Electronic Supplementary Material (ESI) for Chemical Communications

Separation of isomers of sulfophthalic acid by guest induced host framework formation with 4,4'-bipyridine.

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Supporting Information

Experimental analysis and characterization of the compounds by HPLC analysis, NMR spectra, I.R spectra, DRS spectra, Powder XRD patterns and crystallographic information of the compounds explained in details.

Experimental Section:

Materials and Apparatus:

50% aqueous weight of 4-sulfophthalic acid which contains 3-sulfophthalic acid as major ingredient was purchased from Aldrich, U.S.A, 4,4'-bipyridine was purchased from Alfa-Aesar U.K and anthracene, phenanthrene and naphthalene were purchased from Spectrochem, India.

HPLC was recorded on Waters 2489, UV/visible detector instrument. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER-AC 200MHz and 400MHz spectrometer. FTIR spectra were recorded with a Perkin Elmer Instrument Spectrum Rx Serial No. 73713. Melting point measurement was carried out using Fisher Scientific instrument Cat. No. 12-144-1.Elemental analysis has been carried out by Perkin Elmer *Series II* 2400 and the powder XRD patterns were recorded with a PHILIPS Holland PW-1710 diffractometer. The DRS spectra was recorded in a VARIAN CARY 5000 UV-Vis-NIR Spectrophotometer.

Synthesis of Complex 1:

The methanolic solution (5mL) of 4,4'-bipyridine (1.229 gm, 0.0078 mol) was added drop wisely to the methanolic solution (5 mL) of the mixtures of 4 and 3-sulfophthalic acids (1:4 according to NMR study) (1.292 gm, 0.0052 mol) and then the mixture was stirred for 5 minutes to make it homogeneous. After that, anthracene (2.805gm, 0.0157 mol) was dissolved in acetone (1mL) and methanol (4mL) mixture and then the solution was added to the previous mixture. After one day, intense red colored crystals suitable for X-ray diffraction were grown. Yield 74.37% with respect to 4-sulfophthalic acid. Mp>300˚C. (Found C, 66.19; H, 3.54; N, 4.68. Calc. for $C_{32}H_{21}N_2O_7S$: C, 66.48; H, 3.63,

,N, 4.84); λ_{max} (nm) 560; $\upsilon_{max}(cm^{-1})$ 3421, 3101, 3056, 2783, 2103, 1718, 1628, 1593, 1491, 1481, 1429, 1361, 1296, 1235, 1176, 1116, 1064, 1032, 856, 813, 787, 736, 702, 670, 608, 557, 533, 475; δ_H(200 MHz; D_6DMSO) 8.982(d, 4H, Py-α-H), 8.558(s, 2H, guest), 8.206(d, 4H, Py-β-H), 8.070(m, 4H, guest), 7.922(s, 1H,4-H3SPA), 7.806(d, 1H,4-H3SPA), 7.674(d, 1H,$_{4\text{-H3SPA}}$), 7.497(m, 4H, guest).

Similar procedure was applied for the synthesis of Complex **2** but only difference is that naphthalene was used as guest in Complex **2**.

Complex 2: Yield 32% with respect to 3-Sulfophthalic acid. Mp>300˚C. (Found C, 52.01; H, 3.62; N, 6.35. Calc for $C_{56}H_{48}N_6O_{12}S_4$: C, 52.28; H, 3.73; N, 6.53; λ_{max} (nm) 400; $\upsilon_{max}(cm^{-1})$ 3853, 3440, 3053, 2901, 2778, 2047, 1700, 1618, 1593, 1482, 1361, 1216, 1194, 1143, 1122, 1037, 1007, 860, 810, 786, 767, 695, 645, 573; 486. δ_H(200 MHz; D_6DMSO) 8.982(d, 4H, Py-*α*-H), 8.097(d, 4H, Py-*β*-H), 7.881(m,4H,guest), 7.748(d, 1H, 3-SPA), 7.607(d, 1H, 3-SPA), 7.5097(m,4H,guest), 7.430(t, 1H, 3-SPA).

Confirmation of SO_4^{2-} ion and the weight % of H_2SO_4 ion present per ml by $BaCl_2$ treatment:

The presence of SO_4^{2-} ion in the aqueous suspended solid was confirmed by perfoming $BaCl_2$ test. The immediate formation of white precipitation of $BaSO_4$ indicates that SO_4^{2-} ion is also present as ingredient in the original compound.

The amount of SO_4^{2-}.ion present in the solution is also determined by carrying out six separate $BaCl_2$ reactions with the original sample in different molar ratios i,e (1:1), (1:2), (1:3), (1:4), (1:5) and (1:6) respectively and in all cases almost same amount of BaSO4 was precipitated. During experiment, we have taken 1ml of the suspended homogeneous mixture of the original sample in each cases and after complete reaction near about 42 mg of $BaSO_4$ was obtained from the reactions. Therefore, the % of SO_4^{2-} ion i,e H_2SO_4 present in the original compound is 2.5%

The interesting thing is that after removal of SO_4^{2-} ion, the crystallization reactions were again carried out in presence of guest molecules and it has been found that in case of

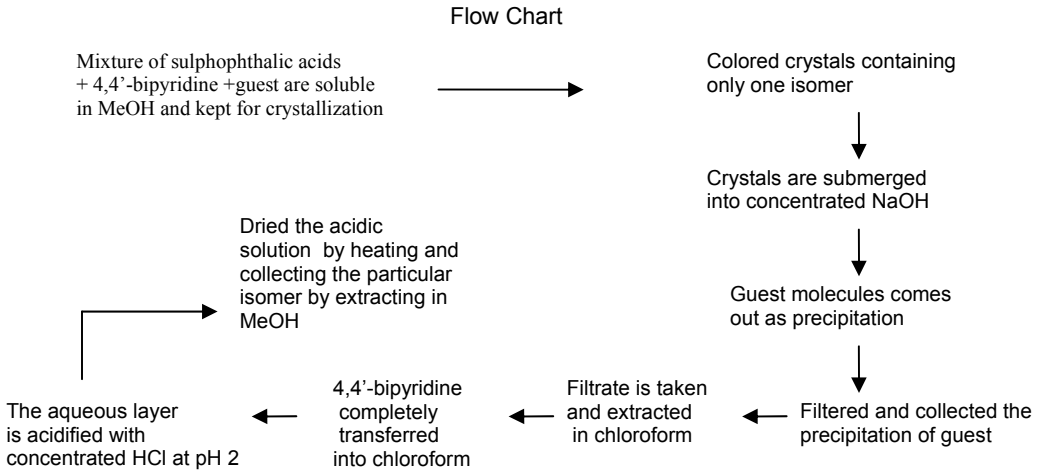
anthracene we got the same crystals as earlier but in case naphthalene, the greenish-yellow colored crystals were not formed only naphthalene precipitated as flakes.

Even after adding excess SO_4^{2-} ion in the form of Na_2SO_4 from outside, the yield the complex **2** was found to be increased and it became maximum when the concentration of sulphate ion was 8% in 1ml of the suspended homogeneous mixture with respect to sulphate ion present in the crude compound. At that concentration of sulphate ion the yield of complex **2** became 38%.

From the above experiments it can be concluded that SO_4^{2-} ion is essential for the formation of the complex **2.**

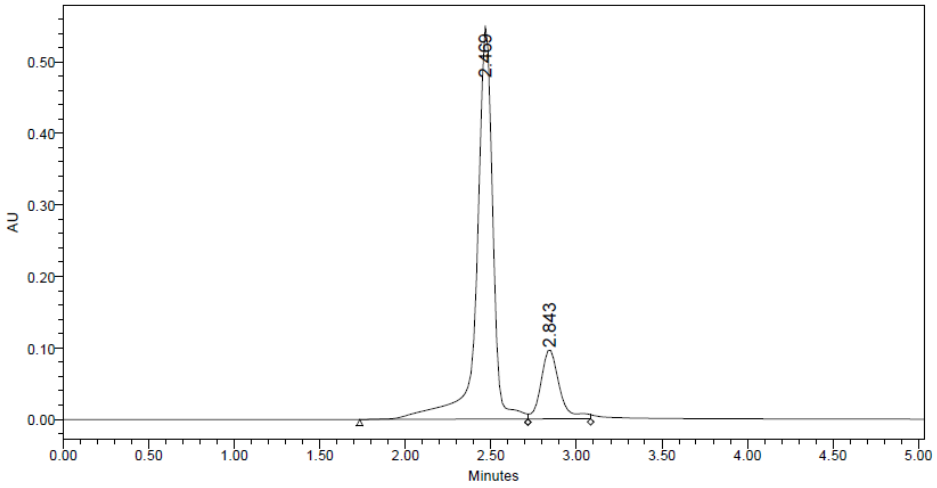
Technique applied for the isolation of isomers from the complexes:

Complexes containing particular isomer could be visually recognized by observing their colors in naked eye. The intense red colored crystals contains 4-isomer whereas the light greenish-yellow colored crystal contains 3-isomer.Isolation of the isomers of sulfophthalic acid from the guest selective host frameworks has been carried out by saponification and solvent extraction technique. The isolated major and minor isomers were well characterized by ^1H and ^{13}C NMR. The amount of 4-sulphophthalic acid and 3-sulphophthalic acid extracted by host-guest complexation technique in **complex 1** and **complex 2** from the mixture were 75% and 32% respectively. The flow chart for the extraction procedure is like the following.



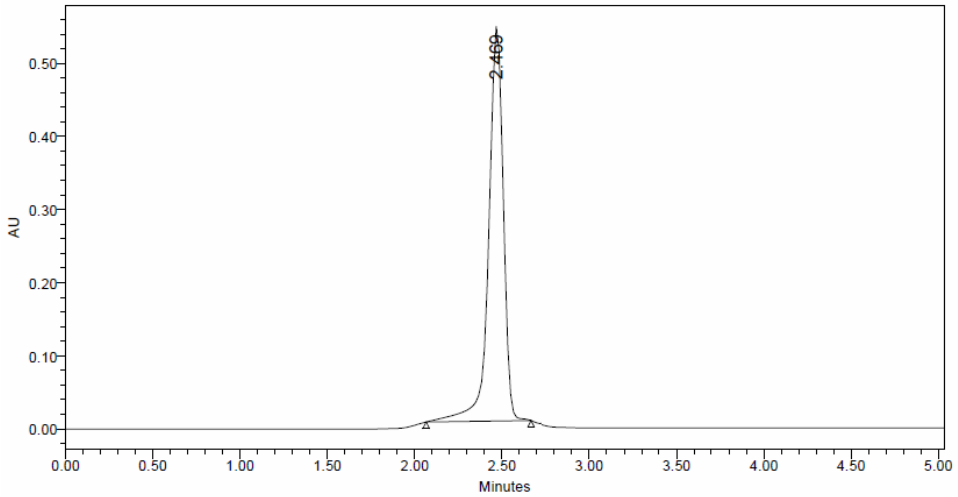
Characterizations of the compounds:

HPLC of the 4-sulfophthalic acid purchased from Aldrich:



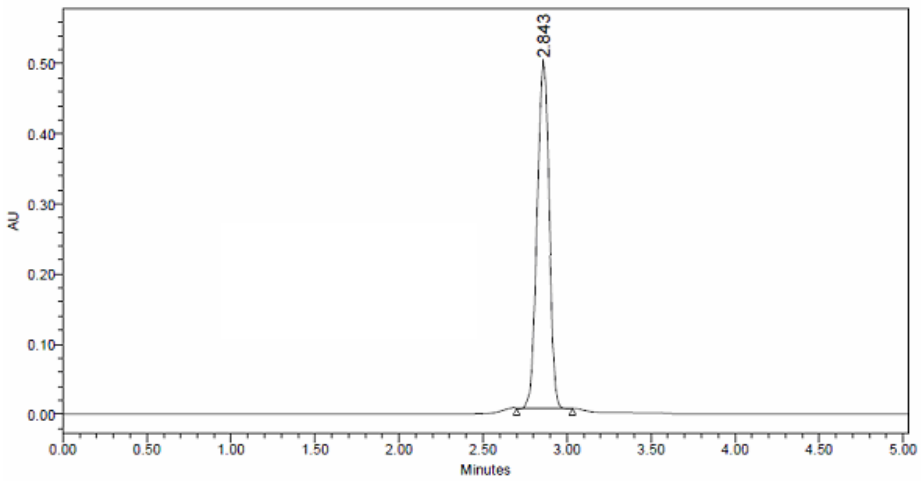
	RT	Area	% Area	Height
1	2.469	3572308	83.15	546038
2	2.843	723846	16.85	96234

HPLC of the 4-sulfophthalic acid



	RT	Area	% Area	Height
1	2.469	3144544	100.00	535830

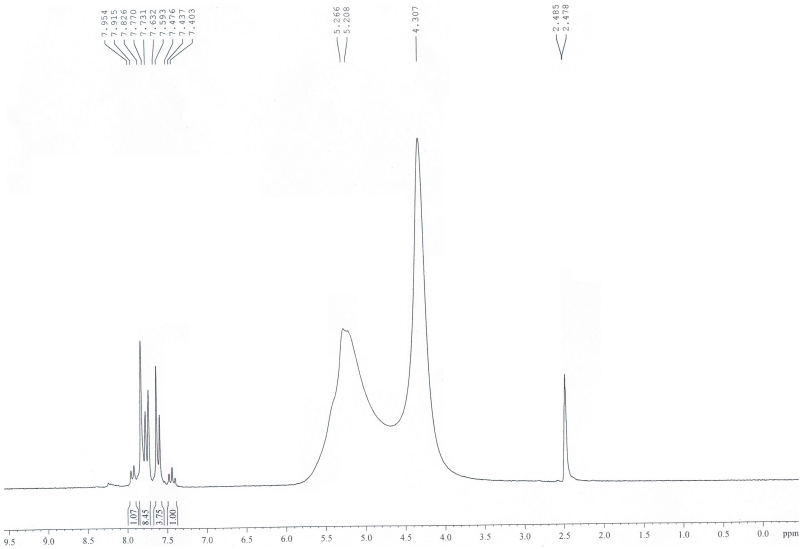
HPLC of the 3-sulfophthalic acid

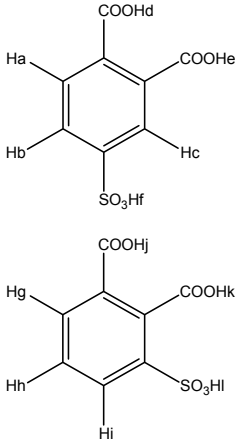


	RT	Area	% Area	Height
1	2.843	2835111	100.00	521048

NMR studies:

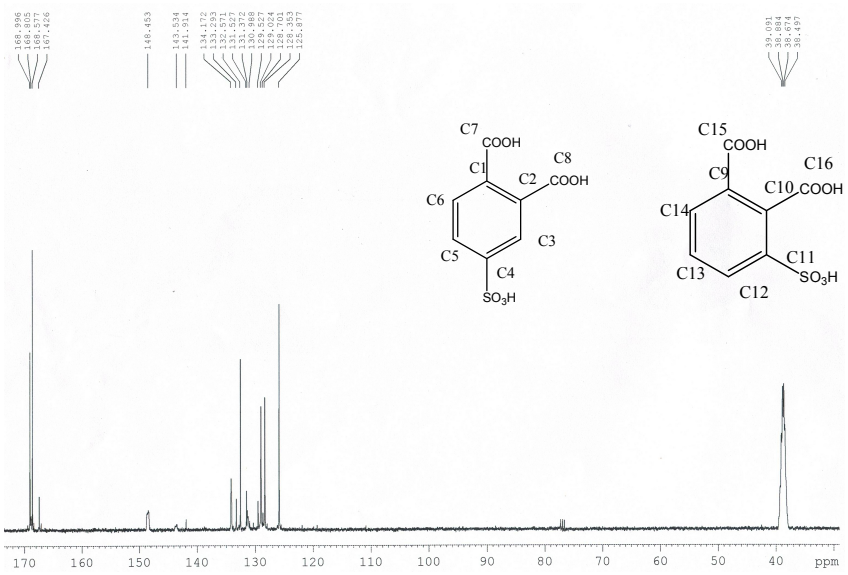
^{1}H NMR of of 4 sulfophthalic acid purchased from Aldrich..





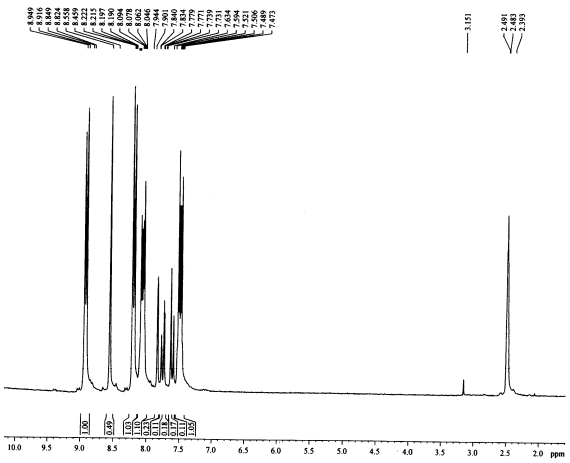
NMR: (D^{6}DMSO, 200MHz), δ_H (ppm): 7.934 (1H, d, 3-H_3SPA,Hl), 7.826 (1H, s, 4-H_3SPA, Hg), 7.750 (1H, d, 4-H_3SPA, Hc), 7.612 (1H, d, 4-H_3SPA, Hb), 7.438 (1H, t, 3-H_3SPA, Hh).

^{13}C NMR of 4 sulfophthalic acid purchased from Aldrich.



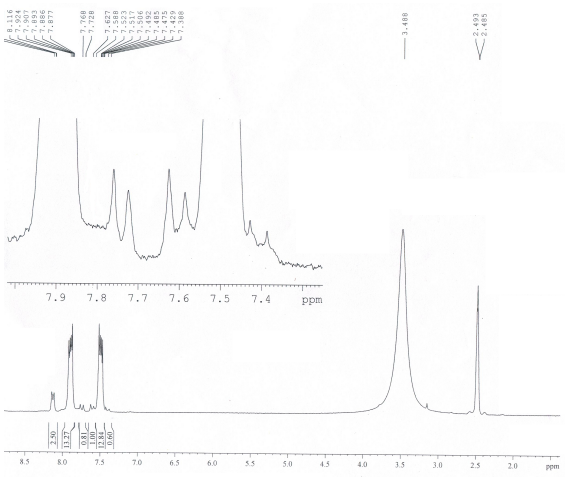
NMR: (D^6DMSO, 200 MHz), δ_C (ppm): 168.996 (C8 of 4-H_3SPA, -COOH group), 168.805 (C7 of 4-H_3SPA, -COOH group), 168.577 (C16 of 3-H_3SPA, -COOH group), 167.426 (C15 of 3-H_3SPA, -COOH group), 148.453 (C4 of 4-H_3SPA ring carbon), 143.534 (C11 of 3-SPA ring carbon), 134.172 (C1 of 4-H_3SPA ring carbon), 133.293 (C13 of 3-SPA ring carbon), 132.571 (C2 of 4-H_3SPA ring carbon), 131.527 (C14 of 3-H_3SPA ring carbon), 130.988 (C9 of 3-H_3SPA ring carbon), 129.527 (C5 of 4-H_3SPA ring carbon), 129.024 (C12 of 3-H_3SPA ring carbon), 128.701 (C10 of 3-H_3SPA ring carbon), 128.353 (C6 of 4-H_3SPA ring carbon), 125.877 (C3 of 4-H_3SPA ring carbon).

^{1}H NMR Complex 1



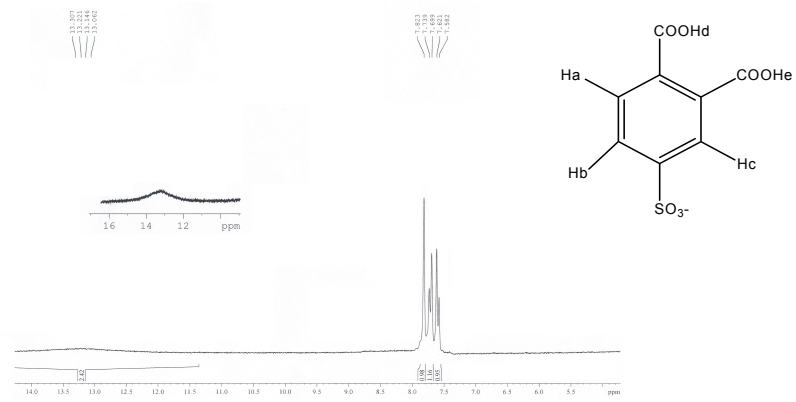
NMR: (D^6DMSO, 200 MHz), δ_H (ppm): 8.982 (d, 4H, Py-α-H), 8.558 (s, 2H, guest), 8.206 (d, 4H, Py-β-H), 8.070 (m, 4H, guest), 7.922 (s, 1H,4-H_3SPA), 7.806 (d, 1H,4-H_3SPA), 7.674 (d, 1H,4-H_3SPA), 7.497 (m, 4H, guest).

^{1}H NMR Complex 2:



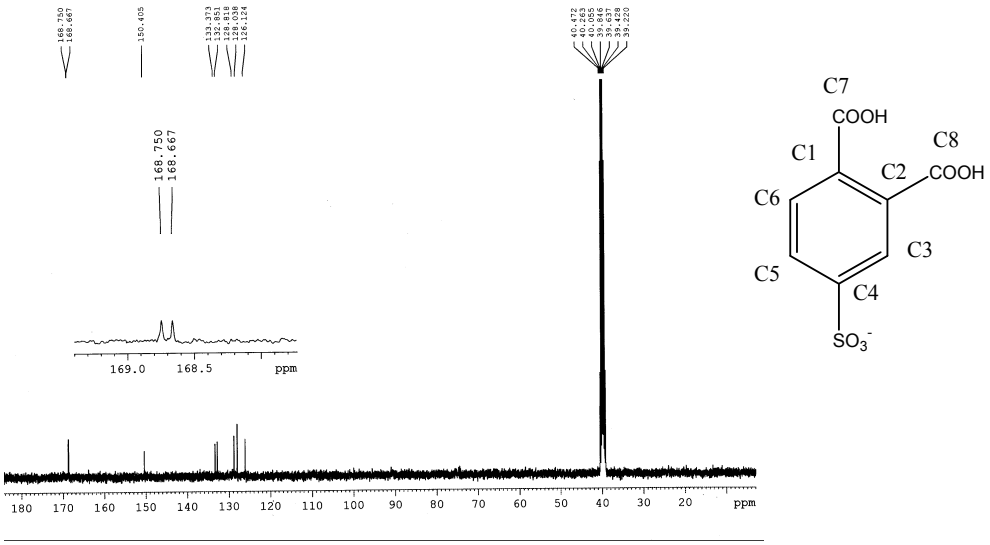
NMR: (D^6DMSO, 200 MHz), δ_H (ppm): 8.982 (d, 4H, Py-*α*-H), 8.097 (d, 4H, Py-*β*-H), 7.881 (m, 4H, guest), 7.748 (d, 1H, 3-H_3SPA), 7.607 (d, 1H, 3-H_3SPA), 7.5097 (m, 4H, guest), 7.430 (t, 1H, 3-H_3SPA).

^{1}H NMR of 4-sulfophthalic acid:



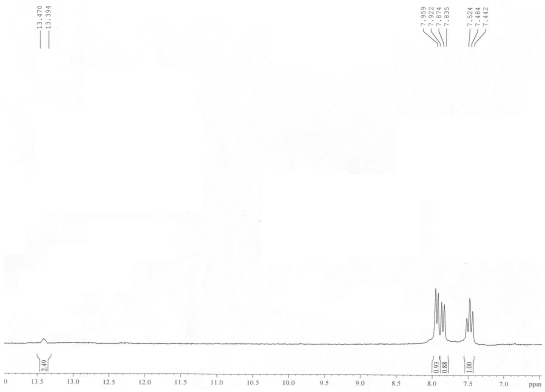
NMR: (D^{6}DMSO, 200 MHz), δ_H (ppm): 13.46 (1H,br, s, He), 13.10 (1H, s, Hd), 7.82 (1H, s, Hc), 7.71 (1H, d, Ha), 7.60 (1H, d, Ha).

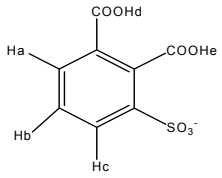
^{13}C NMR of 4-sulfophthalic acid:



NMR: (D^{6}DMSO), δ_C (ppm): 168.750 (C8 of COOH group), 168.667 (C7 of COOH group), 150.405 (C4 of ring carbon), 133.373 (C1 of ring carbon), 132.851 (C2 of ring carbon), 128.818 (C5 of ring carbon), 128.038 (C6 of ring carbon), 126.124 (C3 of ring carbon).

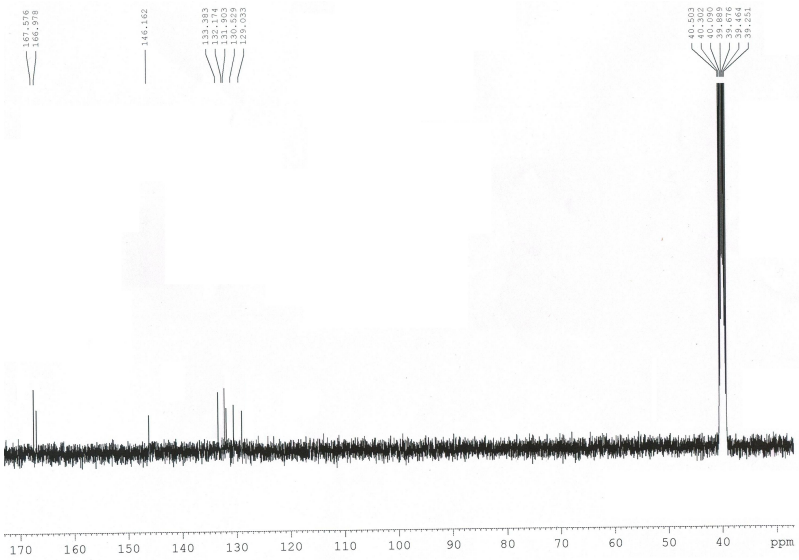
^{1}H NMR of 3-sulfophthalic acid:

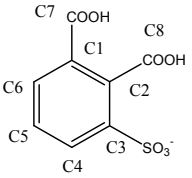




NMR: (D^{6}DMSO), δ_H (ppm)： 13.470 (1H, s, He), 13.394 (1H, s, Hd), 7 940 (1H, d, Hc), 7.804 (1H, d, Ha), 7.483 (1H, t, Hb).

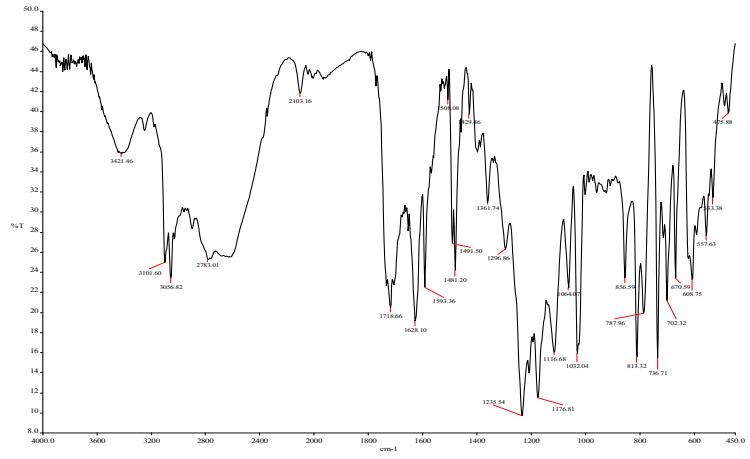
^{13}C NMR of 3-sulfophthalic acid:





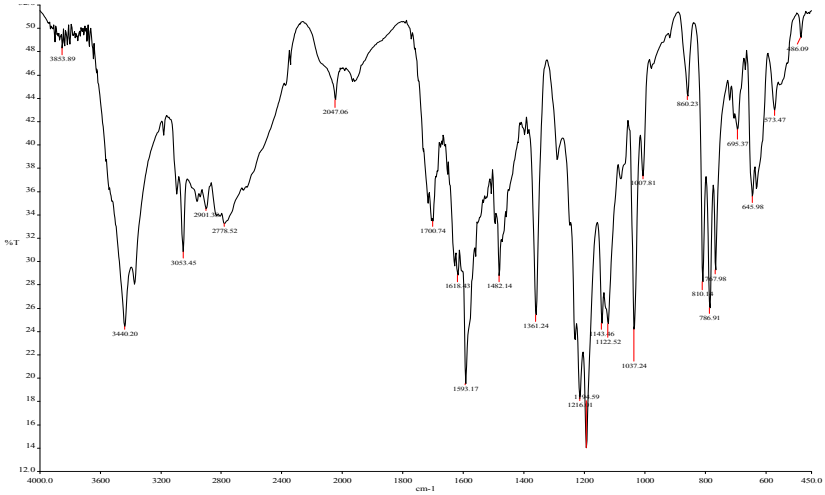
NMR: (D^{6}DMSO), δ_C (ppm)： 167.576 (C8 of –COOH group), 166.978 (C8 of –COOH group), 146.162 (C3 of ring carbon), 133.383 (C6 of ring carbon), 132.174 (C5 of ring caron), 131.903 (C1 of ring carbon), 130.529 (C4 of ring carbon), 129.033 (C2 of ring carbon).

IR spectra of complex 1:



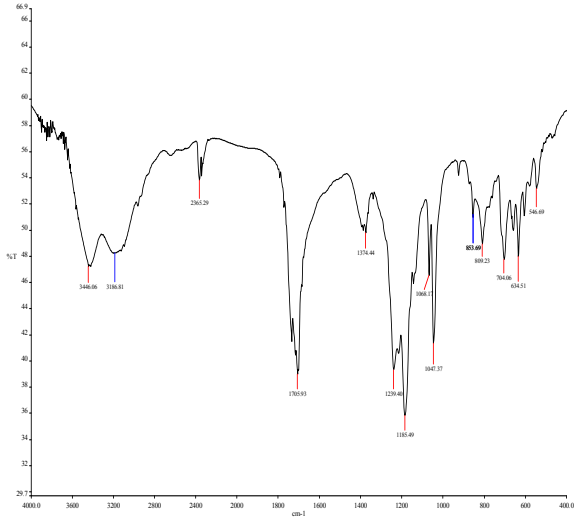
IR(cm^{-1}): 3421.46(asymmetric stretching of hydrogen bonded –COOH group), 2783 O-H stretching (O-H···O hydrogen bonded –COOH group), 1593.36(asymmetric stretching -COO^- group), 1361.74(asymmetric stretching -SO_3^- group).

IR spectra of complex 2



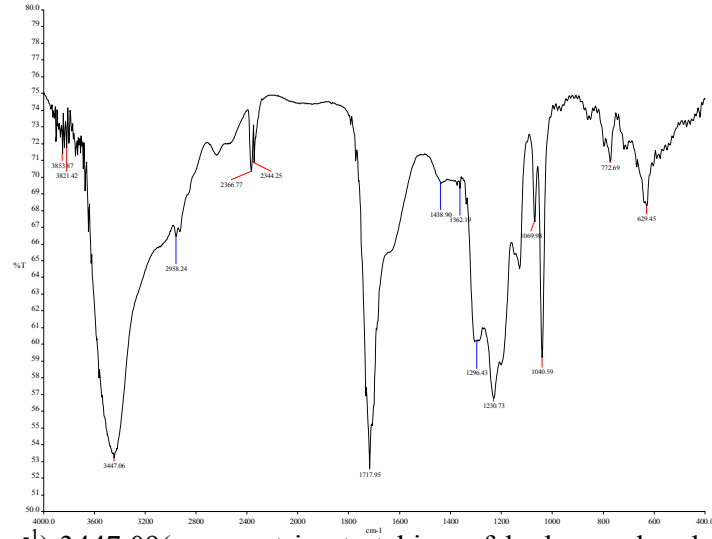
IR(cm^{-1}):3440.20(asymmetric stretching of hydrogen bonded –COOH group), 2778.52(O-H stretching (O-H···O hydrogen bonded –COOH group), 1593.17(COO^- asymmetric stretching), 1361.24(-SO_3^- asymmetric stretching).

IR of 4-sulfophthalic acid:



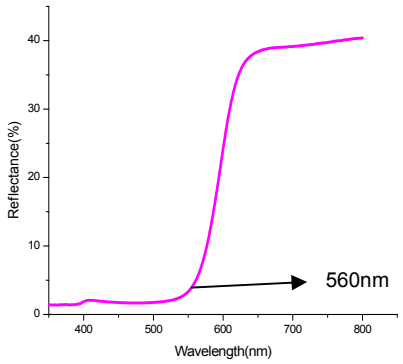
IR($cm^{-}1$):3446.06(asymmetric stretching of hydrogen bonded –COOH group), 1705..93(asymmetric stretching of C=O of free –COOH group) 1374.44(asymmetric stretching of $-SO_3^-$ group).

IR of 4-sulfophthalic acid:

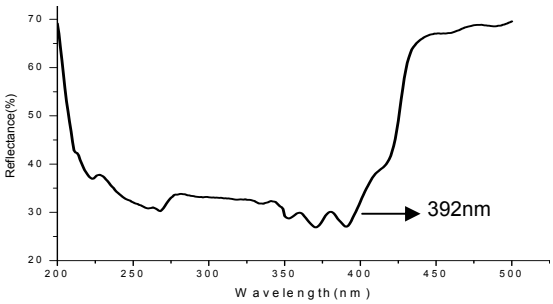


IR(cm^{-1}):3447.09(asymmetric stretching of hydrogen bonded –COOH group), 1717.95 (asymmetric stretching of C=O of free –COOH group), 1362.19 (asymmetric stretching $-SO_3^-$ group).

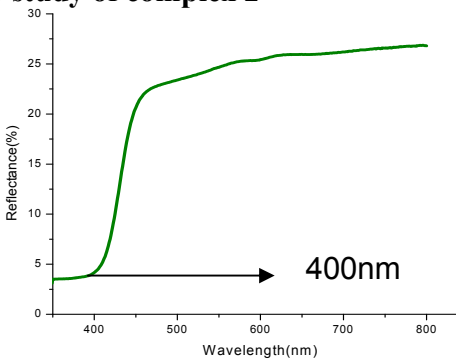
DRS study of complex 1:



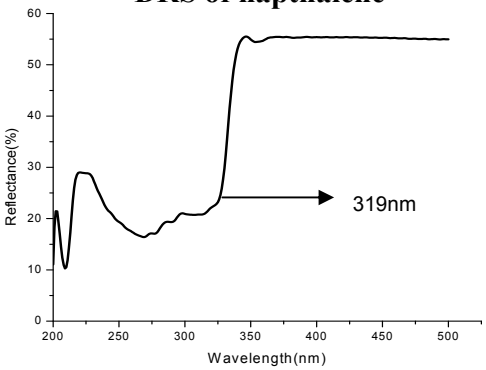
DRS of anthracene



DRS study of complex 2

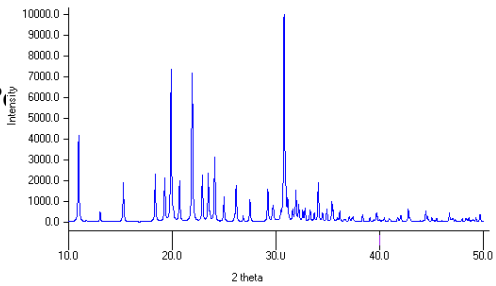


DRS of napthalene

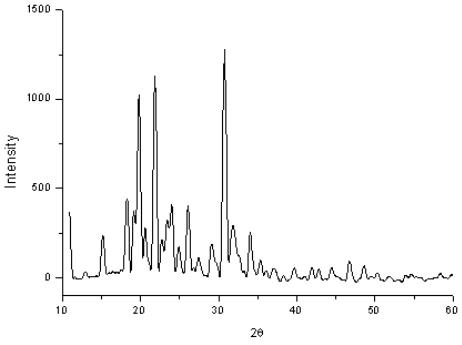


Powder X-rd of complex 1

Calculated

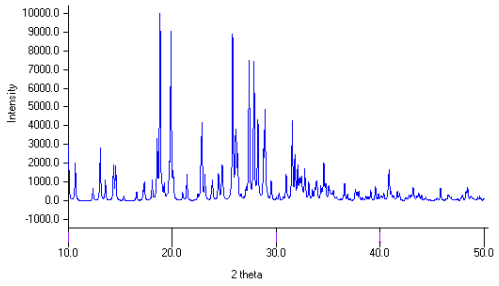


Experimental

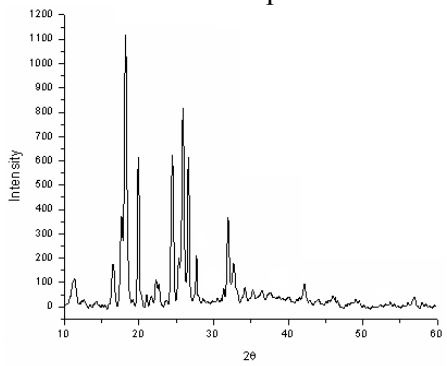


Powder X-rd of complex 2

Calculated



Experimental



X-ray Crystallography: The single crystal data was collected on Bruker APEX-2 CCD X-ray diffractometer that uses graphite monochromated MoKα radiation (λ=0.71073 Å) by hemisphere method. The structures are solved by direct methods and refined by least square methods on F^2 using SHELX-97.[1] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. PLATON was used for the calculation of guest available volumes.[2]

Table S1: Crystallographic parameters of Complexes 1 and 2.

Complexes	**1**	**2**
Formula	$C_{32}H_{21}N_2O_7S$	$C_{56}H_{48}N_6O_{22}S_4$
M. Wt.	577.58	1285.28
***T* (K)**	293	293
System	Monoclinic	Triclinic

Space Group	Cc	P-1
a(Å)	17.683(8)	8.345(4)
b(Å)	11.118(5)	10.533(5)
c(Å)	13.547(6)	16.280(8)
α (°)	90	102.425(13)
β (°)	95.469(13)	93.061(15)
γ (°)	90	93.425(13)
Vol. ($Å^3$)	2651.25	1391.8(12)
Z	4	2
D_{calc} (Mg/m^3)	1.4472(11)	1.5335(13)
R_1 ($I>2\sigma(I)$)		
wR_2 (on F^2, all data)		

Table S2: Important hydrogen bond distances of the complexes 1 and 2.

Complexes	**Type**	H···A (Å)	D···A (Å)	D-H···A (°)
Complex 1	N(11A)-H···O(16)		2.761	
	C(11A)-H···O(17)		3.328	
	N(21A)-H···O(13)		2.551	
	O(11)-H···O(14)		2.559	
Complex 2	N(11B)-H(11B)···O(17)	1.886	2.741	172.660

	C(15B)-H(15B)···O(15)	2.415	3.035	124.007
	O(14)-H(14O)···O(104)	1.716	2.538	167.43
	O(11)-H(11O)···O(102)	1.768	2.534	162.43
	N(21A)-H(21A)···O(101)	2.748	1.974	149.31
	N(11A)-H(11A)···O(104)	2.672	1.813	175.61
	C(15A)-H(15A)···O(103)	3.250	2.612	126.20

References:

(1) G. M. Sheldrick, SHELX-97, *Program for the Solution and Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.

(2) A. L. Spek, *PLATON-A Multi Purpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2002.