Supplementary Material for Chemical Communications

Supplementary Information

Concomitant polymorphs of 2,2',6,6'-tetramethyl-4,4'-terphenyldiol: the β-quinol network reproduced in a metastable polymorph†

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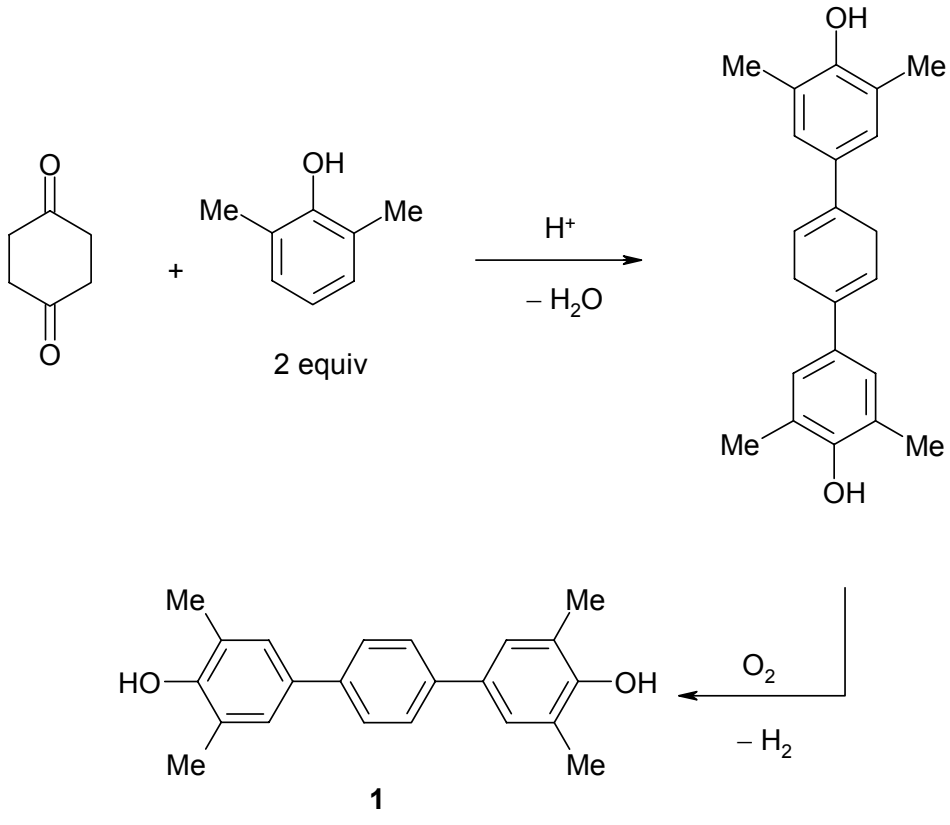
Synthesis of 1

A mixture of cyclohexane-1,4-dione (0.50 g, 8.0 mmol) and 2,6-dimethylphenol (2.30 g, 18.9 mmol) in 1:1 dioxane/water mixture (10 mL) was treated drop wise with concentrated H_2SO_4 (15 mL) at 0 ºC. The reaction mixture was stirred at room temperature for 72 h under O_2 atmosphere. The reaction mixture was neutralized and extracted with ether, dried with anhydrous $MgSO_4$ and solvent evaporated. Pure compound **1** (0.71 g, 50%) was obtained by column chromatography using EtOAc/hexane mixture (3%). The intermediate dihydrobenzene compound was present to the extent of 30% when the reaction was carried without oxygen. **1**: ^{1}H-NMR (DMSO-d_6) δ 2.24 (12 H, s), 7.26 (4 H, s), 7.59 (4 H, s), 8.33 (2 H, s). IR (KBr pellets): 3320, 1597, 1477, 1319 cm^{-1}, m.p. 257-259 °C. Terphenol **2** was prepared in the same way by condensation with phenol.



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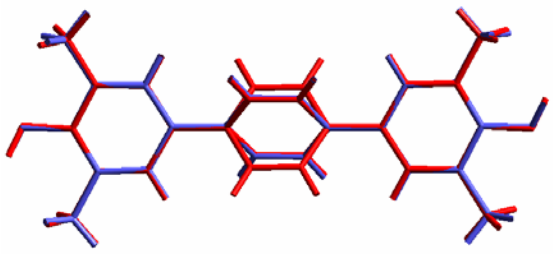

Fig. S1 Different conformations of the central phenyl ring in polymorphs **1a** (blue) and **1b** (red). The conformation of the central phenyl ring in **1a** almost overlaps with the major occupancy of the disordered phenyl ring of **1b**. The minor occupancy phenyl ring has a different orientation.

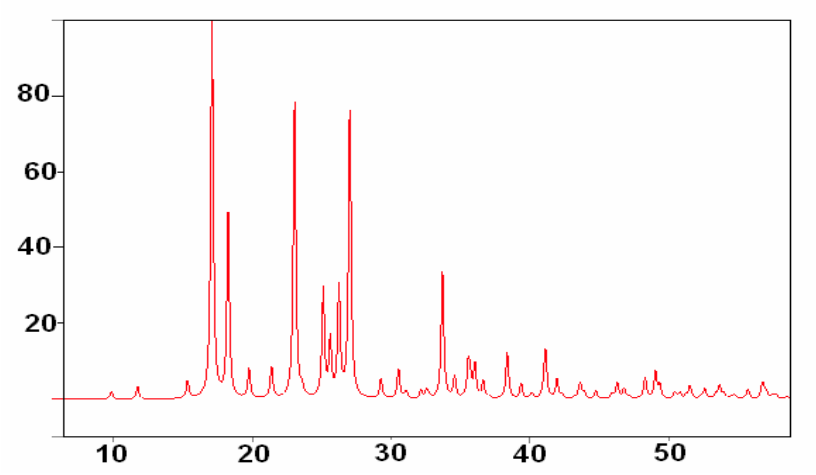

Fig. S2 (a) Simulated trace of the rhombohedral form **1a**.

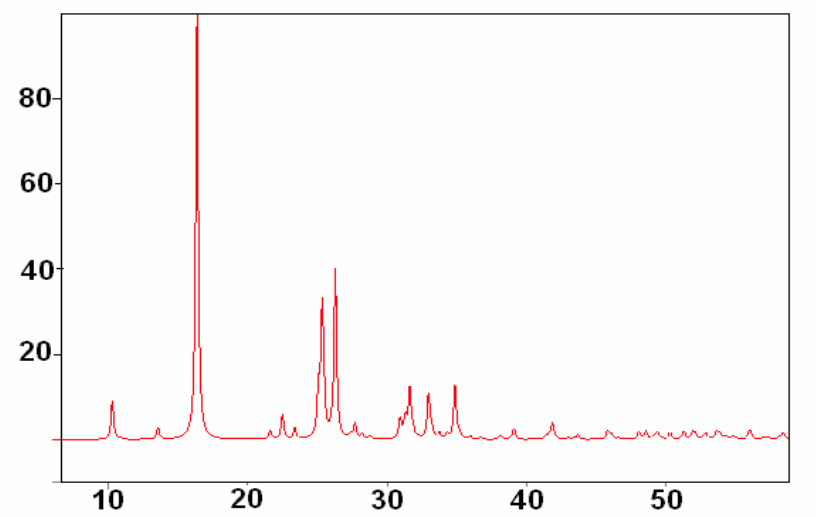

Fig. S2 (b) Simulated trace of the monoclinic form **1b**.

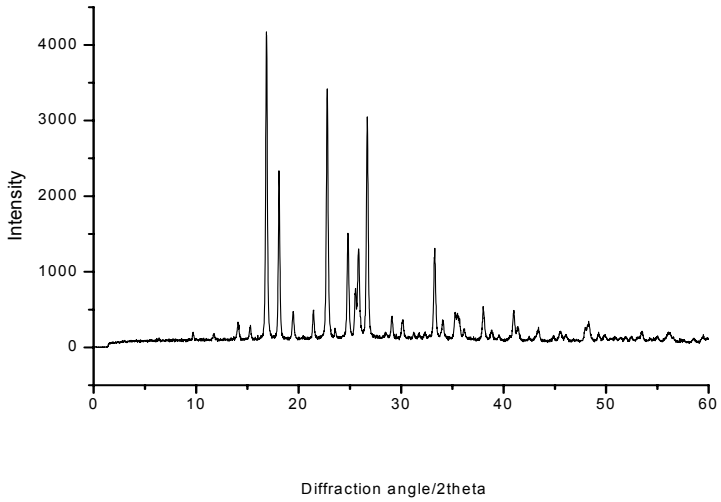

Fig. S2 (c) Experimental PXRD of microcrystalline powder after grinding. This material is mostly form **1a**.

Powder XRD is recorded on INEL XRG3000 instrument using Co-Kα1 radiation (λ=1.788965 Å, 2θ 5-50°).

Differential scanning calorimetry was performed on Mettler Toledo DSC 822e module. The solid (4-6 mg) was placed in crimped but vented aluminum pan and heated from 30-300 °C @ 2K/min maintaining dry nitrogen purge @ 150 mL/min. In the heat–cool–heat cycle for **1a**, the sample was cooled to room temperature @ 5K/min.