

## Supporting Information

### Self-Assembly of Sterically-Rigidified 3-Connecting Benzenetribenzoic Acid in to (3,3) and (6,3) Nets and Stabilization of Water Channel in the Crystal Lattice

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#### Table of Contents

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1.	Experimental details for preparation of <b>MeBTB</b> and its inclusion/multicomponent crystals	S02-04
2.	TGA plots for the inclusion compounds of <b>MeBTB</b>	S04
2.	Details of X-ray crystal structure determinations and refinement	S05-06
2.	The geometrical parameters for important O–H···O hydrogen bonds observed in the inclusion compounds of <b>MeBTB</b>	S06
4.	<sup>1</sup> H and <sup>13</sup> C NMR spectra of <b>MeBTB</b> and its intermediate trinitrile.	S07-8
5.	<sup>1</sup> H NMR spectra for the inclusion compounds of <b>MeBTB</b>	S09-S10

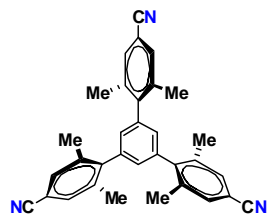
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## EXPERIMENTAL SECTION

All solvents were distilled prior to use. The progress of reactions was monitored by analytical thin layer chromatography (TLC) using aluminum sheets precoated with silica gel. Column chromatography was performed with silica gel (60–120 mesh).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on 500 MHz spectrometer using deuterated solvents. The TGA measurements were carried out on a TGA-DSC1 with a heating rate of 10  $^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. Commercial chemicals were used as received.

**Synthesis of MeBTB.** 1,3,5-Tris(2,6-dimethyl-4-trifluoromethylsulfonyloxyphenyl)benzene preparation has been previously reported by us elsewhere.<sup>1</sup>

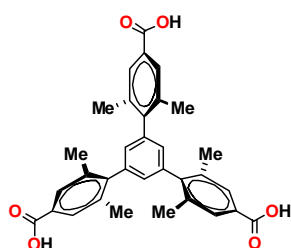
**1,3,5-Tris(2,6-dimethyl-4-cyanophenyl)benzene.** In a pre-heated 50 mL two-necked round-



bottom flask under  $\text{N}_2$  atmosphere were taken 1,3,5-tris(2,6-dimethyl-4-trifluoromethylsulfonyloxyphenyl)benzene (3.0 g, 3.60 mmol) and  $\text{Zn}(\text{CN})_2$  (4.20 g, 36.0 mmol) and 60 mL of anhyd DMF. The contents were allowed to stir for 5 min, and  $\text{Pd}(\text{PPh}_3)_4$  (2.50 g, 2.16 mmol) was introduced. The temperature was slowly raised to 100  $^\circ\text{C}$ . The contents were allowed to stir at this temperature for 8 h. Completion of the reaction was monitored by thin layer chromatography. Later, the reaction was quenched using 10 mL of  $\text{H}_2\text{O}$  and organic matter was extracted with DCM. The combined extracted was washed with brine solution, dried over anhyd  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo to obtain crude product. Short pad Silica gel column chromatography (40%  $\text{CHCl}_3/\text{pet.ether}$ ) was performed to obtain pure product as a colorless solid; yield 98% (1.75 g, 3.53 mmol); mp 248–252  $^\circ\text{C}$ ; IR (KBr)  $\text{cm}^{-1}$  2956, 2923, 2221, 1595, 1560, 1477;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  2.12 (s, 18H), 6.91 (s, 3H), 7.41 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  20.8,

111.5, 119.0, 127.5, 131.0, 137.3, 140.9, 145.6; HRMS  $m/z$  calcd for  $C_{33}H_{27}N_3Cl$  500.1894, found 500.1897  $[M+Cl]^-$ .

**1,3,5-Tris(2,6-dimethyl-4-carboxyphenyl)benzene (MeBTB).** The trinitrile prepared above



was dissolved in 40 mL of glacial AcOH in a two-necked round-bottom flask equipped with a  $CaCl_2$  guard tube. To this was added 70 mL of 60%  $H_2SO_4$  and the contents were refluxed for 12-18 h. After this time period, the reaction mixture was quenched and the organic matter was

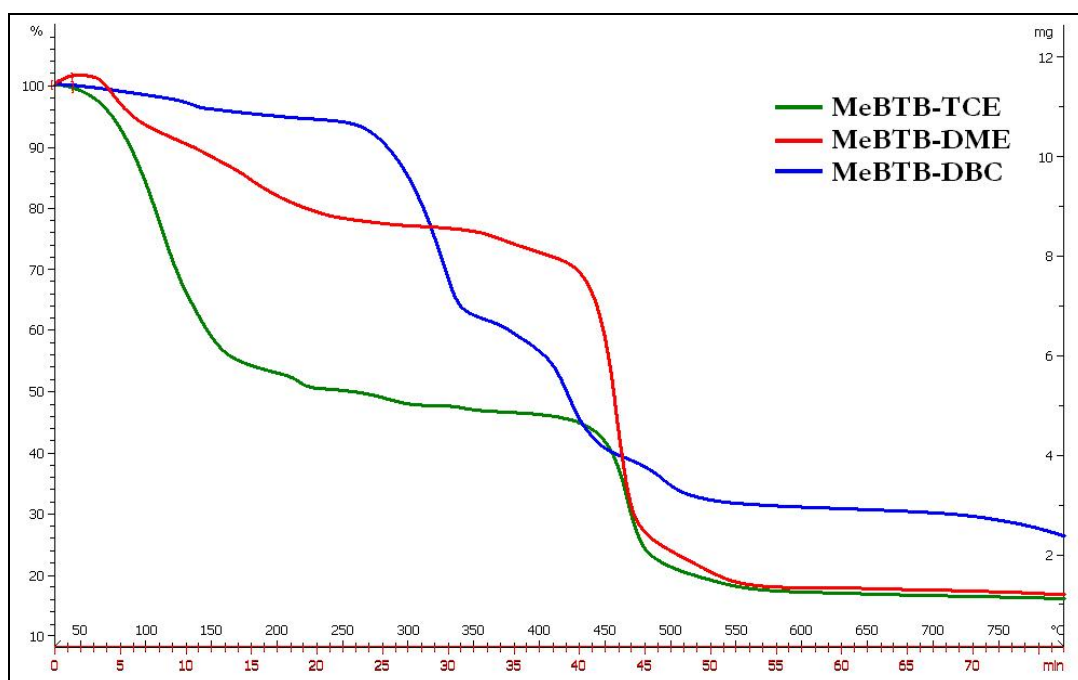
extracted with EtOAc and washed with brine. The organic phase after drying over anhyd  $Na_2SO_4$  was concentrated in vacuo to obtain crude product. The pure triacid was isolated by recrystallization with 50% EtOAc/pet. ether in 97% yield (0.87 g, 1.67 mmol); mp > 300 °C; IR (KBr)  $cm^{-1}$  2978, 2921, 2592, 2541, 1698, 1608, 1594, 1572, 1422;  $^1H$  (400 MHz,  $DMSO-d_6$ )  $\delta$  5.81 (s, 18H), 6.68 (s, 3H), 7.63 (s, 6H);  $^{13}C$  (100 MHz,  $DMSO-d_6$ )  $\delta$  20.8, 127.4, 130.9, 136.2, 141.1, 145.8, 167.8; HRMS  $m/z$  calcd for  $C_{33}H_{29}O_6$  521.1964, found 521.1964  $[M+H]$ .

### Crystallization Experiments with MeBTB

**MeBTB-TCE.** A solution of **MeBTB** (20.0 mg, 0.038 mmol) in 5 mL of 1,1,2,2-tetrachloroethane-MeOH (1:1, v/v) mixture was allowed to undergo slow evaporation. Large prism-shaped crystals of **MeBTB-TCE** were found to develop over a period of 2 weeks.

**MeBTB-DME.** Slow evaporation of the solution of **MeBTB** (20.0 mg, 0.038 mmol) in 5 mL of DME-MeOH (1:1, v/v) mixture led to the formation of long needles of **MeBTB-DME** after 8 days.

**MeBTB-DBC.** Host **MeBTB** (20.0 mg, 0.038 mmol), dibenzo-18-crown-6 (13.7 mg, 0.038 mmol) and KOAc (3.7 mg, 0.038 mmol) were dissolved in 5 mL of MeOH-DME (1:1, v/v) mixture. Slow evaporation of the resultant solution over a period of 4 days yielded cubic crystals of the multicomponent crystals.



**Figure S1.** TGA profiles for the multicomponent crystals of **MeBTB**. Please note that the stepwise %loss observed with heating could not be directly related to the loss of guest species. This is often the case when dealing with inclusion compounds of liquid guests. Presence of more solvent guest, sticking to the crystals when removed from mother liquor, or loss of it on washing leads to results that are erroneous.

## **Details of X-Ray Crystal Structure Determinations and Refinement**

The X-ray diffraction intensity data for all the crystals were collected on a Bruker's SMART CCD. The structure determination and refinement were accomplished with SHELX suite of programs. It should be mentioned that the structure determinations of **MeBTB-TCE** and **MeBTB-DME** were not routine due to high disorder of the guest/water molecules present the crystal lattices. Indeed, the total electron density of the guests is high, and when they are disordered, the overall data quality becomes poor. In addition, the aryl rings of the host **MeBTB**, which is like a propeller with the arms around the central benzene core, flap to some degree increasing the thermal motions of the atoms to a considerable extent. As a consequence, the guest molecules (tetrachloroethane, DME, etc.) needed to be modeled using the constraints and restraints available in SHELX program. In all the structures, the hydrogen atoms were fixed at stereochemical positions and thus were riding with their respective bonded atoms. The hydrogen atoms of water molecules were not included in the refinement. In the following, a brief description of the modeling of disorder is described for each structure.

**MeBTB-TCE.** Tetrachloroethane guests occluded in the crystal lattice were found to be disordered over four positions, and they were given partial occupancies such that they add up to one for each molecule. PART option in the SHELXL program was used along with DFIX and SIMU options to model the disordered TCE. The final occupancies were in the range of 0.17 to 0.33. All the disordered non-hydrogen atoms were refined isotropically.

**MeBTB-DME.** In this structure, DME (dimethoxyethane) and water molecules were found to be disordered. There are two host molecules, two DME and two water molecules in the unit cell. Both DME molecules were found to be disordered over two positions, and were given partial

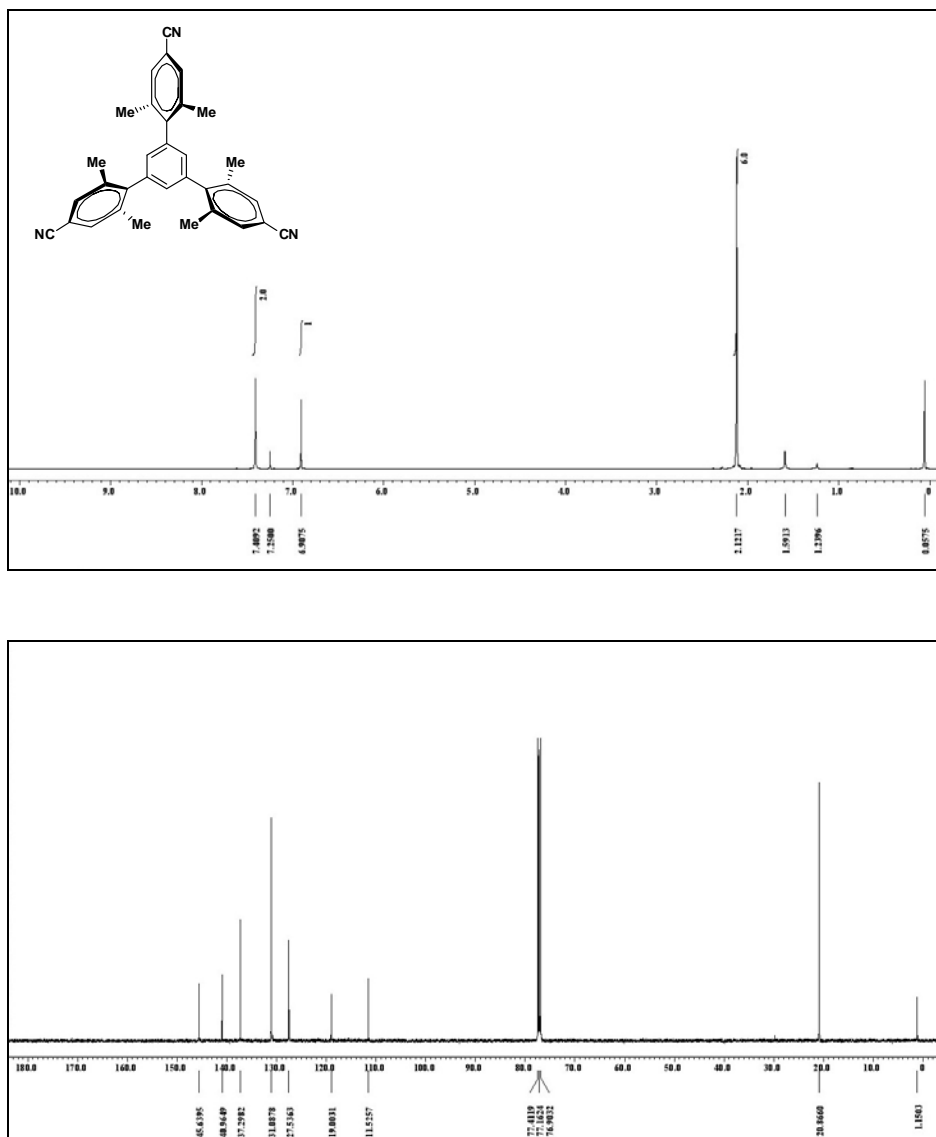
occupancies of x and 1-x, where x represents the occupancy of the major fraction, which was refined to values of 0.618 and 0.606 for the DME molecules. The occupancies of disordered water molecules were fixed with a value of 0.5 (four positions for two water molecules). As in the case of MeBTB-TCE, constrains and restrains available in SHELX (DFIX, SADI and SIMU) were used for modeling. Both DME and water molecules were refined isotropically.

**MeBTB-DBC.** In the case MeBTB-DBC, thermal parameters were found high for the dibenzo-8-crown-6 and DFIX was used as a constraint.

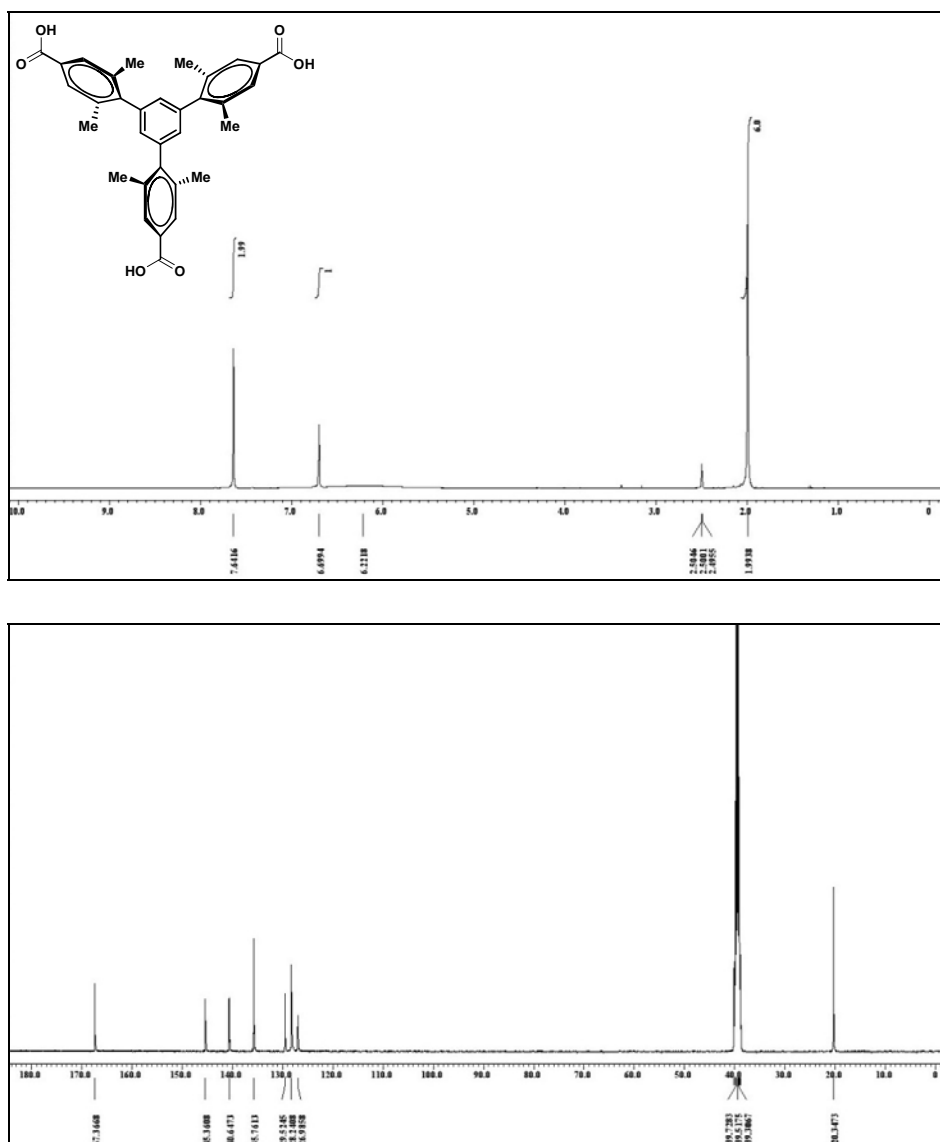
**Table S1.** The Geometrical Parameters for Important O–H···O Hydrogen Bonds Observed in the Multicomponent Crystals of **MeBTB**.

compound	atoms <sup>a</sup>	$d_{O-H\cdots O}$ (Å)	$D_{O\cdots O}$ (Å)	$\theta_{O-H\cdots O}$ (°)
<b>MeBTB-TCE</b>	O1-H···O2	1.77(1)	2.60(1)	166.7(1)
	O3-H···O5	1.76(1)	2.60(1)	177.9(1)
	O6-H···O4	1.79(1)	2.62(1)	178.4(1)
<b>MeBTB-DME</b>	O1A···O4	1.87(1)	2.64(1)	155.7(1)
	O2A-H···O3	1.84(1)	2.61(1)	154.6(1)
	O6-H···O6A	1.88(1)	2.68(1)	164.1(1)
	O5A-H···O8	1.86(1)	2.65(1)	162.2(1)
	O1···O(W1)	-	2.57(1)	-
	O2···O(W2)	-	2.68(1)	-
	O(W1)···O(W2)	-	2.70(1)	-
	O(W2)···O(W1)	-	2.76(1)	-
	O3A···O(W3)	-	2.76(1)	-
	O4A···O(W4)	-	2.77(1)	-
<b>MeBTB-DBC</b>	O1···O(W1)	-	2.71(1)	-
	O2···O6	-	2.48(1)	-
	O3···O5	-	2.55(1)	-
	O4···O(W1)	-	2.94(1)	-
	O5···O(W1)	-	3.05(1)	-
	O(W1)···O(W2)	-	2.87(1)	-

<sup>a</sup> 'W' refers to water molecules.

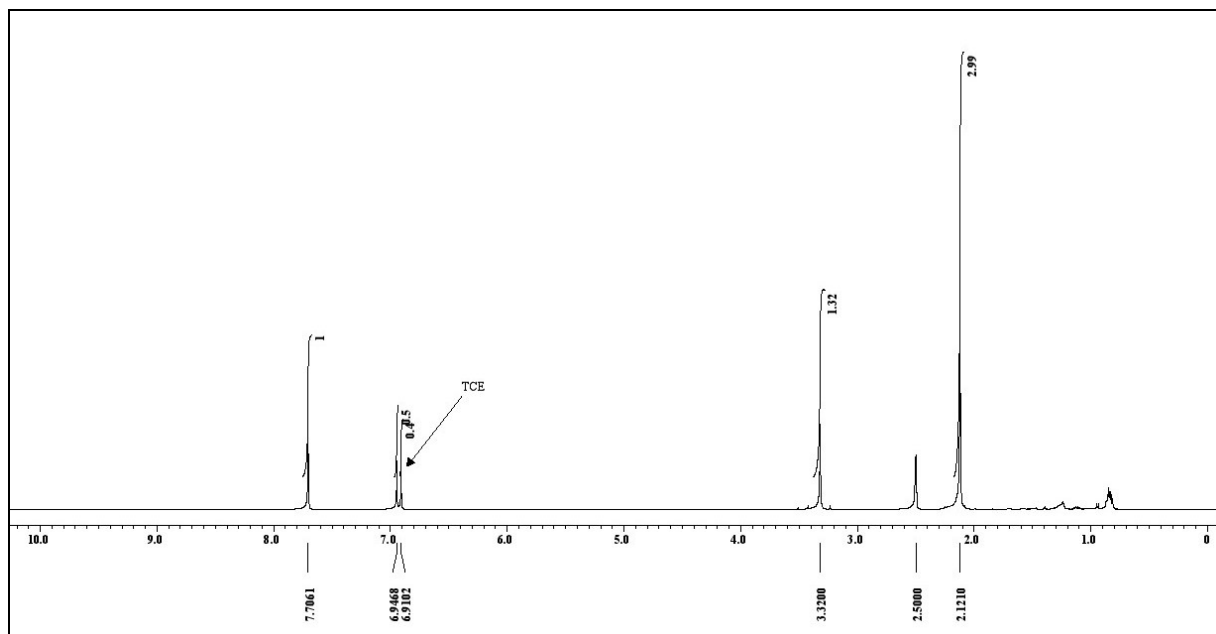


**FIGURE S2.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) and <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) spectra of trinitrile.

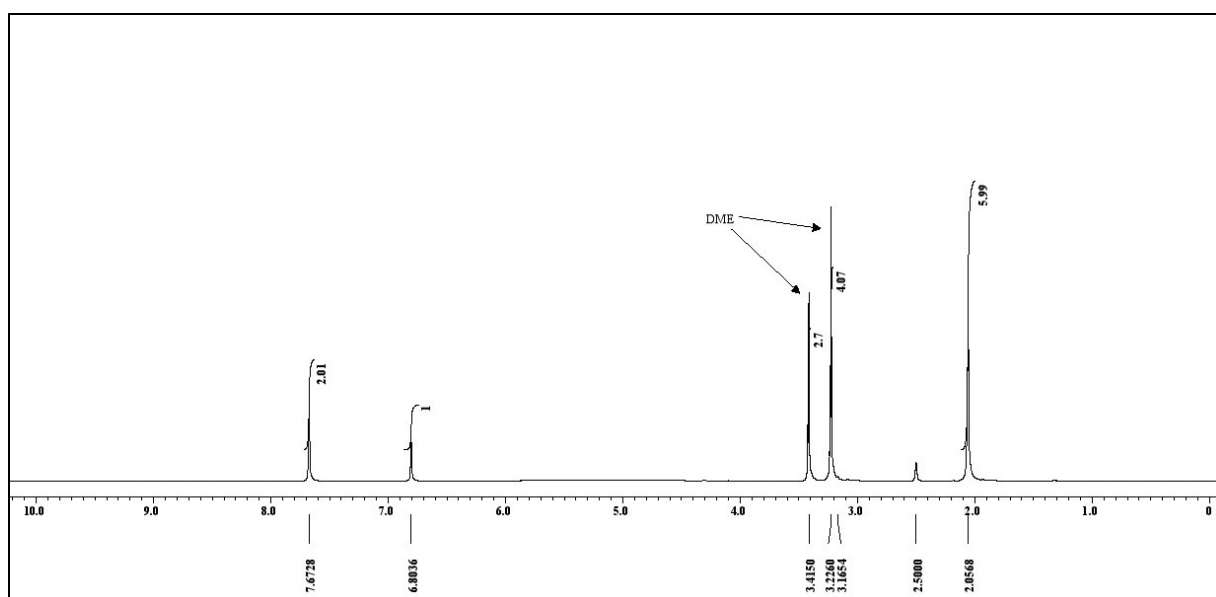


**FIGURE S3.**  $^1\text{H}$  NMR (DMSO- $d_6$ , 400 MHz) and  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz) spectra of MeBTB.

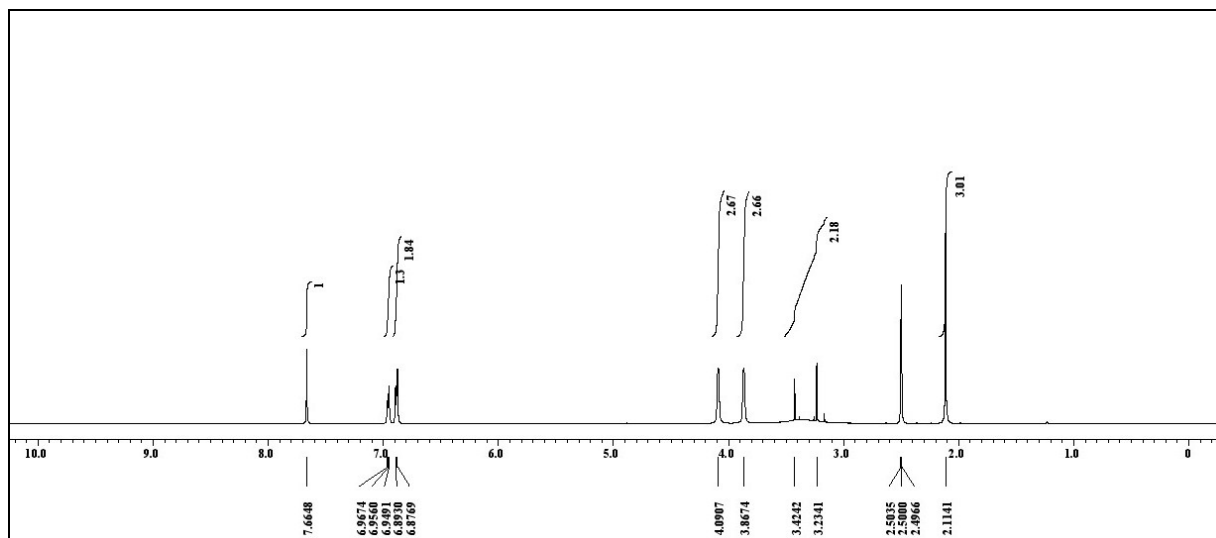




**Figure S4.**  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz) spectrum of the inclusion compound **MeBTB-TCE**.



**Figure S5.**  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ , 500 MHz) spectrum of the inclusion compound **MeBTB-DME**.



**Figure S6.**  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz) spectrum of the multicomponent crystals **MeBTB-DBC**.

## REFERENCES

1. (a) J. N. Moorthy, P. Natarajan, *Chem. —Eur. J.*, 2010, **16**, 7796. (b) J. N. Moorthy, P. Natarajan, A. Bajpai, P. Venugopalan, *Cryst. Growth Des.*, 2011, **11**, 3406.