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

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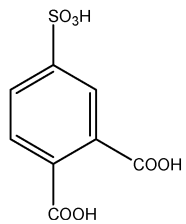
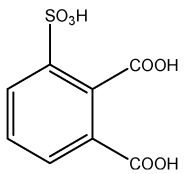
The selective inclusion of aromatic guest molecules in host frameworks formed by 3-sulfophthalic acid or 4-sulfophthalic acid and 4,4′-bipyridine has been effectively utilized for the separation of sulfophthalic acid isomers.

The utility and uniqueness of supramolecular chemistry for the separation of regioisomeric, geometric, diastereomeric and enantiomeric mixtures have been well demonstrated in the literature.[1] The supramolecular methods have been preferred over traditional methods such as chromatography, selective derivatisation and fractional distillation due to the cost effectiveness and also due to the ease of separation. Generally, traditional methods of separation are not feasible for the separation of molecular isomers as they have almost identical properties. The most successful and unconventional methodology is that the host framework selectively chooses one of the components in the mixture as a guest depending on the size or shape selectiveness or the favorable interactions with the host framework. For example, the separation of several positional isomers has been reported by Nassimbeni and Toda *et al.* by using diols as hosts.[2] Ward *et al.* have also demonstrated it but by using two component organic hosts.[3]

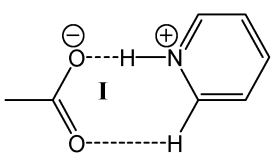
Here we present a new methodology in which the separation of isomers was achieved through selective formation of host networks based on the presence of an aromatic guest molecule. The sulfonation reaction of phthalic acid results in mixtures of 4-sulfophthalic acid (4-H_3SPA) and 3-sulfophthalic acid (3-H_3SPA) due to the nonspecific nature of the reaction. Aldrich sells a chemical with the label of 4-H_3SPA dissolved in water (50% wt. average 4-sulfophthalic acid) and mentions 3-H_3SPA as a major impurity. The ^{1}H NMR of this chemical as purchased reveals that the 4-H_3SPA and 3-H_3SPA are in 4 : 1 ratio. It was also found that the solution contains 2.5% of H_2SO_4 which was confirmed by $BaSO_4$ estimation. The purity of these isomers is of importance for the syntheses of sulfonated phthalocyanine dyes and for their applications.[4] Although some chromatographic methods are published for the separation of these isomers, no simple and convenient separation method for these isomers has been reported.[5] These isomers are of interest to us due to the potential of –COOH and –SO_3H groups to form supramolecular synthons with pyridine derivatives. Both these isomers are indeed capable of forming host networks when reacted with a 4,4′-bipyridine (BIPY) *via* synthons **I**[6] and **II**.[7] In the present report the selective host formation was achieved by automatic choice of guest molecules therefore paving the way for the separation of these sulfophthalic isomers.

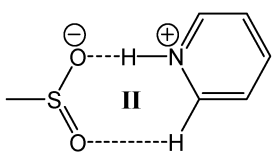


4-H_3SPA



3-H_3SPA





The 4-H_3SPA as purchased from Aldrich was crystallized with BIPY in the presence of aromatic guest molecules such as naphthalene (NAP) and anthracene (ANT) at room temperature in methanol. The single crystal analyses of the resulting crystals reveal the formation of complexes [(4-HSPA)(H_2BIPY)]·ANT, (**1**) and [(3-H_2SPA)$_2$(H_2BIPY)$_3$(SO_4)$_2$]·NAP, (**2**).

In the crystal structure of **1** the asymmetric unit contains one unit each of 4-HSPA, 4,4′-H_2BIPY and anthracene.[8] The deprotonation of –SO_3H and –COOH which is *para* to –SO_3H was confirmed by comparing the S–O (1.488(6), 1.421(8) and 1.452(7) Å) and C–O (1.245(10), 1.256(10) Å) bond lengths. Each 4-HSPA connected to two adjacent 4-HSPA units *via* –COO$^-$···HOOC charge assisted H-bonds (O···O 2.560(8) Å) to form a zig-zag chain along the *c*-axis. These chains are linked into a 3-dimensional network by BIPY *via*

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† Electronic supplementary information (ESI) available: Experimental analysis and characterization of the compounds by HPLC analysis, NMR spectra, IR spectra, DRS spectra, powder XRD patterns and crystallographic information of the compounds explained in detail. CCDC 817472–817473. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11481f

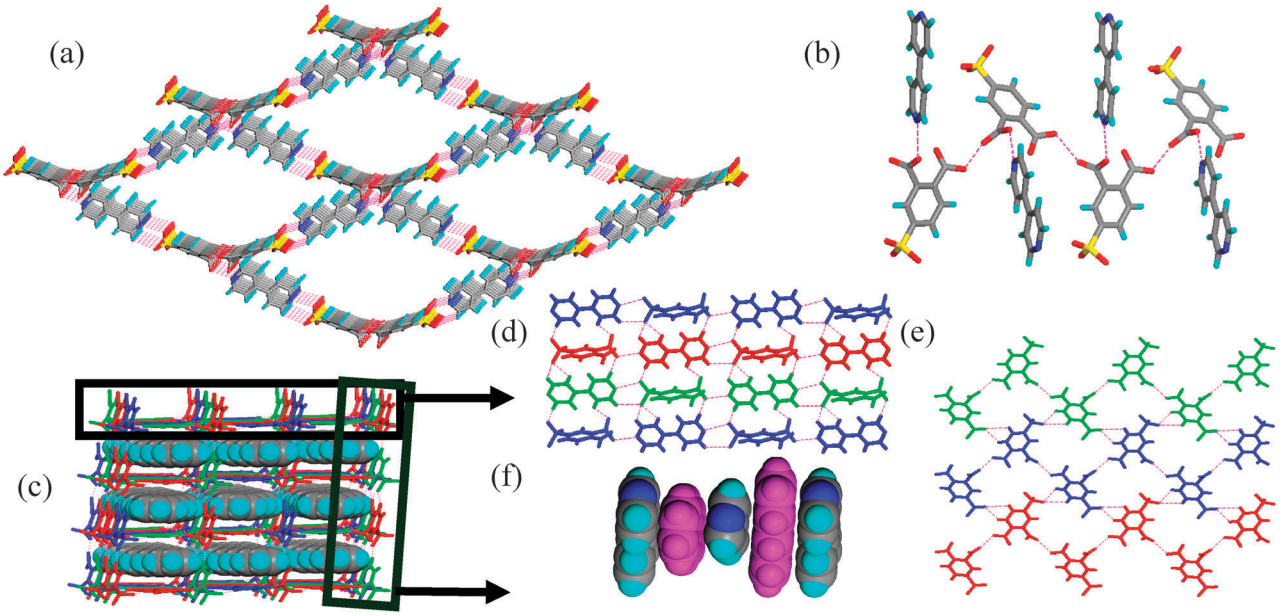

Fig. 1 Illustrations for the crystal structure of **1**: (a) 3D hydrogen-bonded network (along *c*-axis); (b) hydrogen bonding pattern along *c*-axis; (c) triply interpenetrated 3D-networks with guest inclusion (space fill mode); interactions involved between the interpenetrated networks; (d) view in *ab*-plane; (e) view in *bc*-plane; (f) cation–π interaction between H_2BIPY and ANT represented in space fill mode (ANT shown in pink color).

N^+–H···O–C hydrogen bond (N···O: 2.570(9) Å) and synthon-**II** (N···O: 2.755(10) Å and C···O: 3.306(11) Å) (Fig. 1(d) and (e)).

Three such 3D-networks interpenetrate such that there exist continuous channels which are occupied by anthracene units. The interpenetration of networks occurs through the plethora of C–H···O hydrogen bonds. Further anthracene units are included such that they are sandwiched by bipyridinium ions *via* charge-transfer cation–π interactions with a distance as short as 3.392 Å between N^+ and a centroid of one of the outer C_6 rings of the ANT unit (Fig. 1f). As a result the crystals exhibit an intense pink color (λ_{max}: 560 nm).

The asymmetric unit in the crystal structure of **2** contains one unit each of 3-H_2SPA and SO_4^{2-}, one and a half units of H_2BIPY and a half unit of naphthalene.[9] The C–O (1.311(5) and 1.205(5) Å; 1.332(5) and 1.196(5) Å) and S–O bond distances (1.468(4), 1.438(4) and 1.447(4) Å) indicate that the –COOH groups of 3-H_3SPA are not deprotonated and only $–SO_3H$ is deprotonated. The presence of SO_4^{2-} ion in the lattice further confirms the contamination of H_2SO_4 in the Aldrich sample. The SO_4^{2-} ions join the H_2BIPY and 3-H_2SPA units to form two-dimensional layers *via* several O–H···O hydrogen bonds (O···O: 2.534(6), 2.878(5) and 2.542(5) Å) and synthon-**II** (O···N, C···O: 2.665(6), 2.999(7) Å) such that the $–SO_3^-$ groups of 3-H_2SPA point at one side of the layer (Fig. 2a and b). Two such layers are interconnected by H_2BIPY units that sit on the inversion centre *via* synthon-**II** (O···N, C···O: 2.740(7), 3.036(8) Å) (Fig. 2c). As a result the layer has dimension of 16.2 Å and also contains channels to include naphthalene units. The naphthalene units are sandwiched by bipyridinium ions with somewhat longer distance of 4.314 Å between N^+ and a centroid of one of the C_6 rings of the NAP unit indicating a weaker cation–π interaction compared to that of complex **1** (Fig. 2d). The crystals exhibit a greenish yellow color (λ_{max}: 400 nm). The cation–π charge transfer interaction between H_2BIPY and ANT or NAP is confirmed from DRS studies (See ESI). The DRS results indicate that the complexes **1** and **2** exhibit a red shift of 168 nm and 81 nm, respectively, when compared with the λ values of guest molecules.

Furthermore the presence of guest molecules such as phenanthrene or pyrene also resulted in crystals similar to **1** in which exclusively 4-H_3SPA functions as a host component. These crystals also exhibit similar coloration to those of **1**. The colors of the crystals are also helpful as colorimetric indicators in the separation of these isomers. The crystals of **2** contain lower guest accessible volume compared to those of **1**. These results demonstrate that 4-H_3SPA-BIPY forms a host framework for the inclusion of bigger guest molecules while 3-H_3SPA-BIPY-SO_4^{2-} forms a host framework for the inclusion of relatively smaller guest molecules. The bulk purity of these crystals has been verified by ^{1}H NMR, ^{13}C NMR, elemental analysis and XRPD patterns. The isomers from the crystals of **1** or **2** were recovered in the following way. The aromatic guests were precipitated by treating the crystals with aqueous NaOH, and BIPY was removed from the resultant filtrate by extracting with $CHCl_3$. The aqueous portion was treated with conc. HCl until the pH was 2 and water was removed from it by heating the solution. The isomers were recovered by extracting the resultant solid with MeOH. The ^{1}H NMR spectrum of 4-H_3SPA as purchased from Aldrich, pure 4-H_3SPA and pure 3-H_3SPA after separation are shown in Fig. 3 (for details please see ESI).

In a typical reaction, 882 mg of crystals of **1** were produced from 1.292 g of Aldrich solution mixture that contains 503 mg of 4-H_3SPA and 126 mg of 3-H_3SPA. Out of 503 mg of 4-H_3SPA, 374 mg have been included in the crystals of **1** which nearly accounts for 75% of the total amount of 4-H_3SPA in the reaction mixture. Using the above described

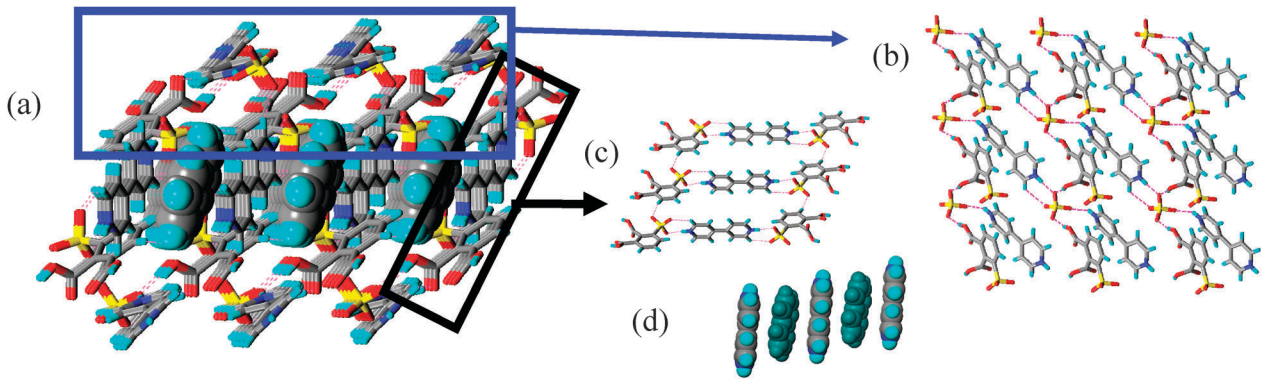

Fig. 2 Illustrations for the crystal structure of **2**: (a) 2D hydrogen-bonded network and inclusion of naphthalene (space fill mode), hydrogen bonding interactions involved in the network formation; (b) *ab*-plane and (c) *bc*-plane; (d) space fill representation of cation–π interaction between H_2BIPY and NAP (green).

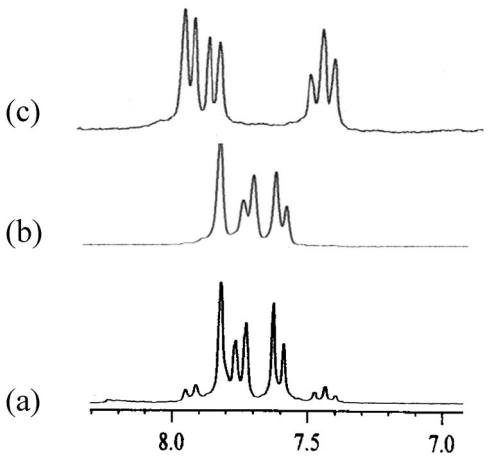

Fig. 3 ^{1}H NMR (in D_6DMSO, 200 MHz) spectra of (a) 4-H_3SPA as purchased from Aldrich, (b) pure 4-H_3SPA after separation, (c) pure 3-H_3SPA after separation.

workup procedure 97% of the isomer from the crystals of **1** was recovered. On the other hand, only 32% of 126 mg of 3-H_3SPA has been included in the crystals of **2**.

In summary, we have shown that the hydrogen bonded host frameworks of complexes **1** and **2** are selectively chosen by the guest molecules. Using this selectivity, the isomers of sulfophthalic acid were separated with ease. The presence of sulfate ion plays a significant role in the formation of complex **2**.

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8 Crystal data for **1**: $C_{32}H_{24}N_2O_7S$, M = 580.59, monoclinic, *Cc*, a = 17.683(8) Å, b = 11.118(5) Å, c = 13.547(6) Å, β = 95.469(13)°, V = 2651(2) Å^3, T = 293(2) K, Z = 4; 2364 reflections out of 3764 (R_{int} = 0.0750) with $I > 2\sigma(I)$, R_1 = 0.0789 ($I > 2\sigma(I)$) and wR_2 = 0.2082 (all data), Flack parameter = 0.5(2).

9 Crystal data for **2**: $C_{56}H_{48}N_6O_{22}S_4$, M = 1285.24, triclinic, $P\bar{1}$, a = 8.345(4) Å, b = 10.533(5) Å, c = 16.280(8) Å, α = 10.425(13)°; β = 93.061(15)°; γ = 93.425(13)°; V = 1391.7(12) Å^3, T = 293(2) K, Z = 1; 2915 reflections out of 4613 (R_{int} = 0.0472) with $I > 2\sigma(I)$, R_1 = 0.0778 ($I > 2\sigma(I)$) and wR_2 = 0.2308 (all data).

