Design and synthesis of Piezochromic materials exploring intermolecular charge transfer: chalconoids bound to *p*-sulfonatocalix[6]arene macrocycle

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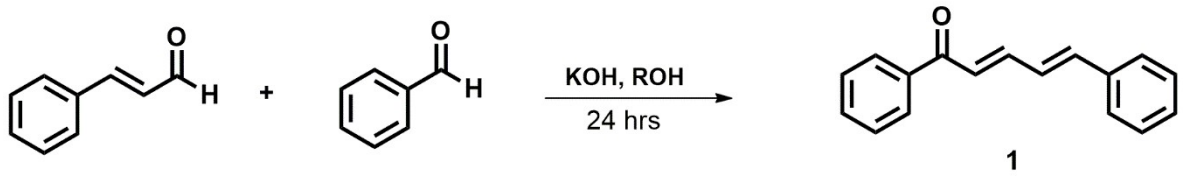
Synthesis of chalcone:

General Procedure:

All chalcones were synthesized according to the literature.[1, 2] Ketone (0.2g, 0.00078 mmol) was taken in equimolar mixture of methanol and ethanol under nitrogen condition. Further the corresponding aldehyde (0.153 g, 0.00078 mmol) was added into the reaction mixture. This was followed by further addition of KOH (0.52 g, 0.0093 mmol). The reaction mixture was stirred for 24 hrs at room temperature which was monitored using thin layer chromatography. Moreover, 10% HCl solution (10 mL) was added to the reaction mixture that yielded precipitate which further purified on silica gel chromatography. The products obtained in good yields were subsequently identified using the ^{1}H NMR, ^{13}C NMR, IR, HRMS spectroscopy experiments.

Chalcone 1 (C1):



1

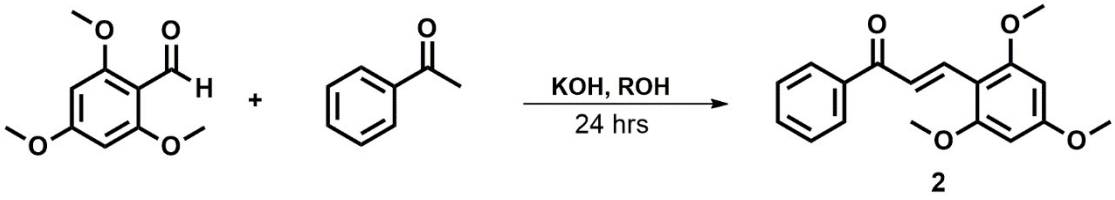
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 7.98 (m, 1H), 7.67 – 7.57 (m, 1H), 7.55 – 7.48 (m, 2H), 7.43 – 7.32 (m, 2H), 7.12 (d, *J* = 14.9 Hz, 1H), 7.07 – 7.03 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 190.53, 144.85, 141.92, 138.22, 136.15, 132.59, 129.23, 128.87, 128.59, 128.40, 127.31, 126.98, 125.49.

ν_{max} (cm^{-1}): 3010, 2920, 2854, 1650, 1579, 1451-1147, 989.

Mass: $C_{17}H_{15}O$ m/z = 235.1121 [M+H] calculated m/z = 235.1138

Chalcone 2 (C2):



2

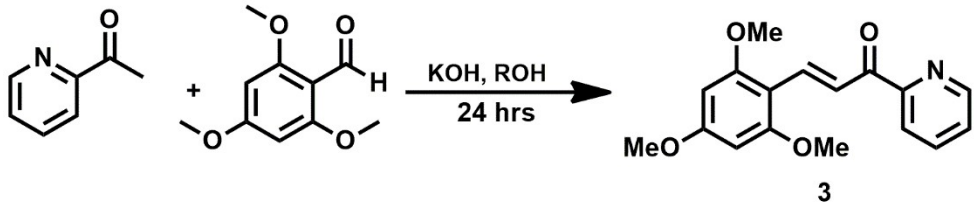
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 15.9 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.90 (d, *J* = 15.9 Hz, 1H), 7.59 – 7.45 (m, 4H), 6.15 (s, 2H), 3.89 (d, *J* = 19.7 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 192.18 (s), 163.18 (s), 161.76 (s), 139.36 (s), 136.08 (s), 131.98 (s), 128.40 (d, *J* = 7.5 Hz), 122.02 (s), 106.61 (s), 90.59 (s), 55.61 (d, *J* = 42.4 Hz).

ν_{max} (cm^{-1}): 3011, 2964-2837, 1644-1543, 1201-1110, 997.

Mass: $C_{18}H_{19}O_4$ m/z = 299.1286 [M+H] calculated m/z = 299.1278

Chalcone 3 (C3):



2-acetylpyridine (1.331 g, 11 mmol) and benzaldehyde (1.06 g, 1.02 mL, 10 mmol) were added to 100 mL distilled water cooled to 4-8 °C and shaken thoroughly forming a fine emulsion. 10 mL of 10 % of NaOH aqueous solution was then added and shaken again for 30 seconds and the reaction left at 4-8 °C. After 24 h the solid product was filtered, dried and recrystallised from EtOH to give the chalcone (2.02 g, 97%) as pale green crystals.[3, 4]

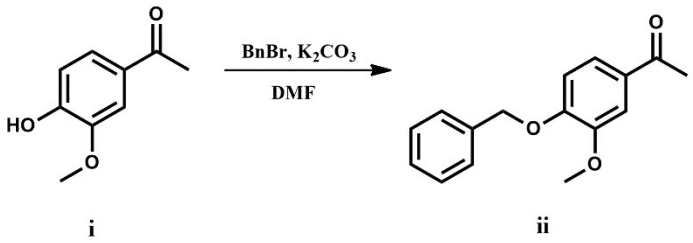
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.77 (ddd, *J* = 4.7, 1.6, 1.0 Hz, 1H), 8.41 – 8.35 (m, 1H), 8.20 (d, *J* = 16.2 Hz, 1H), 8.08 – 7.99 (m, 2H), 7.64 (ddd, *J* = 7.2, 4.7, 1.6 Hz, 1H), 6.34 (s, 2H), 3.90 (d, *J* = 19.5 Hz, 10H), 3.33 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ 190.22, 163.97, 162.05, 154.85, 149.55, 137.95, 135.66, 127.49, 122.72, 120.28, 105.92, 91.59, 56.63, 56.08.

ν_{max} (cm^{-1}): 2974-2934, 1654, 1563, 1332, 1058.

Mass: $C_{17}H_{18}NO_4$ m/z = 300.1229 [M+H] calculated m/z = 300.1238

Chalcone 4 (C4):

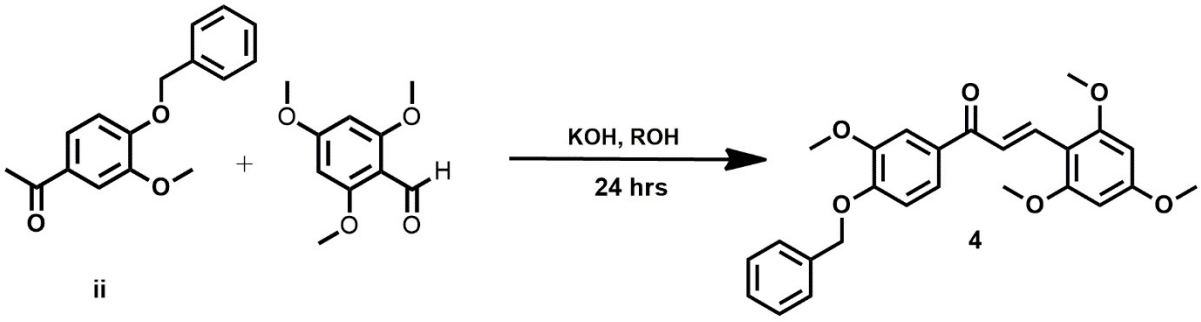


To a solution of acetophenone (1.25 g) in DMF (15 ml), K_2CO_3(1.09 g) was added. The resultant suspension was stirred for 15 minutes at room temperature. To this, 1ml benzyl bromide was added and allowed the reaction mixture to stir for 21 hours at room

temperature and reaction monitored through TLC. The reaction mixture was quenched by water and extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulphate and dried to give compound (ii) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.20 (m, 7H), 6.90 (dd, *J* = 11.6, 8.1 Hz, 1H), 5.39 – 5.10 (m, 2H), 4.14 – 3.79 (m, 3H), 2.73 – 2.46 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 196.75, 152.46, 149.55, 136.33, 130.79, 128.68, 128.11, 127.21, 123.07, 112.22, 110.64, 70.82, 56.06, 26.18.



Synthesized compound 4 as per general procedure.

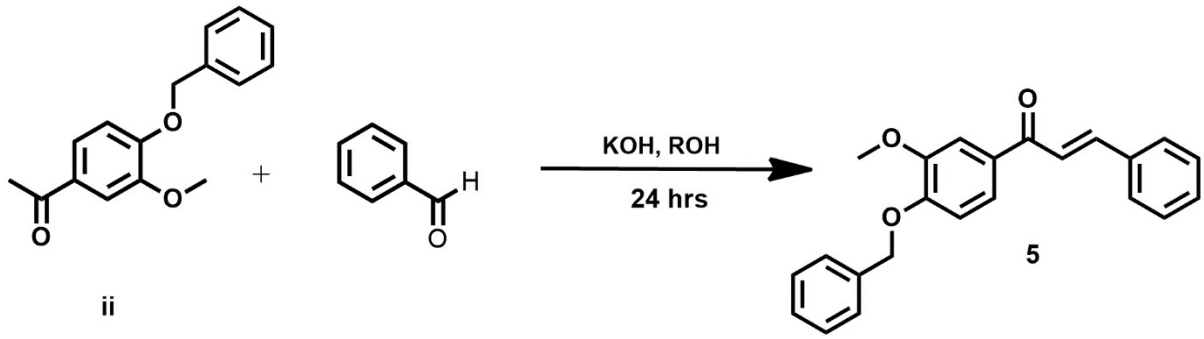
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 15.8 Hz, 1H), 7.90 (d, *J* = 15.8 Hz, 1H), 7.73 – 7.65 (m, 1H), 7.66 – 7.56 (m, 1H), 7.56 – 7.32 (m, 5H), 6.99 – 6.90 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 190.42, 162.97, 161.57, 151.85, 149.47, 136.49, 135.23, 128.64, 128.19, 127.21, 122.50, 122.18, 121.83, 112.35, 111.58, 90.63, 70.97, 56.07, 55.81, 55.38.

ν_{max} (cm^{-1}): 2361, 1568-1416, 1259-1159, 1027.

Mass: $C_{26}H_{26}O_6$ m/z = 435.1807 [M+H] calculated m/z = 434.1729

Chalcone 5 (C5):



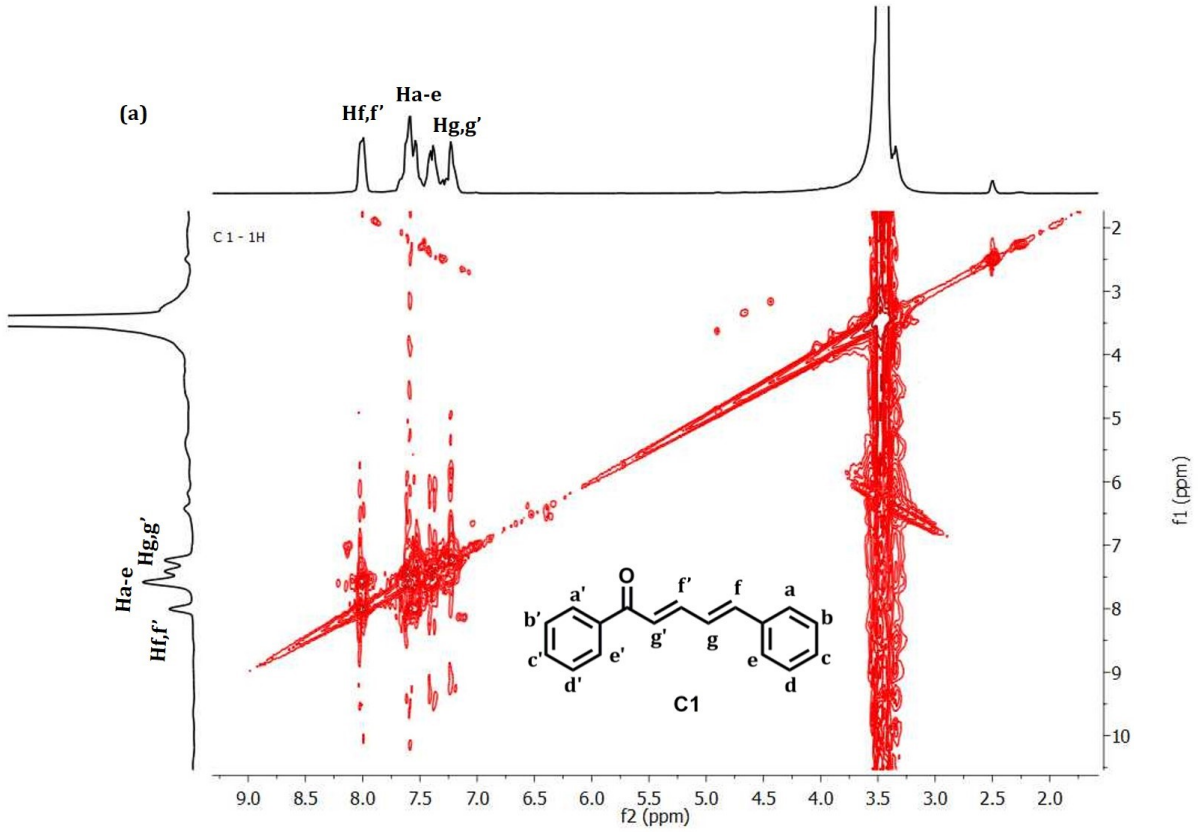
Synthesized compound 5 as per general procedure.

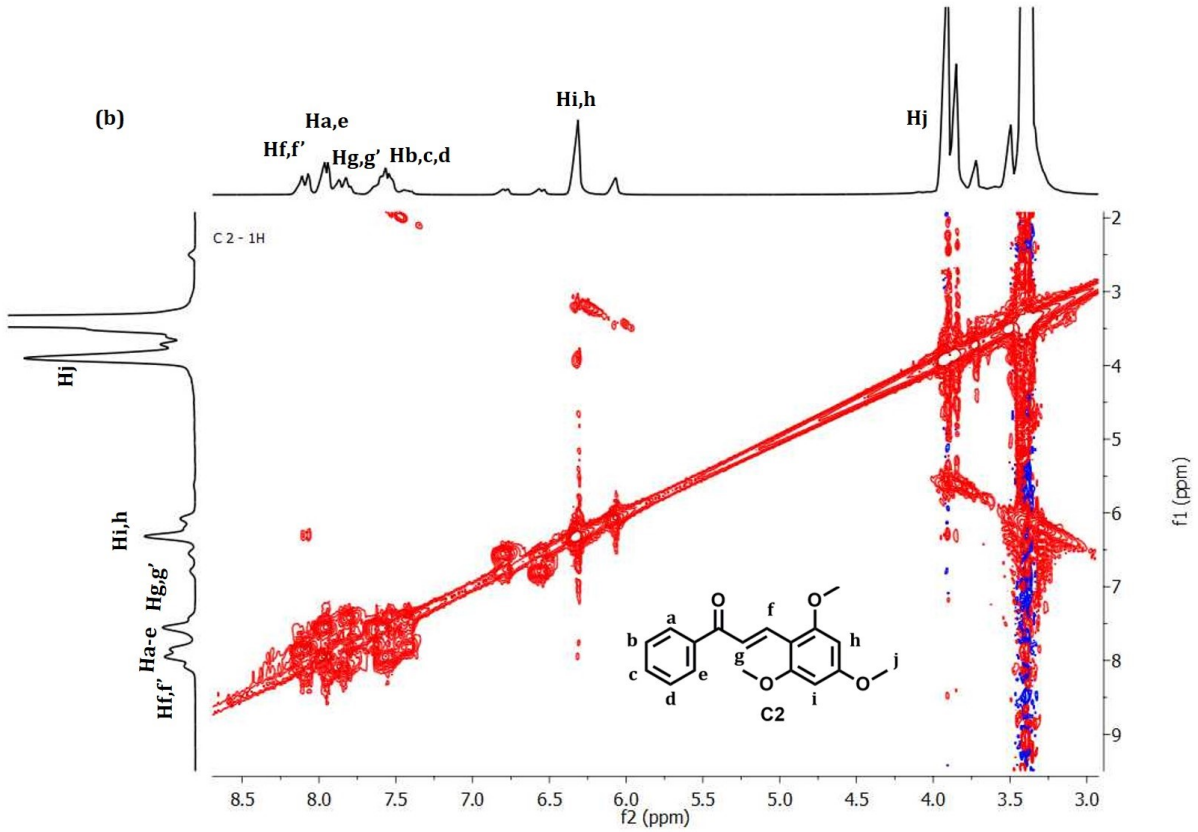
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 2.0 Hz, 1H), 7.57 (d, J = 2.0 Hz, 1H), 7.52 (dd, J = 8.4, 2.0 Hz, 1H), 7.48 – 7.32 (m, 5H), 6.92 (d, J = 8.4 Hz, 1H), 5.26 (s, 2H), 3.97 (s, 3H), 2.57 (s, 3H).

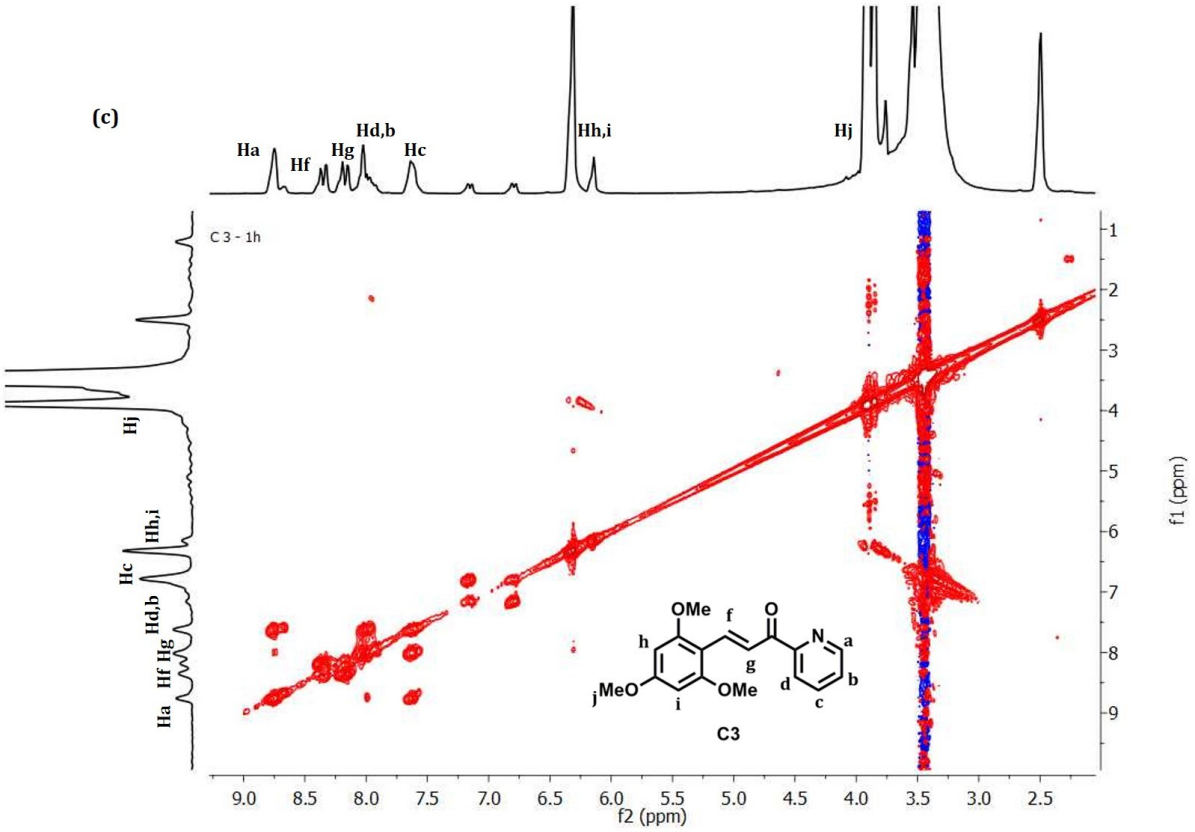
^{13}C NMR (101 MHz, $CDCl_3$) δ 196.63, 152.40, 149.60, 136.39, 130.79, 128.66, 128.12, 127.19, 123.08, 112.17, 110.58, 70.83, 56.09, 26.39.

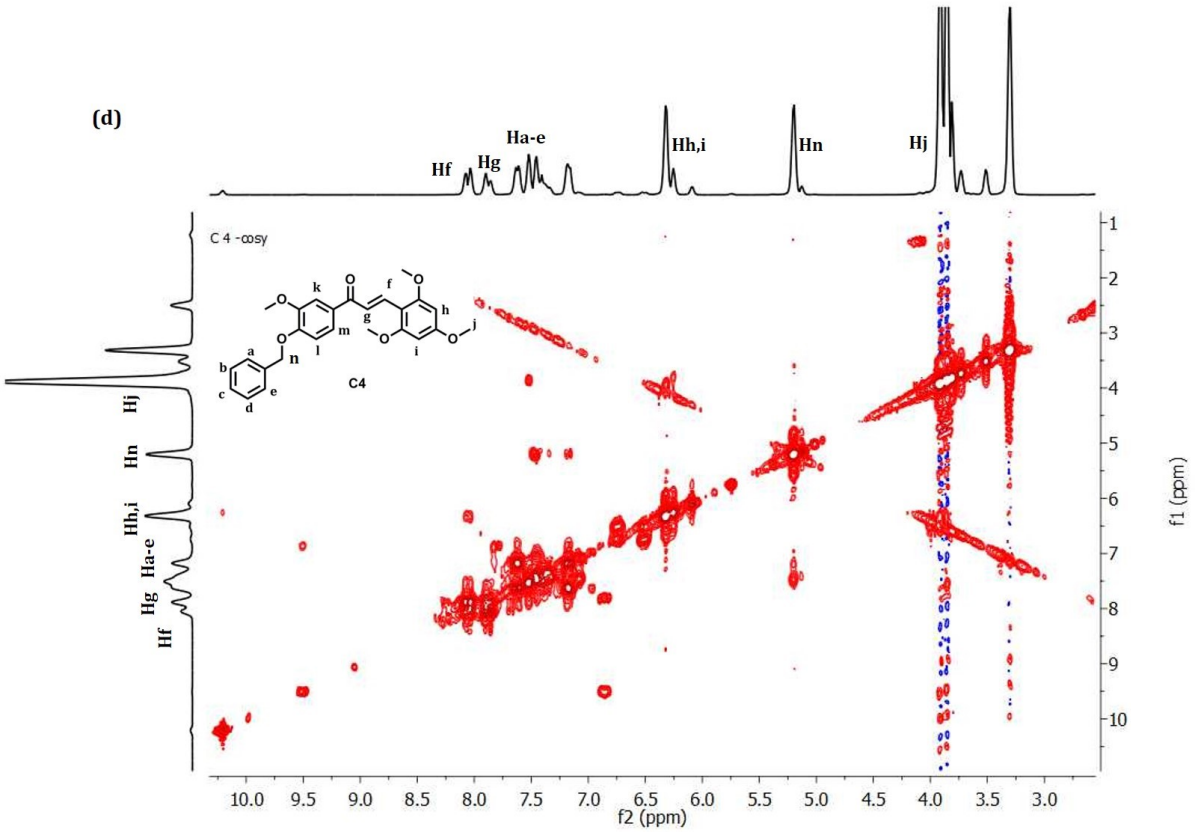
ν_{max} (cm^{-1}): 3027, 2924, 1583-1416, 1259-1146, 988.

Mass: $C_{23}H_{21}O_3$ m/z = 345.1497 [M+H] calculated m/z = 344.1412


(a)
Hf,f'
Ha-e
Hg,g'
C 1 - 1H
Ha-e
Hg,g'
Hf,f'
a'
f'
f
a
b'
b
g'
g
c'
e'
e
c
d'
d
C1
f1 (ppm)
f2 (ppm)


(b)
Hf,f'
Ha,e
Hg,g'
Hb,c,d
Hi,h
Hj
C 2 - 1H
Hj
Hi,h
Hg,g'
Ha-e
Hf,f'
a
f
O
h
b
g
j
c
e
O
O
d
i
C2
f1 (ppm)
f2 (ppm)


(c)
Ha
Hf
Hg
Hd,b
Hc
Hh,i
Hj
C 3 - 1h
OMe
MeO
OMe
C3
f2 (ppm)
f1 (ppm)


(d)
Hf
Hg
Ha-e
Hh,i
Hn
Hj
C 4 -cosy
C4
f2 (ppm)
f1 (ppm)

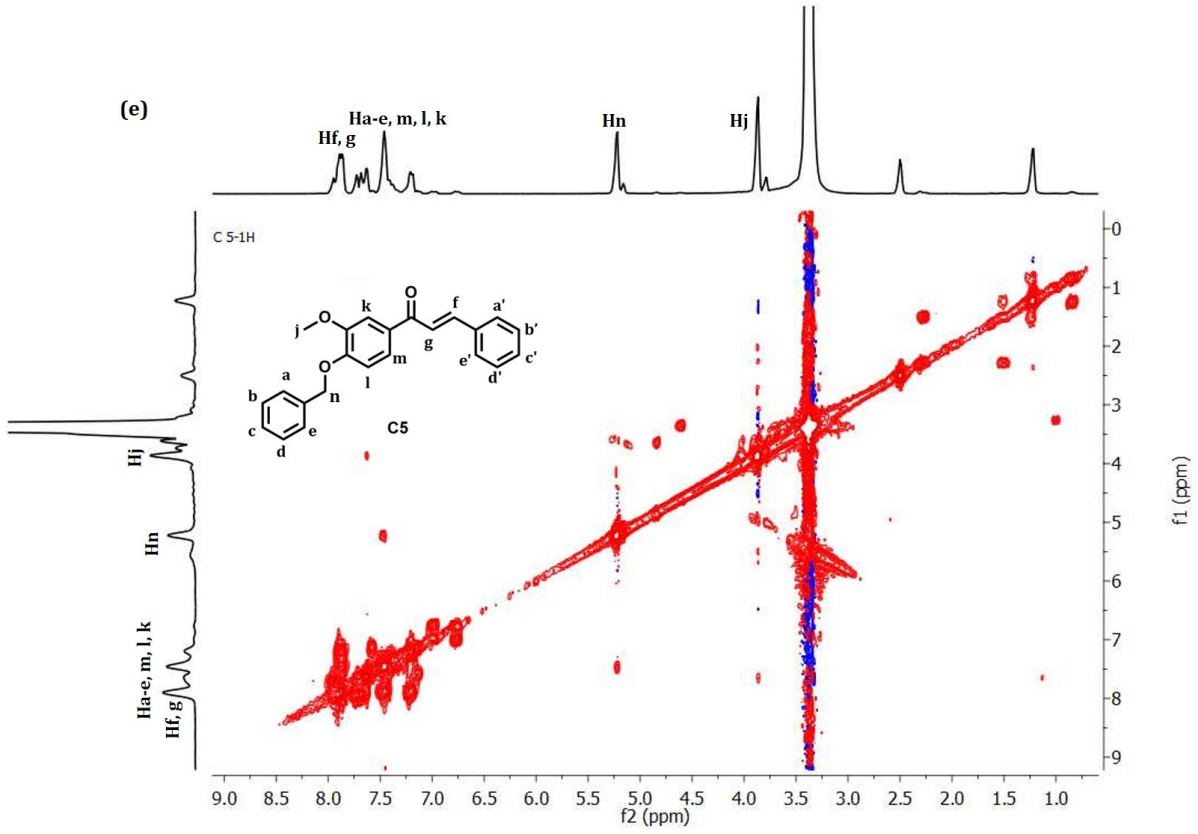
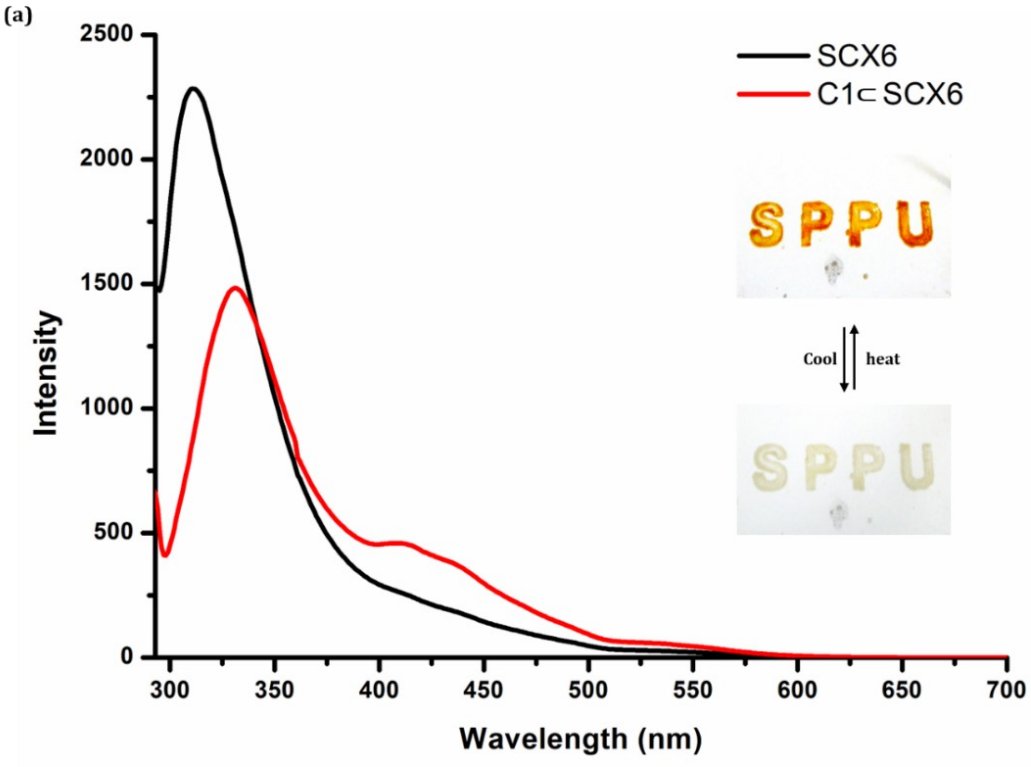
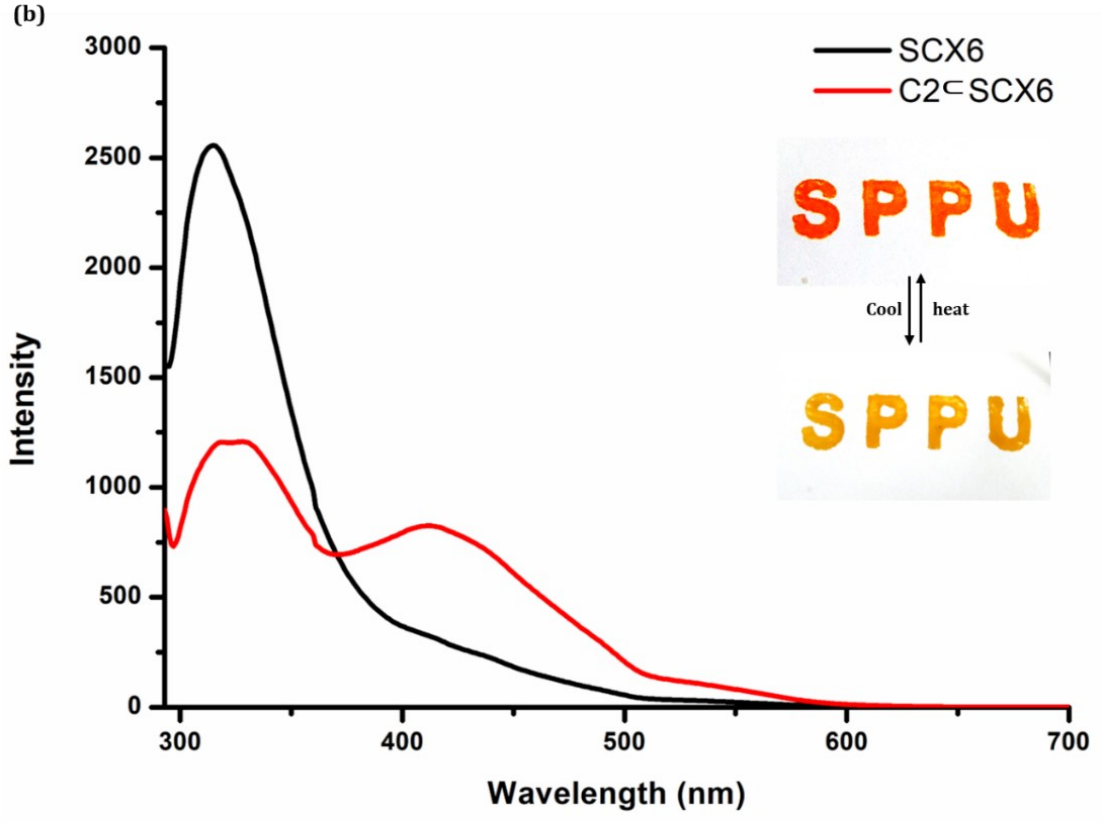
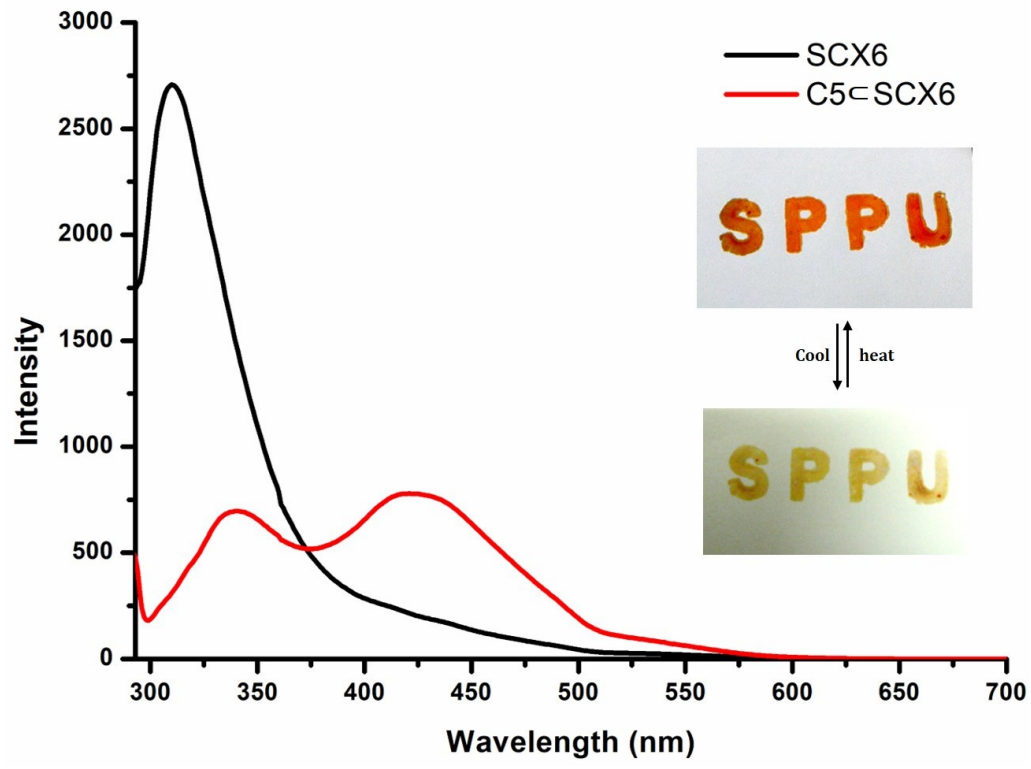


Fig. S1: Selected region of the 2D COSY NMR spectra of (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6; and (e) C5⊂SCX6 in DMSO-d_6.


(a)
SCX6
C1⊂SCX6
Intensity
Wavelength (nm)
Cool
heat
SPPU
SPPU


(b)
SCX6
C2⊂SCX6
Intensity
Wavelength (nm)
Cool
heat
SPPU
SPPU

(d)


SCX6
C5⊂SCX6
Intensity
Wavelength (nm)
Cool
heat
SPPU
SPPU

(c)

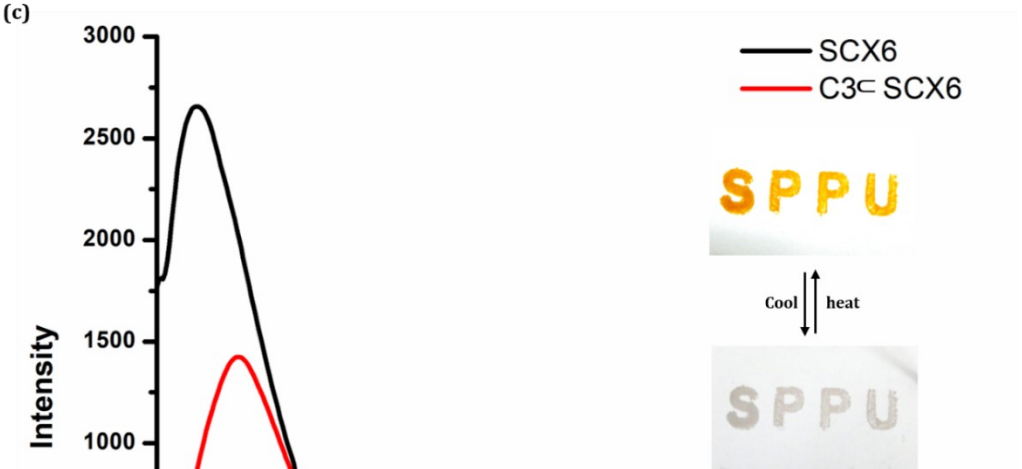
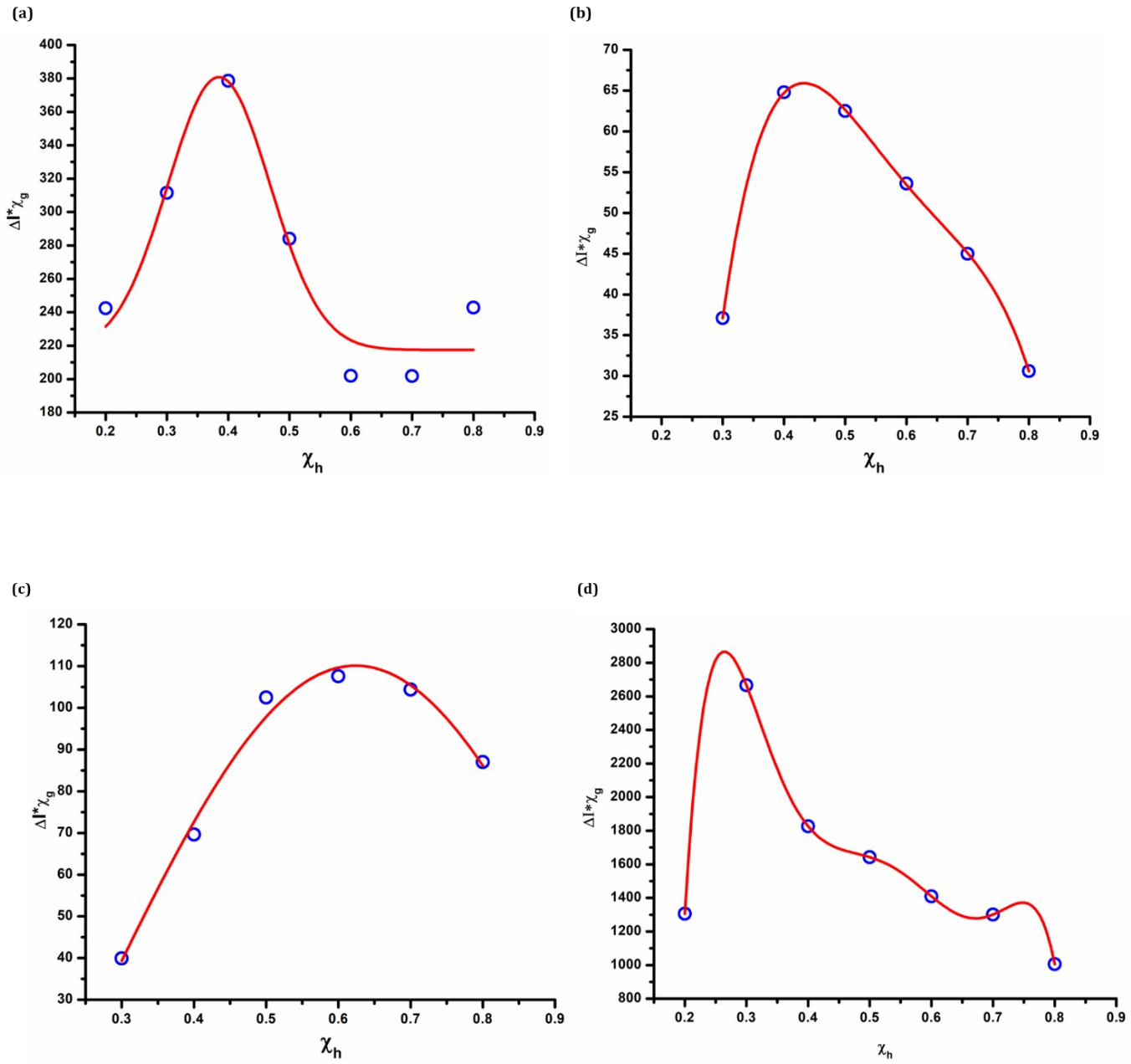

SCX6
C3⊂ SCX6
Intensity
Cool
heat
SPPU
SPPU

Fig. S2: Emission spectra of (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; and (d) C5⊂SCX6 with the treatment of mechanical stimuli. Insets: change in colour of chalcone complexes on applying heat under visible light.



(e)

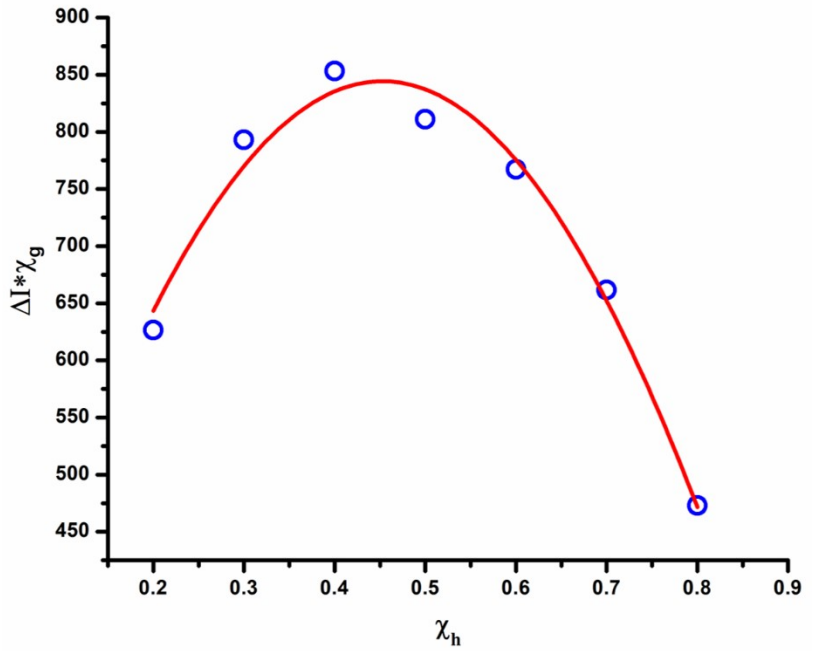


Fig. S3: Job's plot for (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6 and (e) C5⊂SCX6 complexes. 0.0025 mM where ΔI change in intensity, $\chi_{g/h}$ mole ratio of host and guest.

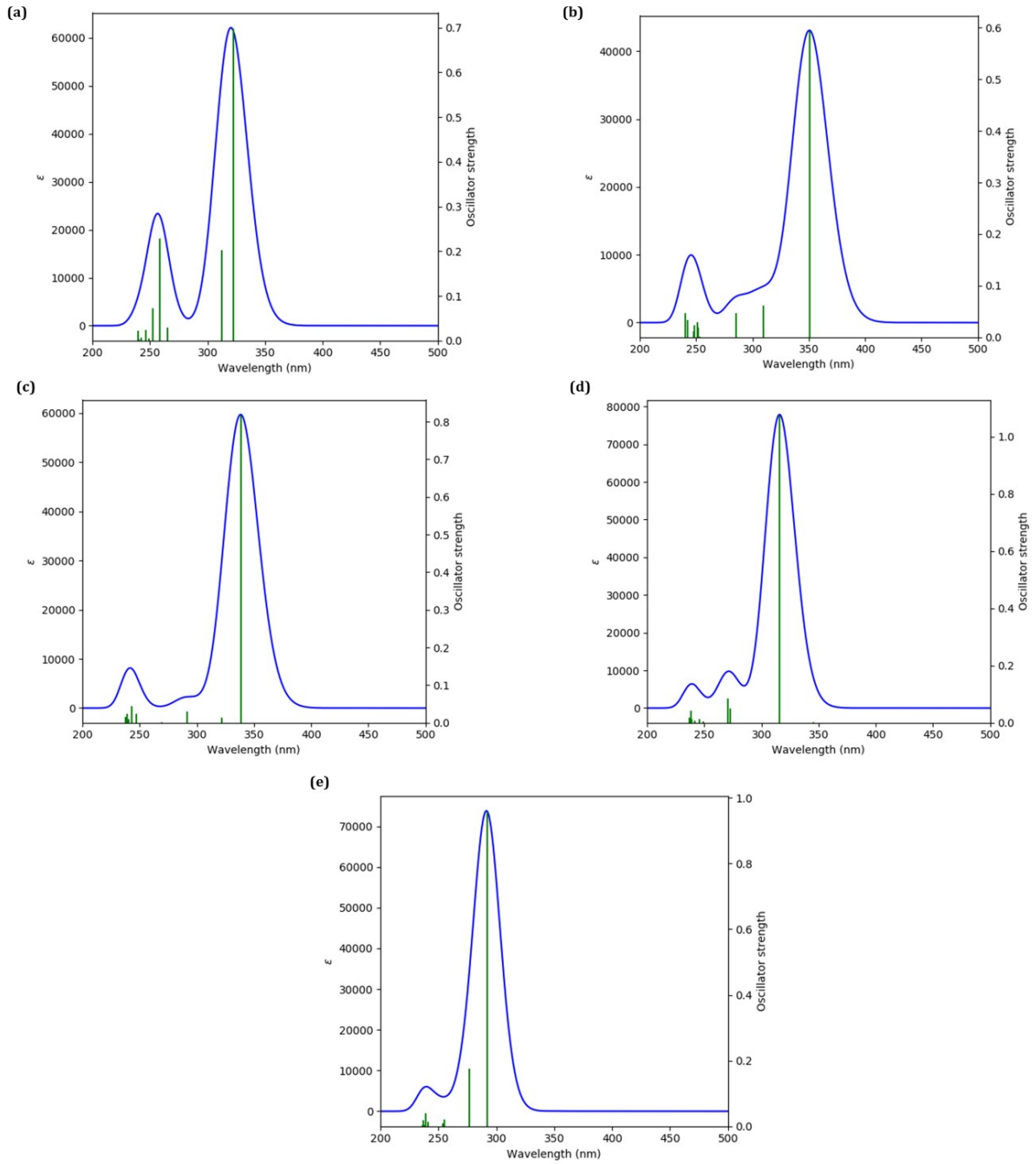
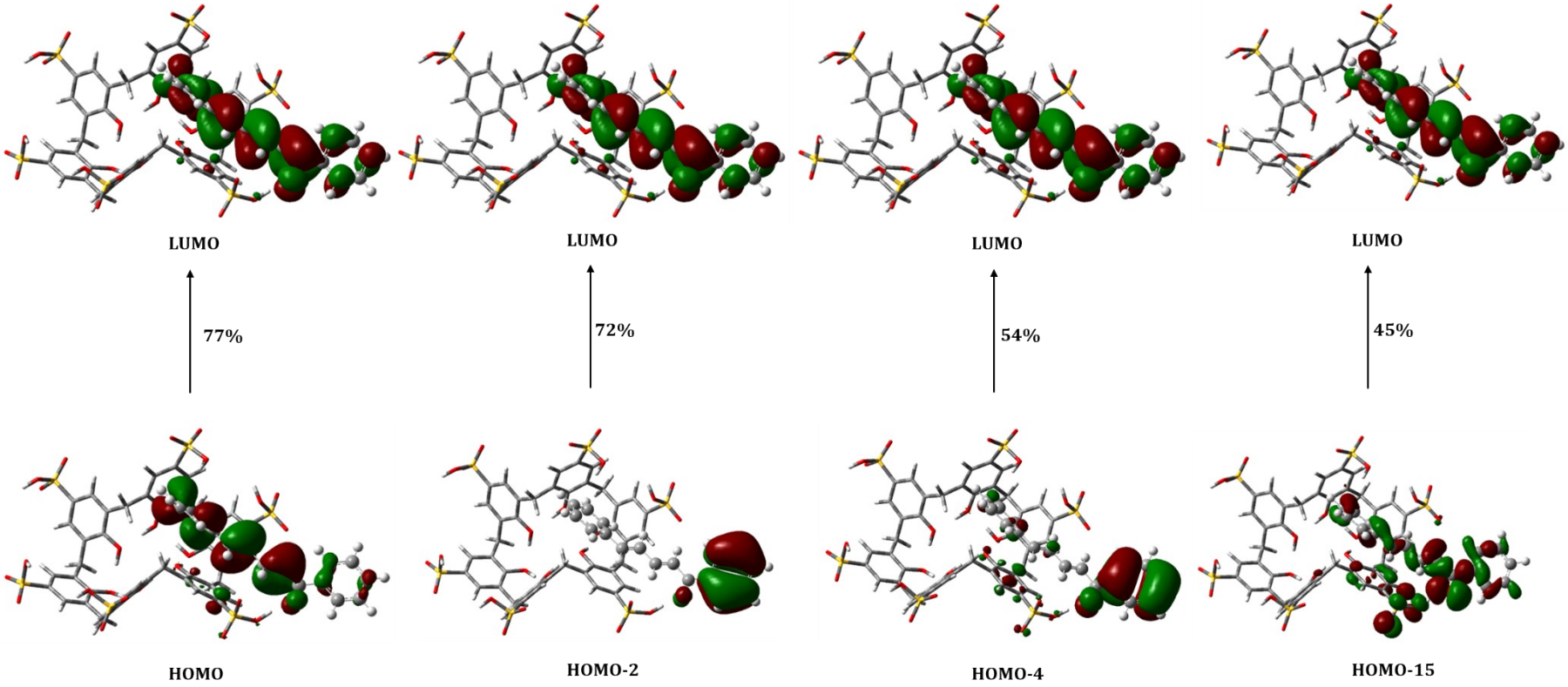
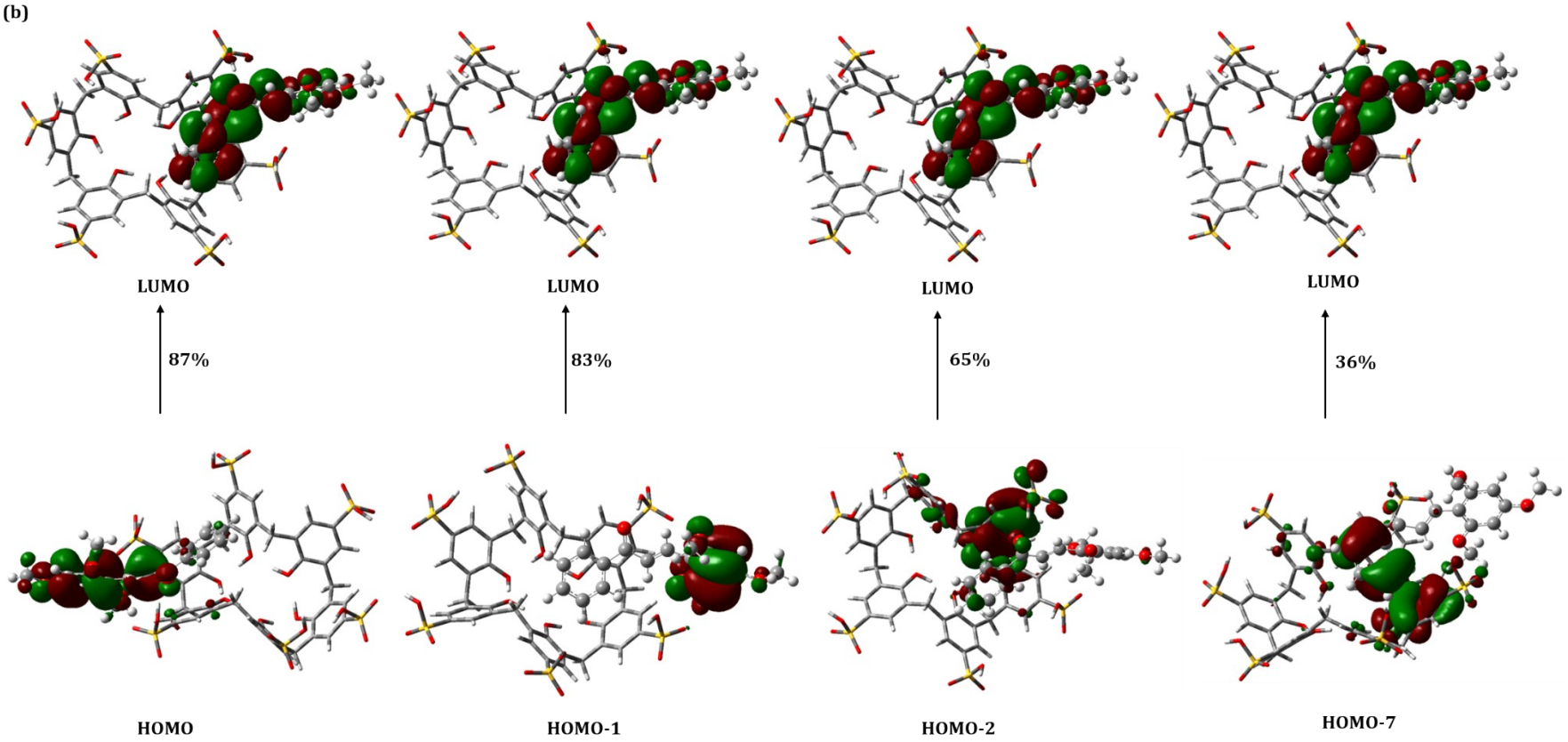
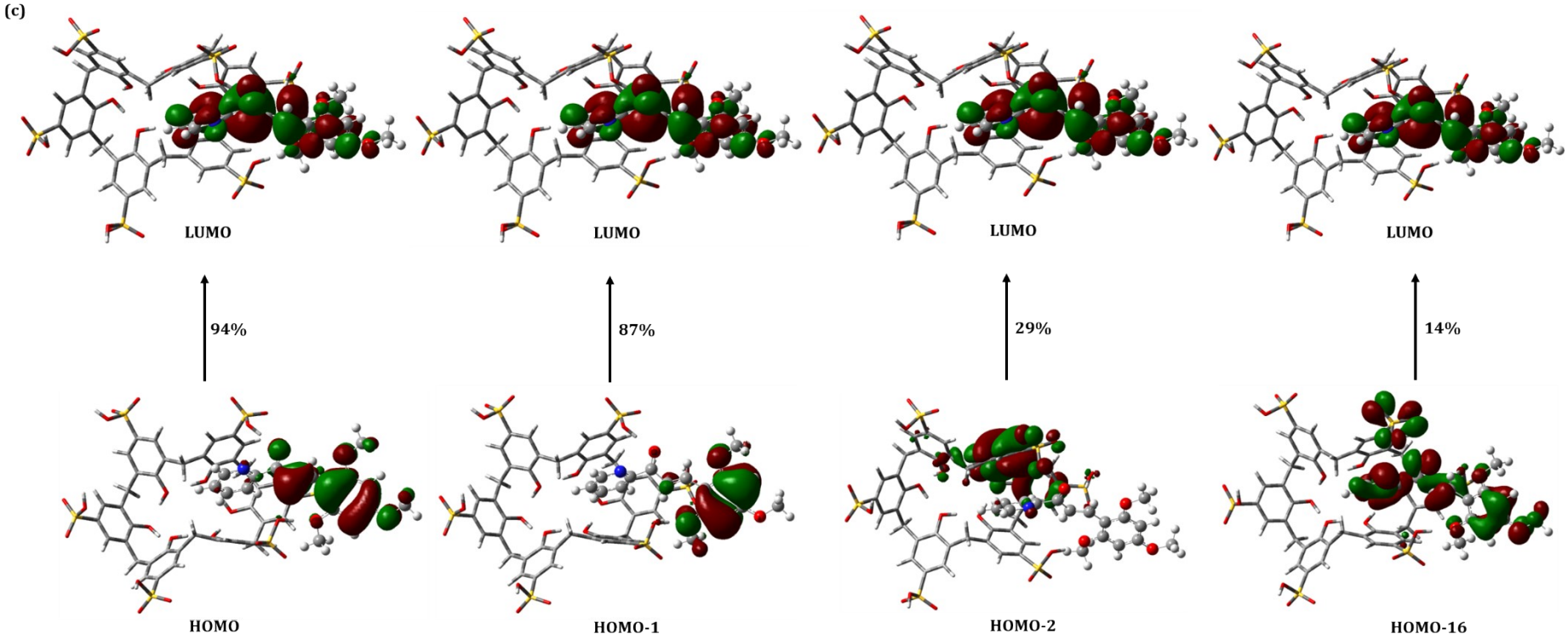


Fig. S4: TDDFT electronic spectra in (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6 and (e) C5⊂SCX6 complexes.

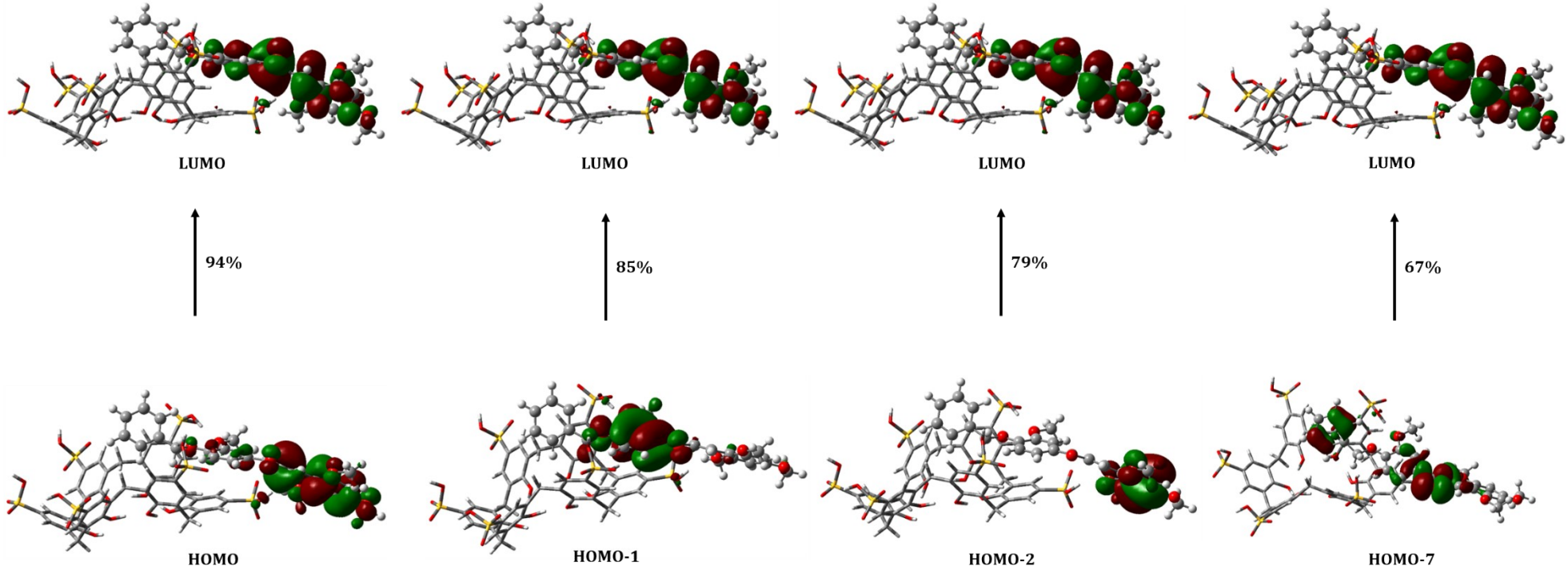
(a)




(b)
LUMO
LUMO
LUMO
LUMO
87%
83%
65%
36%
HOMO
HOMO-1
HOMO-2
HOMO-7


(c)
LUMO
LUMO
LUMO
LUMO
94%
87%
29%
14%
HOMO
HOMO-1
HOMO-2
HOMO-16

(d)



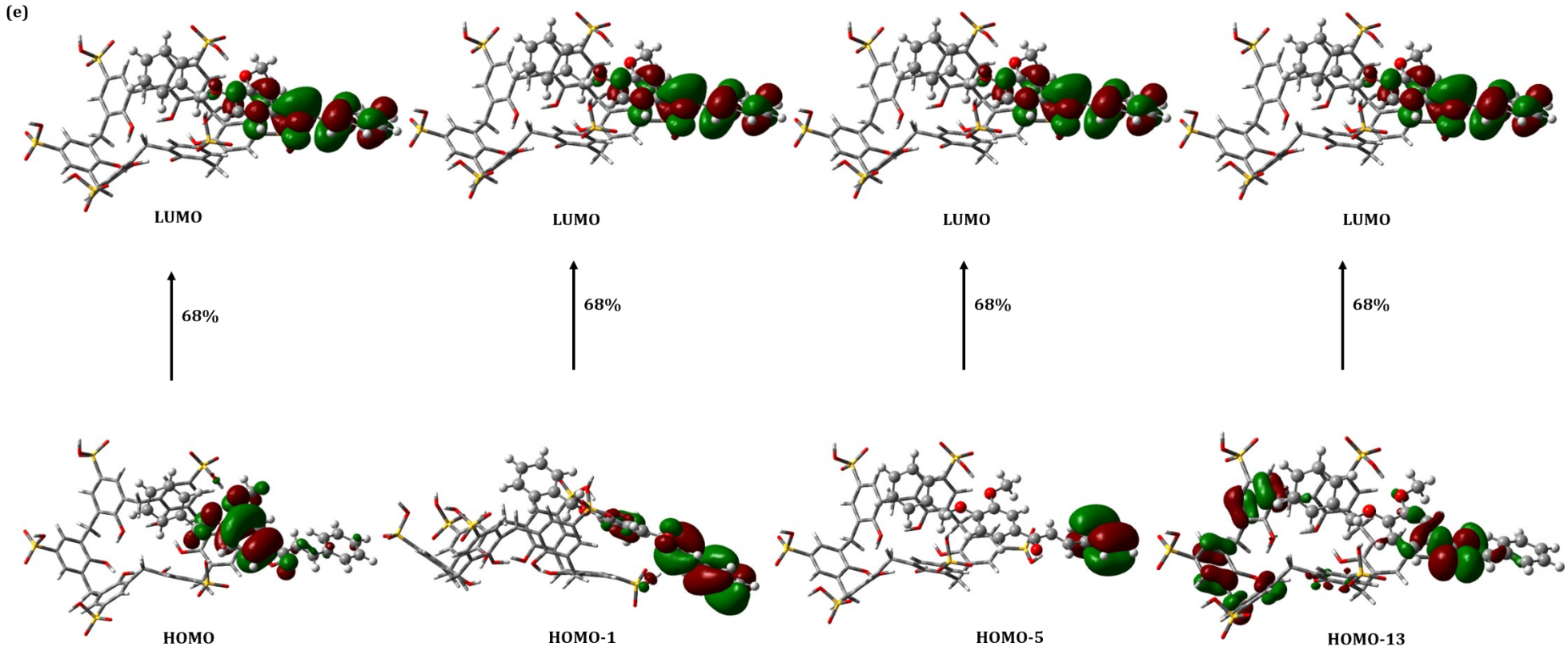
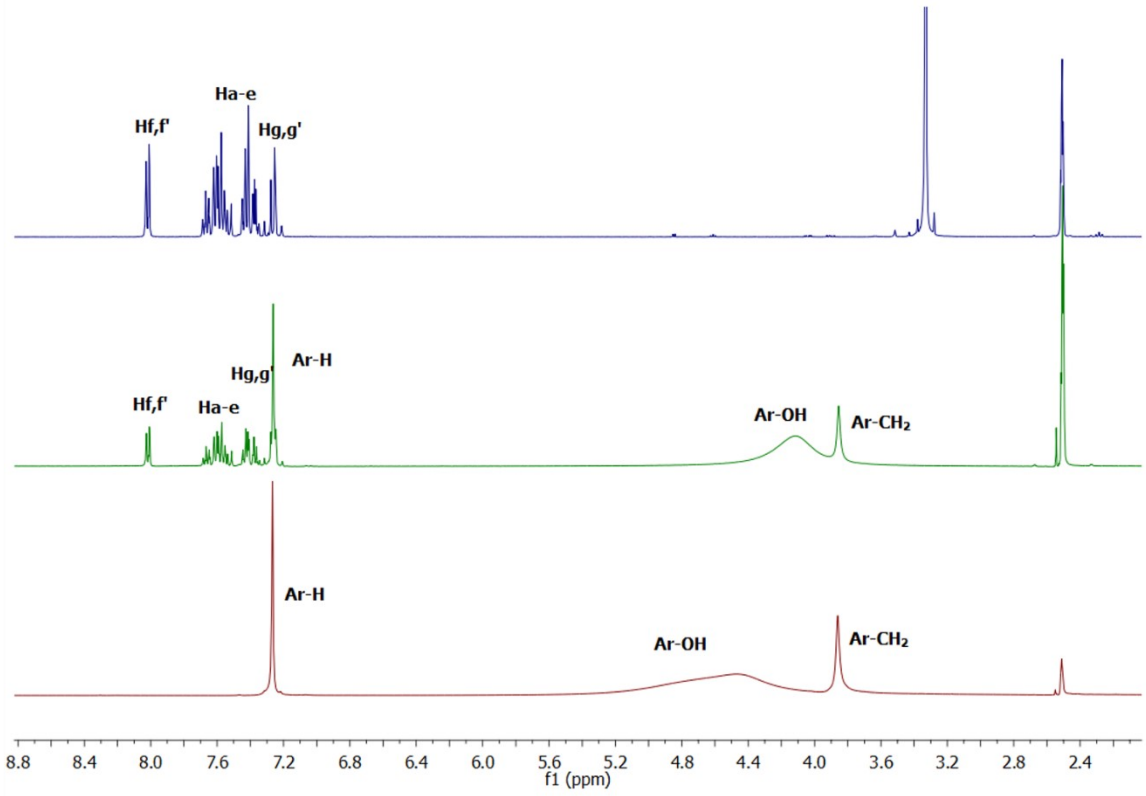
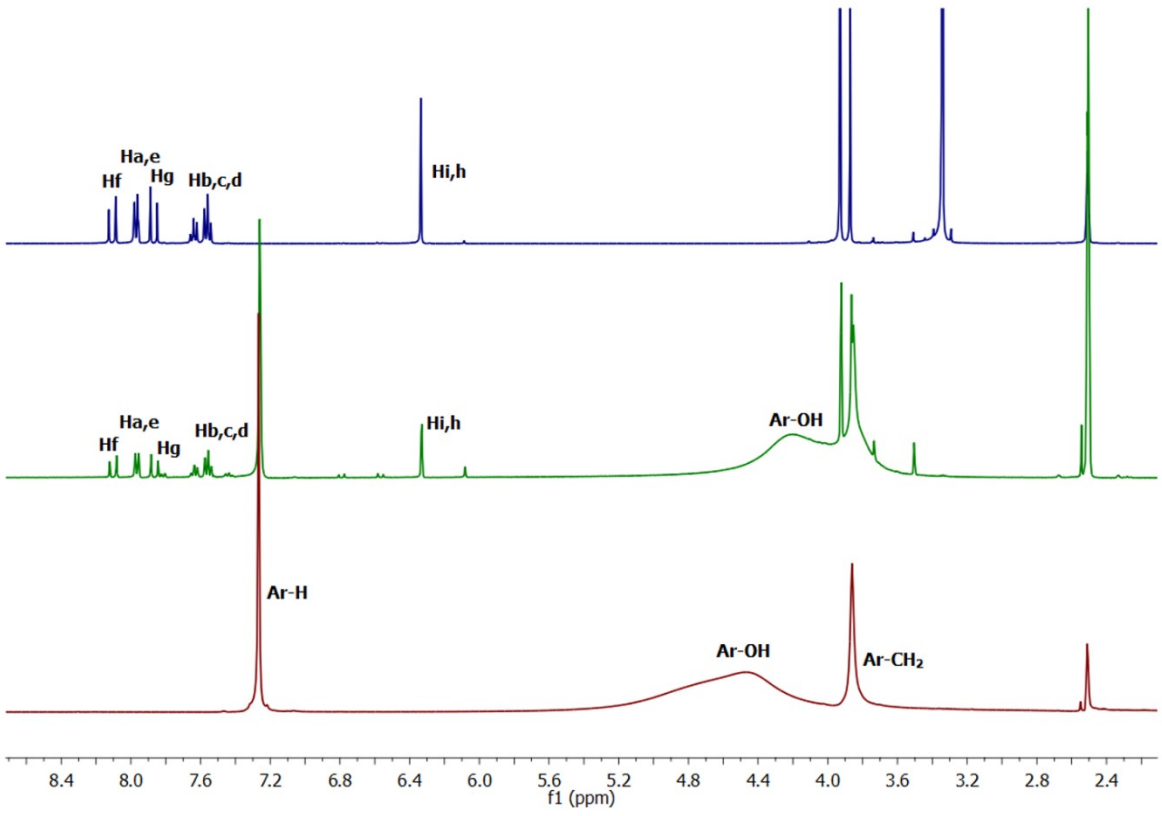


Fig. S5: MO's accompanying electronic transitions in (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6; and (e) C5⊂SCX6 complexes.

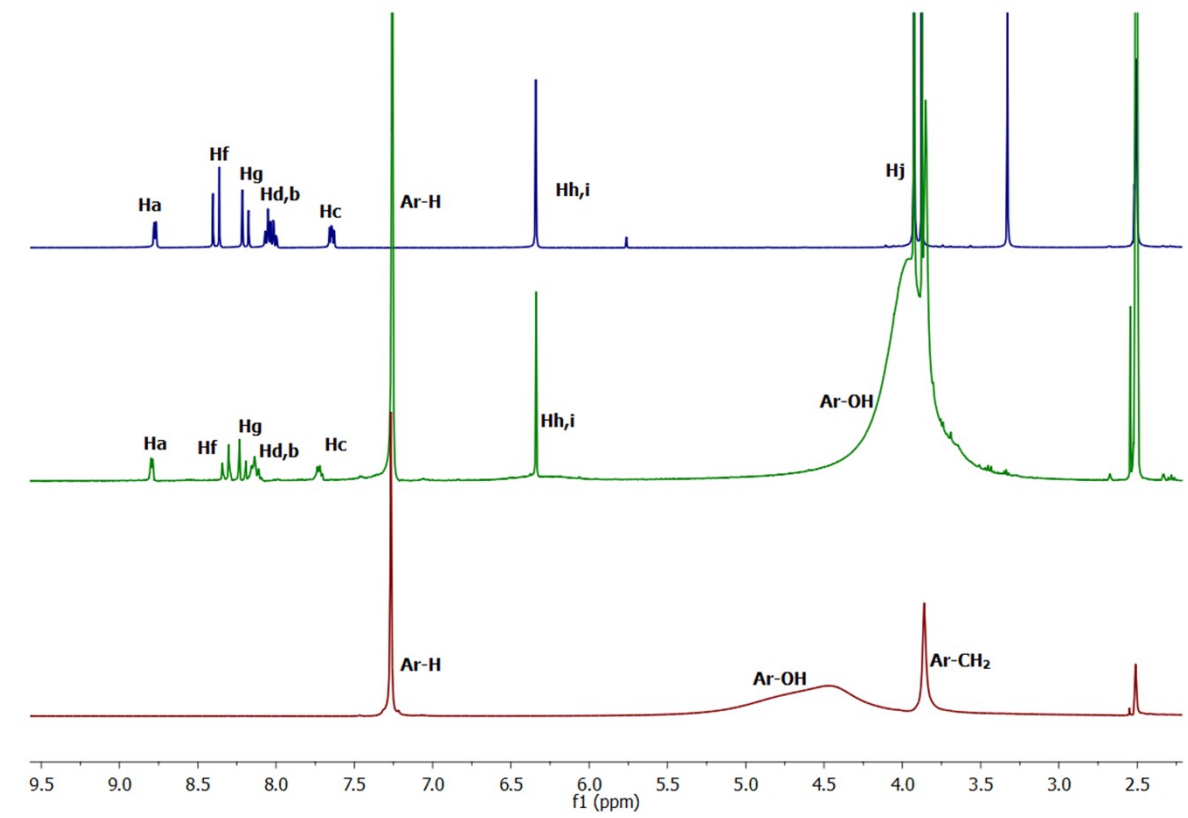
(a)


Hf,f'
Ha-e
Hg,g'
Ar-H
Hg,g'
Hf,f'
Ha-e
Ar-OH
Ar-CH2
Ar-H
Ar-OH
Ar-CH2
8.8
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
f1 (ppm)

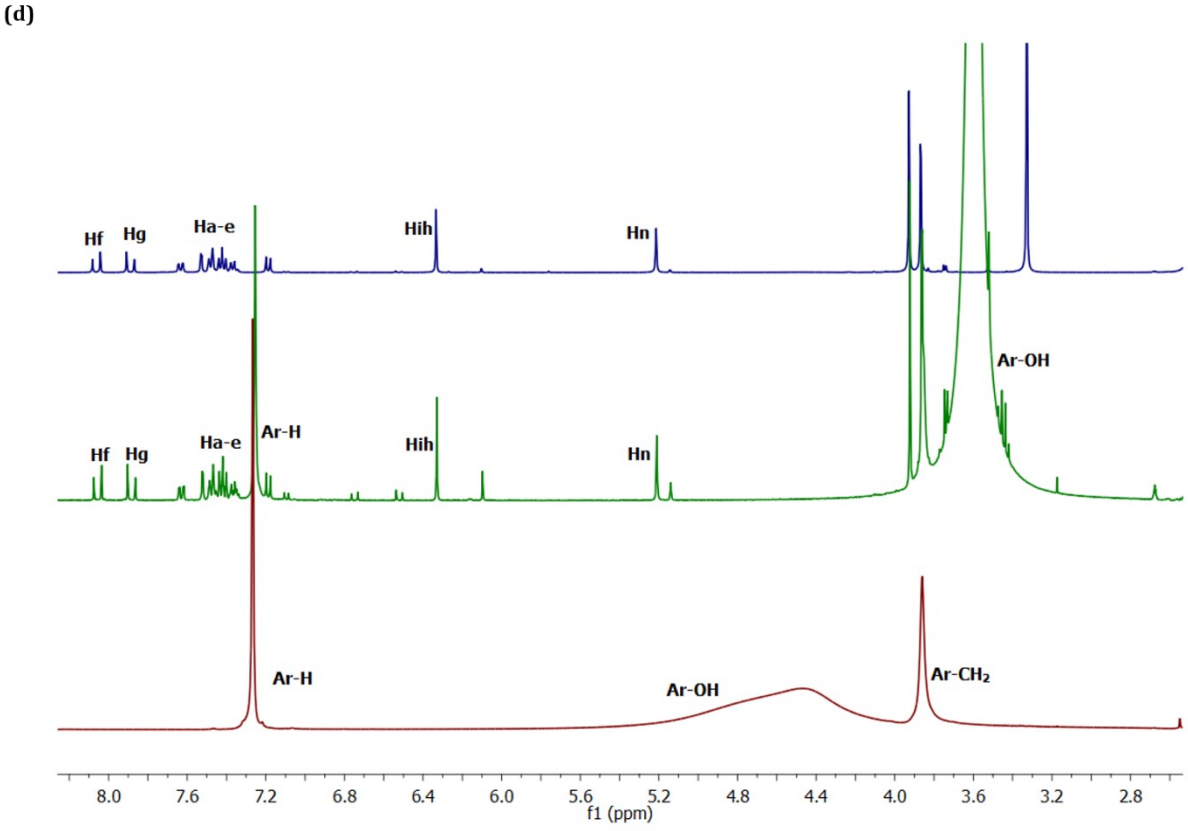
(b)


Ha,e
Hf
Hg
Hb,c,d
Hi,h
Ha,e
Hf
Hg
Hb,c,d
Hi,h
Ar-OH
Ar-H
Ar-OH
Ar-CH2
8.4
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
f1 (ppm)

(c)


Ha
Hf
Hg
Hd,b
Hc
Ar-H
Hh,i
Hj
Ar-OH
Ar-CH₂
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
f1 (ppm)

(d)


Hf
Hg
Ha-e
Hih
Hn
Ar-OH
Ar-H
Ar-CH₂
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
f1 (ppm)

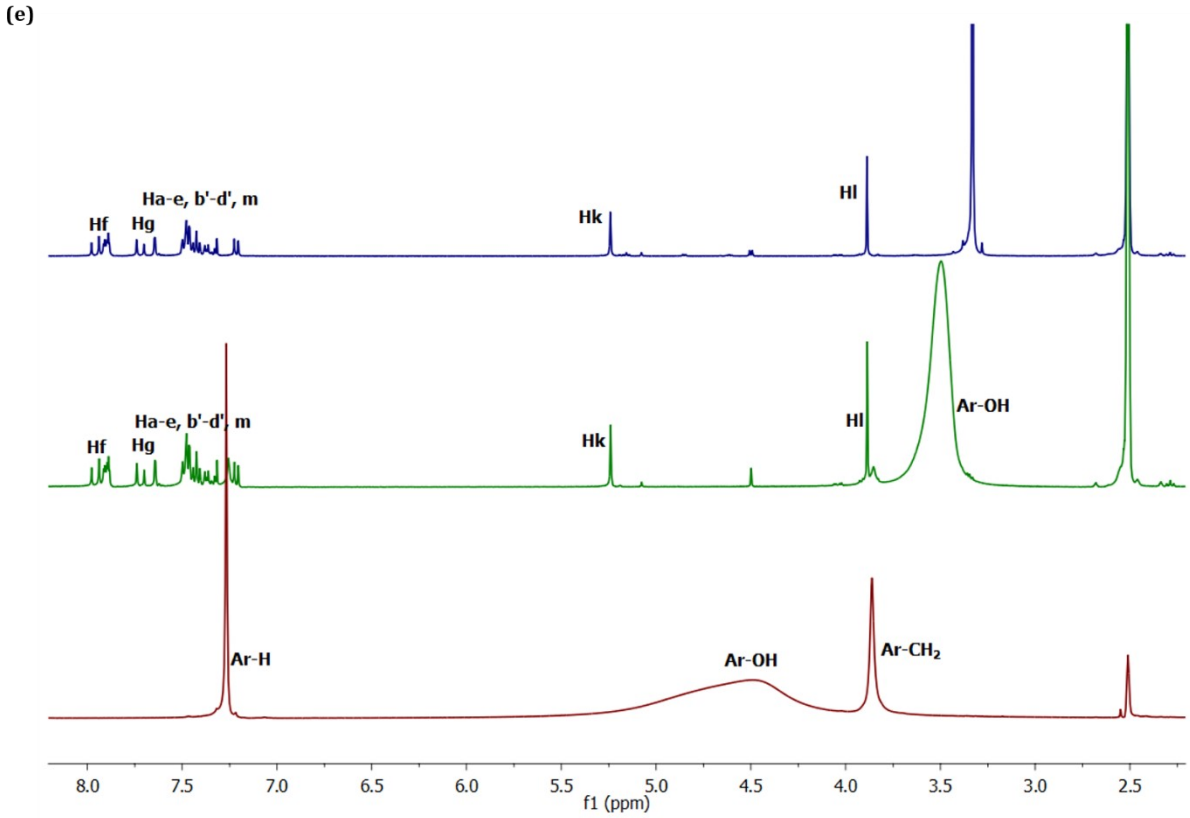


Fig. S6: ^{1}H NMR spectra of 1:1 complexes (in DMSO-d_6): (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6; and (e) C5⊂SCX6 with individual host and guests.

Table S1: A comparison of Chemical shifts and change in chemical shifts in SCX6 (0.01 mM), C1-C5 (0.001 or 0.01 mM) and C1-C5⊂SCX6 complexes. Data refer to DMSO-d_6.

	C1	C2	C3	C4	C5	C1⊂SCX6	C2⊂SCX6	C3⊂SCX6	C4⊂SCX6	C5⊂SCX6	ΔδC1	ΔδC2	ΔδC3	ΔδC4	ΔδC5
Hf,f'	8.02	8.11	8.38	8.06	7.96	8.02	8.1	8.34	8.06	7.96	0	-0.01	-0.04	0	0
Ha-e	7.52			7.4	7.41	7.54			7.41	7.41	0.02			0.01	0
Hg,g'	7.26	7.87	8.2	7.89	7.72	7.26	7.86	8.21	7.88	7.72	0	-0.01	0.01	-0.01	0
Hih		6.34	6.34	6.33			6.33	6.34	6.33			-0.01	0	0	
Hj		3.9	3.9	3.89	3.89		3.93	3.93	3.92	3.85		0.03	0.03	0.03	-0.04
Hc			7.64					7.7					0.06		
Hbcd		7.6	8.04				7.56	8.1				-0.04	0.06		
Ha,e		7.97	8.77		7.9		7.96	8.79		7.9		-0.01	0.02		0
Hk				7.63	7.64				7.63	7.64		0		0	0
Hm				7.53					7.52			0		-0.01	
Hn				5.21	5.24				5.21	5.24		0		0	0
Hl				7.19	7.22				7.19	7.21		0		0	-0.01
Ar-H	7.27	7.27	7.27	7.27	7.27	7.25	7.25	7.26	7.25	7.26	-0.02	-0.02	-0.01	-0.02	-0.01
Ar-OH	4.5	4.5	4.5	4.5	4.5	4.21	3.56	3.85	3.6	3.5	-0.29	-0.94	-0.65	-0.9	-1
Ar-CH_2	3.86	3.86	3.86	3.86	3.86	3.84	3.85	3.88	3.85	3.89	-0.02	-0.01	0.02	-0.01	0.03

Table S2: ^{1}H NMR chemical shifts (ppm) of SCX6, C1-C5 guests and their complexes by DFT.

	C1	C2	C3	C4	C5	SCX6	C1⊂SCX6	C2⊂SCX6	C3⊂SCX6	C4⊂SCX6	C5⊂SCX6
Hj	-	4.31	4.47	4.49	5.15	-	-	3.79	5.07	6.07	5.33
Hf	9.42	9.74	9.77	10.02	9.49	-	8.07	9.40	10.29	10.45	9.98
Hf'	-	-	-	-	-	-	9.57	-	-	-	-
Hg	8.91	9.51	9.29	9.45	9.36	-	7.63	8.71	8.02	10.01	10.13
Hh	-	7.68	7.72	7.41	-	-	-	7.59	7.28	-	-
Hi	-	7.68	7.66	7.35	-	-	-	7.82	7.66	6.07	-
Ha	9.93	9.74	10.40	8.93	8.95	-	10.0	9.61	9.81	9.06	7.88
Hn	-	-	-	5.94	5.95	-	-	-	-	5.13	5.12
Hk	-	-	-	8.85	8.88	-	-	-	-	9.32	9.98
Hb-e	9.19	9.18	9.08	9.03	9.11	-	8.29	7.35	4.72	8.86	9.18
H3	-	-	-	-	-	6.19	14.92	12.55	11.97	10.40	9.89
H1	-	-	-	-	-	10.54	10.98	10.87	11.85	11.84	11.84
H4	-	-	-	-	-	4.60	2.89	5.13	4.37	3.80	3.83
H2/2’	-	-	-	-	-	9.22	8.53	8.81	8.63	8.54	8.45

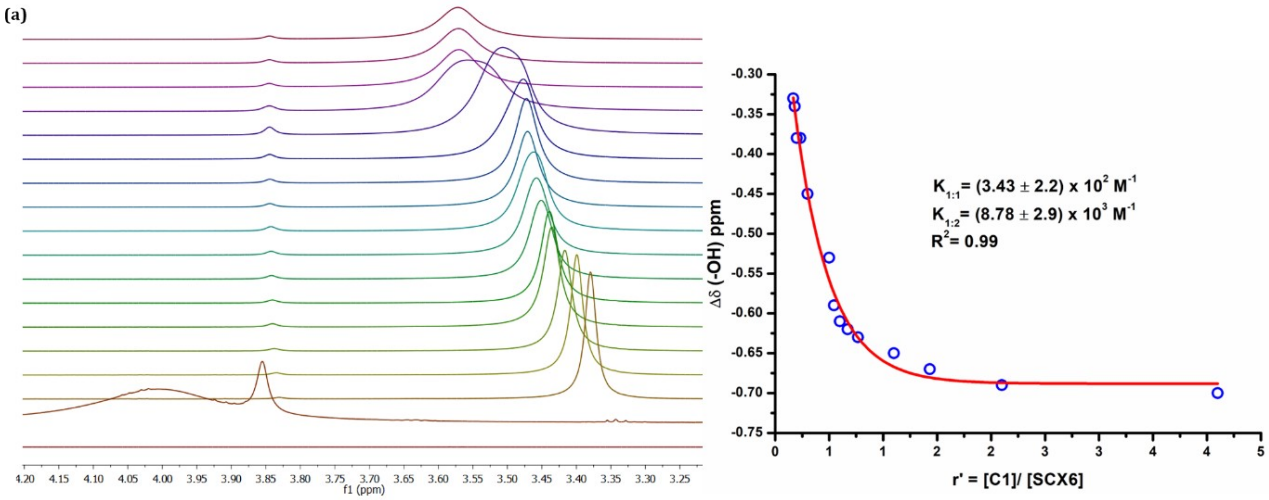


Figure S7: Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of C1 at the concentration of 0.01M upon addition of SCX6; (1) 0 mM; (2) 0.24 m; (3) 0.47 mM; (4) 0.69 mM; (5) 0.91 mM; (6) 1.1 mM; (7) 1.3 mM; (8) 1.5 mM; (9) 1.7 mM; (10) 1.8 mM; (11) 2 mM; (12) 3.3 mM; (13) 4.3 mM; (14) 5 mM; (15) 5.5 mM; (16) 6 mM; (17) 6.4 mM selected region of titration spectra of C1⊂SCX6 showing changes in δ_H of –OH against the increasing amount of SCX6.

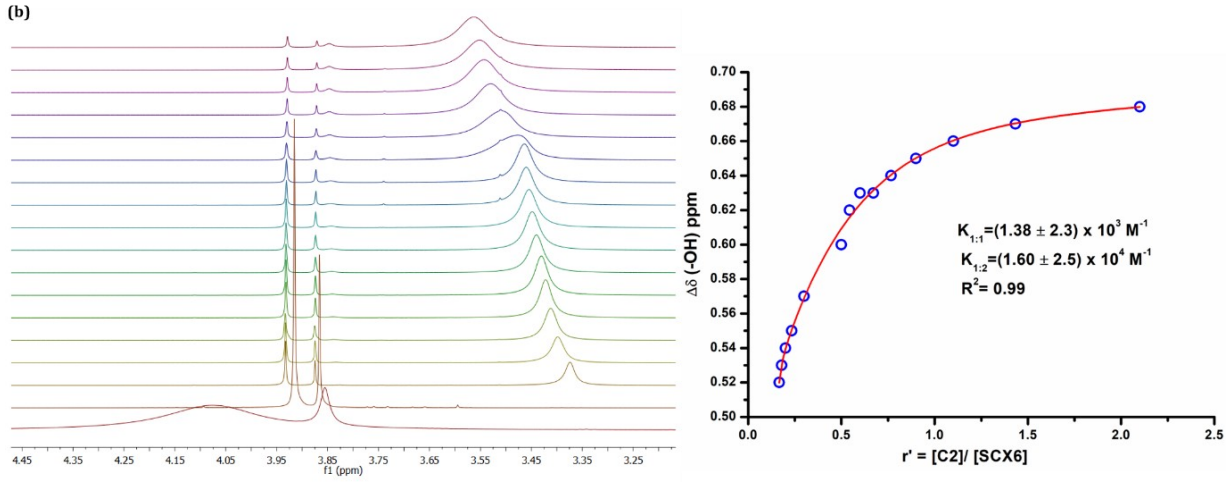


Figure S8 : Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of C2 at the concentration of 0.001M upon addition of SCX6; (1) 0 mM; (2) 0.24 m; (3) 0.47 mM; (4) 0.69 mM; (5) 0.91 mM; (6) 1.1 mM; (7) 1.3 mM; (8) 1.5 mM; (9) 1.7 mM; (10) 1.8 mM; (11) 2 mM; (12) 3.3 mM; (13) 4.3 mM; (14) 5 mM; (15) 5.5 mM; (16) 6 mM; selected region of titration spectra of C2⊂SCX6 showing changes in δ_H of –OH against the increasing amount of SCX6.

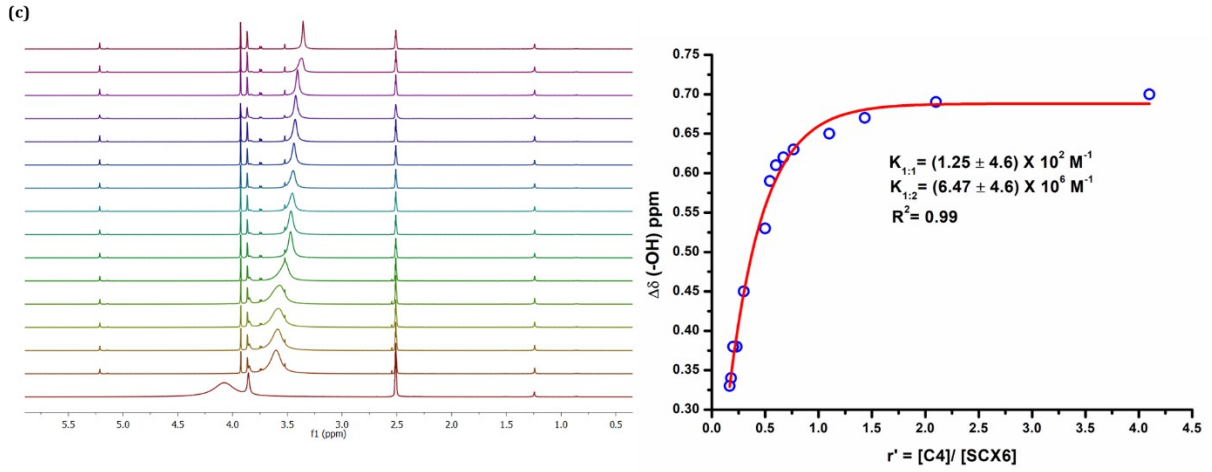


Figure S9: Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of C4 at the concentration of 0.01M upon addition of SCX6; (1) 0 mM; (2) 0.24 m; (3) 0.47 mM; (4) 0.69 mM; (5) 0.91 mM; (6) 1.1 mM; (7) 1.3 mM; (8) 1.5 mM; (9) 1.7 mM; (10) 1.8 mM; (11) 2 mM; (12) 3.3 mM; (13) 4.3 mM; (14) 5 mM; (15) 5.5 mM; (16) 6 mM; (17) 6.4 mM selected region of titration spectra of C4⊂SCX6 showing changes in δ_H of –OH against the increasing amount of SCX6.

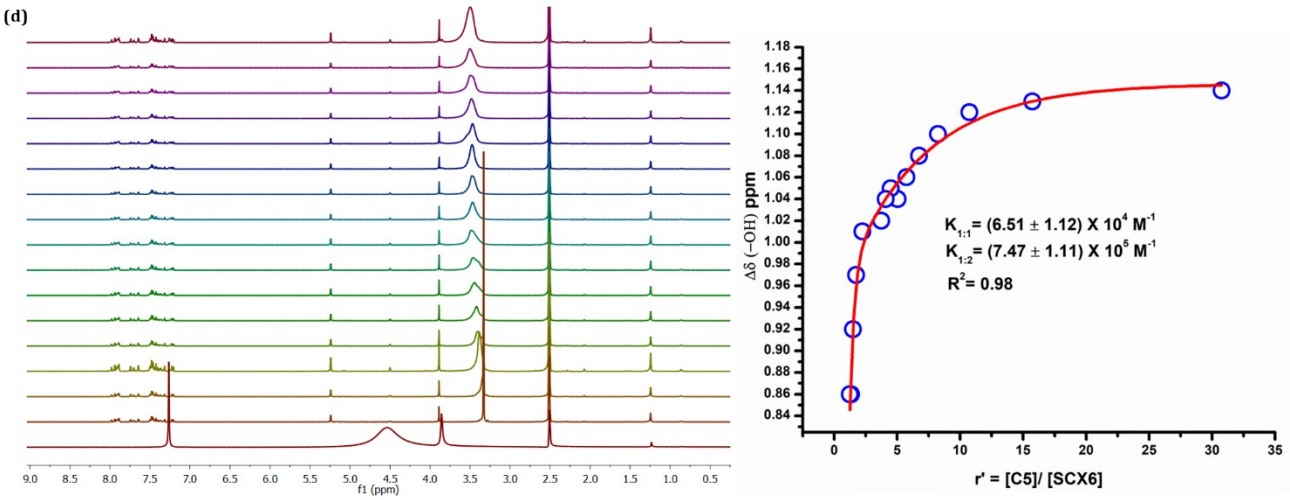
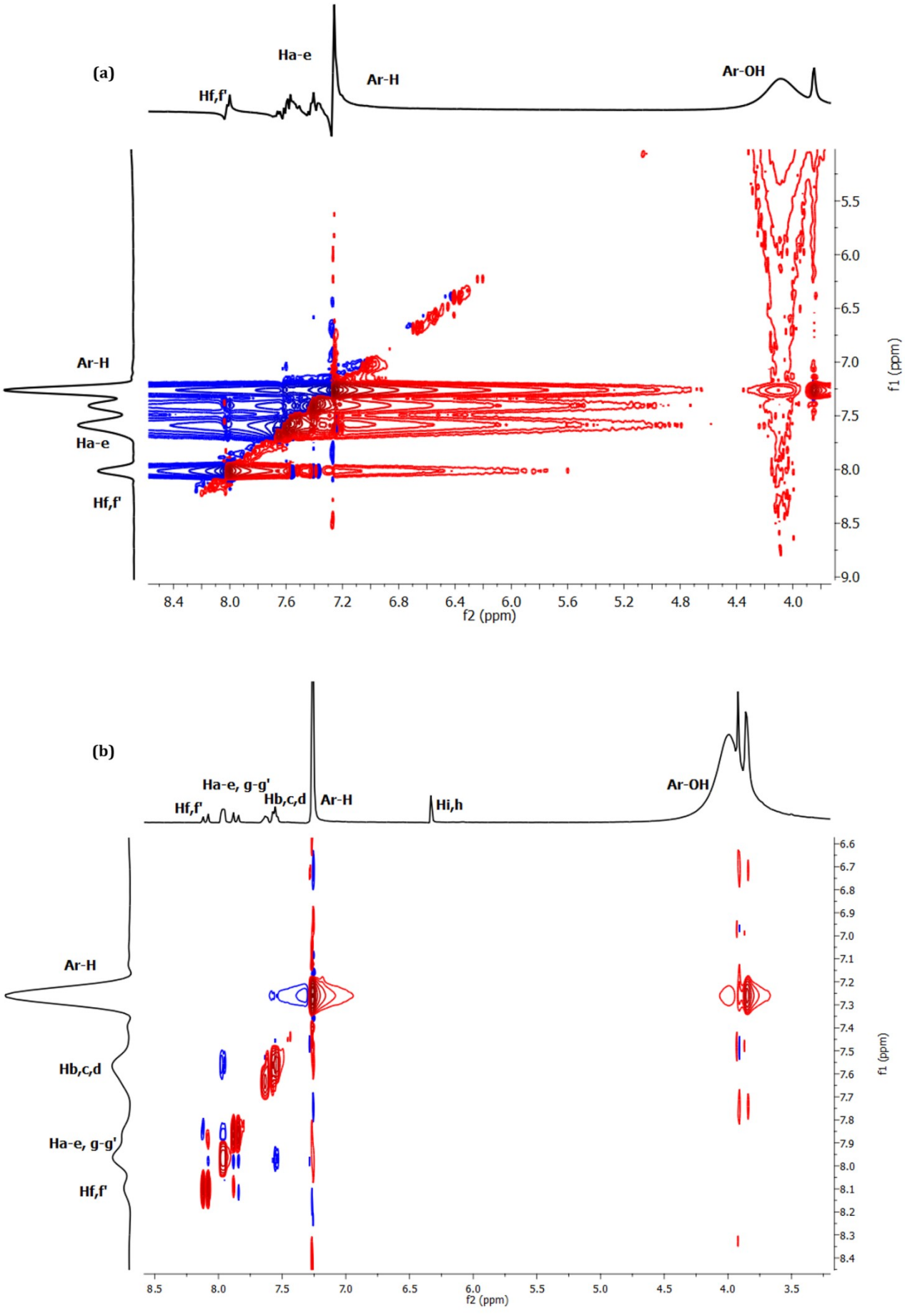
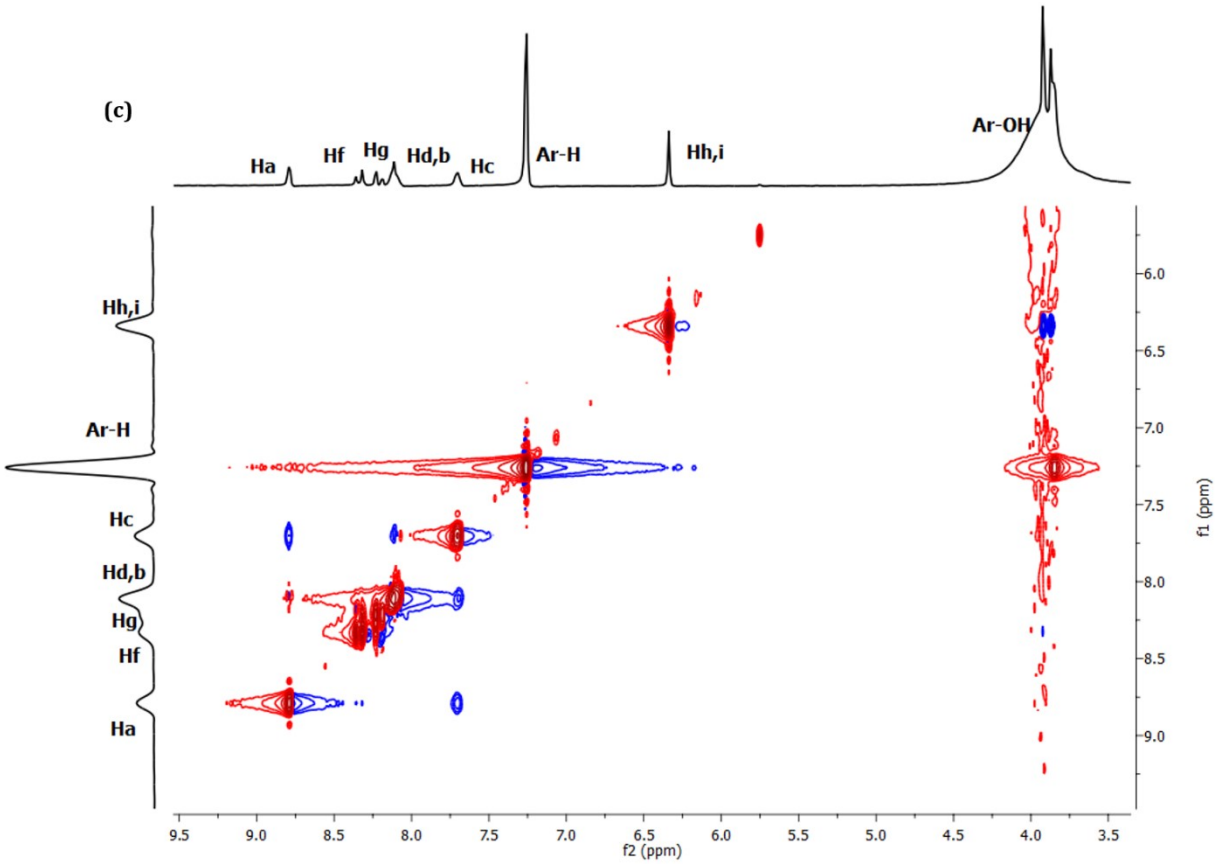
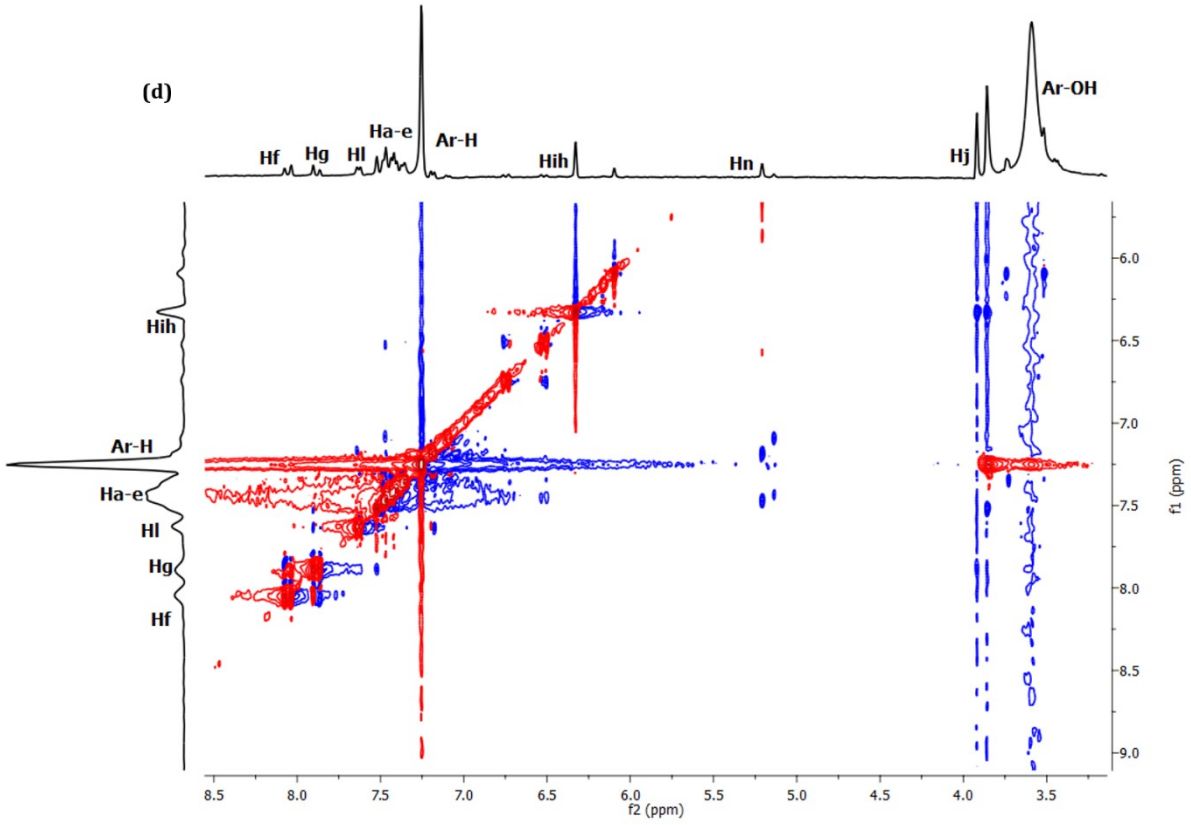


Figure S10: Partial ^{1}H NMR spectra (400 MHz, DMSO-d_6, 298 K) of C5 at the concentration of 0.0075 M upon addition of SCX6; (1) 0 mM; (2) 0.24 mM; (3) 0.47 mM; (4) 0.69 mM; (5) 0.91 mM; (6) 1.1 mM; (7) 1.3 mM; (8) 1.48 mM; (9) 1.66 mM; (10) 1.83 mM; (11) 2 mM; (12) 3.33 mM; (13) 4.28 mM; (14) 5 mM; (15) 5.55 mM; (16) 6 mM selected region of titration spectra of C5⊂SCX6 showing changes in δ_H of –OH against the increasing amount of SCX6.


(a)
Ha-e
Hf,f'
Ar-H
Ar-OH
Ar-H
Ha-e
Hf,f'
f1 (ppm)
f2 (ppm)
(b)
Ha-e, g-g'
Hf,f'
Hb,c,d
Ar-H
Hi,h
Ar-OH
Ar-H
Hb,c,d
Ha-e, g-g'
Hf,f'
f1 (ppm)
f2 (ppm)


(c)
Ha
Hf
Hg
Hd,b
Hc
Ar-H
Hh,i
Ar-OH
f2 (ppm)
f1 (ppm)


(d)
Hf
Hg
Hl
Ha-e
Ar-H
Hih
Hn
Hj
Ar-OH
f2 (ppm)
f1 (ppm)

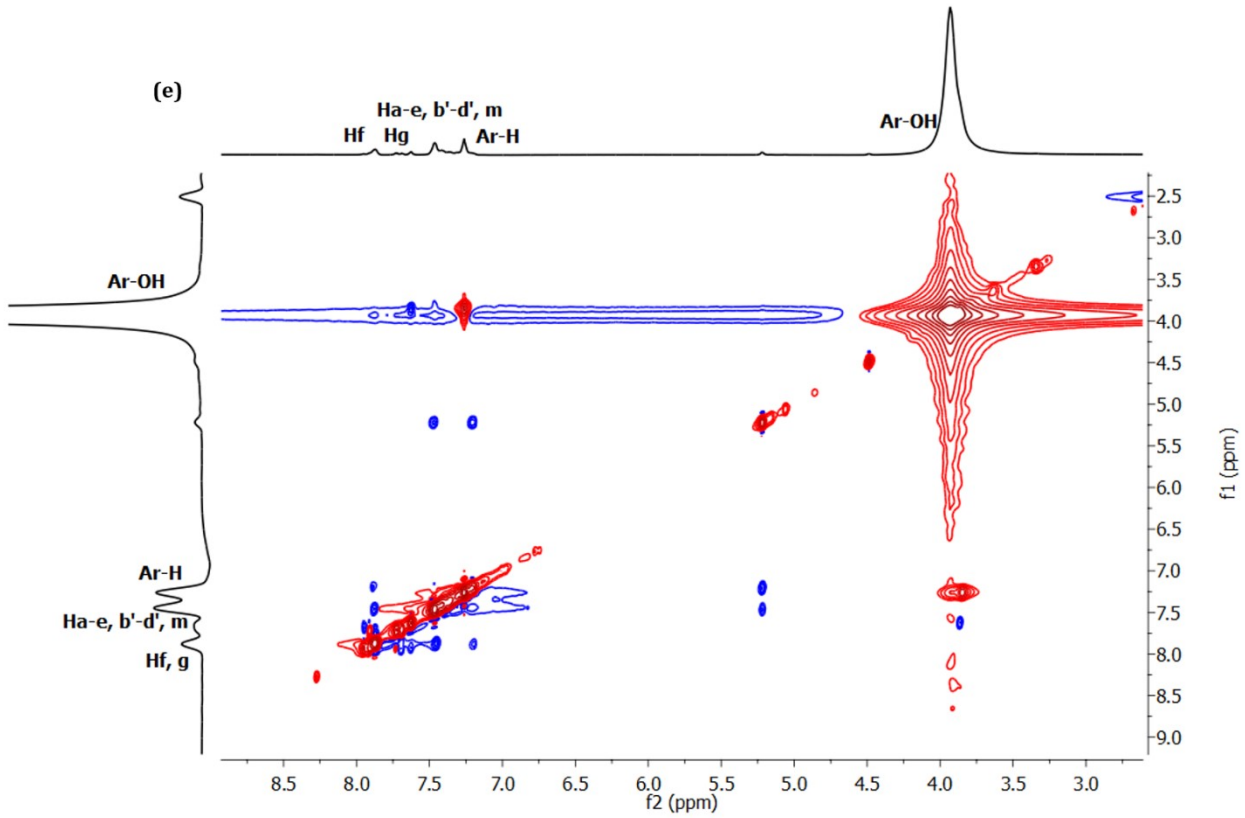


Fig. S11: Selected region of the 2D NOESY NMR spectra of (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6; and (e) C5⊂SCX6 in DMSO-d_6.

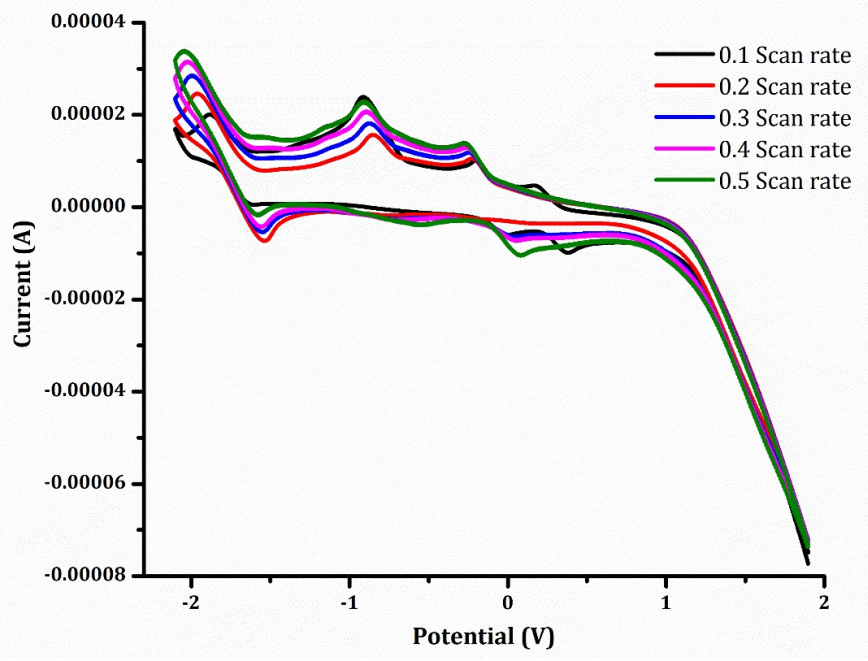


Fig. S12: Cyclic voltammograms of independent C3 in 0.1 M TBAP/ acetonitrile: DMSO using Pt working electrode at 0.1 to 0.5 V s^{-1} scan rate.

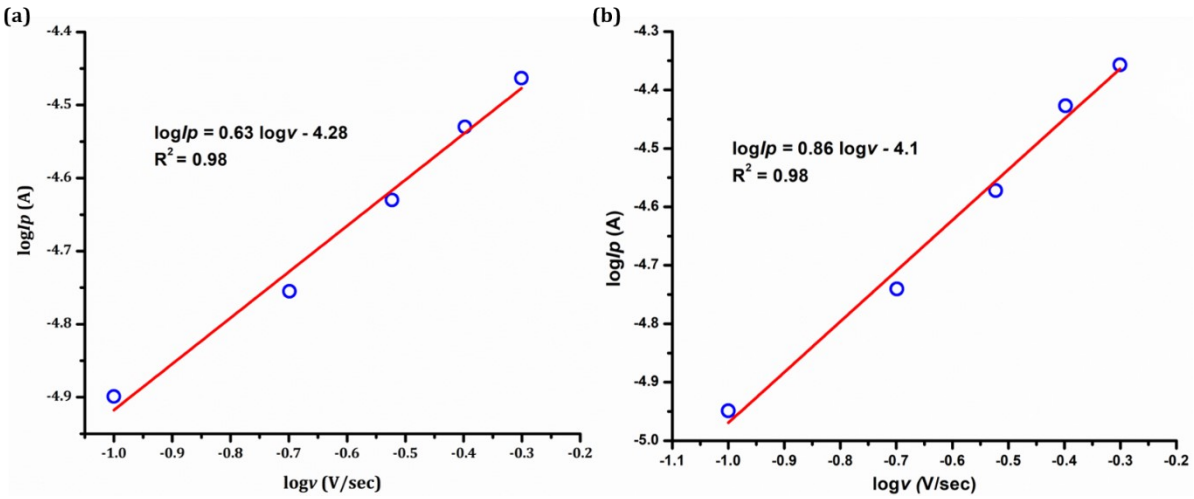
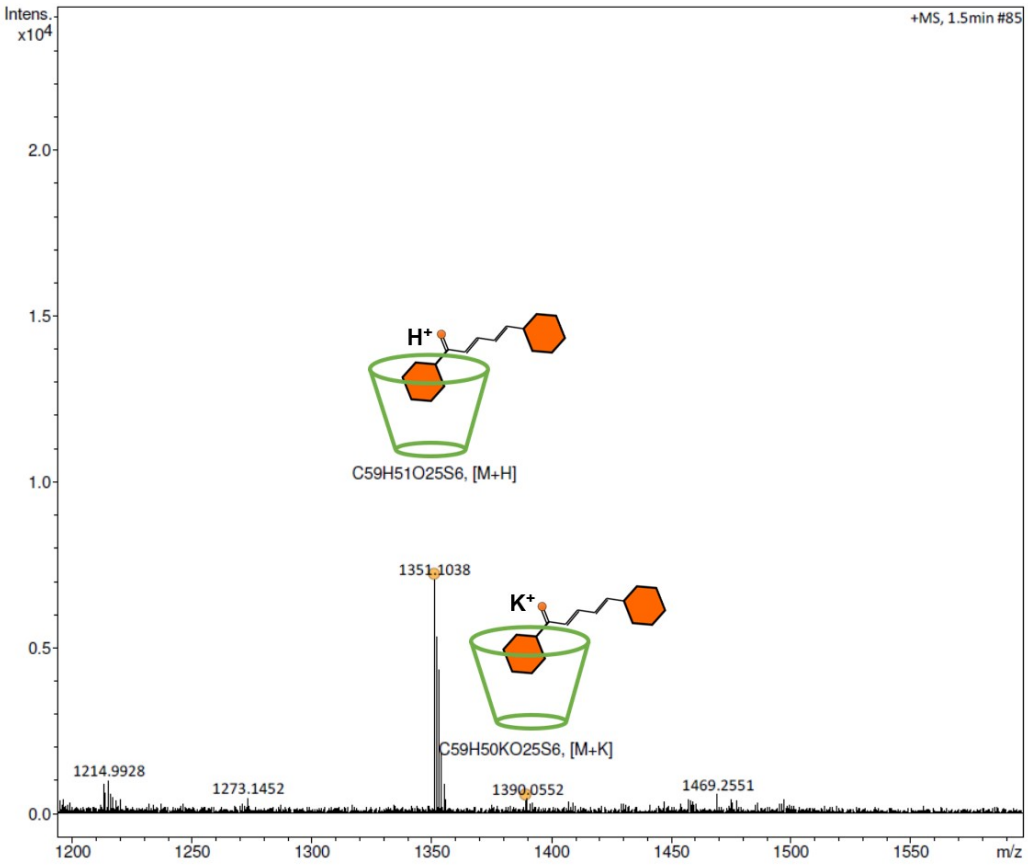


Fig. S13: Plot for log of peak current vs scan rate for (a) 1:1 C3⊂SCX6; and (b) 1:2 C3⊂SCX6 complexes.

Table S3: Second-order perturbation energies ($E^{(2)}$) of C1-C5 and SCX6 complexes.

Complex	Donor	Acceptor	Interaction	$E^{(2)}$ Kcal/mol
C1⊂SCX6	Lp(2) C1=O1	Lp*(1) H3—Oa	n → n*	52.22
	BD(2) C1=O1	Lp*(1) H3	π → n*	3.06
	Lp(2) O1	Lp*(1) H3	n → n*	5.41
	Lp*(1) H3	BD*(1) S1=Oc	n → n*	40.71
	Lp(1) S1=Od	BD*(1) C2—Hf	n → σ*	1.83
C2⊂SCX6	Lp(1) O2	BD*(1) Cb—H2	n → σ*	1.61
	Lp(2) O2	BD*(1) Cb—H2	n → σ*	1.06
	Lp(2) O1	BD*(1) Oa—H3	n → σ*	20.43
	Lp(1) O1	BD*(1) Oa—H3	n → σ*	8.27
	BD*(2) Cd—Cc	BD*(2) C12—C13	π* → π*	1.18
C3⊂SCX6	Lp*(1) N1	BD*(1) H3	n* → π*	0.18
	Lp(2) O2	BD*(1) Oa—H3	n → σ*	5.51
	Lp(2) O1	BD*(1) Oa—H3	n → σ*	21.00
	Lp*(1) O1	BD*(1) Oa—H3	π* → σ*	6.97
	BD*(2) C11—N1	BD*(2) Cb—Cc	π* → π*	0.12
C4⊂SCX6	Lp(2) O2	BD*(1) Oa—H3	n → σ*	7.33
	Lp*(1) O2	BD*(1) Oa—H3	n* → π*	0.29
	Lp(1) O2	BD*(1) Oa—H3	n → σ*	12.00
	BD(2) C2—C3	BD*(1) Oa—H3	π → σ*	5.91
C5⊂SCX6	Lp(2) O2	BD*(1) Oa—H3	n → σ*	5.41
	Lp(1) O2	BD*(1) Oa—H3	n → σ*	10.90
	BD(2) C2=C3	BD*(1) Oa—H3	π → σ*	6.15
	BD*(2) Cf—Ce	BD*(2) C13—C14	π* → π*	3.40

(a)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1.5
1.0
0.5
0.0
H+
C59H51O25S6, [M+H]
1351.1038
K+
C59H50KO25S6, [M+K]
1214.9928
1273.1452
1390.0552
1469.2551
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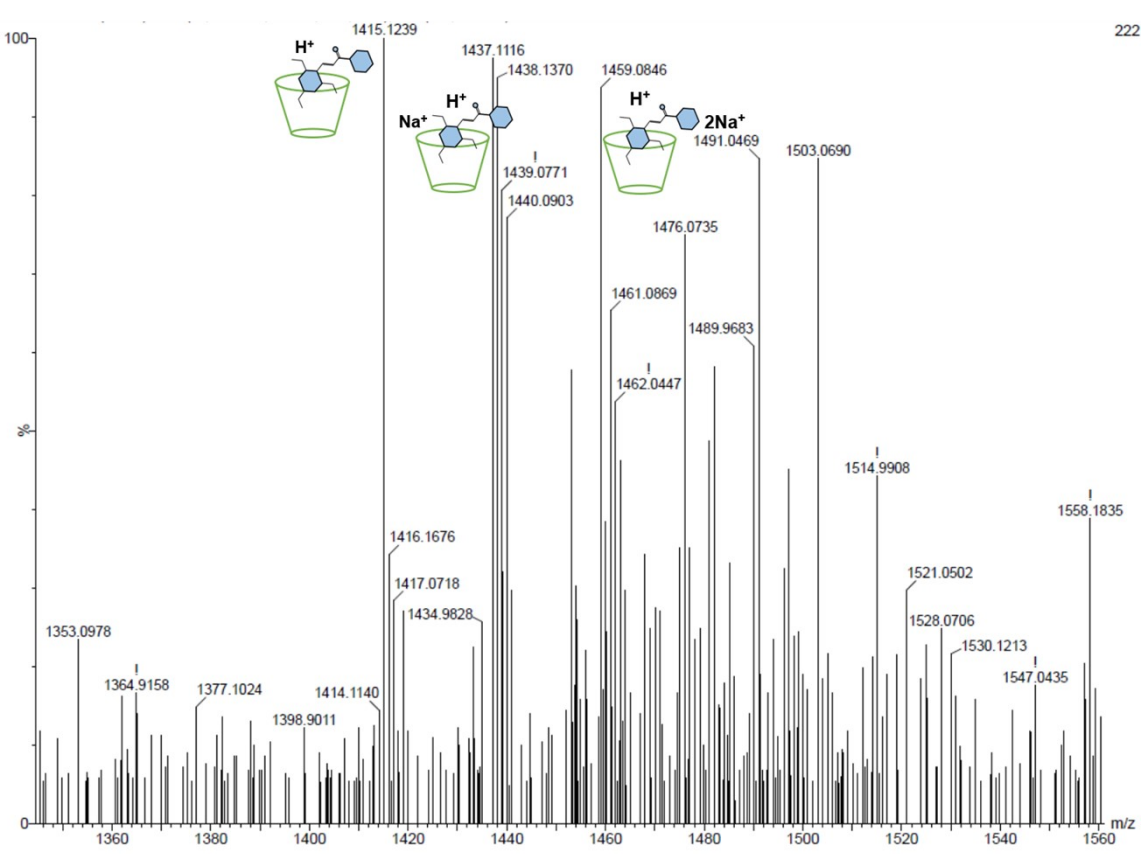
1250
1300
1350
1400
1450
1500
1550
m/z

(b)


100
%
0
222
H+
1415.1239
1437.1116
1438.1370
Na+
H+
1459.0846
H+
2Na+
1491.0469
1503.0690
1439.0771
1440.0903
1476.0735
1461.0869
1489.9683
1462.0447
1514.9908
1558.1835
1416.1676
1417.0718
1434.9828
1521.0502
1528.0706
1530.1213
1547.0435
1353.0978
1364.9158
1377.1024
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1460
1480
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1540
1560
m/z

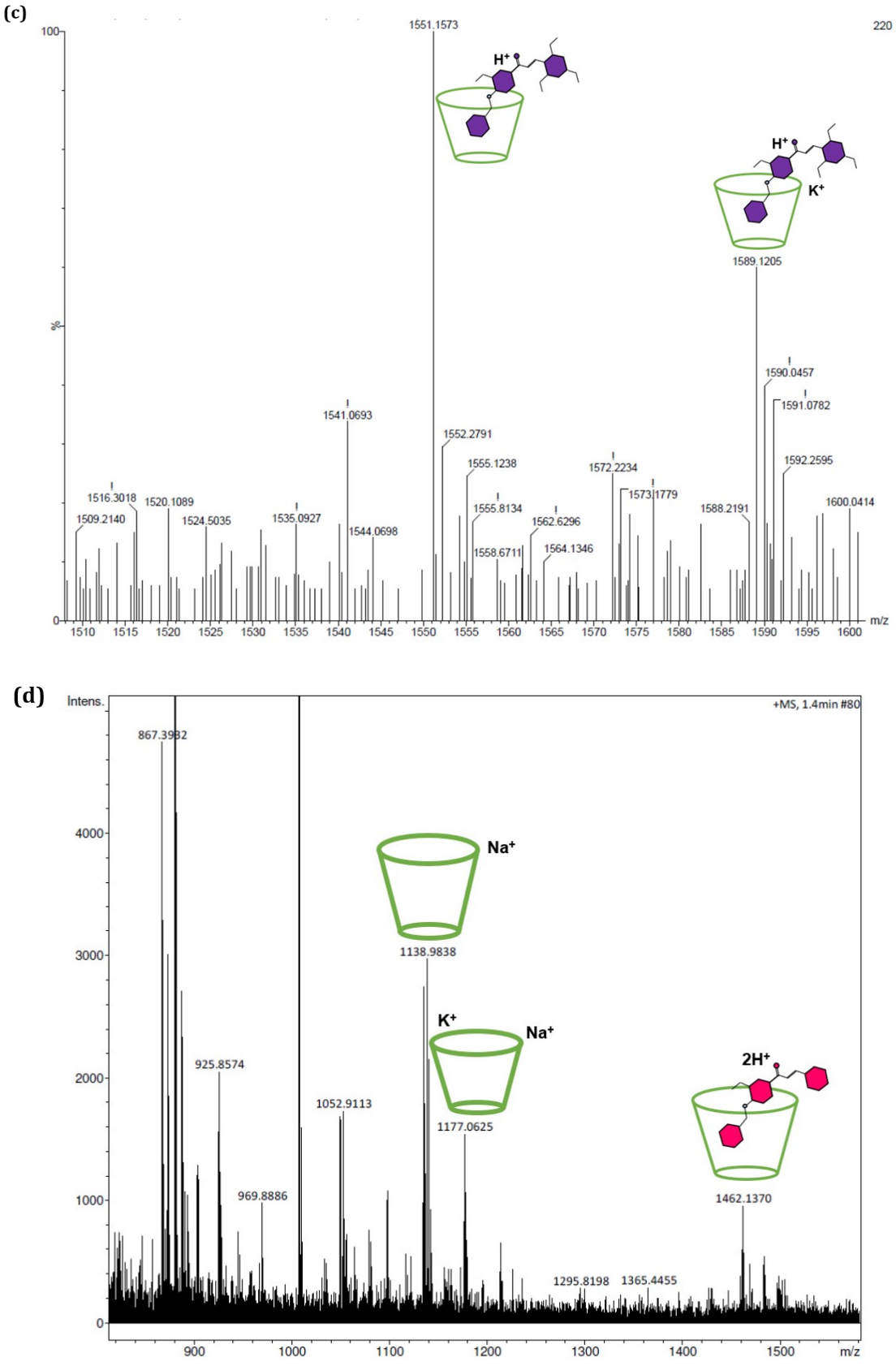


Fig. S14: Successive fragmentations of (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C4⊂SCX6; and (d) C5⊂SCX6 with schematic representation.

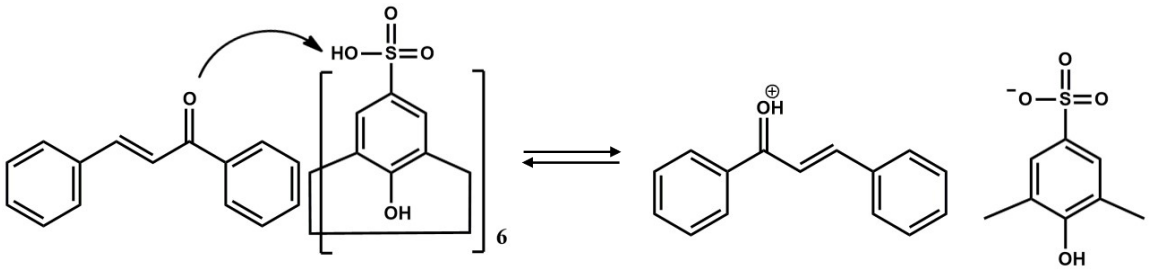
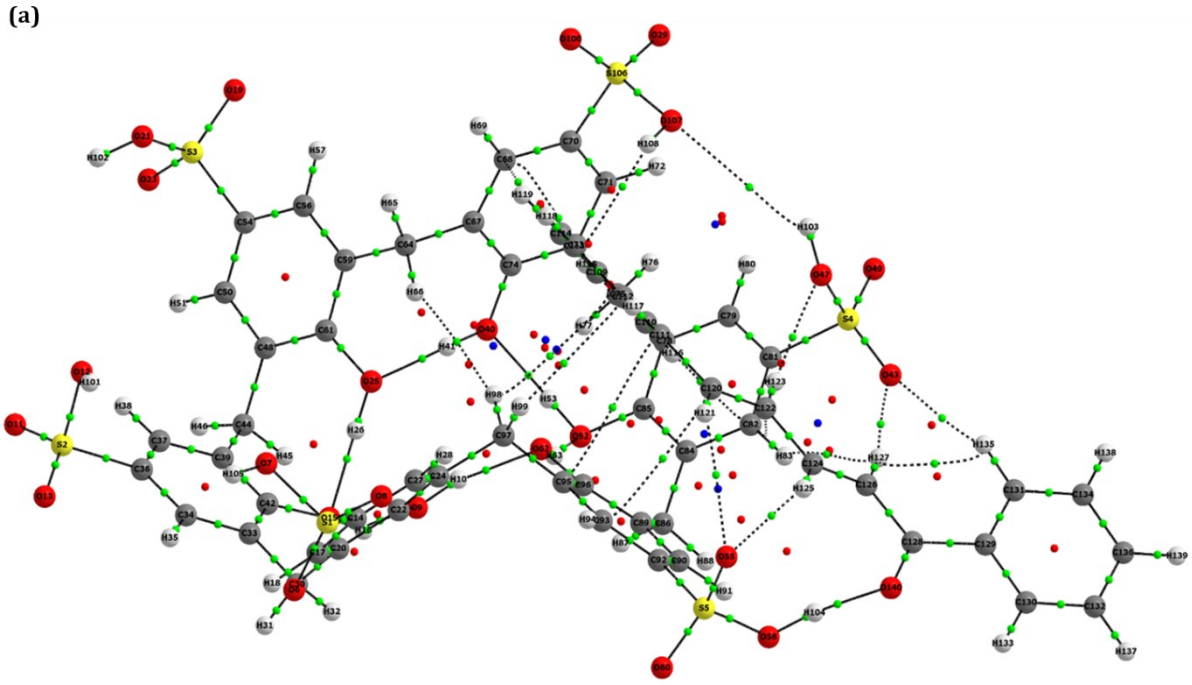
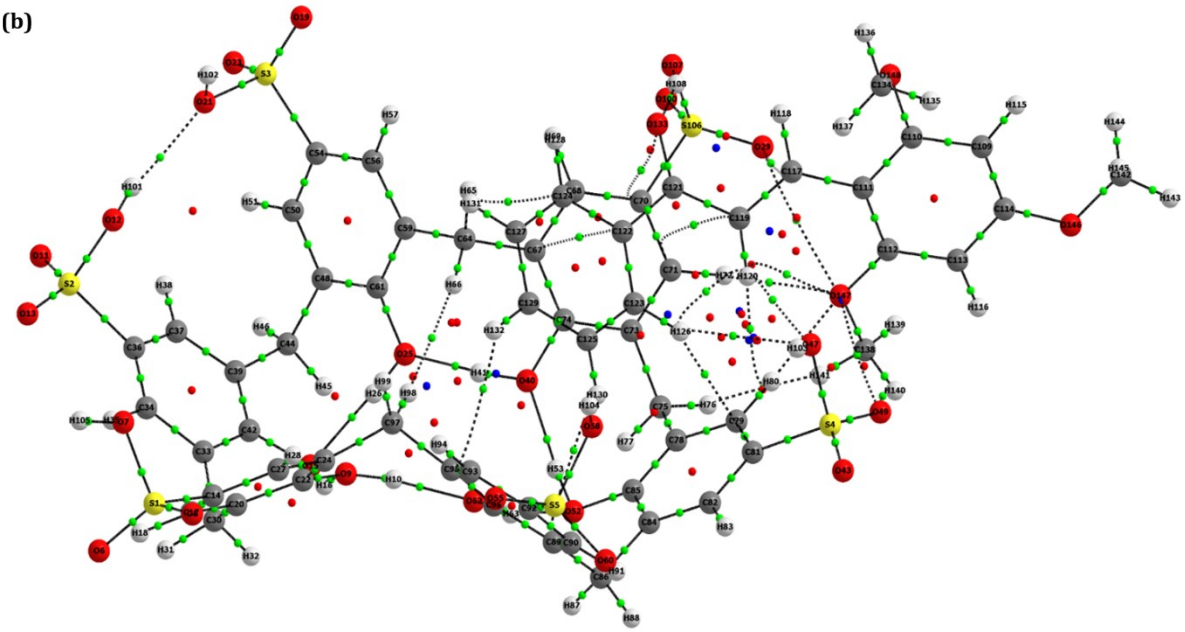


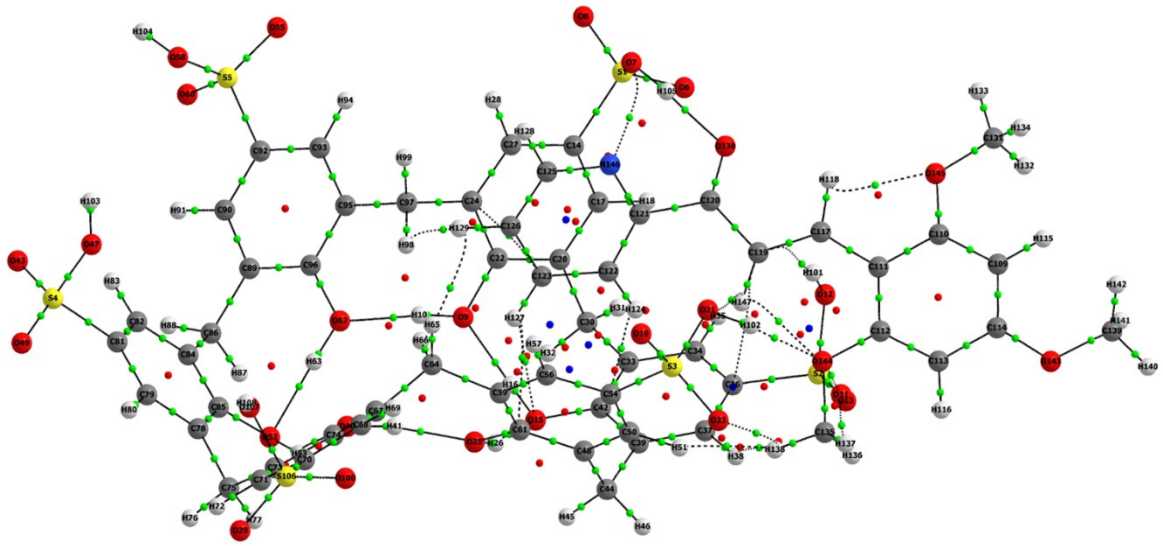
Fig. S15: Proton transfer in inclusion complexes of C1-C5⊂SCX6 in decluttering experiment in mass spectroscopy.



(b)



(c)



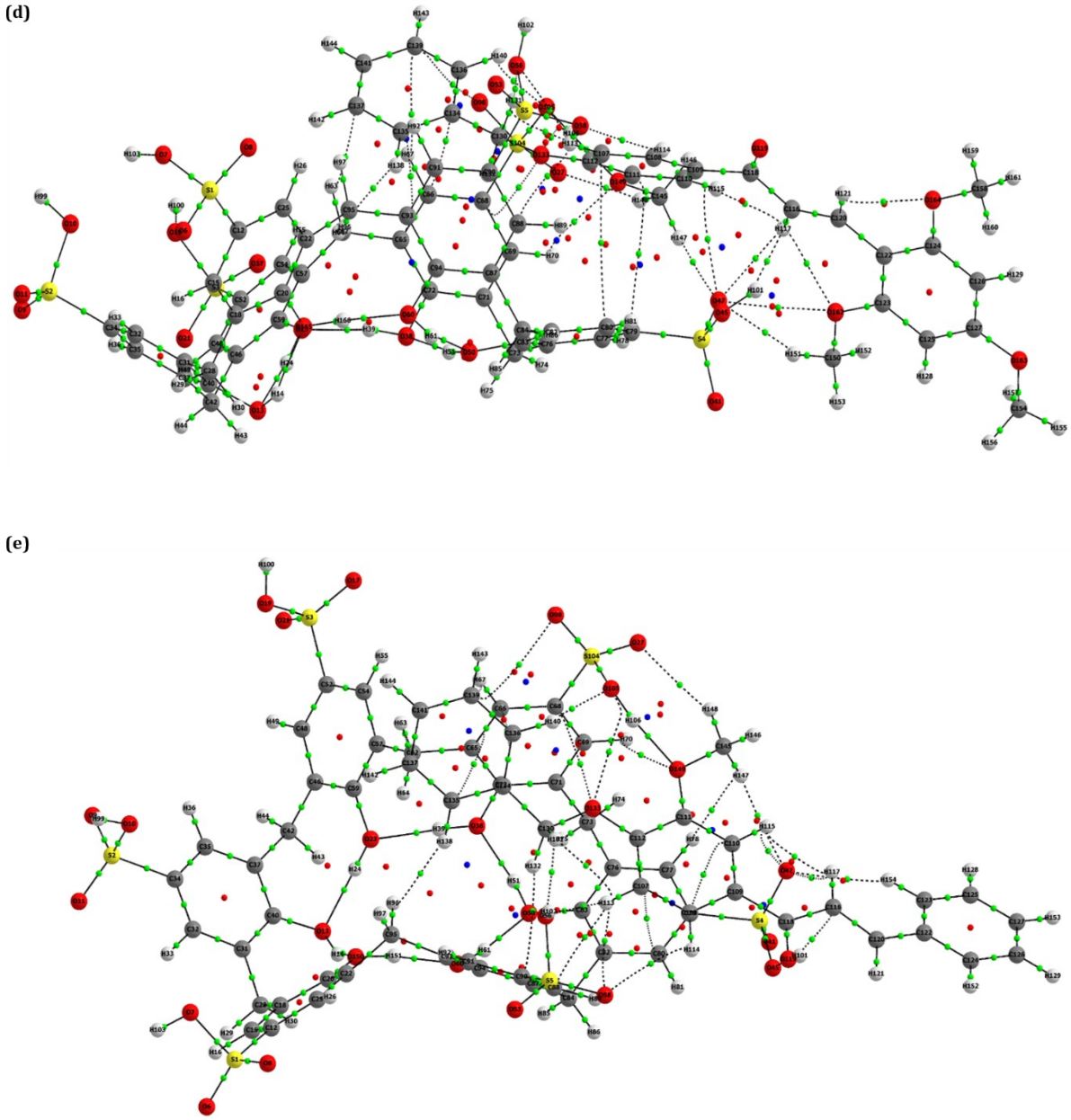


Fig. S16: Molecular graphs of (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6; and (e) C5⊂SCX6 from QTAIM analysis respectively.

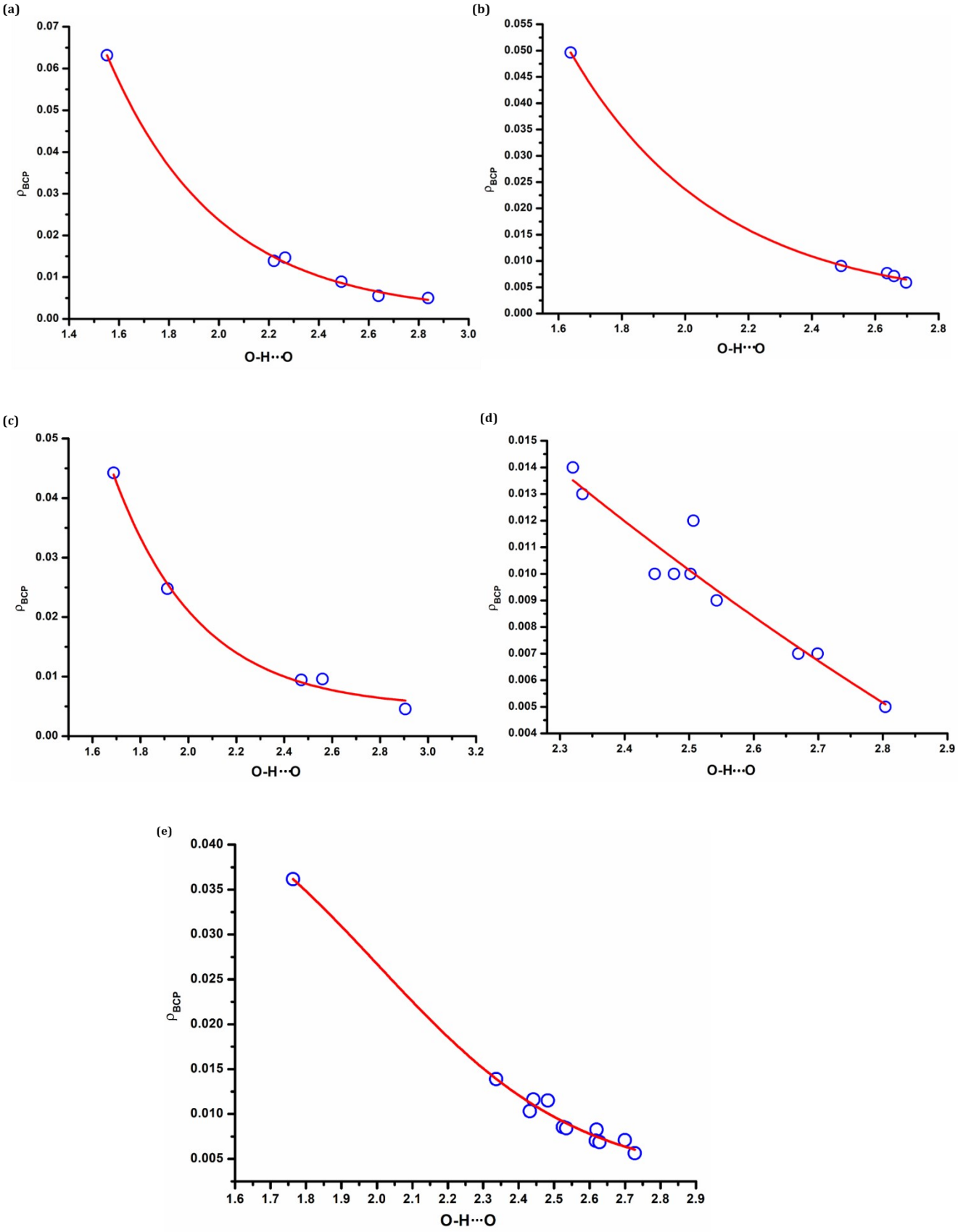


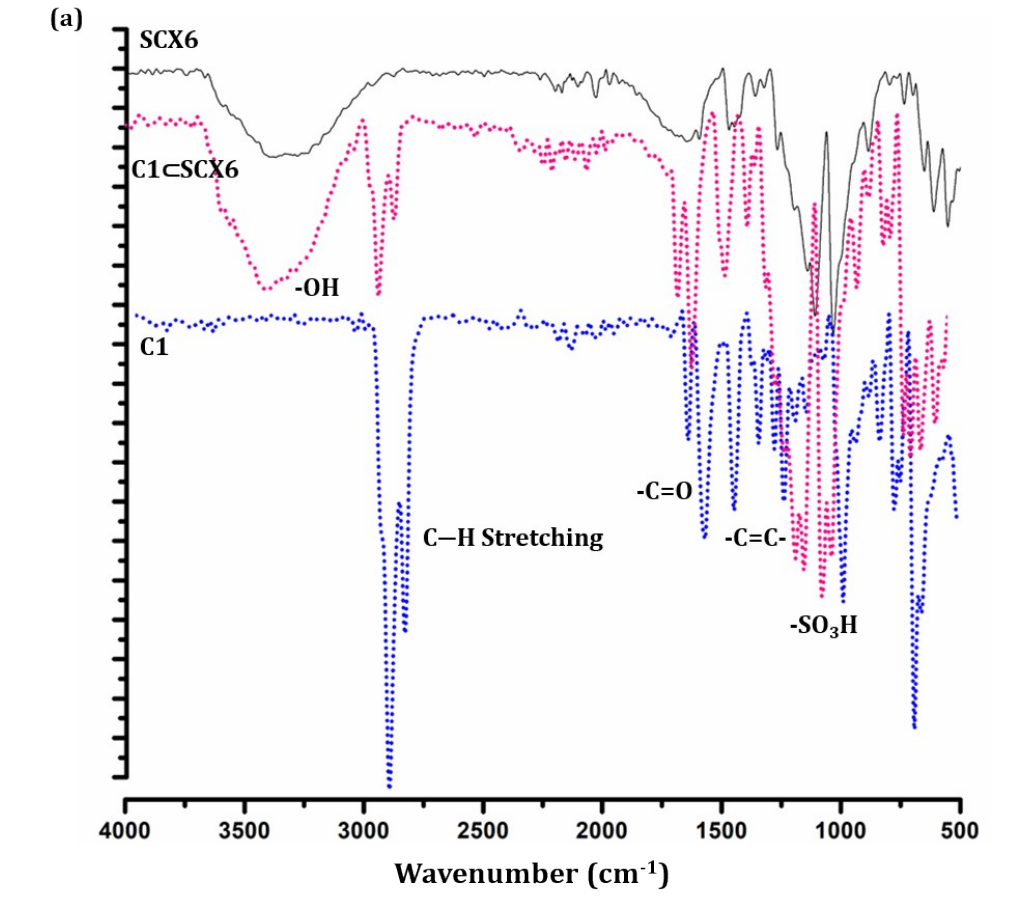
Fig. S17: Correlation of ρ_{CP} with O—H···O hydrogen bonds distances of (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6; and (e) C5⊂SCX6 complexes.

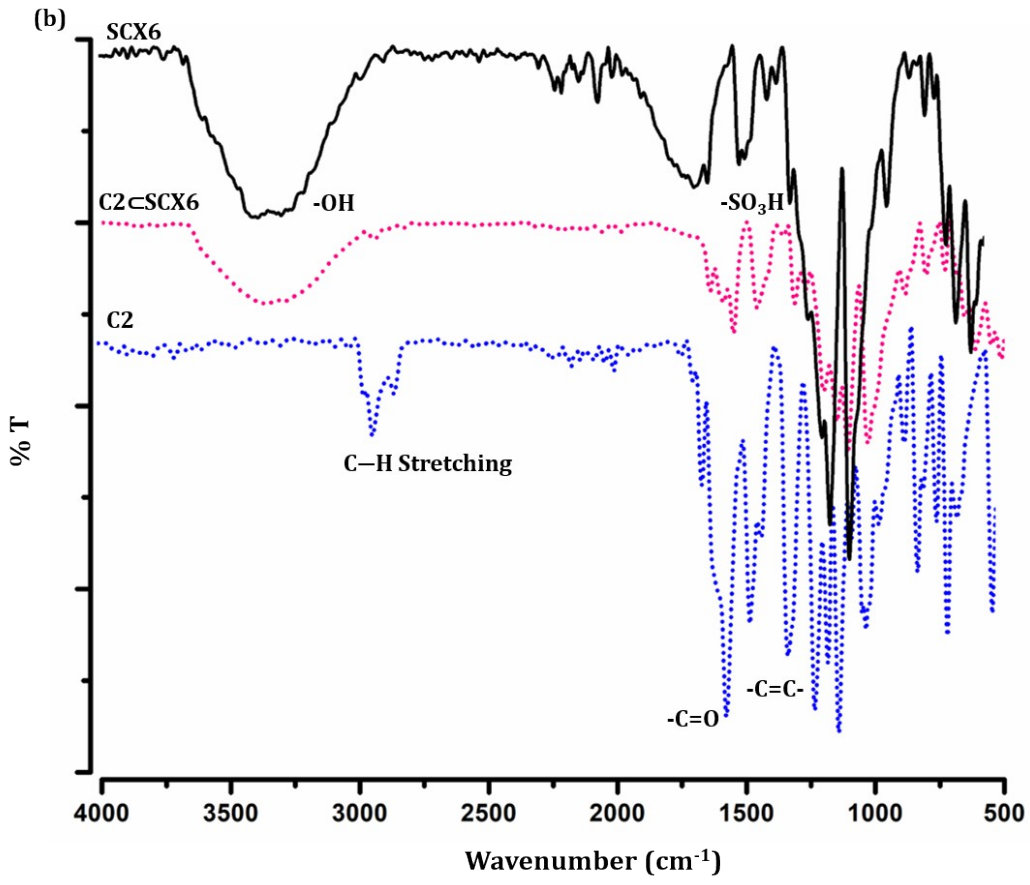
Table S4: QTAIM parameters ρ_{BCP}, $\Delta^2\rho_{BCP}$, Ellipticity(ϵ), V_{BCP}, G_{BCP}, H_{BCP} are given in au.

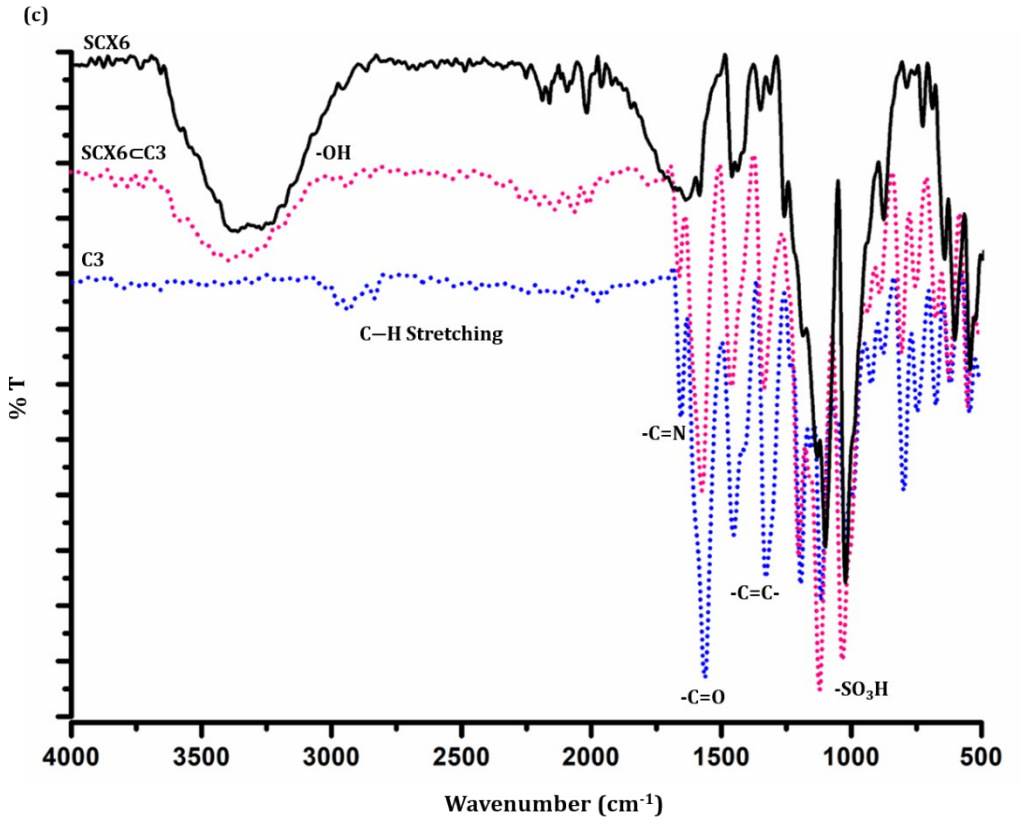
atom	rho	$\Delta^2\rho$	ε	V	G	H	(-G)/V
			SCX6⊂C1				
H98 - C109	0.00409	0.01179	6.61617	-0.0021	0.00251	0.000441	1.213663
H83 - H127	0.00434	0.01406	3.31964	-0.0023	0.00291	0.000602	1.260493
O55 - H121	0.00499	0.01724	0.27886	-0.003	0.00367	0.000643	1.212703
O43 - H135	0.00555	0.0202	0.7339	-0.0035	0.00429	0.00076	1.215297
H99 - C112	0.00615	0.01647	0.72333	-0.0029	0.00353	0.00059	1.200749
C95 - C111	0.00634	0.01793	3.39981	-0.003	0.00377	0.000718	1.235564
C82 - H123	0.00686	0.02099	0.63409	-0.0035	0.00437	0.000883	1.25359
C68 - H119	0.00725	0.02228	0.51984	-0.0037	0.00466	0.000913	1.243857
C82 - H116	0.00729	0.02029	1.19989	-0.0036	0.00434	0.000736	1.204444
C93 - C120	0.0073	0.02184	0.70711	-0.0036	0.00451	0.000952	1.267717
O47 - H123	0.00891	0.02898	0.08481	-0.0056	0.00641	0.000832	1.149104
C68 - H115	0.00914	0.03138	17.4914	-0.0053	0.00659	0.001258	1.236023
H108 - C114	0.00933	0.0282	1.45187	-0.0044	0.00573	0.001323	1.300477
O43 - H127	0.01388	0.05265	0.05082	-0.0091	0.01114	0.002026	1.222393
O55 - H125	0.01466	0.05099	0.04337	-0.0095	0.01114	0.001608	1.168677
H104 - O140	0.06316	0.1515	0.01484	-0.0683	0.0531	**-0.01523**	0.777152
atom	rho	$\Delta^2\rho$	ε	V	G	H	(-G)/V
			SCX6⊂C2				
H108 - O133	0.04965	0.15237	0.04651	-0.0512	0.04463	**-0.00654**	0.872205
O49 - H140	0.00902	0.03295	0.14341	-0.006	0.00711	0.001126	1.188106
O49 - O147	0.00719	0.02799	0.21303	-0.0057	0.00637	0.000627	1.109157
O29 - C117	0.00833	0.02659	0.36082	-0.0051	0.00585	0.000797	1.157728
C70 - O133	0.00818	0.02652	0.64427	-0.0046	0.00564	0.000994	1.214132
O47 - H120	0.00767	0.02587	0.16195	-0.0049	0.00566	0.000805	1.165706
C95 - H132	0.00826	0.02551	1.24367	-0.0042	0.0053	0.001082	1.256763
C81 - H126	0.00868	0.02543	1.73371	-0.0043	0.00532	0.001041	1.243452
O47 - H126	0.00713	0.02261	0.1186	-0.0045	0.00507	0.000579	1.128838
H72 - O147	0.00591	0.02018	0.13449	-0.0037	0.00436	0.000683	1.185598
C89 - H130	0.00644	0.01818	2.24866	-0.0033	0.00391	0.000634	1.19347
H76 - H141	0.00612	0.01672	0.10713	-0.0031	0.00365	0.000534	1.171649
H65 - C124	0.00524	0.01531	0.21407	-0.0025	0.00316	0.000663	1.265094
O29 - O147	0.00304	0.01439	3.09133	-0.0022	0.00291	0.000684	1.306864
H66 - H98	0.00106	0.00368	0.16103	-0.0004	0.00067	0.000247	1.581176
atom	rho	$\Delta^2\rho$	ε	V	G	H	(-G)/V
			SCX6⊂C3				
H102 - O144	0.02481	0.09658	0.08866	-0.0201	0.02214	0.002001	1.09934
H101 - C119	0.01824	0.05297	0.83419	-0.0091	0.01119	0.002057	1.225326
O11 - O144	0.01087	0.04458	0.48405	-0.0089	0.01002	0.00113	1.127181
O11 - H136	0.00946	0.03871	0.41106	-0.0067	0.00817	0.001508	1.226392
O21 - H147	0.00959	0.03709	0.29072	-0.0063	0.00779	0.001478	1.234046
C61 - H127	0.01039	0.03499	1.14384	-0.0058	0.00727	0.001479	1.255485
O7 - N146	0.00864	0.03257	1.61689	-0.0058	0.00697	0.001169	1.201413
H98 - H129	0.00762	0.02552	0.38626	-0.0041	0.00525	0.001133	1.275468

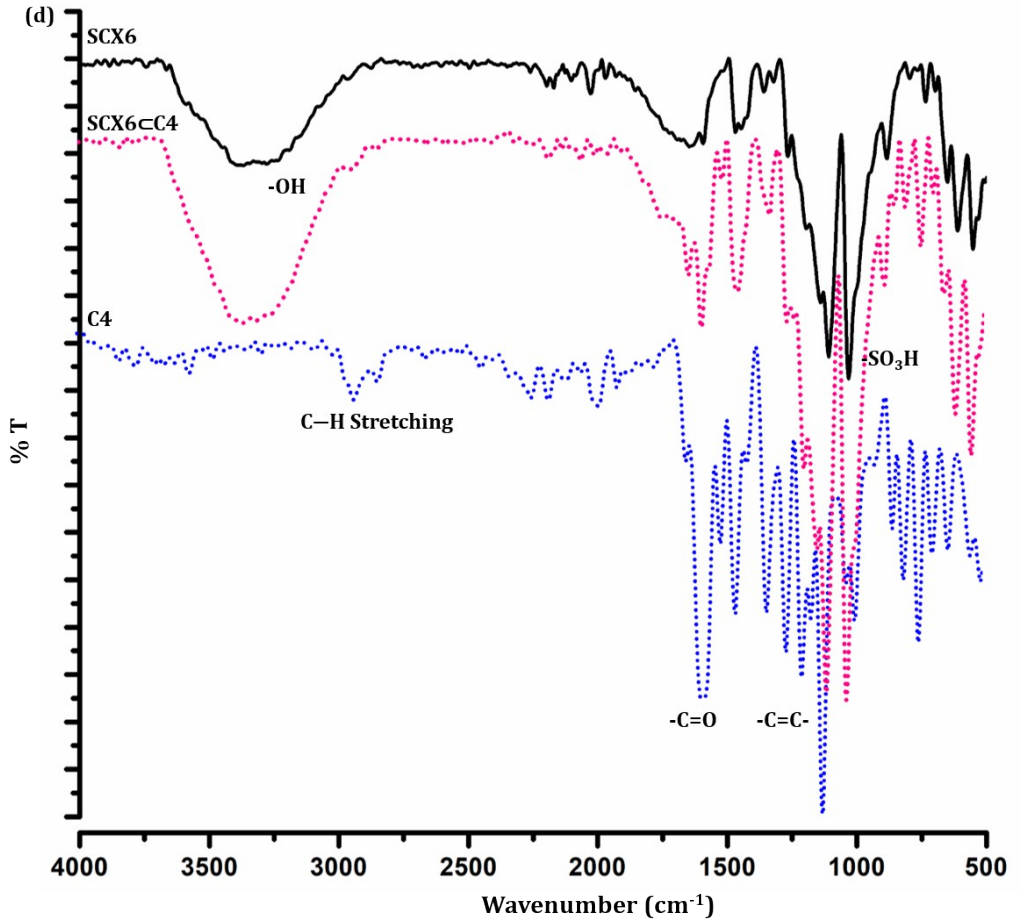
C42 - H124	0.00823	0.02501	2.40404	-0.0043	0.00527	0.000981	1.228618
C24 - C123	0.00765	0.02243	3.25225	-0.0037	0.00467	0.000933	1.249399
H66 - H129	0.00662	0.02198	0.12049	-0.0036	0.00455	0.000947	1.263056
O15 - H127	0.00456	0.01486	0.40253	-0.0028	0.00326	0.000458	1.163688
atom	rho	$\Delta^2\rho$	ε	V	G	H	(-G)/V
			SCX6⊂C4				
H101 - C116	0.02214	0.06201	0.13401	-0.0147	0.01511	0.000395	1.026849
O105 - H140	0.01427	0.05224	0.26038	-0.0096	0.01135	0.001707	1.176965
O47 - H151	0.01327	0.04602	0.09527	-0.0088	0.01016	0.001344	1.152398
O47 - H115	0.01216	0.04511	0.61036	-0.0084	0.00983	0.001452	1.173394
O105 - O133	0.00997	0.03956	1.46013	-0.0076	0.00873	0.001164	1.153928
O47 - H117	0.01001	0.03265	0.0071	-0.0065	0.00731	0.000849	1.131343
O27 - H148	0.01005	0.0323	0.0537	-0.0062	0.00714	0.00094	1.151711
O47 - O162	0.0082	0.03211	0.96691	-0.0066	0.00732	0.000707	1.106878
H96 - H138	0.00895	0.03059	0.45576	-0.005	0.00635	0.001303	1.258429
O56 - H131	0.00896	0.02971	0.09155	-0.0057	0.00656	0.00087	1.152954
H63 - C137	0.00878	0.02764	0.62636	-0.0047	0.0058	0.001114	1.237983
O56 - H113	0.00847	0.02752	0.17437	-0.0054	0.00615	0.000733	1.135365
H70 - O149	0.00741	0.02582	0.3022	-0.0047	0.00559	0.000864	1.182741
O58 - H113	0.00701	0.02345	0.64257	-0.0045	0.00516	0.000702	1.157505
C88 - H113	0.00767	0.02344	1.3748	-0.0039	0.00489	0.000974	1.248914
O58 - H114	0.00485	0.0182	0.26051	-0.0031	0.00381	0.000738	1.240078
H67 - C139	0.00608	0.01751	1.54478	-0.0029	0.00366	0.000718	1.244135
C90 - H132	0.00564	0.01676	1.45829	-0.003	0.0036	0.000588	1.195154
C66 - C136	0.00557	0.01583	4.439	-0.0026	0.00328	0.000682	1.262813
C65 - C135	0.00534	0.01369	4.27311	-0.0024	0.00292	0.0005	1.206441
C79 - C111	0.00455	0.01093	2.09658	-0.002	0.00236	0.000373	1.187626
O98 - C139	0.00328	0.01077	0.89339	-0.0016	0.00216	0.000534	1.328818
C80 - C107	0.00301	0.00735	0.44619	-0.0013	0.00156	0.000278	1.217018
atom	rho	$\Delta^2\rho$	ε	V	G	H	(-G)/V
			SCX6⊂C5				
H101 - C116	0.02112	0.05726	0.14959	-0.0129	0.01362	0.000695	1.053776
O105 - H140	0.0139	0.05074	0.28314	-0.0094	0.01103	0.00166	1.177237
O105 - O133	0.01057	0.04176	1.04875	-0.008	0.00923	0.001212	1.151179
O47 - H115	0.01151	0.04095	0.28293	-0.0077	0.00897	0.001272	1.165345
O47 - H117	0.01162	0.03893	0.11599	-0.0076	0.00869	0.001049	1.137376
O27 - H148	0.01032	0.03345	0.05894	-0.0064	0.00737	0.000992	1.155486
H96 - H138	0.00885	0.02975	0.41378	-0.0049	0.00618	0.001259	1.255894
H70 - O149	0.00828	0.02906	0.35096	-0.0054	0.00632	0.000951	1.177293
O56 - H113	0.00855	0.02803	0.16602	-0.0055	0.00623	0.000775	1.142045
O56 - H131	0.00841	0.02783	0.09247	-0.0053	0.00614	0.00082	1.154222
C88 - H113	0.0086	0.0273	1.37413	-0.0045	0.00567	0.001161	1.257771
H63 - C137	0.00864	0.02707	0.60837	-0.0046	0.00567	0.001093	1.238646
O58 - H113	0.0071	0.02415	0.79337	-0.0045	0.00529	0.000744	1.163588
O47 - H154	0.00703	0.02224	0.16924	-0.0043	0.00491	0.00065	1.152618
O47 - H147	0.00688	0.02222	0.21354	-0.0042	0.00489	0.000669	1.158681
O58 - H114	0.00564	0.02062	0.17129	-0.0036	0.00437	0.000787	1.219832
H67 - C139	0.00592	0.0169	1.53094	-0.0029	0.00354	0.000684	1.239412

C90 - H132	0.00553	0.01653	1.57432	-0.003	0.00356	0.000572	1.191368
C66 - C136	0.00529	0.01505	7.61885	-0.0025	0.00311	0.000649	1.263286
C79 - C110	0.0059	0.01481	1.64625	-0.0026	0.00317	0.000529	1.200151
C65 - C135	0.00506	0.0129	6.40929	-0.0023	0.00276	0.000469	1.205162
C68 - O133	0.0037	0.01241	1.21482	-0.002	0.00256	0.000545	1.271009
H78 - H147	0.0033	0.01079	0.0902	-0.0016	0.00217	0.000529	1.322758
O98 - C139	0.00319	0.01046	0.8519	-0.0016	0.00209	0.000523	1.333121
C80 - C107	0.00336	0.00821	1.69609	-0.0015	0.00175	0.000298	1.20467


(a)
SCX6
C1⊂SCX6
-OH
C1
-C=O
C—H Stretching
-C=C-
-SO3H
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


(b)
SCX6
C2⊂SCX6
-OH
-SO3H
C2
C—H Stretching
-C=O
-C=C-
% T
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


(c)
SCX6
SCX6⊂C3
C3
-OH
C—H Stretching
-C=N
-C=C-
-C=O
-SO3H
% T
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)


(d)
SCX6
SCX6⊂C4
C4
-OH
C—H Stretching
-C=O
-C=C-
-SO3H
% T
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

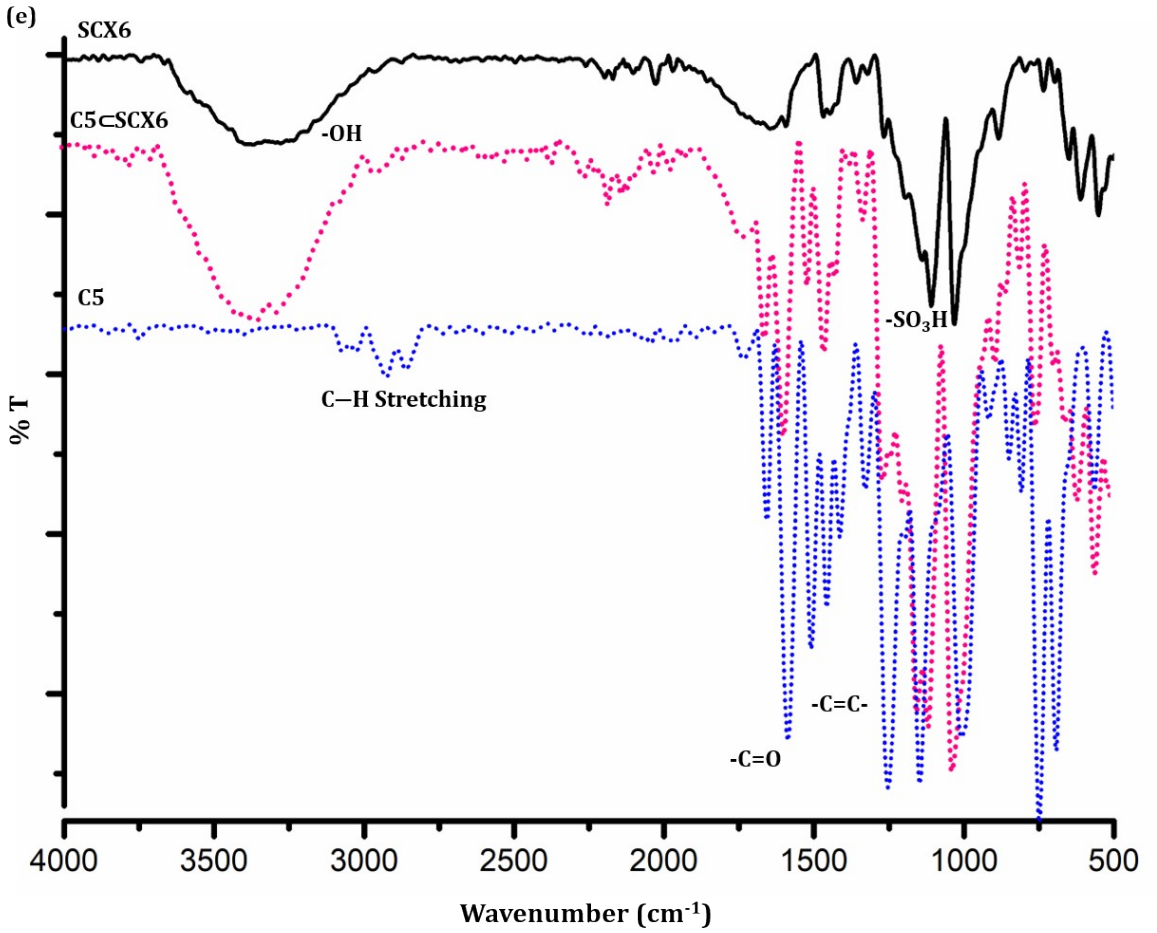


Fig. S18: Infrared spectra of (a) C1⊂SCX6; (b) C2⊂SCX6; (c) C3⊂SCX6; (d) C4⊂SCX6 and (d) C5⊂SCX6.

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