

**Trimorphs of 4-bromophenyl 4-bromobenzoate. Elastic, brittle, plastic.**

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**Supporting Information**

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## S1: Synthesis of 1: 4-bromophenyl 4-bromobenzoate

4-Bromobenzoyl chloride was prepared from 4-bromobenzoic acid. 100 Mg of 4-bromobenzoic acid was taken in a 100 ml RB flask. Excess of thionyl chloride ( $\text{SOCl}_2$ ) was then added in the flask. The mixture was refluxed for 4 hours at  $90^\circ\text{C}$ . Nitrogen atmosphere was maintained during the reflux. After that, excess  $\text{SOCl}_2$  was removed from the reaction mixture under reduced pressure. The crude was then dissolved in dry dichloromethane (DCM) and was kept on a stirrer at room temperature. A solution of 4-bromophenol (1 equivalent) in DCM was slowly added in that. A pinch of tetrabutylammonium hydrogen sulphate was then added in the reaction mixture. Then, a solution of potassium carbonate ( $\text{K}_2\text{CO}_3$ ) (2.5 equivalent) was poured in that. The reaction was left for overnight. The reaction mixture was washed with water four times and finally with brine. Solvent from the extracted solution was removed under reduced pressure. The solid product was purified through crystallization and the pure sample was used for further experiments.

## S2: SCXRD experiment

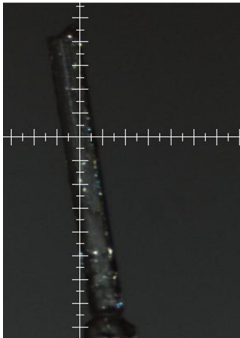
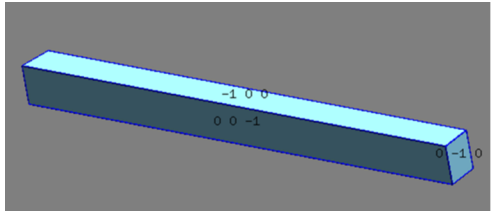
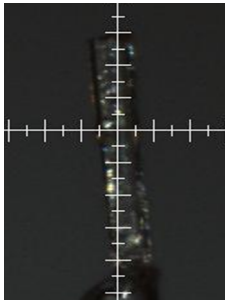
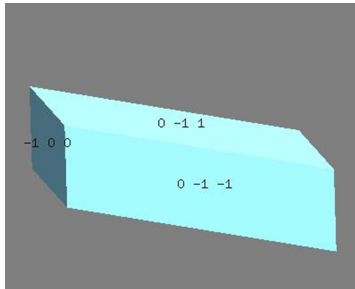
Single crystal X-ray diffraction (SCXRD) data of all the polymorphs were collected on a Rigaku Mercury 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromator  $\text{Mo K}\alpha$  radiation, with an attached low temperature gas spray cooler. The data were processed with the Rigaku CrystalClear 2.0 software.<sup>1,2</sup> Structure solution and refinements were executed using SHELX97<sup>3</sup> implemented in the WinGX suite.<sup>4</sup> All the non-hydrogen elements were refined anisotropically and hydrogen atoms were refined isotropically. The crystallographic data are given in the supplementary information, (S3).

1. Rigaku Mercury375R/M CCD. Crystal Clear-SM Expert 2.0 rc14; Rigaku Corporation: Tokyo, Japan, 2009.
2. J. Pflugrath, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 1999, **55**, 1718.
3. G. M. Sheldrick, SHELX-97: Program for the Solution and Refinement of Crystal Structures, 1997 (University of Göttingen: Göttingen).
4. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

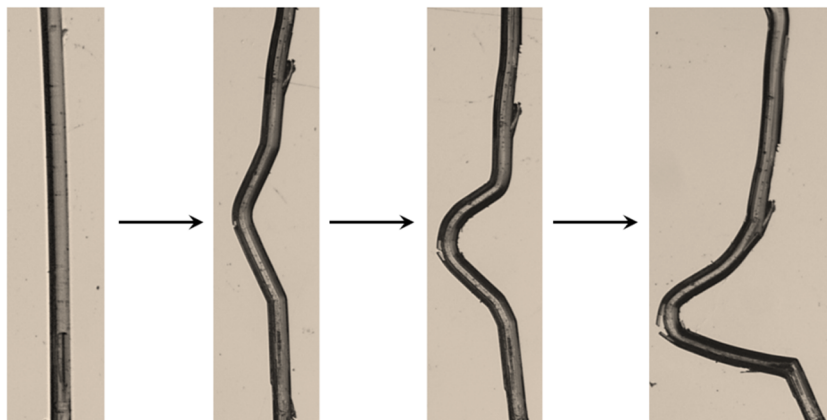
**S3: Crystallographic information table**

Compounds	1_Form-I	1_Form-II	1_Form-III
Formula	C <sub>13</sub> H <sub>8</sub> Br <sub>2</sub> O <sub>2</sub>	C <sub>13</sub> H <sub>8</sub> Br <sub>2</sub> O <sub>2</sub>	C <sub>13</sub> H <sub>8</sub> Br <sub>2</sub> O <sub>2</sub>
Molecular weight	356.01	356.01	356.01
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P2<sub>1</sub>/n</i>	<i>Pna2<sub>1</sub></i>	<i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>
<i>a</i> (Å)	15.484(13)	7.859(5)	3.8549(9)
<i>b</i> (Å)	4.021(3)	6.118(4)	11.732(2)
<i>c</i> (Å)	19.824(15)	24.872(17)	27.480(5)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90.285(12)	90	90
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1234.2(17)	1195.9(14)	1242.8(4)
<i>Z</i>	4	4	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.916	1.977	1.902
F(000)	688.0	688.0	688.0
Temp. (K)	100	100	100
<i>R</i> <sub>1</sub>	0.0514	0.0756	0.0567
<i>wR</i> <sub>2</sub>	0.1399	0.1966	0.1666
Goodness-of fit	1.026	1.096	0.995
CCDC No.	1833685	1833686	1833687

#### S4: Face indexing images

Compound	Crystal image	Indexed faces
1 (Form-I)		
1 (Form-III)		

#### S5: Progressive plastic bending in form-III of 1

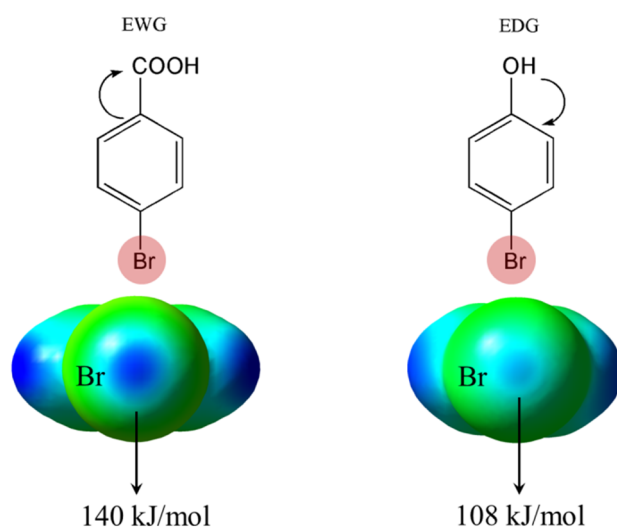


## S6: Computation method

Electrostatic surface potential maps were calculated for model compounds, 4-bromobenzoic acid and 4-bromophenol. Each of the compounds represents the two different bromine groups in the compound **1**. Atomic coordinates were obtained from GaussView5.0.8. All the DFT calculations were performed in Gaussian 09.<sup>6</sup> B3LYP function and 6-311G (d, p) basis set were used. Electrostatic surface potentials were mapped using molecular electron density 0.004 electron/Å. Colour coding was used to indicate relative distribution of charges. Blue colour indicates positive charge.

6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09; Gaussian, Inc.: Wallingford, CT, 2009.

## S7: Electrostatic surface potential (ESP) maps



Calculated electron density maps showing electrostatic surface potential (ESP) distribution for model compounds, 4-bromobenzoic acid and 4-bromophenol. Effect of the electron withdrawing carboxyl group (EWG) in enhancing the positively charged  $\sigma$ -hole on bromine compared to the electron donating phenolic group (EDG).

**S8: Attachment energy calculation**

Attachment energies for crystals of form-I and form-III are calculated using Morphology module. Dreiding force field was used. Crystal graphs were first generated. Calculated crystal graphs are then used to generate growth morphology. Attachment energies are finally obtained from the calculated morphologies.