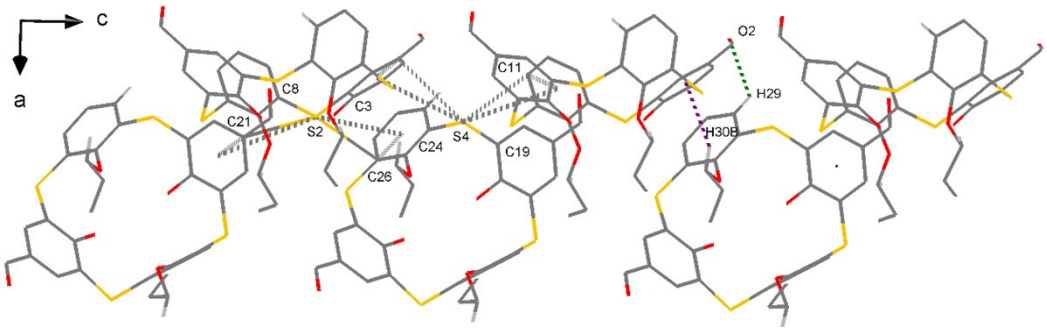


Figure S4 View along the crystallographic *b* axis, the intermolecular C-H···O, C-H···π and S···π interactions are green, violet and gray dot lines, respectively, observed in the triply helical nanotubes of **8**. Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity.

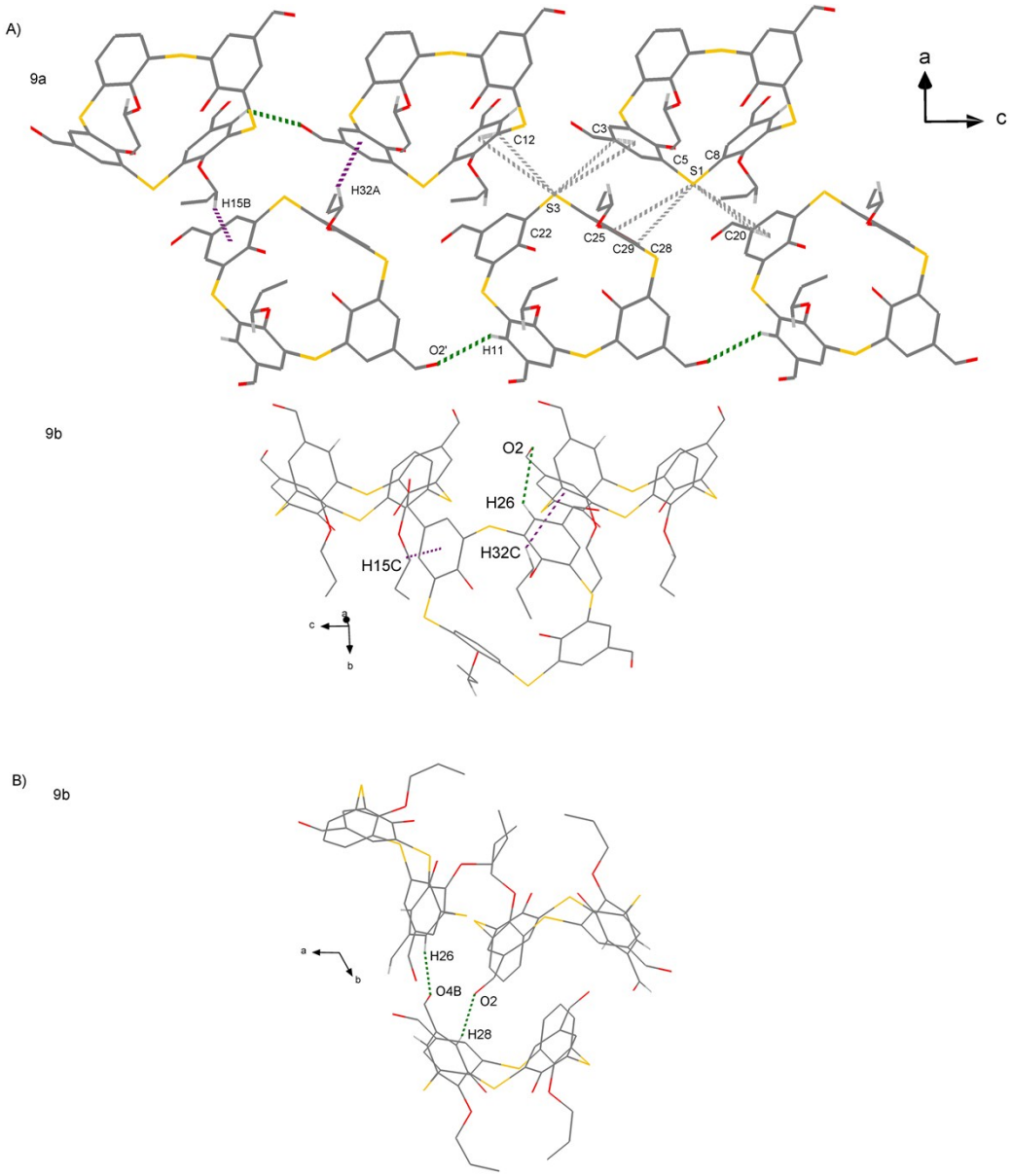


Figure S5

(A) View along the crystallographic *b* axis, the intermolecular C-H···O, C-H···π and S···π interactions are green, violet and gray dot lines, respectively, observed in the triply helical nanotubes of **9a** and **9b**.

(B) The C-H···O interactions observed in neighbouring nanotubes of **9b**. C-H···O interactions shown as dashed green lines.

Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity.

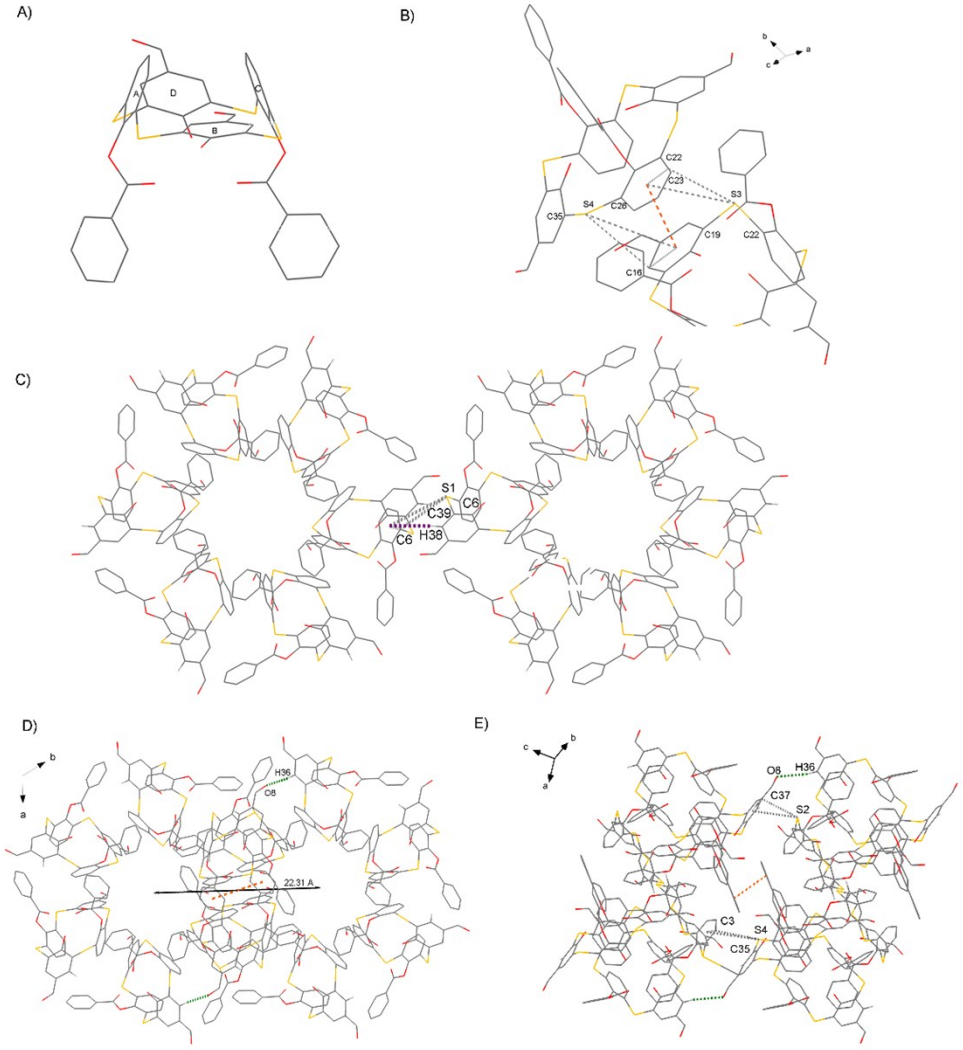


Figure S6

(A) Schematic of the structure of **10.**

(B) The S···π interactions and π···π interactions observed in hexameric disc.

(C) Non-covalent interactions the same layer neighbouring hexameric of **10·H_2O** observed in 2D network.

(D) The different layer neighbouring hexameric of **10·H_2O** observed in 3D network.

(E) Non-covalent interactions the adjacent layer neighbouring hexameric of **10·H_2O** observed in 3D network.

C-H···O interactions, C-H···π interactions, and S···π interactions are green, violet and gray dot lines, respectively. Hydrogen atoms (except for those involved in hydrogen bonding) and H_2O are omitted for clarity.

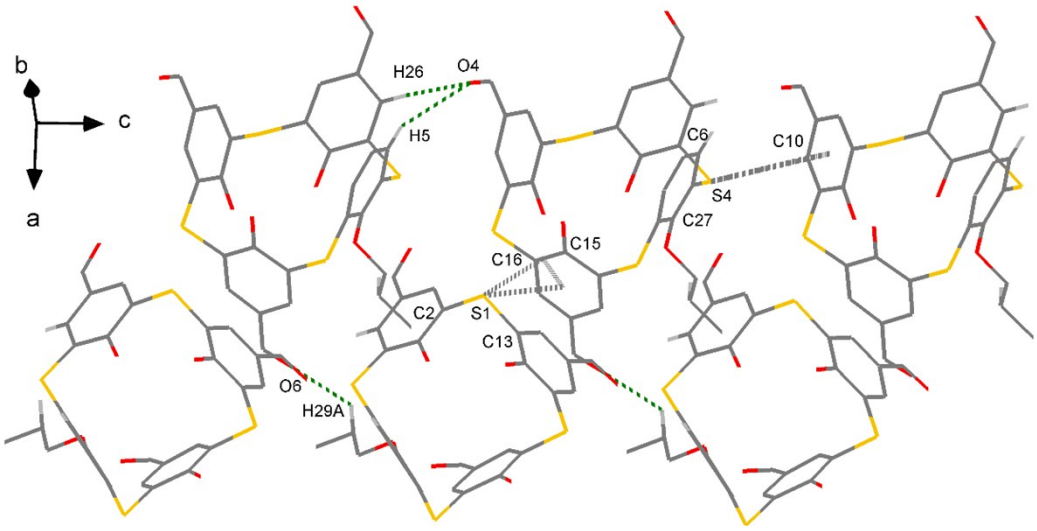


Figure S7 View along the crystallographic *b* axis, the intermolecular C-H···O and S···π interactions are green and gray dot lines, respectively, observed in the triply helical nanotubes of **11**. Hydrogen atoms (except for those involved in hydrogen bonding) are omitted for clarity

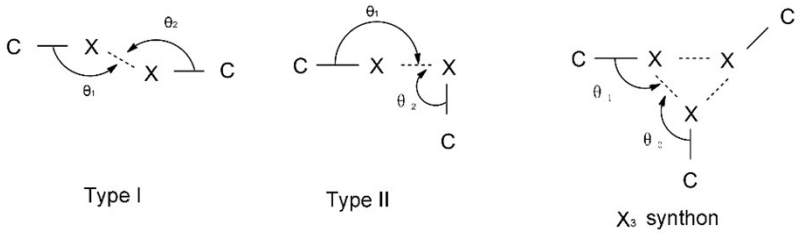


Figure S8 Schematic representations of Type I, Type II, and X_3 synthon halogen···halogen contacts. The angles: Type I (θ_1=θ_2=140–180º) and Type II (θ_1=150–180º, θ_2=90–120º). The X_3 synthon is a trigonal array of halogen atoms with attractive electrophile-nucleophile Type II contacts.

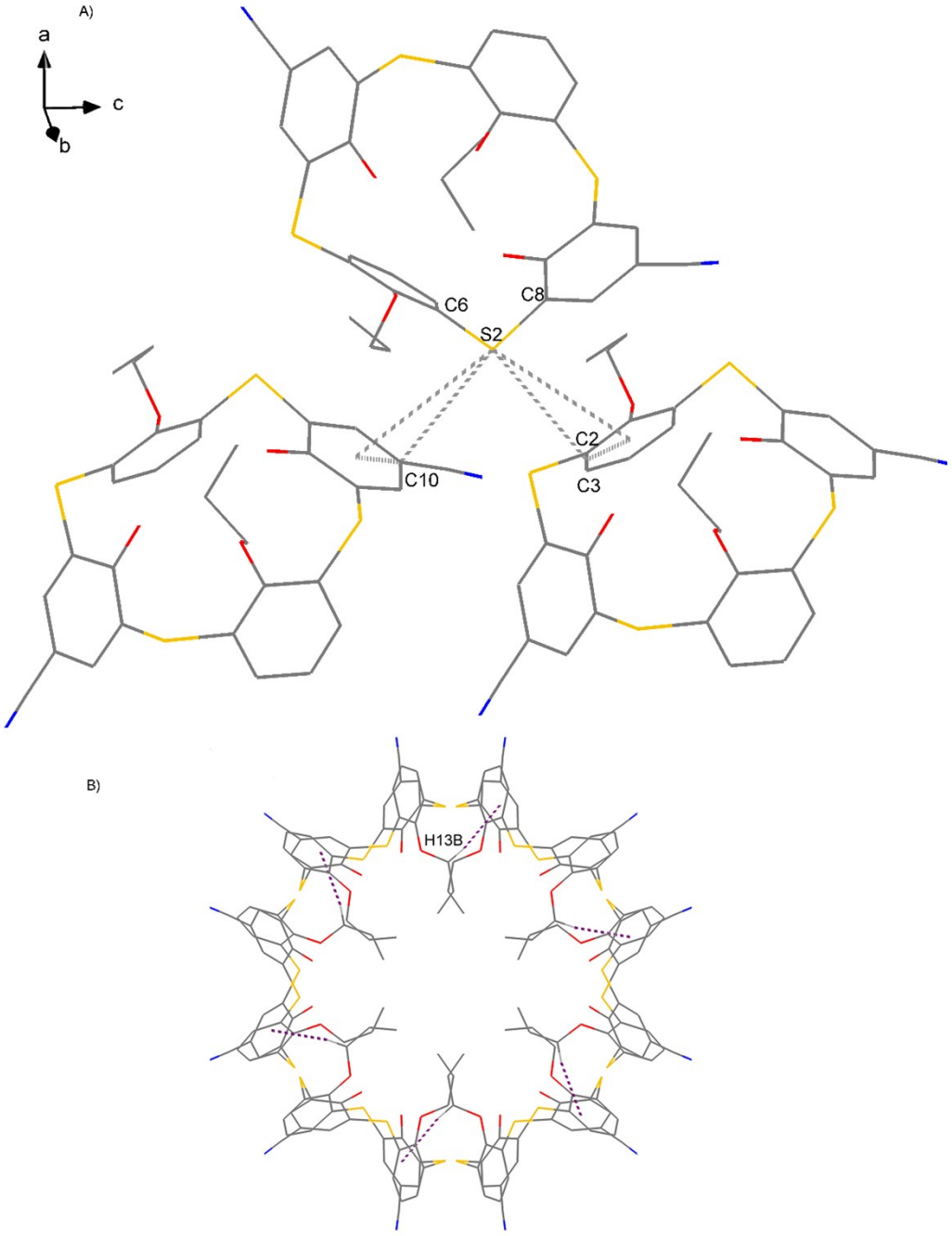
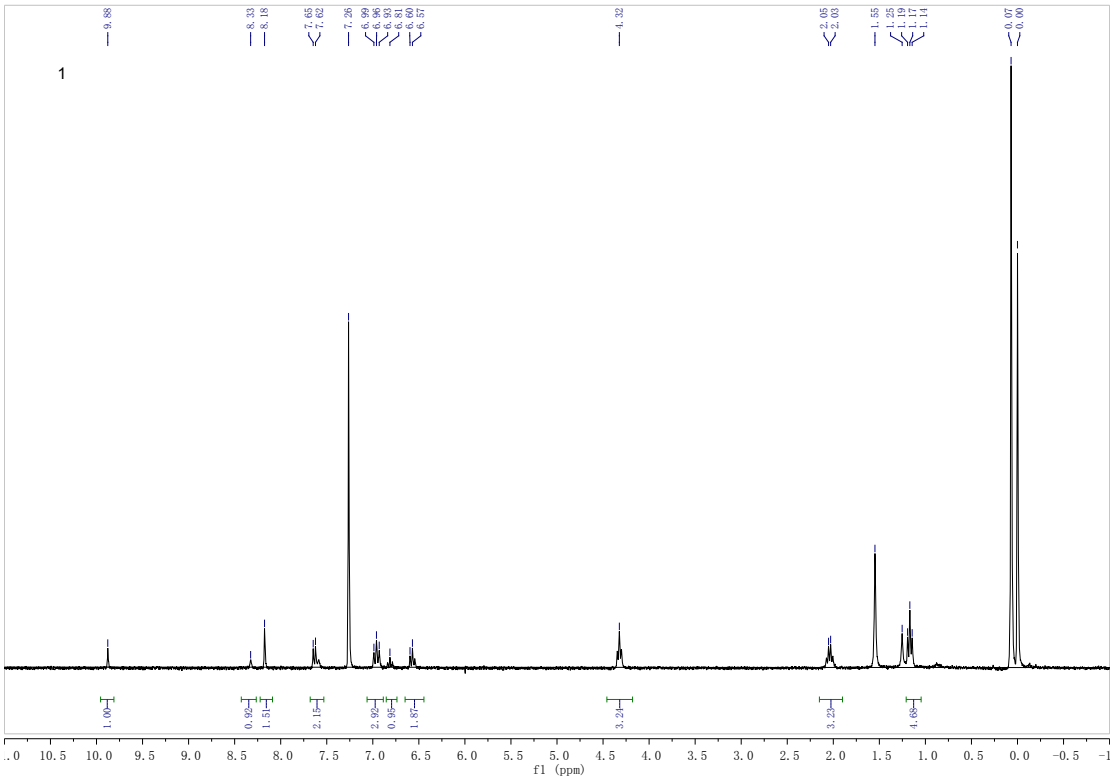


Figure S9

(A)The intermolecular S···π interactions are gray dot lines observed in the triply helical nanotubes of **12·CHCl$_3$**.

(B) Structure of **12·CHCl$_3$** showing hexameric discs through the C-H···π interactions. C-H···π interactions shown as dashed orange lines.

Figure S10 [1]HNMR and ESI – MS of compound **7**



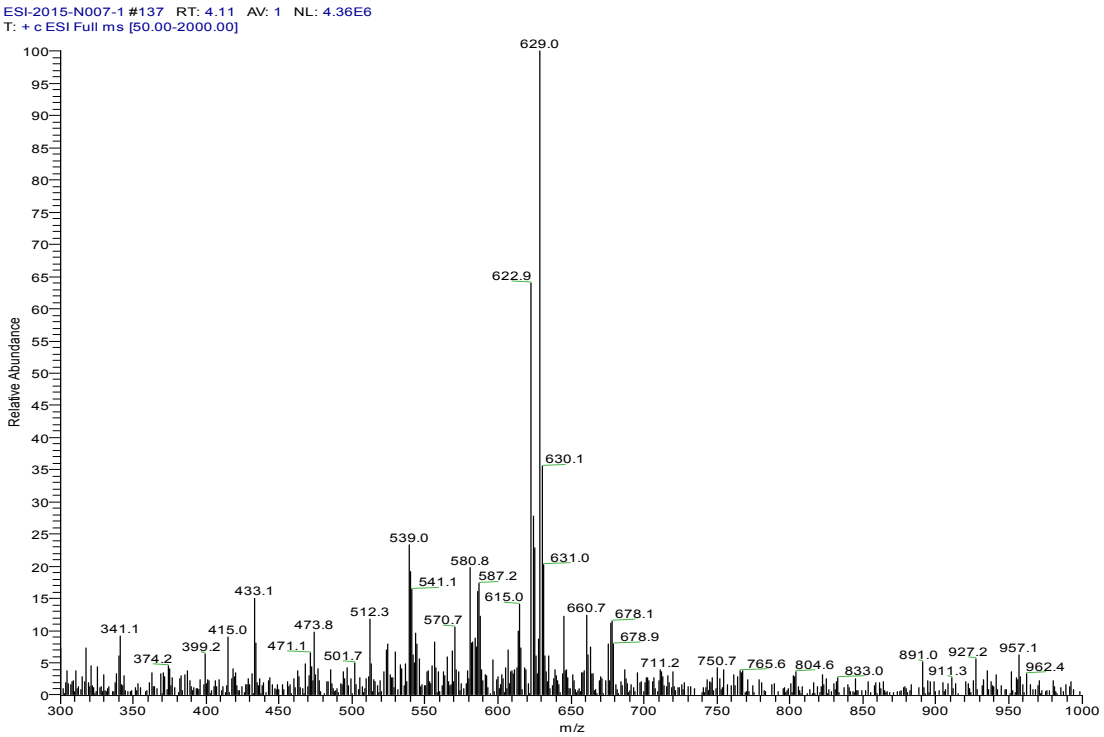
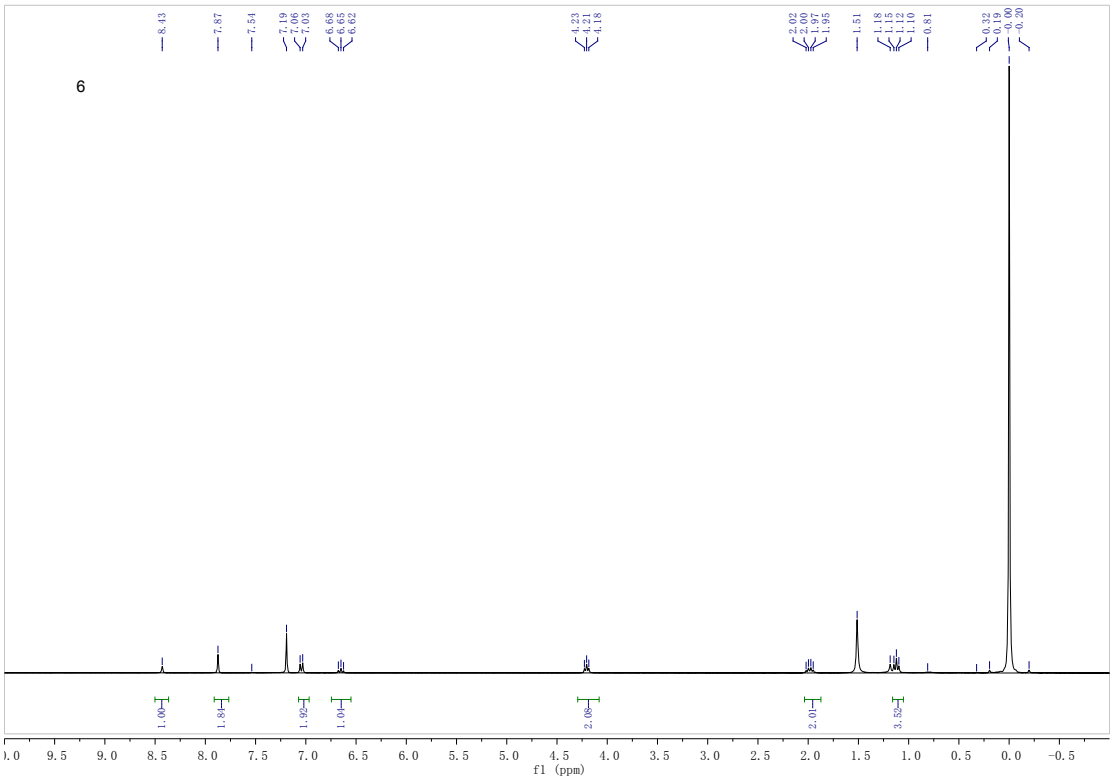


Figure S11 [1]HNMR and ESI – MS of compound **12**



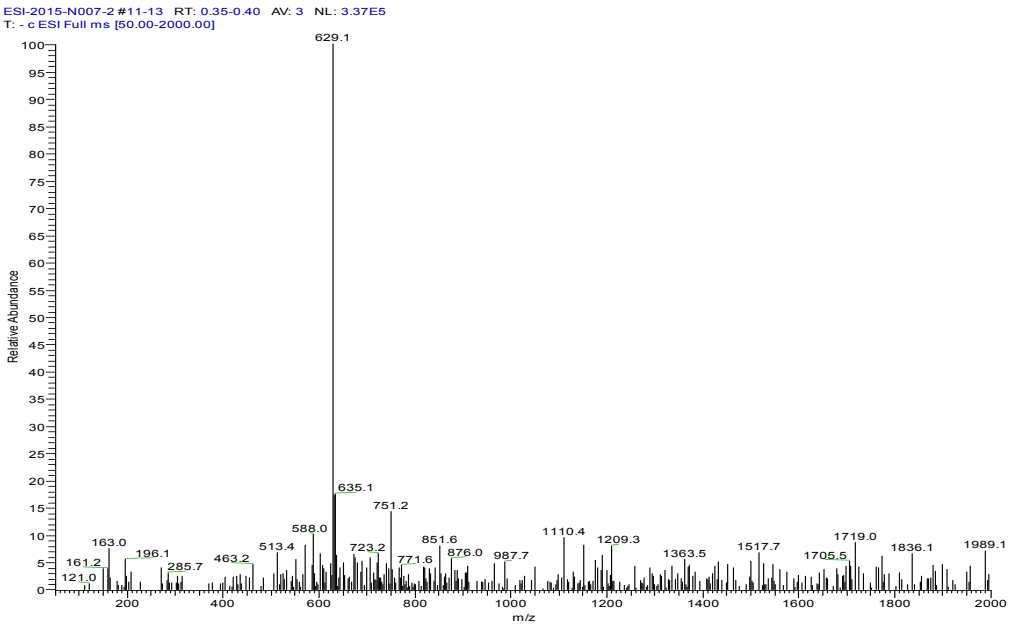


Table S1 Dihedral angles of aromatic rings and reference molecular plane R of the seven compounds

Compound	Plane AR (°)	Plane BR (°)	Plane CR (°)	Plane DR (°)
2	70.34	35.71	71.19	30.57
7·$CHCl_3$	71.09(68.14)	33.52(30.60)	73.51(76.51)	37.89(38.77)
8	77.15	32.69	65.91	44.37
9	75.11	43.26	69.95	38.63
10·H_2O	110.16	20.73	109.25	28.42
11	78.60(80.25)	89.92(89.43)	73.46(70.94)	43.25(35.64)
12·$CHCl_3$	68.73	43.97	68.73	43.97

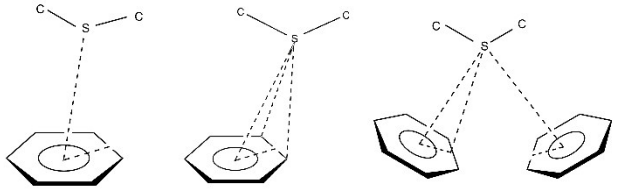
( ) represents the disordered molecular

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

Compound	Plane AC (°)	Plane BD (°)
2	38.48	113.72
7·$CHCl_3$	35.40	109.6(110.63)
8	36.96	102.97
9	34.97	98.10
10·H_2O	39.42	130.59
11	27.98(29.39)	46.84(52.80)
12·$CHCl_3$	42.54	92.06

( ) represents the disordered molecular

Table S3 The three types of S···π interactions in compounds **7-12** and their metric parameters



Compound	Type	S···Cg	Symmetry	r / Å	d / Å		α / α'(°)	φ (°)
7·CHCl$_3$	III	S(2)···Cg(1)	1/3+x-y, -1/3+x, 2/3-z	4.357	C(6)	3.820	74.72/154.99	58.52
		S(2)···Cg(4)	1/3+x-y, -1/3+x, 5/3-z	4.150	C(30)	3.599	168.48/71.26	57.52
	III	S(4)···Cg(2)	1/3+y, 2/3-x+y, 2/3-z	4.193	C(14)	3.536	76.30/177.34	53.13
		S(4)···Cg(3)	1/3+y, 2/3-x+y, 5/3-z	4.127	C(19) - C(20)	3.742	159.21/72.13	63.21
8	III	S(2)···Cg(3)	1+y, 1-x+y, 2-z	4.495	C(21)	3.701	165.26/61.41	47.79
		S(2)···Cg(4)	1+y, 1-x+y, 1-z	4.216	C(26)	3.675	77.09/163.53	58.16
	III	S(4)···Cg(1)	x-y, -1+x, 1-z	4.258	C(5)	3.658	75.23/170.75	55.75
		S(4)···Cg(2)	x-y, -1+x, 2-z	4.174	C(11)	3.572	163.49/67.04	55.17
9	III	S(1)···Cg(3)	1/3+y, 2/3-x+y, -1/3-z	4.152	C(20)	3.739	175.33/74.07	63.31
		S(1)···Cg(4)	1/3+y, 2/3-x+y, 2/3-z	4.149	C(28) - C(29)	3.684	69.63/159.33	59.29
	III	S(3)···Cg(1)	1/3+x-y, -1/3+x, 2/3-z	4.252	C(3)	3.645	167.27/67.43	55.43
		S(3)···Cg(2)	1/3+x-y, -1/3+x, -1/3-z	4.167	C(12)	3.696	74.92/160.11	60.88
10·H$_2$O	II	S(1)···Cg(1)	1-x, -y, -z	4.753	C(5)	3.775	118.0/83.91	38.51
	II	S(2)···Cg(6)	4/ 3-x+y, -2/3-x, -1/3+z	4.254	C(36) - C(37)	3.588	102.66/87.08	49.43
	II	S(3)···Cg(4)	1+y, 1-x+y, -z	4.082	C(22) - C(23)	3.661	62.1/134.74	61.71
	III	S(4)···Cg(1)	2/3-y, -2/3+x-y, -1/3+z	4.891	C(3)	3.884	167.86/92.13	37.31
		S(4)···Cg(3)	x-y, -1+x-y, -z	4.106	C(16)	3.664	58.79/135.44	62.44
11	II	S(1)···Cg(3)	y, 1-x+y, 1-z	3.979	C(15) - C(16)	3.551	164.08/75.55	60.77
	I	S(3)···Cg(1)	1+x-y, x, 2-z	3.620	C(5)	3.394	129.52/104.0	69.57
	II	S(4)···Cg(2)	x, y, 1+z	4.260	C(10)	3.376	111.79/124.14	42.87
12·CHCl$_3$	III	S(2)···Cg(1)	-x+y, y, 1/2+z	3.946	C(2)-C(3)	3.566	161.62/76.81	62.95
		S(2)···Cg(2)	y, -x+y, 2-z	4.215	C(10)	3.778	71.82/173.38	62.38

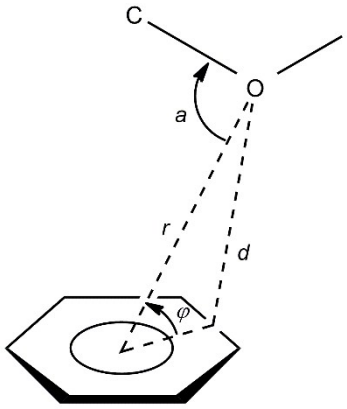
Table S4 π···π interactions for five compounds

Compound	Cg(I)···Cg(J)	Symmetry	α	Cg···Cg	Cg(I)_Perp	Cg(J)_Perp
7·CHCl$_3$	Cg(1)···Cg(1)	1-x,-y,1-z	0	4.050(3)	3.446(2)	3.447(2)
8	Cg(4)···Cg(4)	-x+5/3,-y+1/3,-z+4/3	0	4.047(2)	3.468(1)	3.468(1)
9	Cg(2)···Cg(2)	-x+1, -y, -z	0	4.708(3)	3.431(2)	3.431(2)
10·H$_2$O	Cg(3)···Cg(4)	1+y,1-x-y ,-z	0	3.725(3)	28.216(5)	3.513(2)
	Cg(5)···Cg(5)	5/3-x,1/3-y,1/3-z	0	4.801(5)	-3.323(3)	-3.323(3)
11	Cg(4)···Cg(4)	-x+4/3,-y+5/3,-z+5/3	0	4.300(4)	-3.509(2)	-3.509(2)

Table S5 C-H···π interactions for six compounds

Compound	Atoms involved C-H···Cg	Symmetry	H···Cg	C···Cg	<C-H···Cg
7·CHCl$_3$	C(3) - H(3)···Cg(2)	1-x, -y, 1-z	3.183	4.064(4)	154.8
	C(4) - H(4A)···Cg(3)	1-x, -y, 1-z	3.179	3.818(4)	126.1
	C(5) - H(5)···Cg(4)	1-x, -y, 1-z	3.123	4.007(1)	155.8
	C(7) - H(7A)···Cg(2)	1/3+y, 2/3-x+y, 2/3-z	2.77	3.520(7)	132.6
	C(23) - H(23A)···Cg(4)	1/3+x-y, -1/3+x, 5/3-z	2.93	3.790(10)	136.1
	C(23) - H(23A)···Cg(5)	1/3+x-y, -1/3+x, 5/3-z	2.93	3.43(3)	134.0
	C(13) - H(13)···Cg(1)	1/3+y, 2/3-x+y, 2/3-z	3,138	3.603(4)	112.0
8	C(30) - H(30)···Cg(1)	x-y, x-1, -z+1	2.66	3.438(4)	136
9	C(15') - H(15B)···Cg(3)	1/3+y, 2/3-x+y, -1/3-z	2.96	3.89(3)	161
	C(32') - H(32A) ···Cg(1)	1/3+x-y, -1/3+x, 2/3-z	2.92	3.77(5)	147
	C(15) - H(15C)···Cg(3)	1/3+y, 2/3-x+y, -1/3-z	2.90	3.64(2)	134
	C(32) - H(32C) ···Cg(1)	1/3+x-y, -1/3+x, 2/3-z	2.96	3.61(2)	126
10·H$_2$O	C(38) - H(38)···Cg(1)	1-x, -y, 1-z	3.113	4.041(5)	175.9
11	C(24) - H(24)···Cg(1)	-x+4/3, -y+5/3, -z+5/3	2.65	3.476(9)	148
	C(25) - H(25)···Cg(2)	-x+4/3, -y+5/3, -z+5/3	2.90	3.442(6)	118
	C(25') - H(25')···Cg(2)	-x+4/3, -y+5/3, -z+5/3	2.80	3.526(12)	136
12·CHCl$_3$	C(13) - H(13B)···Cg(2)	-x+ y, y, -1/2+z	2.84	3.682(6)	146.6

Table S6 O···π interactions in compounds **9, 10·H_2O** and **11**



Compound	C–O (C=O)···Cg	Symmetry	*r*/ Å	*d*/ Å		*α*(°)	*φ*(°)
9	C(14) - O(4)···Cg(2)	1-x, -y, -z	3.469(14)	C(12)	3.469	80.1	78.46
	C(14) - O(4)···Cg(3)	1-x, -y, -z	3.443(13)	C(23)	2.972	154.6	58.84
	C(14) - O(4)···Cg(4)	1-x, -y, -z	3.213(15)	C(25) - C(26)	3.147	102.0	76.13
	C(14) - O(4A)···Cg(1)	1-x, -y, -z	3.121(19)	C(6)	2.821	155.7	64.67
	C(14) - O(4A)···Cg(2)	1-x, -y, -z	3.558(19)	C(8)	3.441	75.40	73.90
	C(14) - O(4A)···Cg(4)	1-x, -y, -z	3.24(2)	C(28) - C(29)	3.175	100.15	76.28
10·H_2O	C(40) - O(8)···Cg(1)	1-x, -y, -z	3.832(4)	C(1) - C(2)	3.416	131.6	60.91
11	C(13) - O(3)···Cg(3)	y, 1-x+y,1-z	3.598(2)	C(17) - C(18)	3.197	84.55	60.93

Table S7 Hydrogen bonds of compound **7·CHCl$_3$**

Atoms involved D-H···A	Symmetry	H···A	D···A	<(DHA)
C(24) - H(24A)···Cl(1)		2.86(5)	3.76(3)	134(3)
C(25) - H(25B)···Cl(2)		2.99(9)	4.053(9)	167(6)
C(7) - H(7B)···S(1)		3.02(5)	3.520(5)	112(3)
C(31) - H(31)···S(1)	x, y, 1+z	2.97(5)	3.757(5)	141(4)
C(31') - H(31)···S(1)	x, y, 1+z	2.97(5)	3.757(5)	119(3)
C(23) - H(23A)···S(2)		3.03(5)	3.572(6)	116(3)
C(7) - H(7B)···S(2)	y+1/3, -x+y+2/3, -z+2/3	3.02(6)	3.890(4)	146(4)
C(23) - H(23B)···S(3)		2.83(10)	3.569(7)	140(7)
C(23) - H(23B)···S(3')		2.18(11)	2.92(4)	138(7)
C(20) - H(20)···O(5)	x, y, 1+z	2.64(7)	3.263(6)	127(5)
C(21) - H(21)···O(5)	4/3-x+y, 2/3-x, 2/3+z	2.47(5)	3.128(5)	121(4)
C(22) - H(22)···O(5)	4/3-x+y, 2/3-x, 2/3+z	2.60(4)	3.046(5)	106(3)
O(2) - H(2)···S(1)		2.68(8)	3.077(3)	114(6)
O(4) - H(4)···S(3)		2.43(13)	3.071(6)	114(8)
O(4) - H(4)···S(3')		1.96(14)	2.794(10)	127(9)
O(4') - H(4)···S(3)		2.43(13)	3.38(13)	140(13)
O(4') - H(4)···S(3')		1.96(14)	3.01(11)	151(13)
O(2) - H(2)···O(1)		2.01(10)	2.758(4)	167(8)
O(4) - H(4)···O(3)		1.81(14)	2.834(10)	147(10)
O(4') - H(4)···O(3)		1.81(14)	2.67(4)	128(11)

Table S8 Hydrogen bonds of compound **8**

Atoms involved D-H···A	Symmetry	H···A	D···A	<(DHA)
C(30) - H(30B)···S(2)	x-y, x-1, -z+1	3.05(3)	3.845(4)	138.8(6)
C(30) - H(30A)···S(4)		2.95(1)	3.453(4)	112.5(3)
C(12) - H(12)···O(2)	4/3-y, x-y-1/3, z+2/3	2.59(3)	3.388(4)	141.4(1)
C(13) - H(13)···O(2)	-x+y+5/3, -x+4/3, z+1/3	2.46(6)	3,.266(4)	142.5(2)
C(29) - H(29)···O(2)	x-y, x-1, -z+1	2.87(1)	3.269(4)	106.4(2)
C(6) - H(6)···O(5)	-x+5/3, -y+1/3, -z+4/3	2.52(2)	3.399(4)	154.3(2)
C(7) - H(7)···O(5)	-x+5/3, -y+1/3, -z+4/3	2.58(3)	3.444(5)	150.8(1)
C(11) - H(11)···O(5)	-x+5/3, -y+1/3, -z+7/3	2.39(3)	3.176(4)	139.4(2)
O(1) - H(1A)···S(2)		2.64(3)	3.058(2)	114(3)
O(1B) - H(1B)···S(4)		2.61(3)	3.098(2)	120(3)
O(1) - H(1A)···O(3)		2.01(2)	2.781(3)	162(4)
O(4) - H(4A)···S4		1.93(2)	2.707(3)	157(3)

Table S9 Hydrogen bonds of compound **9**

Atoms involved D-H···A	Symmetry	H···A	D···A	<(DHA)
C(15) - H(15C)···S(1)		2.71(13)	3.25(6)	119(8)
C(15') - H(15C)···S(1)		2.71(13)	3.58(4)	134(8)
C(2) - H(2)···S(2)	x, y, z+1	3.09(7)	3.909(5)	139(5)
C(15') - H(15D)···S(2)		3.03(7)	3.52(2)	117(5)
C(15) - H(15D)···S(3)	y+1/3, -x+y+2/3, -z-1/3	3.00(10)	4.05(5)	152(3)
C(15') - H(15D)···S(3)	y+1/3, -x+y+2/3, -z-1/3	3.00(10)	3.90(2)	162(5)
C(32) - H(32C)···S(3)		2.90(15)	3.51(2)	117(11)
C(32) - H(32D)···S(4)		3.01(10)	3.57(3)	112(8)
C(19) - H(19)···O(2)	-x+1, -y, -z	2.54(7)	3.421(9)	150 (4)
C(24) - H(24)···O(2)	-x+1, -y, -z	2.79(15)	3.464(13)	133(12)
C(26) - H(26)···O(2)	x-y+1/3, x-1/3, -z+2/3	2.99(4)	3.462(8)	108(3)
C(28) - H(28)···O(2)	-x+1, -y, -z+1	2.49(8)	3.302(9)	161(5)
C(11) - H(11) ···O(2')	x, y, z-1	2.61(7)	3.30(2)	130(5)
C(28) - H(28)···O(2')	-x+1, -y, -z+1	2.95(7)	3.53(4)	128(4)
C(21) - H(21)···O(4B)	-x+y+4/3, -x+2/3, z-1/3	2.92(6)	3.65(3)	134(3)
C(26) - H(26)···O(4B)	-x+y+4/3, -x+2/3, z-1/3	2.09(6)	3.11(2)	164(4)
C(26) - H(26)···O(6)	-y+2/3, x-y-2/3, z+1/3	2.74(5)	3.452(9)	126(3)
O(1) - H(1')···S(1)		2.50(17)	3.014(7)	119(7)
O(5) - H(5)···S(3)		2.6(2)	2.982(5)	125(12)
O(1) - H(1)···S(4)		2.42(11)	2.993(10)	117(7)
O(1) - H(1')···O(3)		2.24(16)	2.893(9)	151(7)
O(1) - H(1)···O(7)		2.04(13)	2.922(7)	148(8)
O(5) - H(5)···O(7)		2.3(2)	2.942(7)	149(12)

Table S10 Hydrogen bonds of compound **10·H_2O**

Atoms involved D-H···A	Symmetry	H···A	D···A	<(DHA)
C(11) - H(11)···O(1)	1-y, x-y, z	2.852(3)	3.693(8)	151.2(3)
C(36) - H(36)···O(8)	y+2/3, -x+y+1/3, -z+1/3	2.735(1)	3.657(6)	170.0(3)
O(7) - H(7)···S(1)		2.51(6)	3.034(3)	122.8(4)
O(3) - H(3)···S(3)		2.644(4)	3.080(3)	114.9(3)
O(7) - H(7)···O(2)		2.04(5)	2.725(4)	140.9(2)
O(3) - H(3)···O(6)		1.92(1)	2.663(4)	150.7(5)

Table S11 Hydrogen bonds of compound **11**

Atoms involved D-H···A	Symmetry	H···A	D···A	<(DHA)
C(28) - H(28B)···S(2)	x, y, z+1	3.06(5)	4.006(4)	165.4(6)
C(28') - H(28D)···S(2')	x, y, z+1	3.01(5)	3.885(6)	150.4(3)
C(10) - H(10)···S(4')	x, y, -1+z	3.04(5)	3.500(5)	112.0(3)
C(28') - H(28D)···S(4')		2.59(1)	3.203(6)	121.2(4)
C(3) - H(3A)···O(2)	-x+y+1/3, -x+5/3, z-1/3	2.53(1)	3.233(4)	143.8(2)
C(7) - H(7)···O(2)	-y+5/3, x-y+4/3, z+1/3	2.53(1)	3,133(4)	122.5(4)
C(12) - H(12)···O(2)	-x+y+1/3, -x+5/3, z-1/3	2.75(2)	3,644(4)	168.2(1)
C(14) - H(14)···O(2)	-y+5/3, x-y+4/3, z-2/3	2.90(1)	3,490(4)	122.5(3)
C(5) - H(5)···O(4)	x, y, z+1	2.82(1)	3,702(5)	159.2(3)
C(10) - H(10)···O(4)	-x+4/3, -y+5/3, -z+2/3	2.63(1)	3.310(4)	130.9(1)
C(26) - H(26)···O(4)	x, y, z+1	2.91(1)	3.778(6)	155.1(5)
C(26) - H(26)···O(5)	-x+4/3, -y+5/3, -z+5/3	2.73(1)	3.539(7)	145.8(3)
C(29) - H(29A)···O(6)	y, -x+y+1, -z+2	2.54(1)	3.174(13)	122.9(2)
C(17') - H(17')···O(6')	y, -x+y+1, -z+1	2.43	3.34($)	165.5(6)
O(3) - H(3)···S(1)		2.54(2)	3.030(3)	119.8(2)
O(5) - H(5A)···S(2)		2.57(1)	3.072(5)	120.7(4)
O(1) - H(1)···S(4)		2.52(1)	3.000(2)	118.7 (1)
O(1) - H(1)···S(4')		2.48(1)	3.041(4)	126.7 (2)
O(3) - H(3)···O(1)		2.36	2.919(3)	126.5(1)
O(5) - H(5A)···O(4)	-x+4/3, -y+5/3, -z+2/3	2.02	2.690(5)	138.2(5)
O(5') - H(5')···O(4)	-x+4/3, -y+5/3, -z+2/3	2.58	2.99(1)	112.9(5)
O(1) - H(1)···O(7)		2.19	2.985(6)	163.6(3)
O(1) - H(1)···O(7')		2.28	3.040(16)	155.0(1)

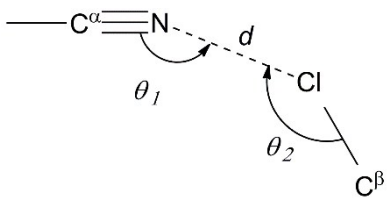
Table S12 Hydrogen bonds of compound **12·CHCl$_3$**

Atoms involved D - H···A	Symmetry	H···A	D···A	<(DHA)
O(2) - H(2)···S(2)		2.61	3.059(7)	114.8
O(2) - H(2)···O(1)		2.31	2.810(8)	119.6

Table S13 The Cl···Cl interactions of compound **12·CHCl$_3$**

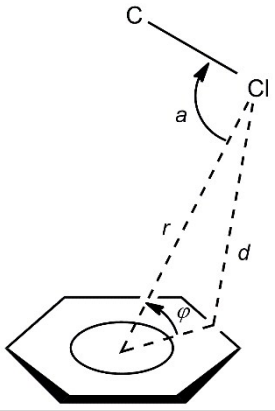
	Symmetry	d(Cl···Cl)/Å	d(C···Cl) /Å	$\theta_1 = \theta_2$(°)
C(17) - Cl(2)···Cl(2) - C(17)	1-x, 2-y, -z	2.921	4.492	151.43

Table S14 The cyano···Cl interactions of compound **12·CHCl$_3$**



	Symmetry	d(N···Cl)/Å	d(C$^{\alpha}$···Cl) /Å	d(C$^{\beta}$···N) /Å	θ_1(°)	θ_2(°)
C$^{\alpha}$ - N(1)···Cl(3) - C$^{\beta}$	x-y, x, 2-z	2.779	3.786	4.285	147.94	149.85

Table S15 The Cl···π interactions of compound **12·CHCl$_3$**



C - Cl···Cg	Symmetry	r/ Å	d/ Å		α(°)	φ(°)
C(17) - Cl (1)···Cg(1)	y, 1-x+y, 1-z	3.403(6)	C(1) - C(6)	3.470	104.52(12)	83.20
C(17) - Cl (1)···Cg(2)	x, 1+x-y, -1/2+z	3.928(3)	C(7)	3.448	106.87(10)	60.14

Table S16 Sums of the van der Waals radii (vdW) of C and phenyl ring with common lp-containing atoms (atom LP)[S2]

Atom LP	vdW radii/ **Å**	vdW(LP) + vdW(C^a)/ **Å**	vdW(LP) + vdW(Phenyl ring)/ Å
H	1.20	2..90	3.05
O	1.52	3.22	3.37
Cl	1.75	3.40	3.45
S	1.80	3.50	3.65
N	1,55		
C^a	1.70		
Phenyl ring[S3]	1.85		

Reference

S2 Bondi, *J. Phys. Chem.*, 1964, 68, 441–451.

S3 F. Malone, C. M. Murray, M. H. Charlton, R. Docherty and J. Lavery, *J. Chem. Soc.*, *Faraday Trans*, 1997, 93, 3429–3436.

Table S17 The partial site occupation factors of four compounds

Compound	Split atoms	Occupation factors
7·$CHCl_3$	C(26)-C(31), S(3), O(4)/C(26')-C(31'), S(3'), O(4')	0.859(16)/0.141(16)
8	C(14)-C(16)/C(14')-C(16')	0.826(8)/0.174(8)
9	C(15)-C(17)/C(15')-C(17')	0.57/0.43
	C(32)-C(34)/C(32')-C(34')	0.66/0.34
	C(14)/C(14B)	0.75/0.25
	O(4), O(4A)/O(4B),	0.375, 0.375/0.25
	O(2)/O(2')	0.69/0.31
	O(6)/O(6')	0.78/0.22
11	C(15)-C(30), S(2), S(3), S(4), O(5), O(6), O(7)/	0.707(3)/0.293(3)
	C(15')-C(30'), S(2'), S(3'), S(4'), O(5'), O(6'), O(7')	