*Supporting Information*

# A Dense $I^1O^3$ Hybrid Superhydrophobic Network, Pb(H-BTMB), Exhibits Selectivity Towards $CO_2$ Gas Sorption

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## *Index*:

1. Syntheses ----------S2
2. Experiments and instruments----------S3-S4
3. X-ray structural parameter tables----------S5
4. X-ray powder patterns ----------S6
5. Thermo-gravimetric analysis----------S7
6. Gas adsorption study---------- S8-S10
7. Contact angle measurements ----------S11-S13
8. X-ray crystal structures----------S14-S15

**Syntheses:**

**Chemicals used in this work:**

$Pb(NO_3)_2$ was purchased from Merck, *N*,*N*-dimethylformamide (DMF)and methanol (MeOH) were purchased from SD fine (India) used as received without further purification. Benzene-1, 3, 5-tris(*m*-benzoic acid) ($H_3$BTMB) was prepared according to reported[1] procedure.

**Synthesis of [Pb(H-BTMB)(DMF)]**: A solid mixture of $H_3$BTMB (11 mg, 0.025 mmol), Benzoic Acid (12.21 mg,0.1 mmol) and $Pb(NO_3)_2$ (15.16 mg,0.038 mmol) was dissolved in a mixture of DMF/MeOH/$H_2O$ (0.5/0.25/0.25 mL) in an 2-mL glass vial. To the reaction mixture Benzoic acid (0.1 mmol) used for lowering the nucleation of crystal growth and 20 μL of NaOH (0.01 M) was added as a deprotonating agent and the initial pH was 6.0. The whole reaction mixture was heated in a temperature controllable oven from room temperature to 100 °C, over a period of 4 h and then at 100 °C for 48 h. The oven was cooled from 100 °C to room temperature naturally. The product contains homogeneous colorless block shaped crystals, which were isolated by washing with MeOH and dried in air. Yield: 13.7 mg, 83% based on $H_3$BTMB. Elemental microanalysis for **[Pb(H-BTMB)(DMF)]** ≡ $C_{30}H_{23}NO_7Pb$, calculated (%): C, 50.27; H, 3.23; N, 1.95. Found (%): C, 50.18; H, 3.19; N, 1.91. FT-IR (4000-400 $cm^{-1}$): 3750 (w), 3055 (w), 1647(w), 1586 (w), 1523 (vs), 1457(w), 1408 (m), 1368 (vs), 1275 (m), 1240 (m), 1162 (w), 913 (m), 866 (m), 808 (s), 759 (vs), 680 (vs), 619 (m), 520 (m), 416 (s).

**Large scale synthesis of [Pb(H-BTMB)(DMF)]:** The large scale synthesis of **[Pb(H-BTMB)(DMF)]** were achieved in similar reactions conditions, but quantified by 10 times to that of above in Teflon lined auto clave of 100 ml capacity. The products were homogeneous single crystals yielded 75%.

**General characterization techniques:** Thermo-gravimetry analysis was obtained using a Rigaku TG8120 under flowing nitrogen with 10 K $min^{-1}$ ramp rate. Powder X-ray diffraction was obtained using a Rigaku RINT powder diffractometer with Cu Kα anode. Gas adsorption isotherms were obtained using Belsorp Mini volumetric adsorption instrument from BEL JAPAN, INC. FTIR spectra were recorded at 298 K temperature by Cary 639 FTIR with Diamond ATR, Agilent technologies, USA.

**Contact angle measurements**: Contact angels were measured on powder samples using HOLMARC contact angle meter with rotatable substrate holder, automated dispenser & temperature control, model No: HO-IAD-CAM-01B, Holmarc Opto-Mechtronics, India. The powder samples were spread on Aluminum substrate bed and pressed with the help of glass slide to make inform surface. On the pressed powder samples, 20 μL of water droplet was released slowly by using automated 100 μL dispenser. The contact angles were measured at room temperature and high temperatures from 40 ° C, to 90 ° C with 10 ° C intervals by heating substrate bed with temperature controller.

**X-ray Diffraction and Crystal Structures of [Pb(H-BTMB)(DMF)]**: Single crystal X-ray diffraction measurements were performed at 223 K with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF / VariMax rotating-anode X-ray generator with confocal mono-chromated MoKα radiation. Data were processed using Crystal Clear TM-SM (Version 1.4.0). The crystal structures were solved and refined using the WinGX suite of programs using the SHELXS-97[2] and SHELXL-97[3], respectively. The final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for the hydrogen atoms. Locating the position of the Pb atom was done based on a systematic approach. The aromatic hydrogen atoms were introduced in the calculated positions and refined isotropically. The solvent DMF molecule has disorder problem due adsorption nature of **Lead (Pb) metal.** In this context the routine SQUEEZE was employed in structural solution. Crystal data and structure refinement parameters for **[Pb(H-BTMB)(DMF)]** is listed in table S1 for both as refined with solvent molecules and also SQUEEZE data.

**The below PLAT213 alerts are generated in CIF check because there is a large amount of disorder in the structure due to adsorption problem of Lead (Pb) metal**. Heavy metals like Pb compounds very commonly shows adsorption problems at –50 $^{0}$ C temperature. It is in this context we have squeezed the structure to remove solvent

molecule in the final refinement. Both the data are reporting in this publication.

**Alert level A**

| | | |
|---|---|---|
| PLAT213_ALERT_2_A Atom O5 | has ADP max/min Ratio ..... | 8.0 prolat |
| PLAT213_ALERT_2_A Atom C4 | has ADP max/min Ratio ..... | 5.7 prolat |
| PLAT213_ALERT_2_A Atom C7 | has ADP max/min Ratio ..... | 7.3 prolat |

**References:**

S1. He, Y.; Bian, Z.; Kang, C.; Cheng, Y.; Gao, L. *Tetrahedron*. **2010**, *66*, 3553.

S2. Sheldrick, G. M. Program for crystal structure solution, University of Göttingen, Germany, 1997.

S3. Sheldrick, G. M. Program for crystal structure refinement, University of Göttingen, Germany, 1997.

**Table S1.** Crystal data and structure refinement parameters for **Pb[(H-BTMB)(DMF)]**

| Parameters | **[Pb(H-BTMB)(DMF)]** | **After squeeze Pb(H-BTMB)** |
|---|---|---|
| Empirical Formula | $C_{30}H_{23}NO_7Pb$ | $C_{27}H_{16}O_6Pb$ |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | *Pccn* | *Pccn* |
| Crystal size (mm) | 0.2× 0.2 × 0.2 | 0.2× 0.2 × 0.2 |
| *a (Å)* | 20.989(6) | 20.989(6) |
| *b (Å)* | 29.784(9) | 29.784(9) |
| *c (Å)* | 7.425(2) | 7.425(2) |
| Volume ($Å^3$) | 4642(2) | 4642(2) |
| *Z* | 8 | 8 |
| Formula mass | 716.68 | 643.59 |
| $\rho_{calc}$ ($gcm^{-3}$) | 2.051 | 1.842 |
| $\lambda$ *(MoK$\alpha$) Å* | 0.71073 | 0.71073 |
| $\mu$($mm^{-1}$) | 7.326 | 7.310 |
| $\theta$ range (˚) | 1.37 to 31.55 | 1.37 to 31.55 |
| Total data collected | 7992 | 7992 |
| Unique data | 7192 | 7192 |
| Observed data (I > 2σ(I)) | 2906 | 2811 |
| R indexes [I > 2 σ(I)] | $R_1$ = 0.0867, $wR_2$ = 0.1920 | $R_1$ = 0.0813, $wR_2$ = 0.1798 |
| Goodness of fit | 0.964 | 0.922 |

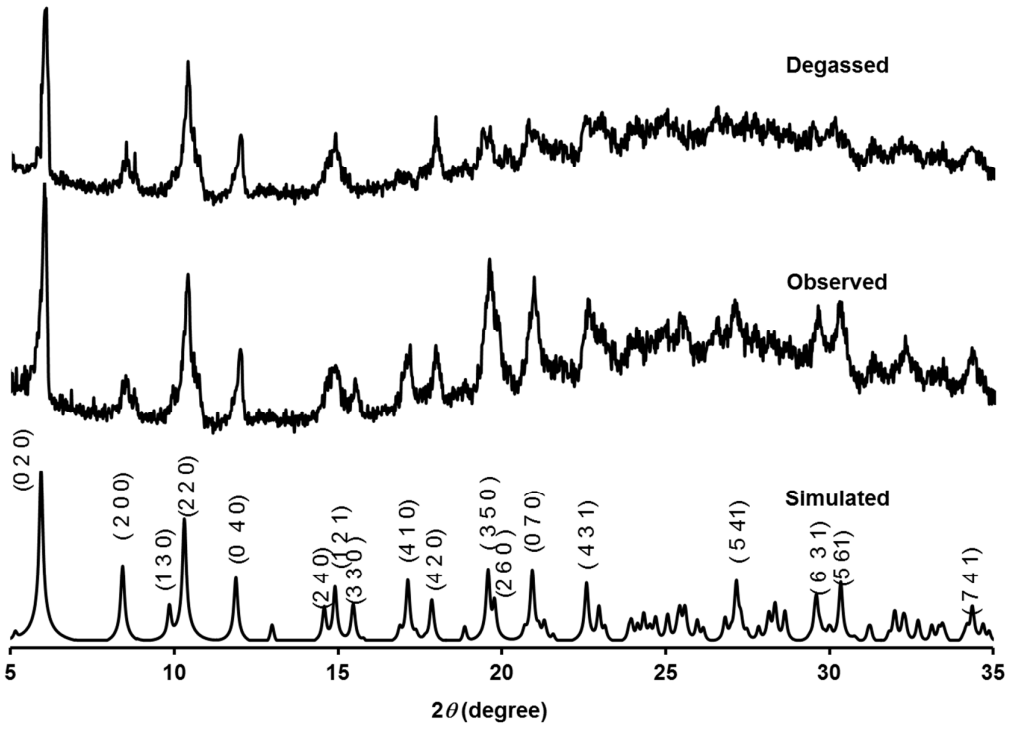


**Figure S1.** Powder X-ray diffraction patterns of **[Pb(H-BTMB)(DMF)]** simulated (bottom), observed (middle) and degassed at 275 ° C (top).

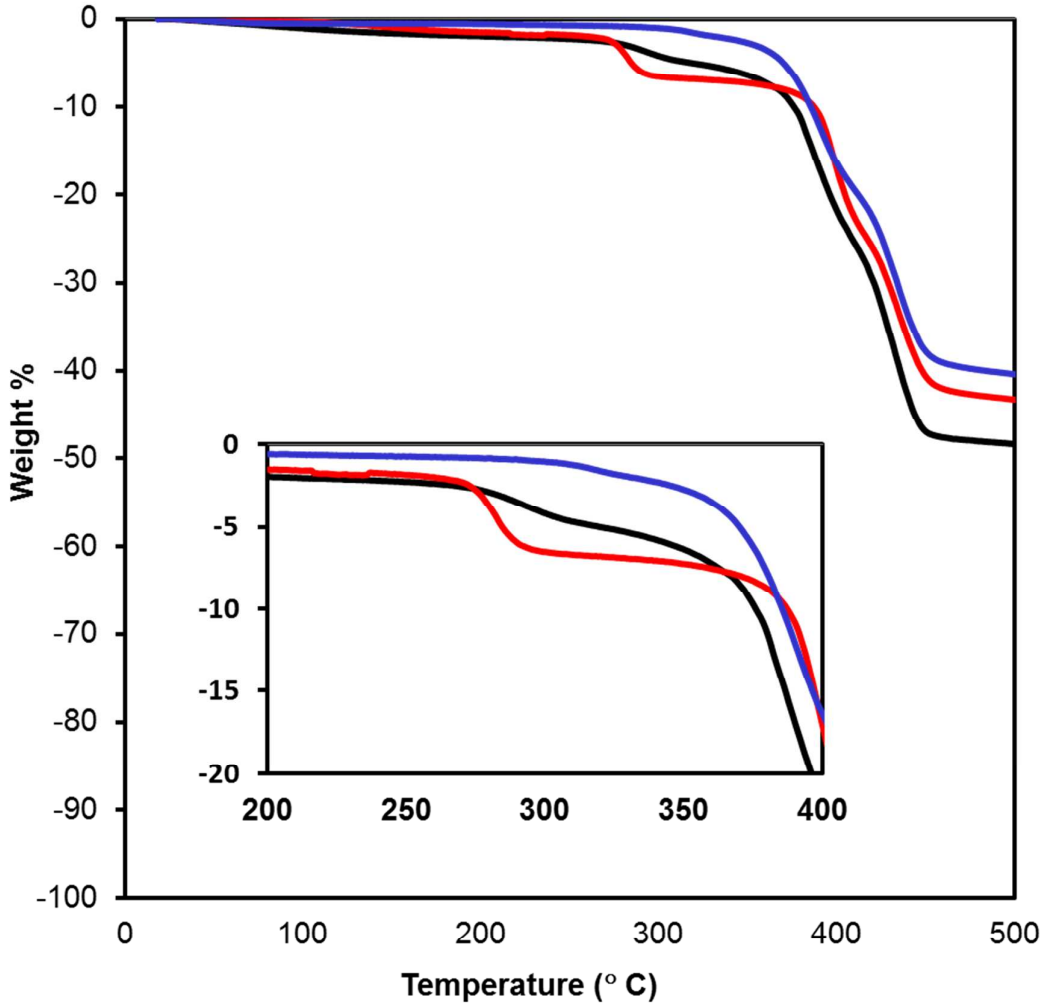


**Figure S2.** Thermo-gravimetric analysis (TGA) measured under $N_2$ flow of **[Pb(H-BTMB)(DMF)]** as synthesized (Black), exchanged with methanol (red) and activated at 275 °C (Blue).

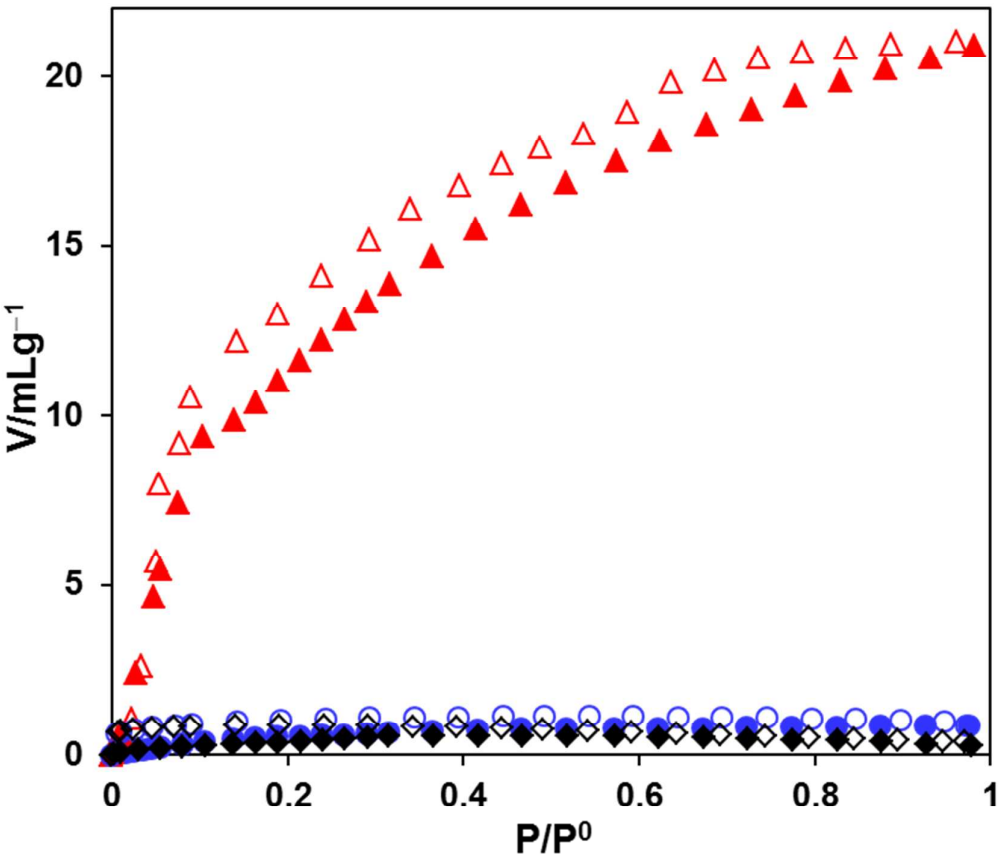


Figure S3. Adsorption isotherms of **Pb(H-BTMB)** for $CO_2$ (red), $C_2H_4$ (blue), and $C_2H_6$ (Black) at 273 K. Filled and open symbols are adsorption and desorption data, respectively.

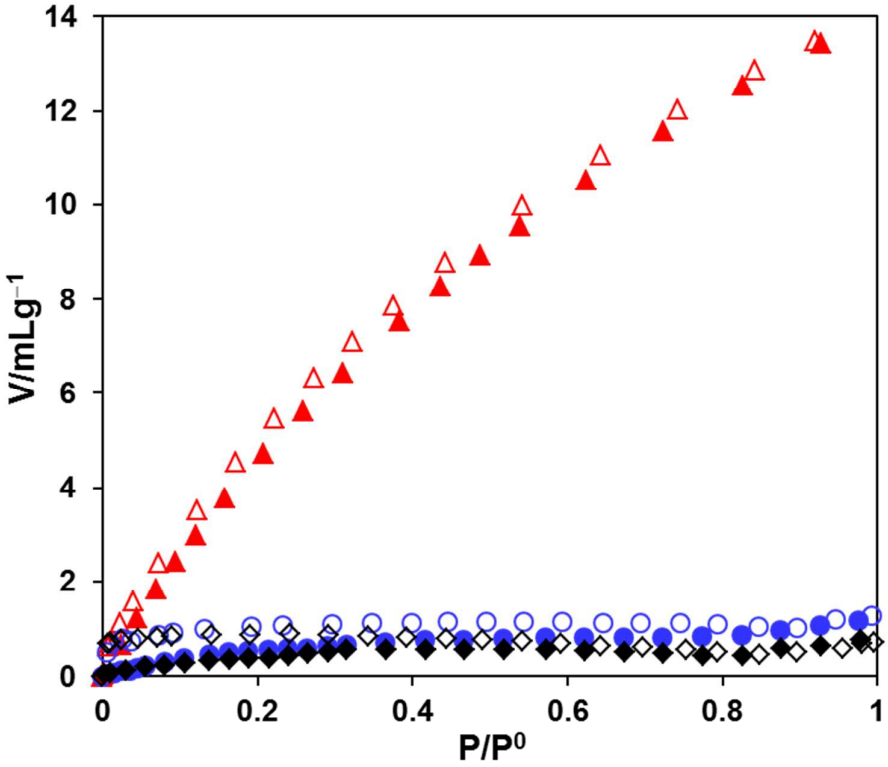


Figure S4. Adsorption isotherms of **Pb(H-BTMB)** for $CO_2$ (red), $C_2H_4$ (blue), and $C_2H_6$ (Black) at 298 K. Filled and open symbols are adsorption and desorption data, respectively.

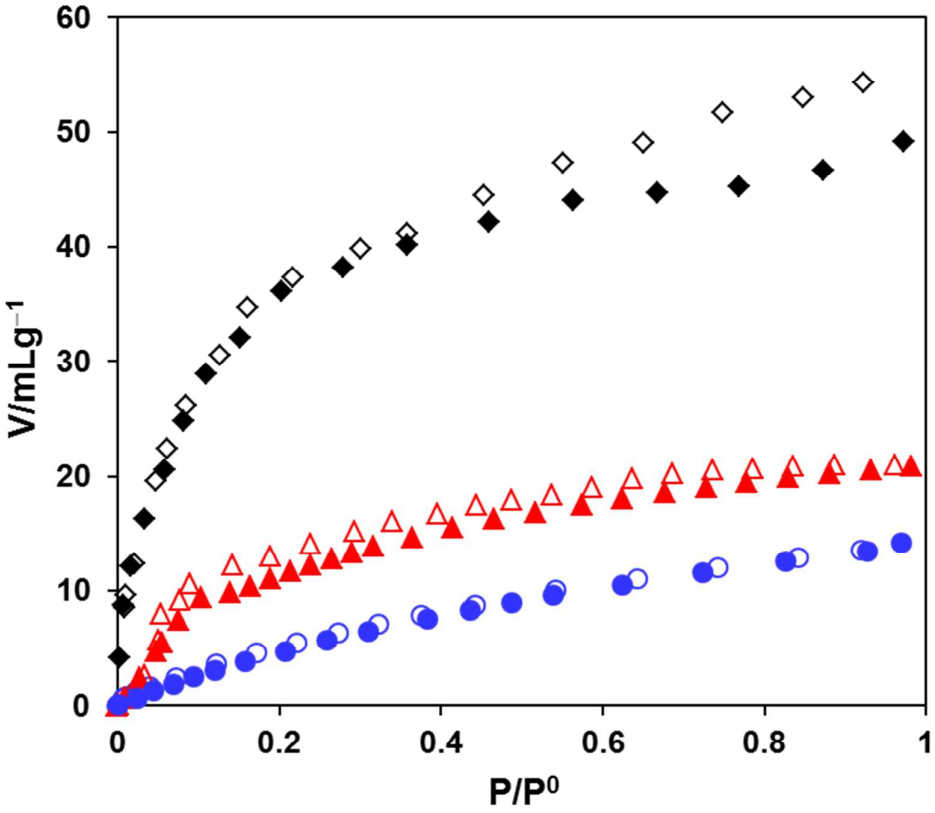


Figure S5. Adsorption isotherms of **Pb(H-BTMB)** for $CO_2$, (black) at 195 K, (red) at 273 K, and (blue) at 298 K. Filled and open symbols are adsorption and desorption data, respectively.

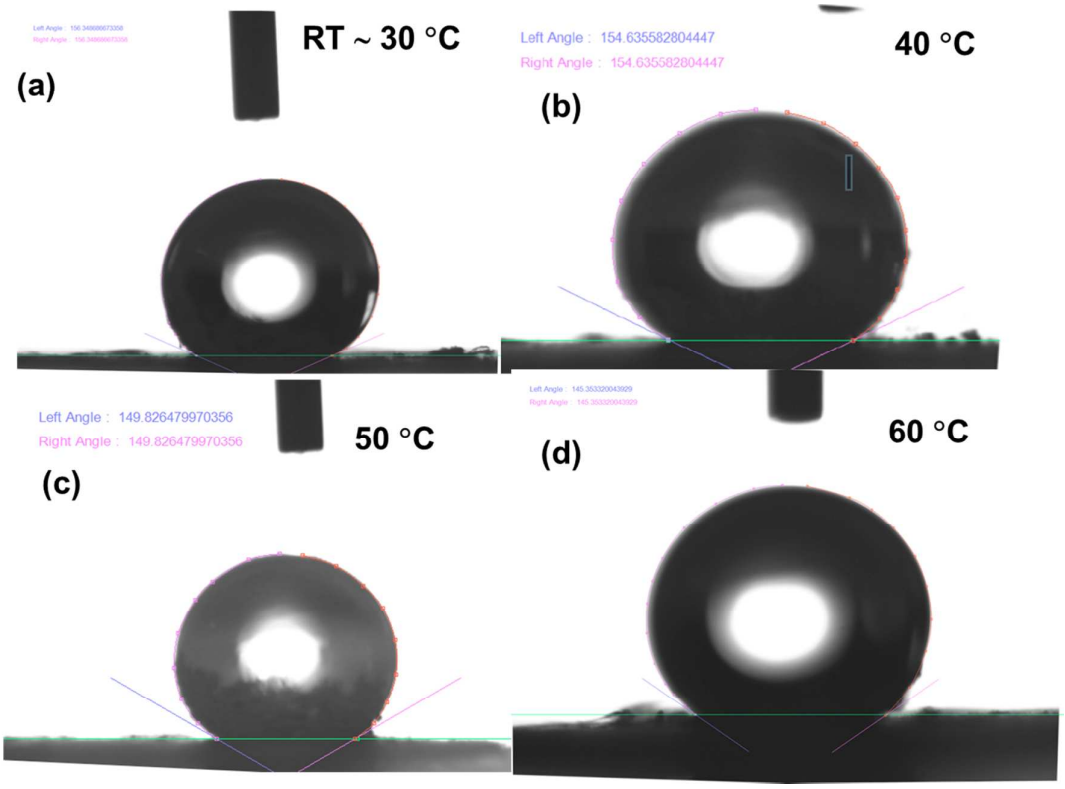


**Figure S6**. Picture showing contact angle measured at (a) room temperature (b) 40 ° C, (c) 50 ° C and (d) 60 ° C on the powder samples of **[Pb(H-BTMB)(DMF)]**.

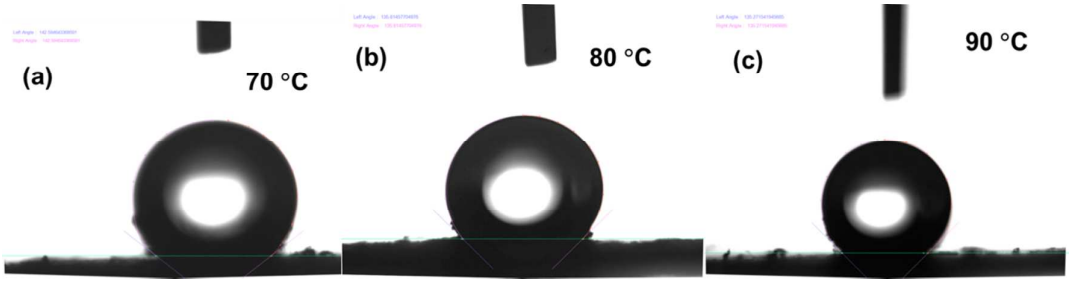


**Figure S7**. Picture showing contact angle measured at (a) 70 ° C, (b) 80 ° C and (c) 90 ° C on the powder samples of **[Pb(H-BTMB)(DMF)]**.

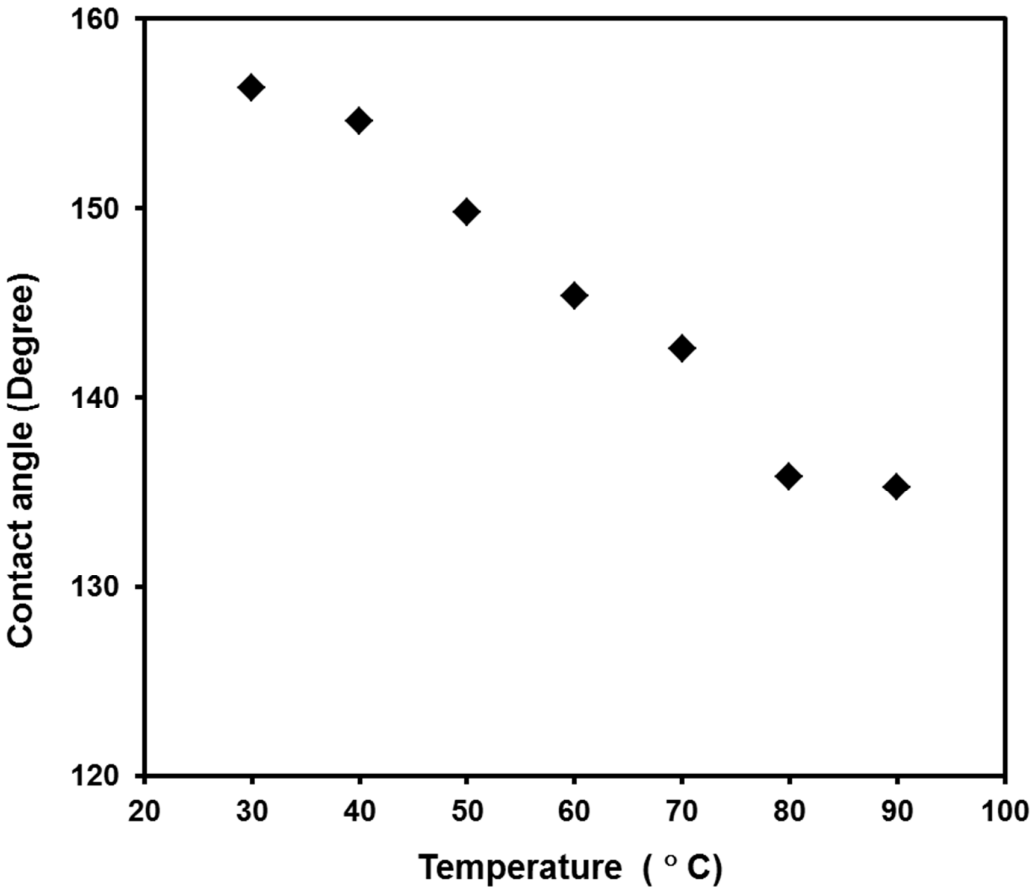


**Figure S8**. Graph shows contact angles Vs temperatures on powder samples of **[Pb(H-BTMB)(DMF)]**.

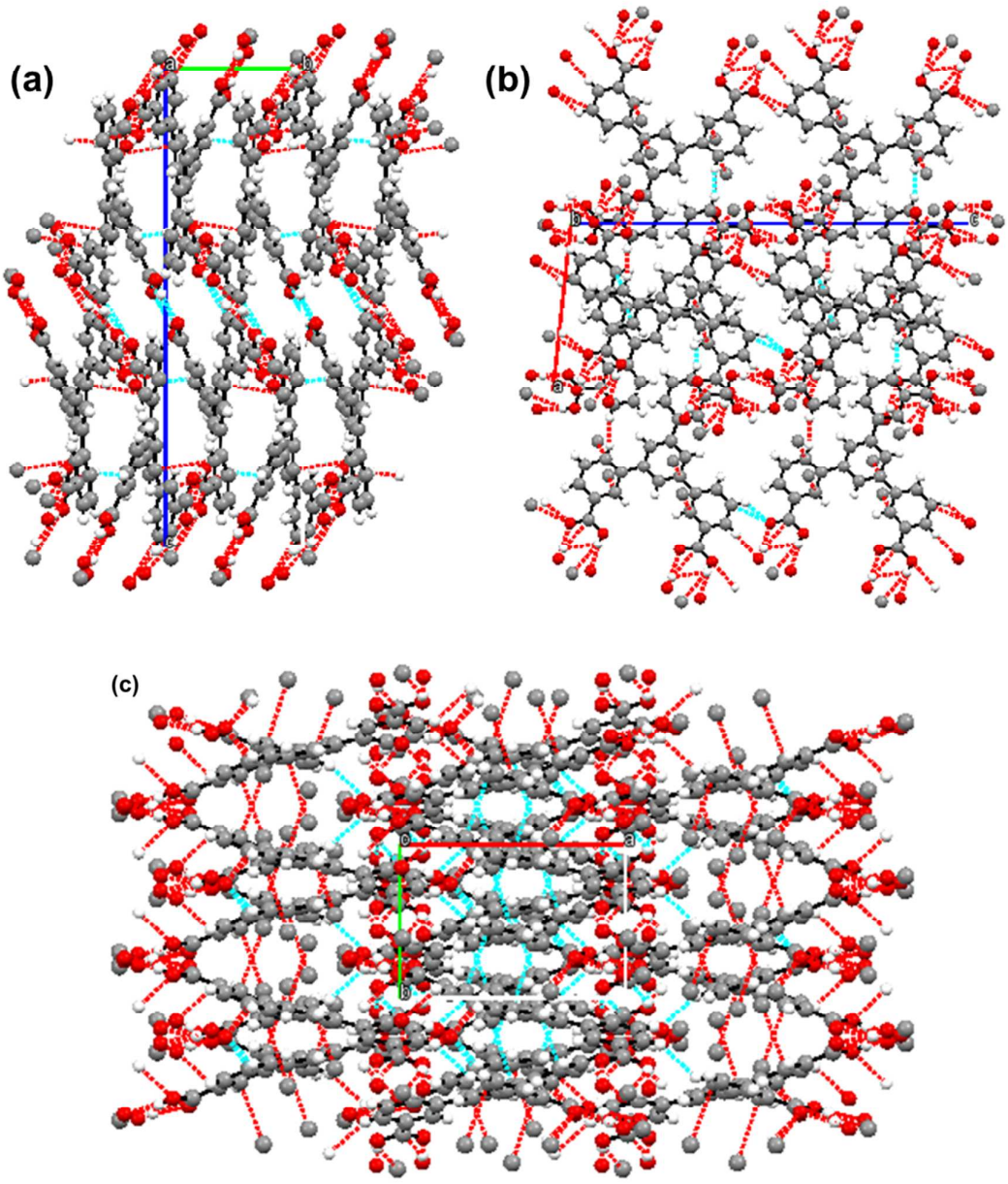


**Figure S9**. Single crystal X-ray structures of **$H_3$BTMB**, viewed along the *a*-axis (a), *b*-axis (b) and *c*-axis (c). Dotted lines of cyan colors are possible of hydrogen bonding and dotted lines of red color represented the short contacts.

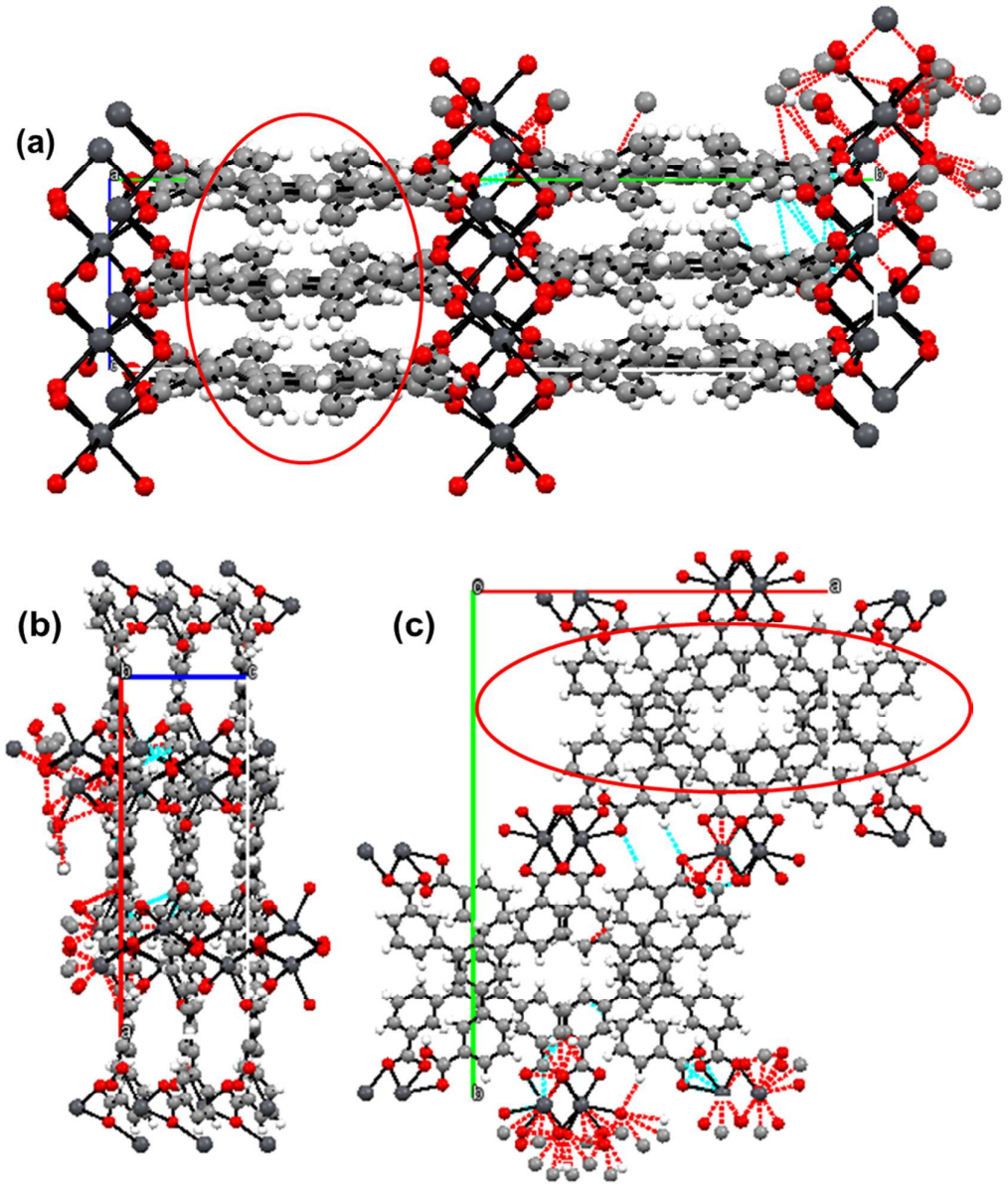


**Figure S10**. Single crystal X-ray structures of **[Pb(H-BTMB)(DMF)]**, viewed along the *a*-axis (a), *b*-axis (b) and *c*-axis (c). Dotted lines of cyan colors are possible of hydrogen bonding and dotted lines of red color represented the short contacts. The circled area represents more of hydrocarbon rich surface.