

## Hexagonal crystalline inclusion complexes of 4-iodophenoxy trimesoate

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### Supplementary Information (ESI)

(6 pages)

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**(i) Preparation of benzene-1,3,5-tricarboxylic acid tris(4-iodophenyl) ester (2)**

This compound was prepared using procedures similar to those previously reported.<sup>1</sup> 1,3,5-Benzenetricarbonyl trichloride (2.0 mmol, 0.53 g), Et<sub>3</sub>N (10 mmol, 1.4 mL), and DMAP (1.0 mmol, 0.12 g) were combined in dichloromethane (15 mL) and cooled to 10 °C. To this reaction mixture, 4-iodophenol (6.6 mmol, 1.45 g) dissolved in dichloromethane (10 mL) was added dropwise. The reaction was allowed to gradually warm to rt and maintained for 4 h. Water was added to the reaction mixture and the layers were separated. The aqueous phase was extracted with additional CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layer was washed with 10% aq. HCl solution, 5% aq. NaOH solution, and brine, followed by drying over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Filtration and removal of the solvent afforded crude product that was subjected to purification by flash column chromatography (SiO<sub>2</sub>, 1:1 hexanes:EtOAc) to afford **2** (1.06 g, 65%) as a colorless solid. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ 7.05 (d, *J* = 4.5 Hz, 6H), 7.79 (d, *J* = 4.5 Hz, 6H), 9.2 (s, 3H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ 90.8, 123.9, 131.2, 136.4, 138.9, 150.5, 163.1. IR (neat) ν (cm<sup>-1</sup>) 1744, 1219. Anal. Calcd. for C<sub>27</sub>H<sub>15</sub>I<sub>3</sub>O<sub>6</sub>: C, 39.71; H, 1.84. Found: C, 39.92; H, 1.89.

X-ray quality single crystals of **2**·3CHCl<sub>3</sub>, **2**·3C<sub>5</sub>H<sub>5</sub>N, and **2**·non-solvated were obtained by slow evaporation of solutions of **2** in CHCl<sub>3</sub>, pyridine, and CH<sub>2</sub>Cl<sub>2</sub>, respectively. In the case of **2**·3CHCl<sub>3</sub> and **2**·3C<sub>5</sub>H<sub>5</sub>N continued contact with the mother liquor over a period of several days resulted in disappearance of crystals of the respective inclusion complexes (hexagonal blocks) and the concomitant formation of crystals of **2**·non-solvated (colorless needles) as determined by X-ray diffraction analysis of randomly

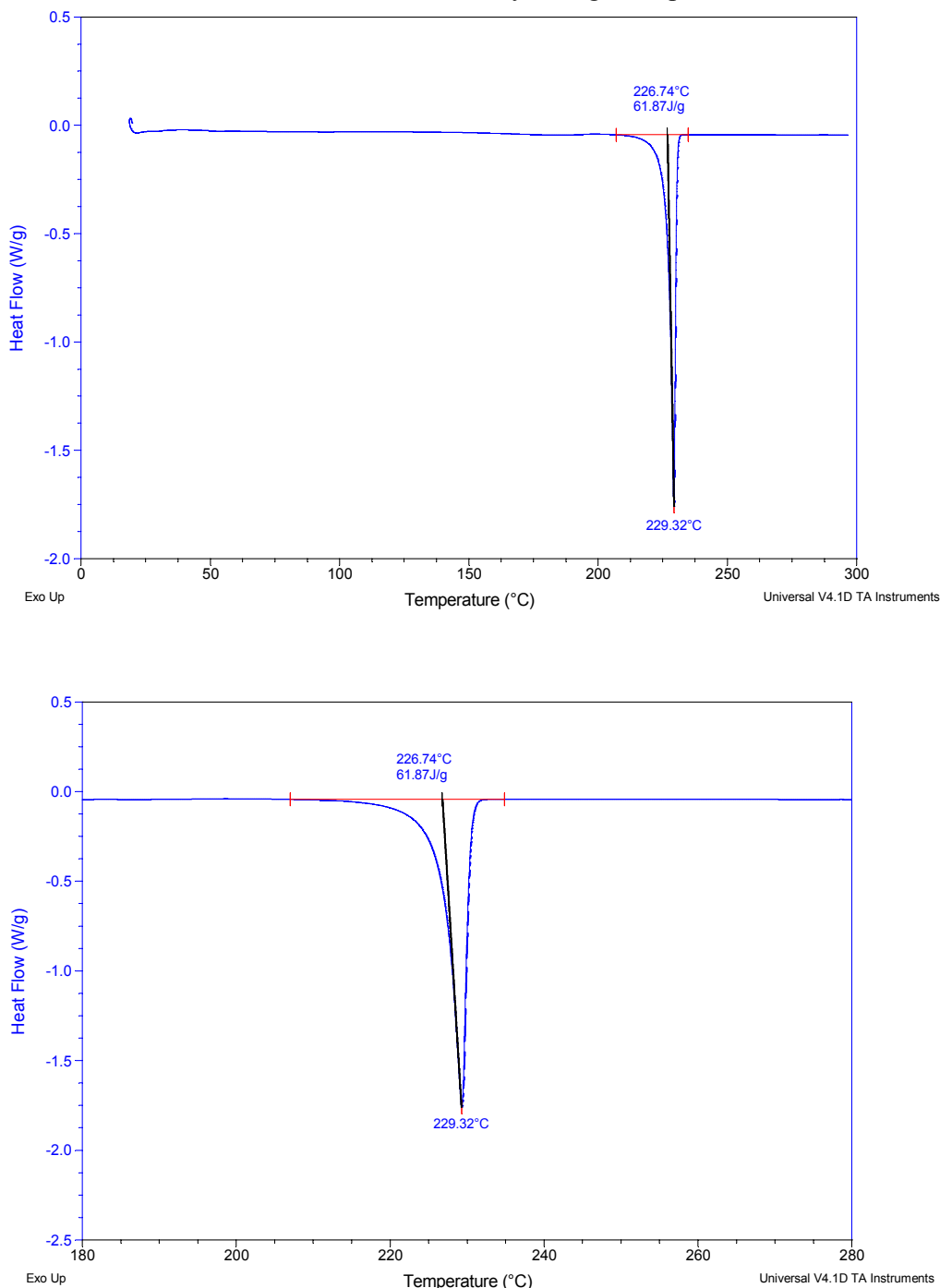
chosen samples. Crystallization yields were not determined. Crystals of  $2 \cdot 1.5C_6H_6$  were obtained upon attempted co-crystallization of **2** and trimesic acid trimethyl ester. Thus, **2** (~ 50 mg) was dissolved in 3 mL of benzene containing an equimolar amount of trimesic acid trimethyl ester. Slow evaporation at room temperature initially deposited hexagonal blocks found to be  $2 \cdot 1.5C_6H_6$ . Over time these crystals were replaced with crystalline needles found to be  $2 \cdot \text{non-solvated}$ . Instability of the crystalline inclusion complexes precluded PXRD analysis, however DSC/TGA analysis of  $2 \cdot 3C_5H_5N$  was performed (as shown below). Thermal and PXRD analyses of  $2 \cdot \text{non-solvated}$  were also obtained.

### References

1. C.-H. Lee and T. Yamamoto, *Bull. Chem. Soc. Jpn.* 2002, **75**, 615.

**(ii) Differential Scanning Calorimetry (DSC) of 2 (non-solvated)**

DSC was performed using a TA instruments 2920 MDSC V 2.6A DSC standard cell module. The sample was placed in crimped but vented aluminum pan and heated from 20 – 300 °C at a rate of 5 °C min<sup>-1</sup> under dry nitrogen. Mp. 226.74 °C.

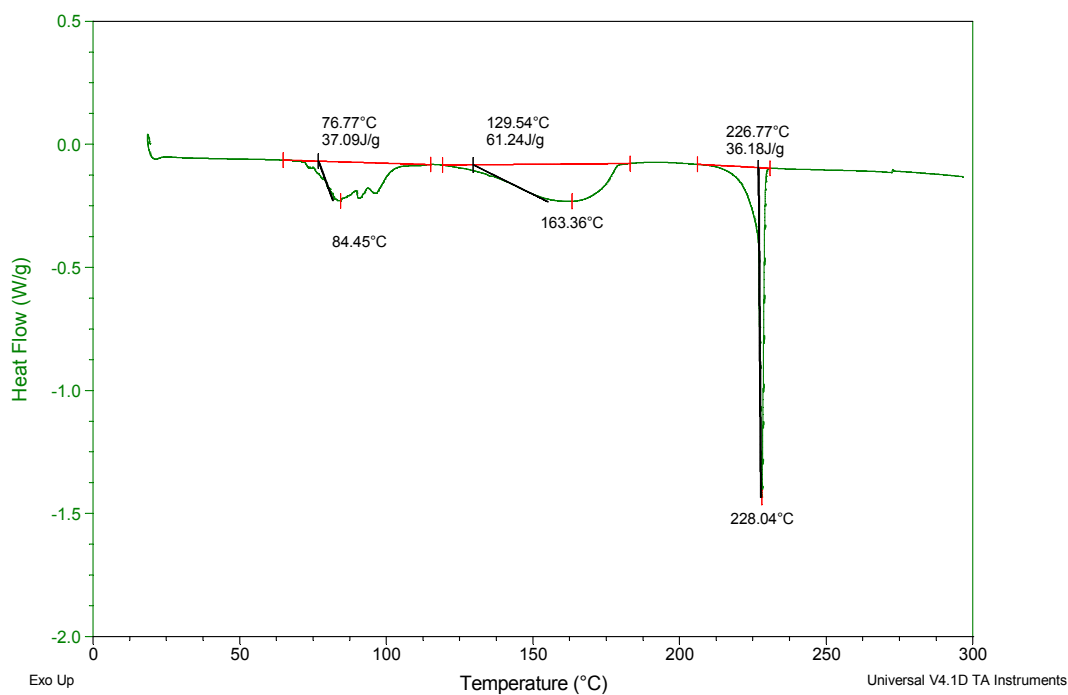


**Figure S1.** DSC trace of 2 (non-solvated form) after crystallization from CH<sub>2</sub>Cl<sub>2</sub>.

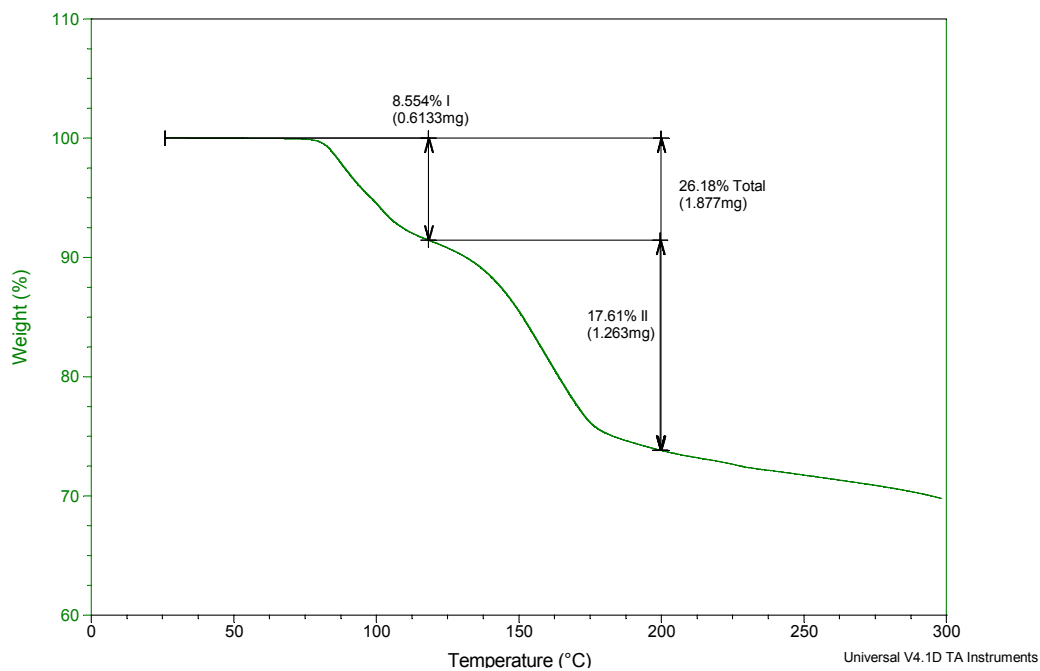
**(iii) DSC/TGA of 2·3C<sub>5</sub>H<sub>5</sub>N**

A thermogravimetric analyzer (TGA, Model 2950, TA Instruments) and a differential scanning calorimeter (DSC, Model 2010, TA instruments) were connected to a thermal analysis operating system (Thermal Analyst 2000, TA Instruments).

Approximately 5-10 mg of the sample in an open aluminum pan was heated in the DSC and TGA from room temperature to 300°C at 5°C/min under nitrogen purge.



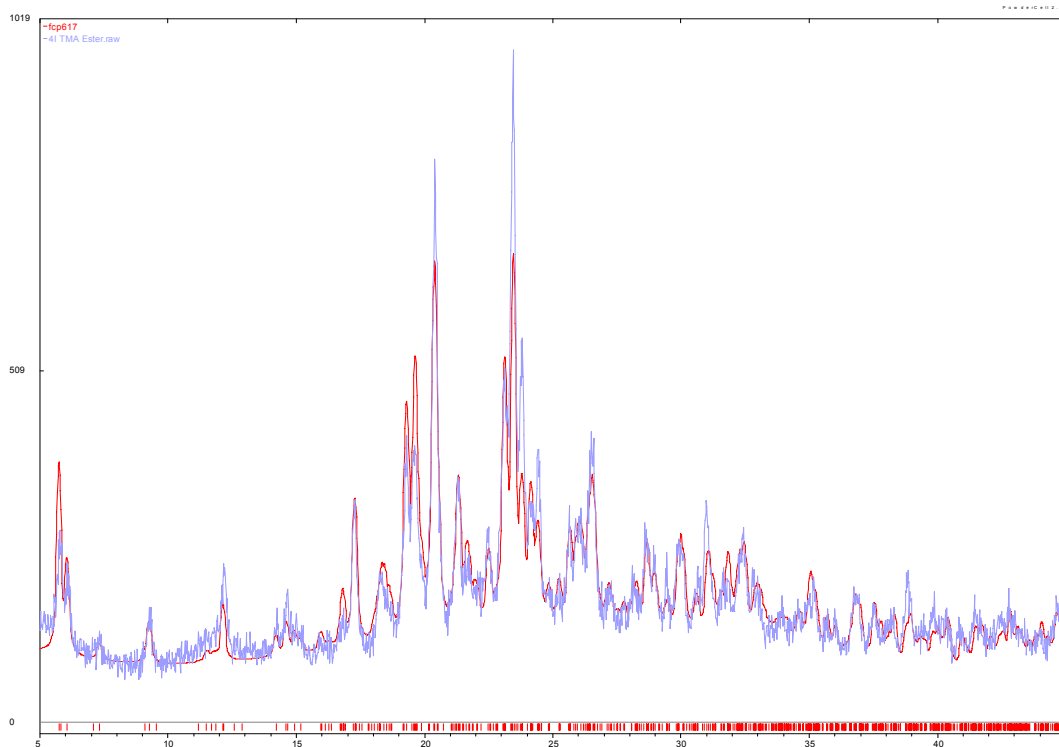
**Figure S2.** DSC trace of 2·3C<sub>5</sub>H<sub>5</sub>N. Loss of pyridine appears to take place in two stages beginning at ~ 77 °C and 130 °C followed by ample melting at ~ 227 °C.



**Figure S3.** TGA of 2·C<sub>5</sub>H<sub>5</sub>N. Weight loss occurs in two stages corresponding to endothermic transitions in the DSC trace. Total observed weight loss is ~ 26% which compares favorably to the calculated value of 22.5% for loss of all pyridine solvates.

#### (iv) X-Ray powder diffraction (PXRD)

X-ray powder diffraction data were recorded on a Siemens D5000 diffractometer using Cu K $\alpha$  X-radiation at 50 kV and 30 mA. Diffraction patterns were collected over a range of 5 - 45°  $2\theta$  at a scan rate of 1°  $2\theta$  min<sup>-1</sup>. The software Powder Cell 2.3 was used for Rietveld refinement (N. Kraus and G. Nolze, *POWDER CELL*, version 2.3; Federal Institute for Materials Research and Testing: Berlin, Germany, 2000).



**Figure S4.** Comparison of Rietveld simulated (red) and experimental (violet) powder patterns for the non-solvated form of **2**. The simulated pattern was calculated from single crystal X-ray diffraction data obtained on crystals grown from CH<sub>2</sub>Cl<sub>2</sub>. Experimental powder pattern was obtained using material purified via flash column chromatography.