

## **Electronic Supporting Information**

### **Linker size dependent Mechanical Properties of Di-imine based Molecular Crystals**

*Deepak Manoharan,<sup>a</sup> Shamim Ahmad,<sup>b</sup> Srinu Tothadi,<sup>c</sup> Franziska Emmerling,<sup>d</sup> Biswajit*

*Bhattacharya,<sup>\*d</sup> Soumyajit Ghosh<sup>\*a</sup>*

<sup>a</sup>Department of Chemistry, SRM Institute of Science and Technology, Kattankulathur, 603 203, Tamil Nadu, India.

<sup>b</sup>Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, Nadia, West Bengal, 741246 India

<sup>c</sup>Analytical and Environmental Sciences Division and Centralized Instrumentation Facility, CSIR-Central Salt and Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar-364002 (India)

<sup>d</sup>BAM Federal Institute for Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany.

\* Email: [soumyajitghosh89@gmail.com](mailto:soumyajitghosh89@gmail.com)

[biswajit.bhattacharya@bam.de](mailto:biswajit.bhattacharya@bam.de)

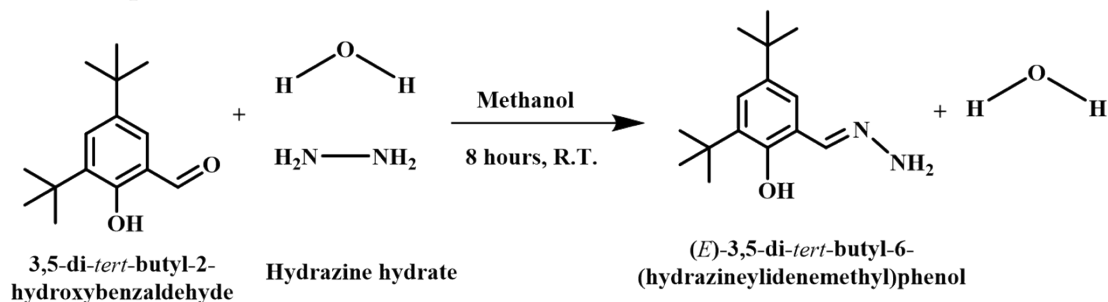
---

<b>Table of Contents</b>	<b>Page No</b>
S1. Synthesis and NMR Spectroscopy	S3-S6
S2. Thermal analysis	S7-S8
S3. Face indexing	S9-S10
S4. Mechanical Flexibility	S10
S5. Elastic strain calculation	S11
S6. Single Crystal X-ray Diffraction	S11-S12
S7. Energy Framework Calculations	S13-S16
S8. Torsion Angles	S17-S18
S9. UV & PL spectrum	S19-S20
S10. Fluorescence Microscopy images	S21-S22
S11. References	S22

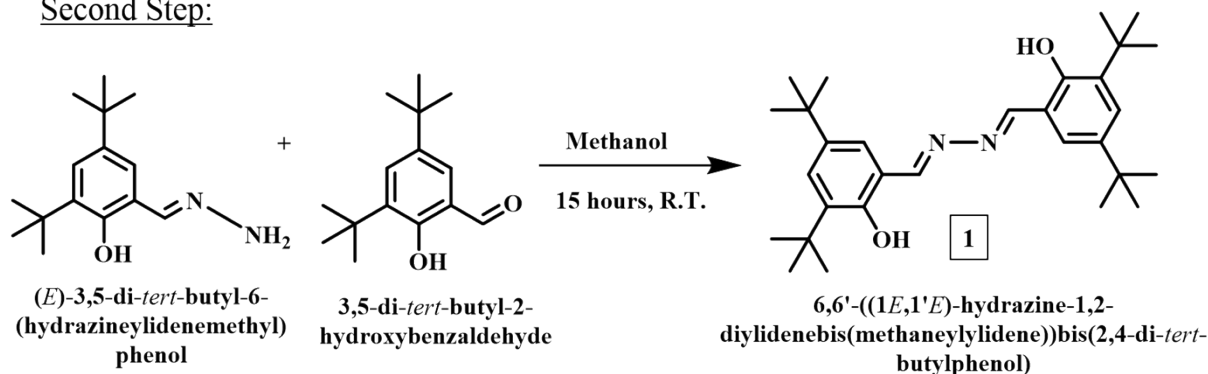
## S1. Synthesis and NMR Spectroscopy

### Synthesis procedure

#### First Step:

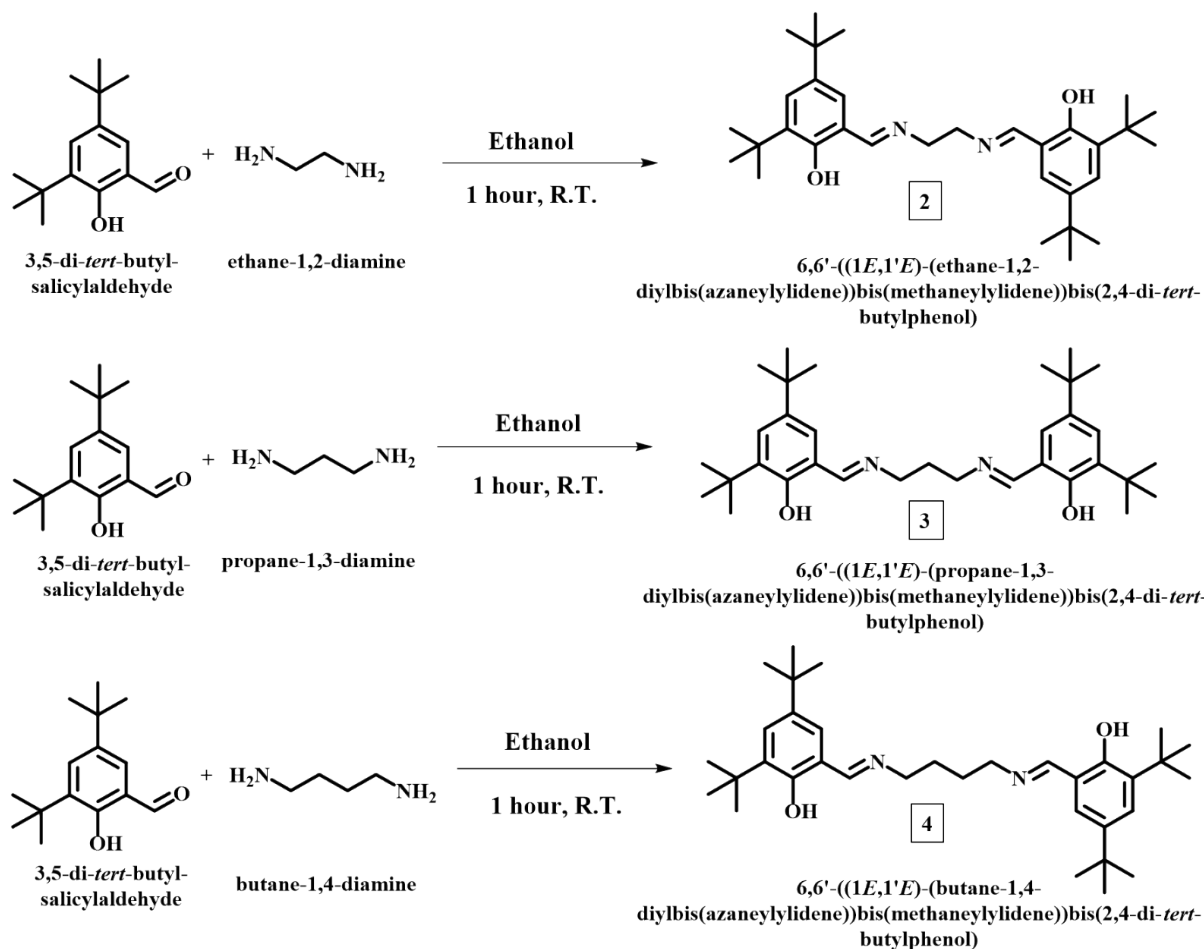


#### Second Step:



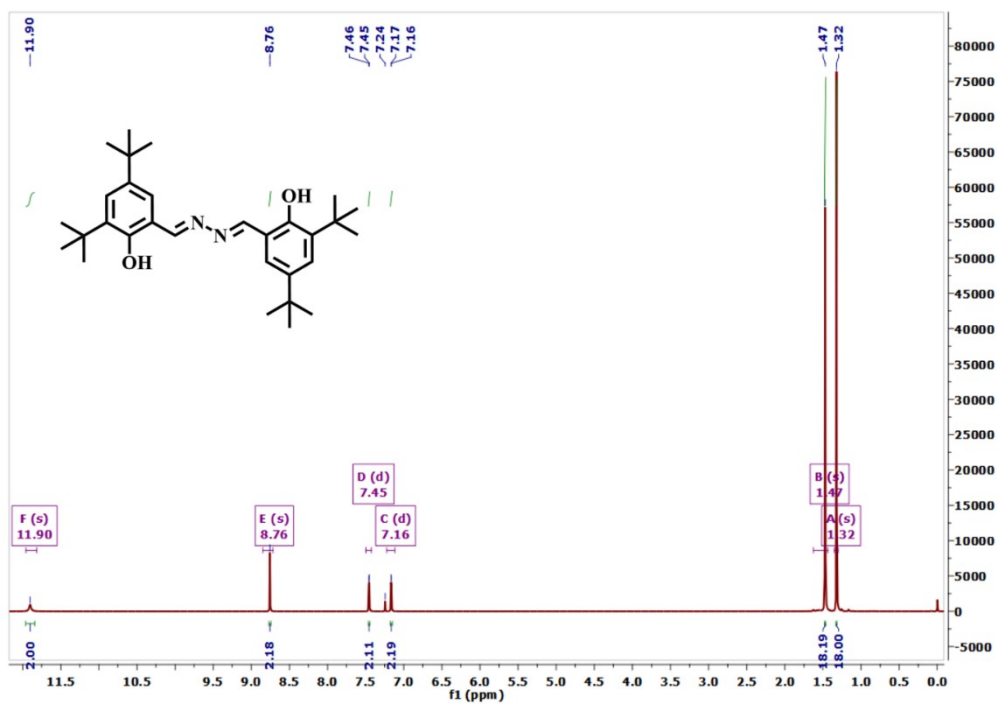
**Scheme 1** Synthesis route of compound **1**.

Compound **1** was synthesized through a two-step process with a reported procedure.<sup>1</sup> In the first step, we dissolved one equivalent of 3,5-ditertiarybutyl salicylaldehyde in 20 ml of methanol and added an excess of hydrazine hydrate to the solution. This mixture was stirred for 8 hours to yield the desired product. The yield of product in first step is 83 %. For the second step, the product obtained in the first step was dissolved in 20 ml of methanol along with another one 1 equivalent 3,5-ditertiarybutyl salicylaldehyde once again. The resulting mixture was stirred for 15 hours, leading to the formation of the final product. We then washed the product with diethyl ether and dried it using a high vacuum pump to obtain Compound **1** with yield of 70 %.



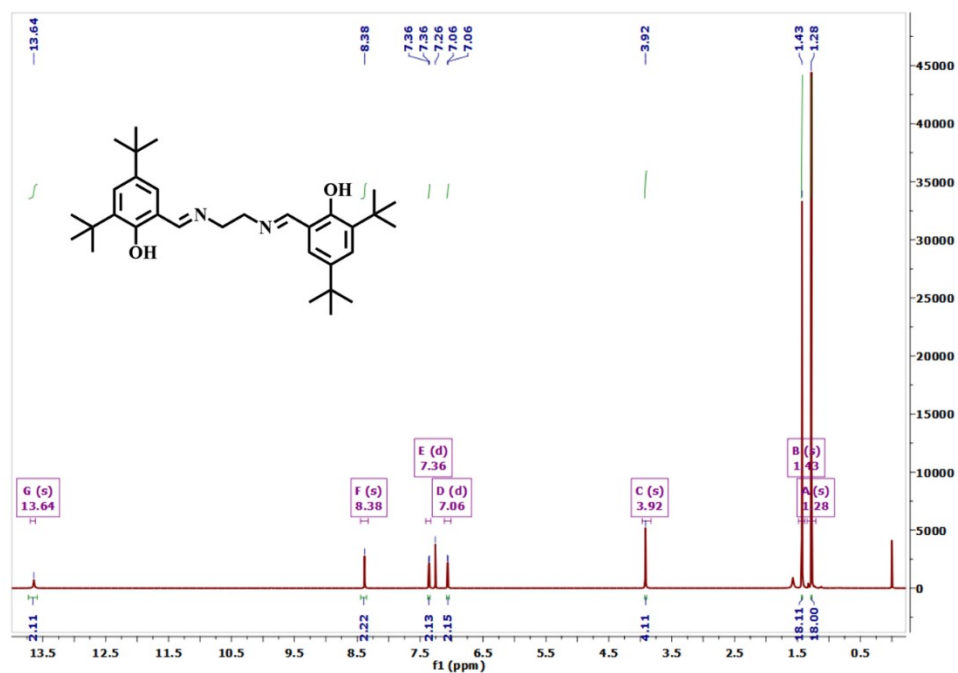
**Scheme 2** Synthesis route of compounds **2**, **3** and **4**.

Compounds **2**, **3**, and **4** were also synthesized using a reported procedure by dissolving 2 equivalents of 3,5-ditertiarybutyl salicylaldehyde in 20 ml of methanol separately, each time with a different diamine (namely ethylenediamine, 1,3 diaminopropane, and 1,4 diaminobutane).<sup>2</sup> The solutions were stirred for 1 hour at room temperature. Following the completion of the reaction, we observed the precipitation of the respective products. These precipitates were then filtered and dried under high vacuum conditions to obtain compounds **2**, **3**, and **4** with the yields of 75 %.



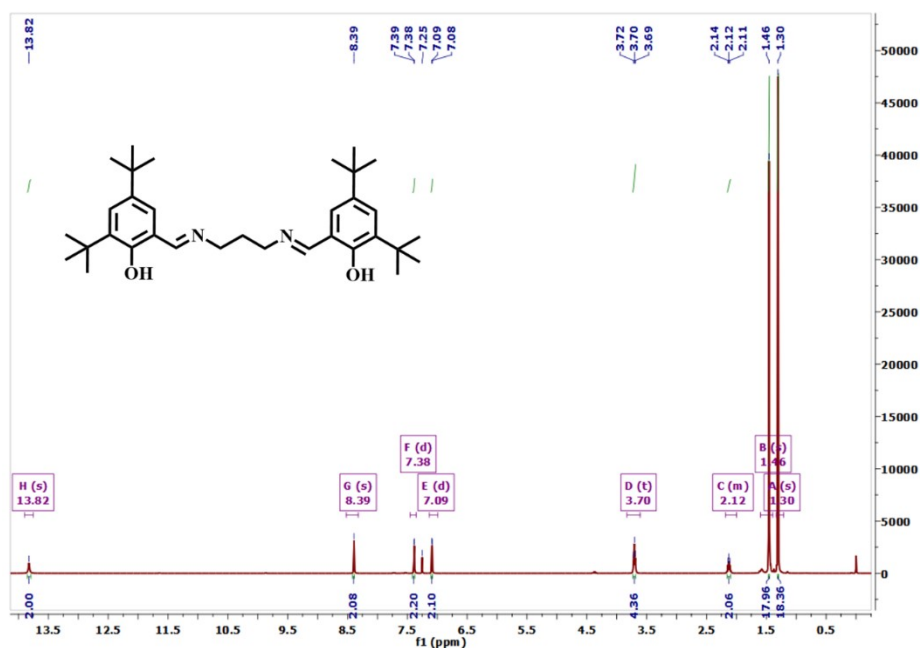
**Fig. S1.1**  $^1\text{H}$  NMR spectrum of crystal 1.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  11.90 (s, 2H), 8.76 (s, 2H), 7.45 (d,  $J = 2.4$  Hz, 2H), 7.16 (d,  $J = 2.4$  Hz, 2H), 1.47 (s, 18H), 1.32 (s, 18H).



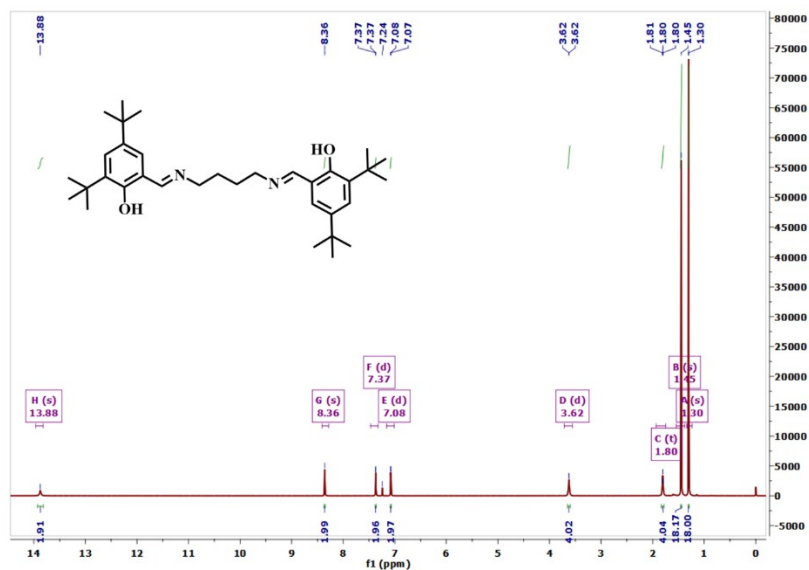
**Fig. S1.2**  $^1\text{H}$  NMR spectrum of crystal 2.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  13.64 (s, 2H), 8.38 (s, 2H), 7.36 (d,  $J = 2.5$  Hz, 2H), 7.06 (d,  $J = 2.4$  Hz, 2H), 3.92 (s, 4H), 1.43 (s, 18H), 1.28 (s, 18H).



**Fig. S1.3**  $^1\text{H}$  NMR spectrum of crystal 3.

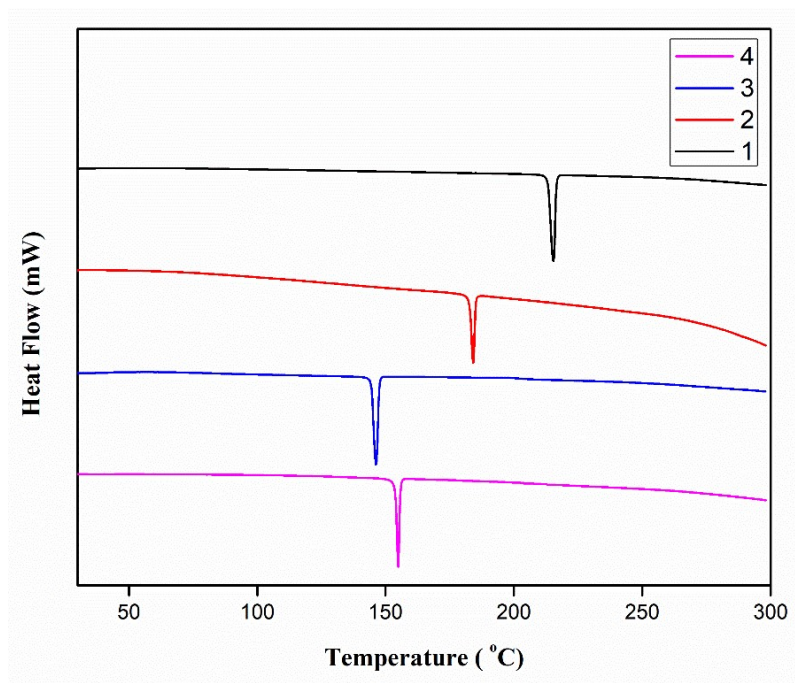
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  13.82 (s, 2H), 8.39 (s, 2H), 7.38 (d,  $J = 2.4$  Hz, 2H), 7.09 (d,  $J = 2.4$  Hz, 2H), 3.70 (t,  $J = 6.4$  Hz, 4H), 2.18 – 2.00 (m, 2H), 1.46 (s, 18H), 1.30 (s, 18H).



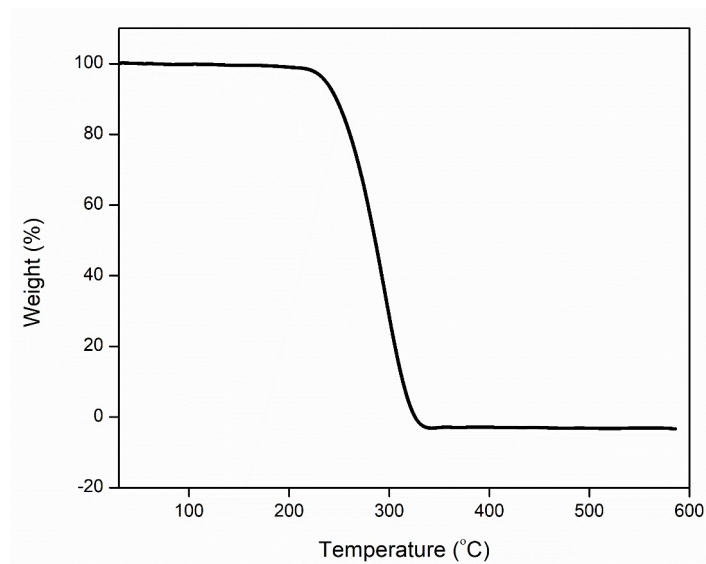
**Fig. S1.4**  $^1\text{H}$  NMR spectrum of crystal 4.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  13.88 (s, 2H), 8.36 (s, 2H), 7.37 (d,  $J = 2.5$  Hz, 2H), 7.08 (d,  $J = 2.4$  Hz, 2H), 3.62 (d,  $J = 0.8$  Hz, 4H), 1.80 (t,  $J = 2.8$  Hz, 4H), 1.45 (s, 18H), 1.30 (s, 18H).

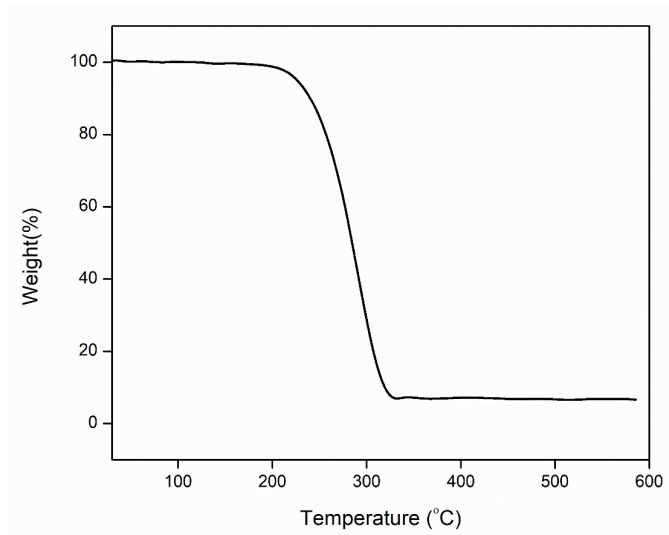
## S2. Thermal analysis



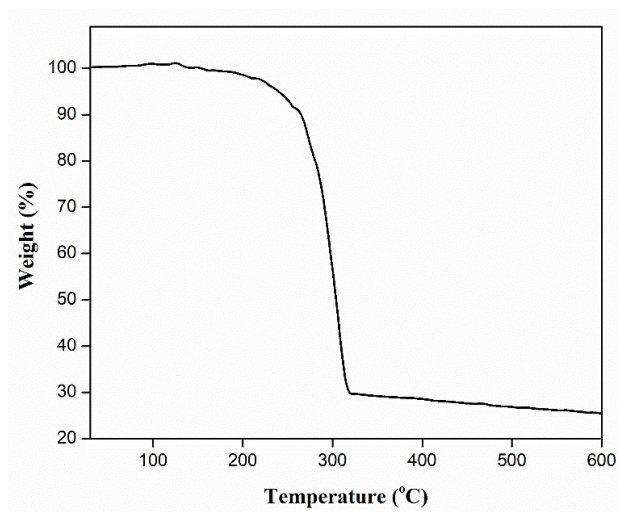
**Fig. S2.1** DSC thermogram of crystals of **1**, **2**, **3** and **4**.



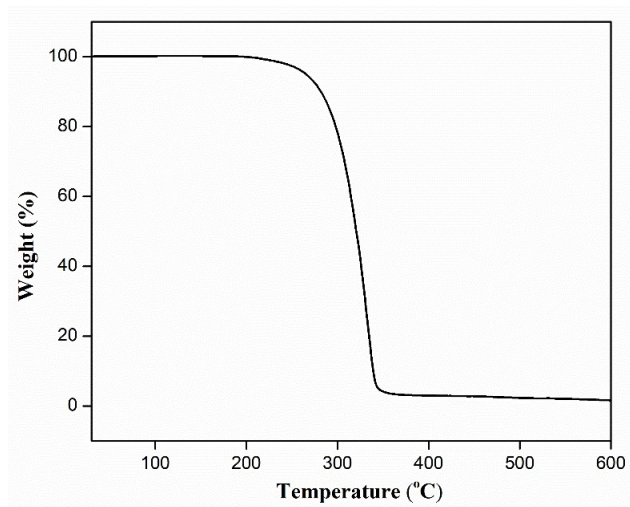
**Fig. S2.2** TGA graph of crystal **1**.



**Fig. S2.3** TGA graph of crystal 2.



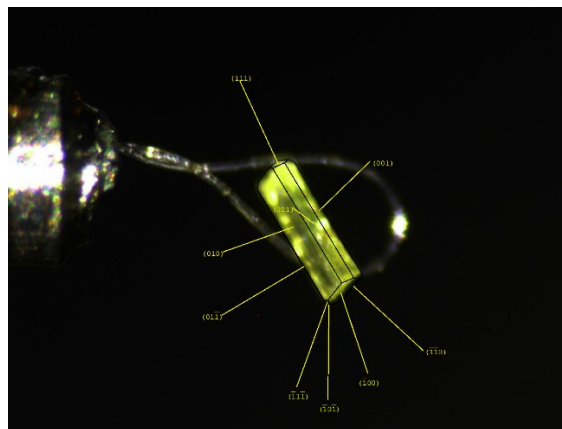
**Fig. S2.4** TGA graph of crystal 3.



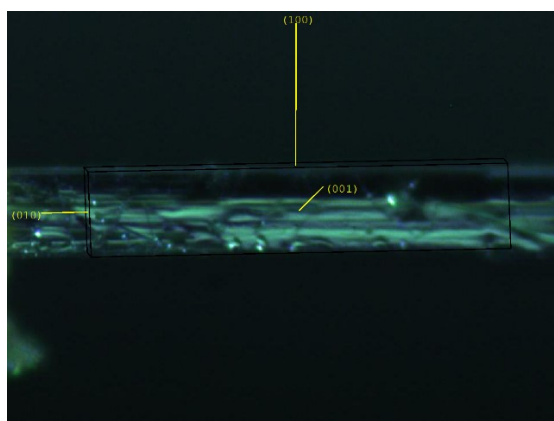
**Fig. S2.5** TGA graph of crystal 4.



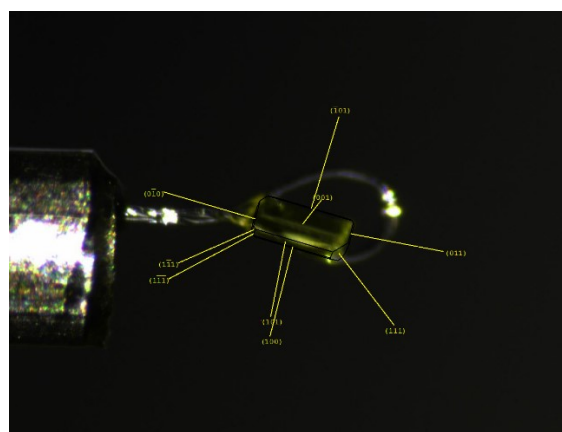
### S3. Face Indexing



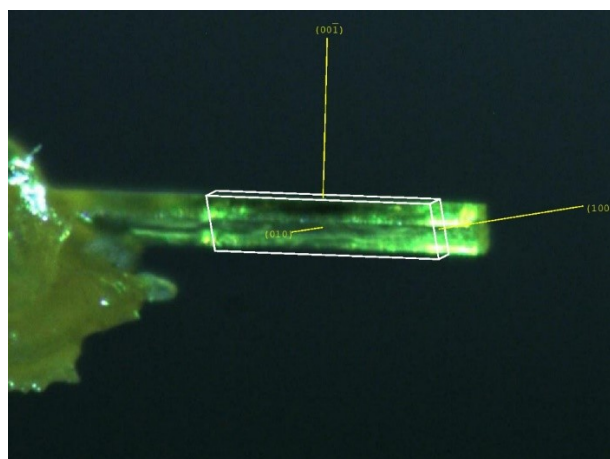
**Fig. S3.1** Face indexing image of pristine crystal of **1**.



**Fig. S3.2** Face indexing image of pristine crystal of **2**

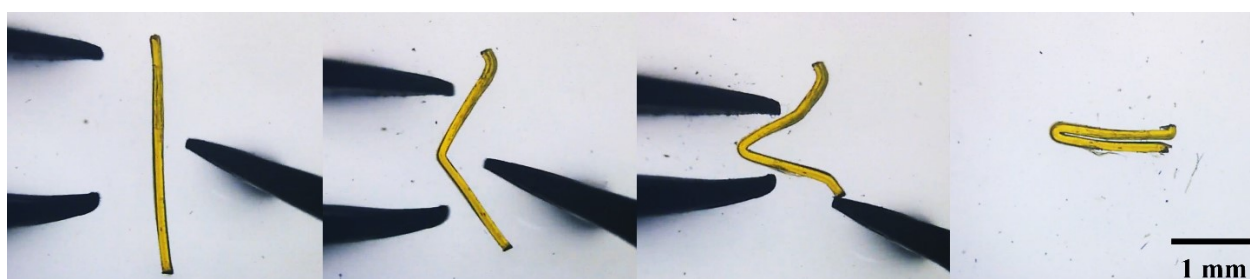


**Fig. S3.3** Face indexing image of pristine crystal of **3**.

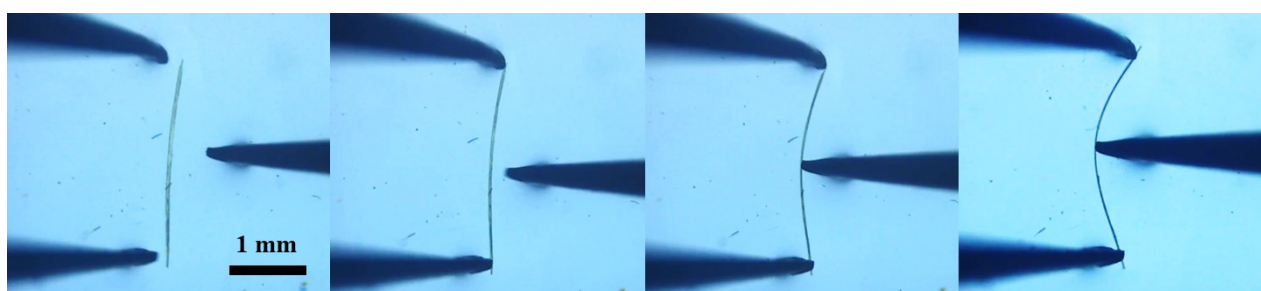


**Fig. S3.4** Face indexing image of pristine crystal of 4.

#### **S4. Mechanical Flexibility**



**Fig. S4.1** Stepwise plastic bending of crystal 2.



**Fig. S4.2** Stepwise elastic bending image of crystal of 4.

## S5. Elastic strain calculation

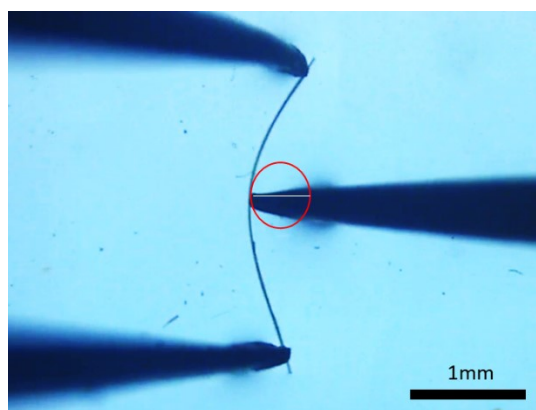


Fig. S5.1 Elastic strain calculation of crystal of 4.

Length = 2.5 mm  
Width = 0.024 mm  
Thickness = 0.019 mm  
Radius of Curvature, (R) = 0.25 mm

$$\begin{aligned}\varepsilon (\%) &= t / 2R \times 100 \\ &= 0.019 / 2 \times 0.25 \times 100 \\ &= 3.8\%\end{aligned}$$

## S6. Single Crystal X-ray Diffraction

Table S6.1. Dimensions of the crystals 1, 2, 3 and 4

Crystal	Crystal Dimension			Morphology
	Length	Width	Thickness	
1	2 mm	0.12 mm	0.08 mm	Needle Shaped
2	2.2 mm	0.4 mm	0.15 mm	Needle Shaped
3	2 mm	0.16 mm	0.08 mm	Needle Shaped
4	2 mm	0.2 mm	0.05 mm	Needle Shaped

**Table S6.2:** Crystallographic Information Table.

Compounds	1	2	3	4
Formula	C <sub>30</sub> H <sub>44</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>32</sub> H <sub>48</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>33</sub> H <sub>50</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>34</sub> H <sub>52</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	464.69	492.75	506.78	520.80
T/K	298	150	298	301
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 1
<i>a</i> /Å	6.4470(15)	18.8769(8)	10.9190(10)	10.1433(12)
<i>b</i> /Å	10.416(3)	6.1559(2)	10.0505(8)	11.0854(13)
<i>c</i> /Å	11.367(3)	26.9215(11)	29.337(3)	15.0978(18)
$\alpha$ /°	82.665(10)	90	90	87.297(5)
$\beta$ /°	87.026(10)	106.511(3)	90.486(3)	78.914(5)
$\gamma$ /°	72.301(9)	90	90	89.006(5)
Volume/Å <sup>3</sup>	721.1(3)	2999.4(2)	3219.3(5)	1664.0(3)
<i>Z</i>	1	4	4	2
$\rho$ , Mg.cm <sup>-3</sup>	1.070	1.091	1.046	1.039
<i>m</i> /mm <sup>-1</sup>	0.066	0.067	0.064	0.063
Reflections	24832	63050	60616	69500
Collected				
Independent	2550	3156	5658	7087
Reflections				
R <sub>int</sub>	0.1034	0.0470	0.0753	0.0929
GOF	1.028	1.040	1.048	1.033
Final R[I > 2 $\sigma$ ]	0.0645	0.0512	0.0834	0.0888
R <sub>1</sub> / wR <sub>2</sub>	0.1514	0.1326	0.2357	0.2633

CCDC Number	2285906	2292993	2285907	2292994
-------------	---------	---------	---------	---------

## S7. Energy Framework Calculations

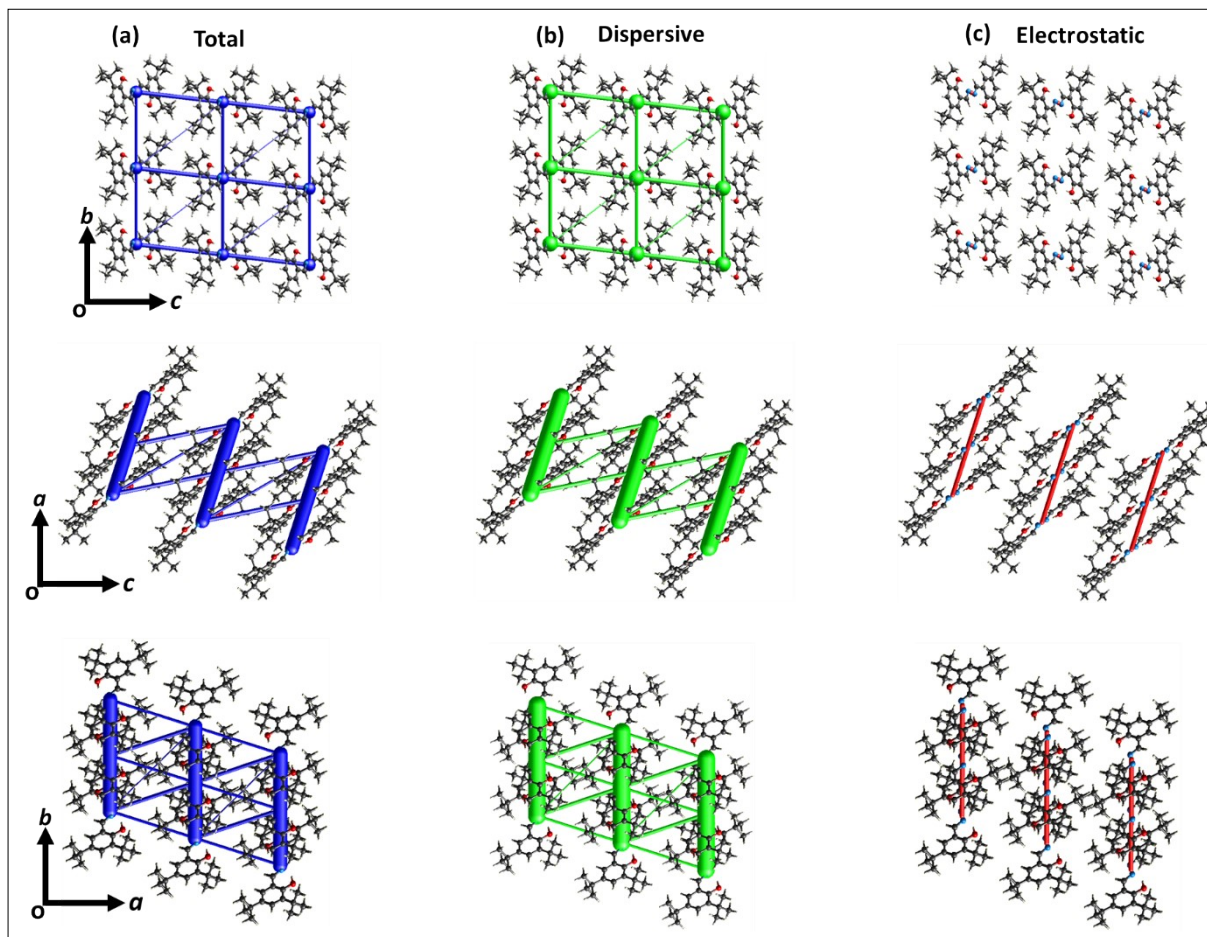
The energy frameworks calculations relating to intermolecular interactions of pristine structures of **1**, **2** and **3** and the uniaxial compressed structures obtained from the DFT calculations were performed using the software suite Crystal-Explorer<sup>3,4</sup> based on B3LYP/DGDZVP molecular wavefunctions. The input structures were taken from the CIF files. The hydrogen atoms were normalized to standard neutron diffraction values. The constructed energy frameworks are based on the crystal symmetry and the total components of the interaction energy including electrostatic, polarization, dispersion, and exchange repulsion components. The scale factors for the electrostatic, polarization, dispersion and exchange repulsion components are 1.057, 0.740, 0.871 and 0.618, respectively. To provide clarity, energies above  $-5 \text{ kJ.mol}^{-1}$  have been omitted and the energy scale factor was set to 100. the cylinder thickness is proportional to the intermolecular interaction energies along the direction of the cylinder.

**Table S7.1** Molecular structure pairs and the interaction energies ( $\text{kJ.mol}^{-1}$ ) obtained from energy frameworks calculation for **1**. Scale factors are in the lower table.

Interaction Energies ( $\text{kJ/mol}$ )									
R is the distance between molecular centroids (mean atomic position) in Å.									
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)									
	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	17.53	B3LYP/DGDZVP	1.9	-0.0	-8.9	0.0	-5.8
	2	x, y, z	17.63	B3LYP/DGDZVP	-1.7	-0.1	-14.9	0.0	-14.9
	2	x, y, z	6.45	B3LYP/DGDZVP	-26.2	-3.2	-119.6	82.3	-83.4
	2	x, y, z	12.89	B3LYP/DGDZVP	0.9	-0.1	-6.2	0.0	-4.5
	2	x, y, z	10.45	B3LYP/DGDZVP	-3.8	-0.7	-25.0	11.7	-19.1
	2	x, y, z	13.90	B3LYP/DGDZVP	-0.5	-0.1	-5.5	0.0	-5.4
	2	x, y, z	10.42	B3LYP/DGDZVP	-3.4	-0.2	-17.0	10.3	-12.3
	2	x, y, z	13.36	B3LYP/DGDZVP	-0.3	-0.5	-29.9	0.0	-26.6

Scale factors for benchmarked energy models				
See Mackenzie et al. IUCrJ (2017)				
Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618



**Fig. S7.1** Visualization of energy frameworks showing total interaction energy (a, blue); electrostatic (b, red) and dispersion (c, green) components for **1**, in the (top) (100); (middle) (010) and (below) (010) faces, respectively. The energy scale factor is 100 and the energy threshold is  $5 \text{ kJ.mol}^{-1}$ .

**Table S7.2** Molecular structure pairs and the interaction energies ( $\text{kJ.mol}^{-1}$ ) obtained from energy frameworks calculation for **2**. Scale factors are in the lower table.

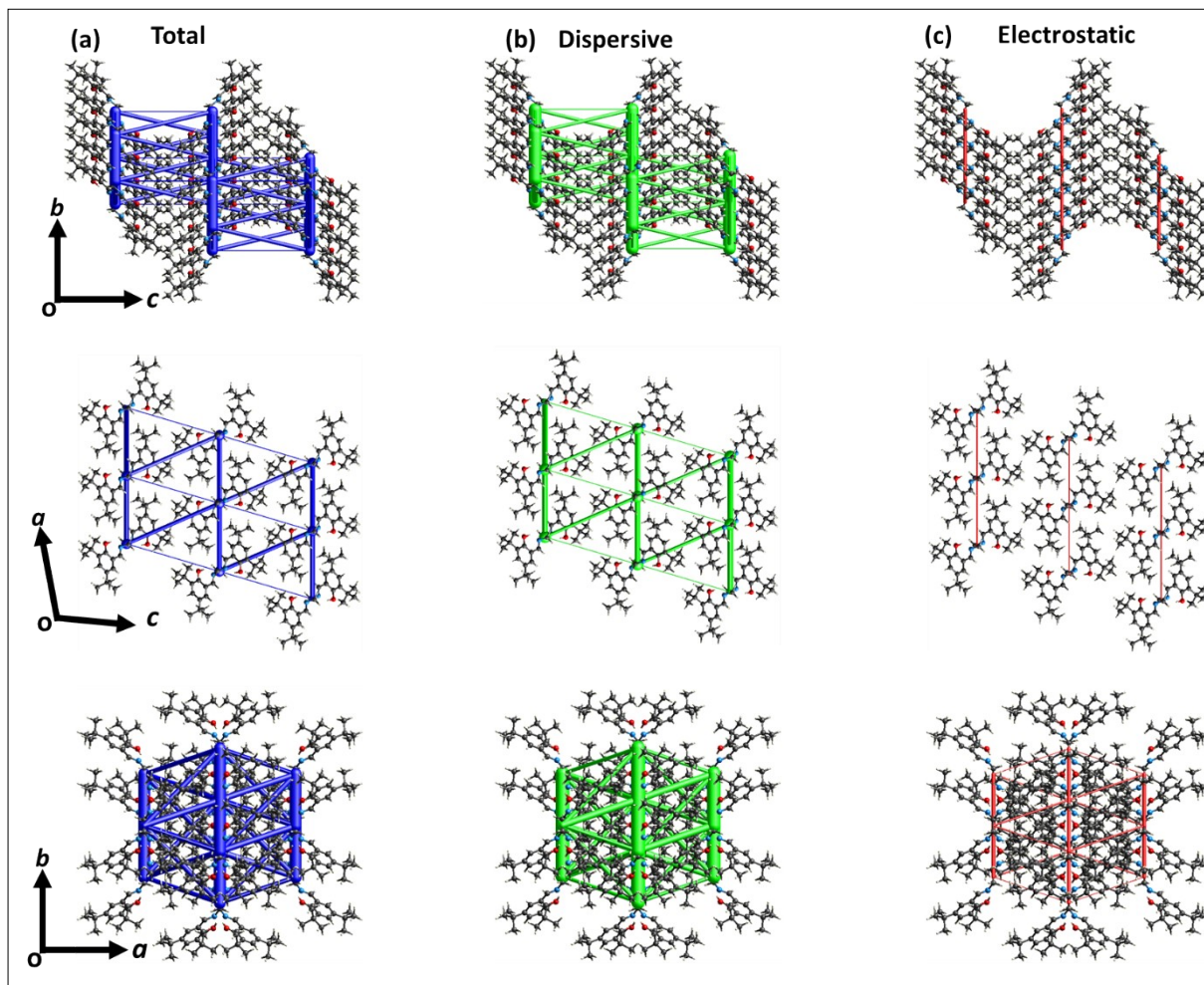
Interaction Energies ( $\text{kJ/mol}$ )  
 $R$  is the distance between molecular centroids (mean atomic position) in  $\text{\AA}$ .

Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symp	R	Electron Density	$E_{\text{ele}}$	$E_{\text{pol}}$	$E_{\text{dis}}$	$E_{\text{rep}}$	$E_{\text{tot}}$
	2	$x+1/2, y+1/2, z$	9.93	B3LYP/DGDZVP	-10.1	-2.4	-47.8	29.3	-36.0
	2	$x+1/2, y+1/2, z$	9.93	B3LYP/DGDZVP	-4.9	-0.4	-20.7	15.4	-14.0
	2	$x, y, z$	6.16	B3LYP/DGDZVP	-22.3	-2.8	-97.3	59.1	-73.9
	4	$-x+1/2, y+1/2, -z+1/2$	14.41	B3LYP/DGDZVP	-4.4	-0.3	-25.8	0.0	-27.4
	2	$x+1/2, y+1/2, z$	13.20	B3LYP/DGDZVP	-3.1	-1.0	-32.4	0.0	-32.2
	2	$x+1/2, y+1/2, z$	18.05	B3LYP/DGDZVP	-0.3	-0.0	-1.8	0.0	-1.9
	2	$-x, y, -z+1/2$	13.46	B3LYP/DGDZVP	-0.8	-0.1	-5.8	0.0	-6.0

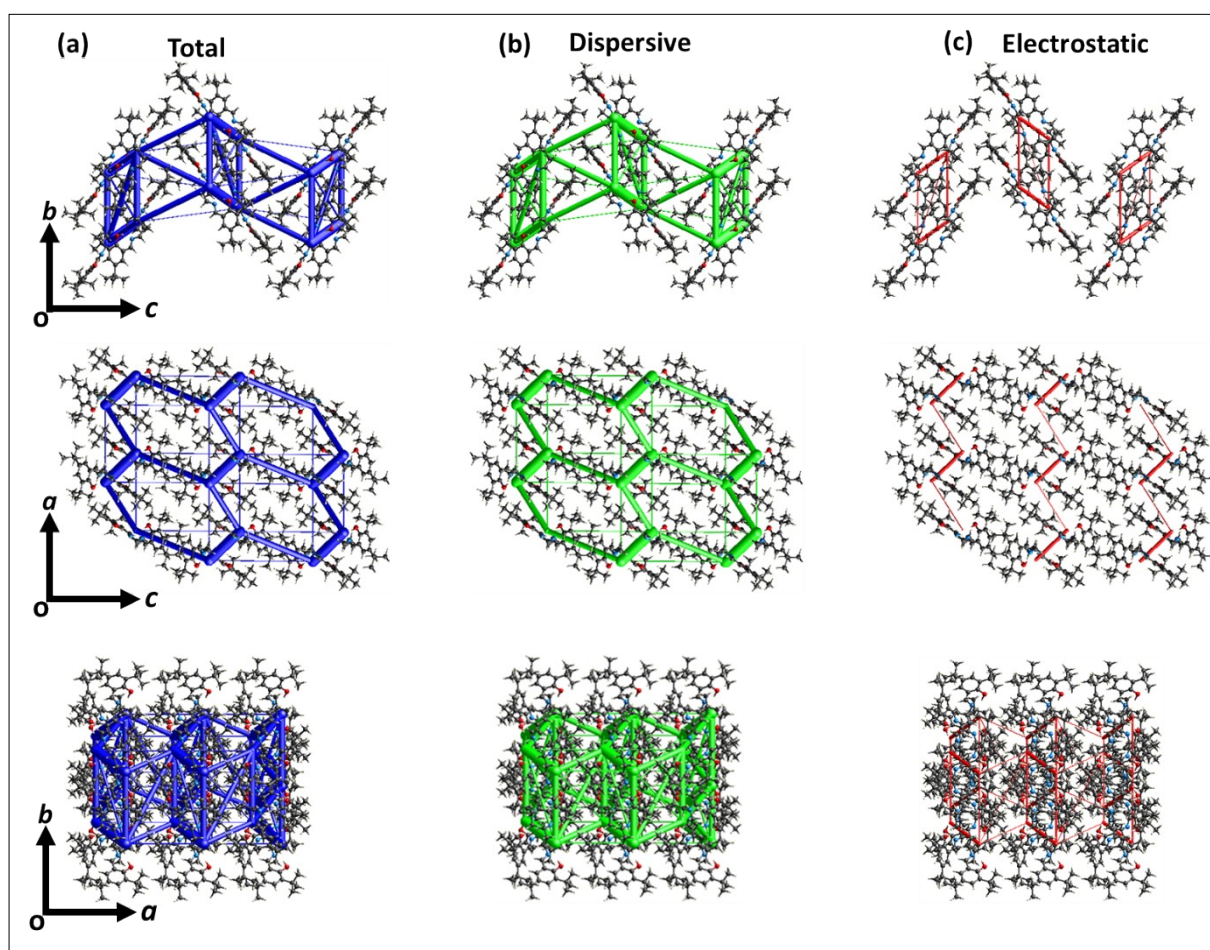
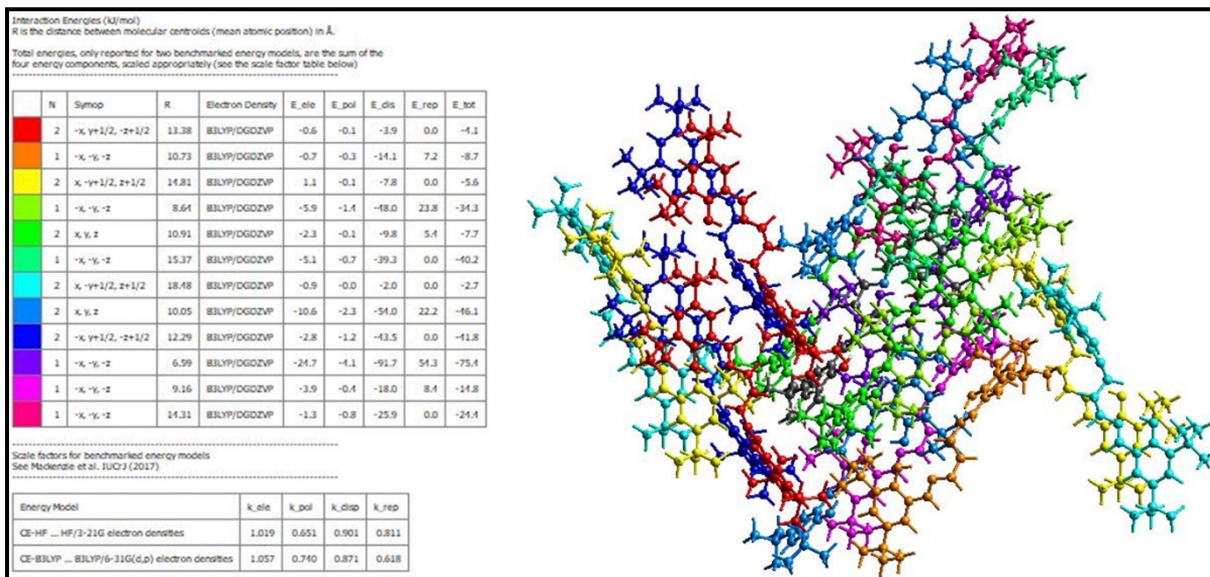
Scale factors for benchmarked energy models  
 See Mackenzie et al. IUCrJ (2017)

Energy Model	$k_{\text{ele}}$	$k_{\text{pol}}$	$k_{\text{dis}}$	$k_{\text{rep}}$
CE+HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618



**Fig. S7.2** Visualization of energy frameworks showing total interaction energy (a, blue); electrostatic (b, red) and dispersion (c, green) components for **2**, in the (top) (100); (middle) (010) and (below) (010) faces, respectively. The energy scale factor is 100 and the energy threshold is  $5 \text{ kJ.mol}^{-1}$ .

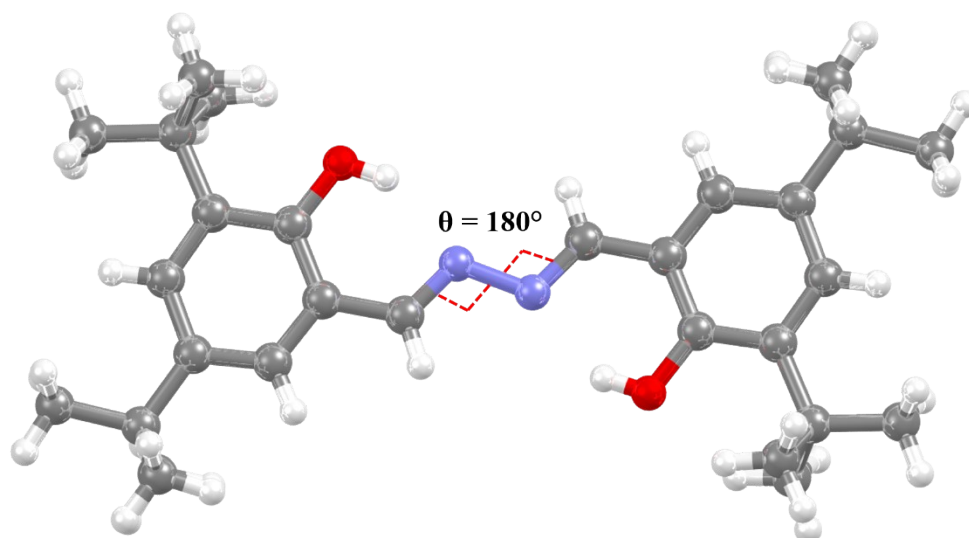
**Table S7.3** Molecular structure pairs and the interaction energies ( $\text{kJ.mol}^{-1}$ ) obtained from energy frameworks calculation for **3**. Scale factors are in the lower table.



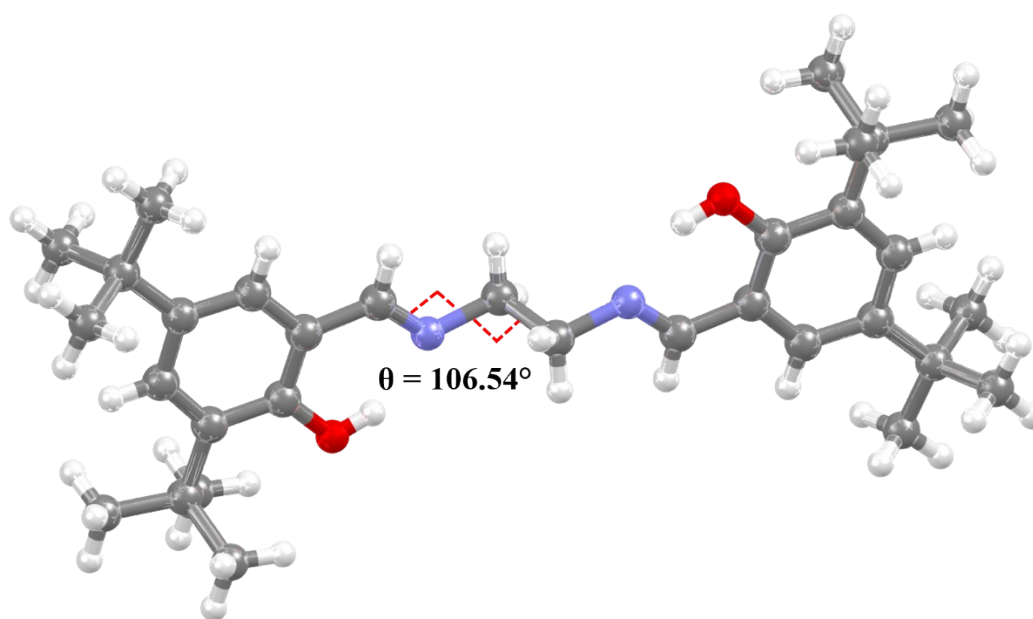
**Fig. S7.3** Visualization of energy frameworks showing total interaction energy (a, blue); electrostatic (b, red) and dispersion (c, green) components for **2**, in the (top) (100); (middle) (010) and (below) (010) faces, respectively. The energy scale factor is 100 and the energy threshold is  $5 \text{ kJ.mol}^{-1}$ .



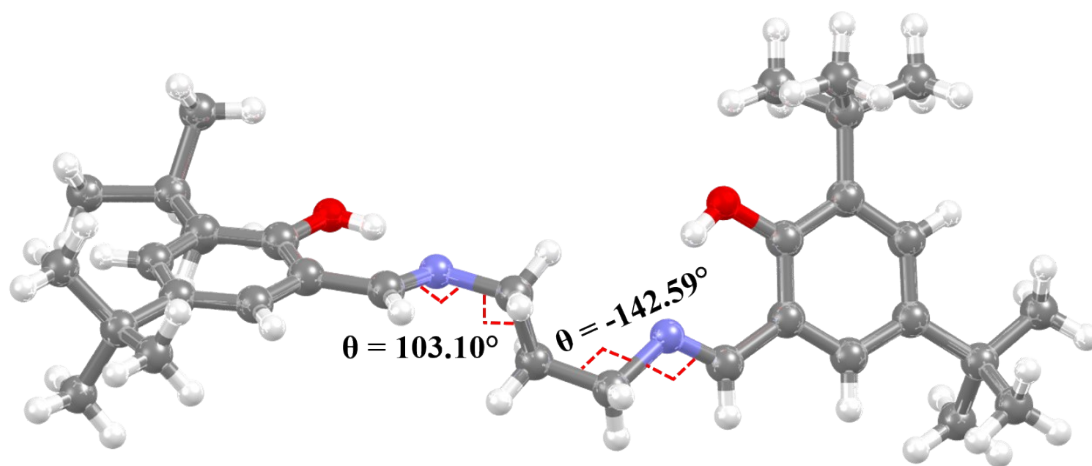
## S8. Torsion Angle Measurement



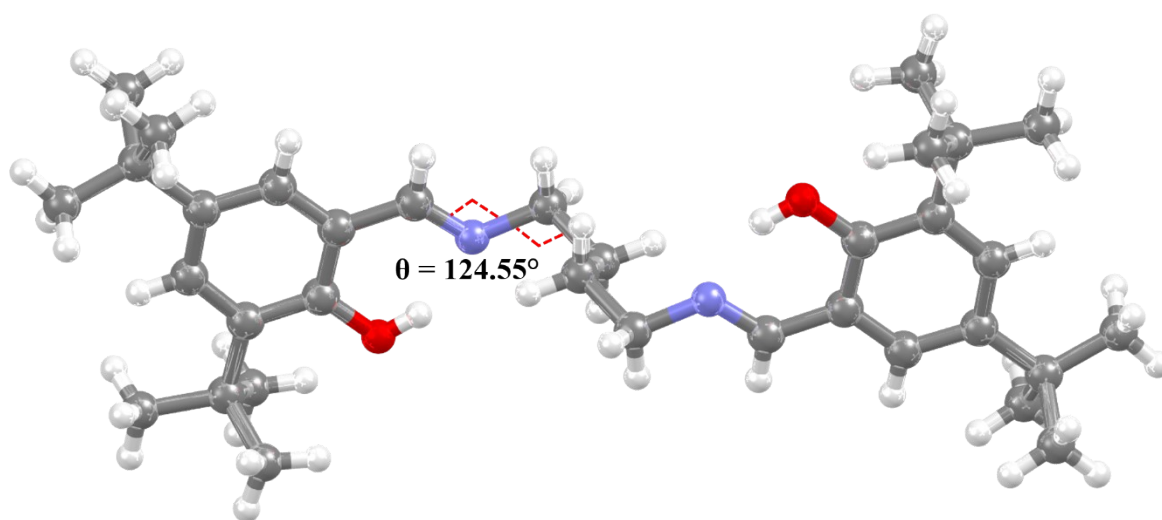
**Fig. S8.1** Torsion angle of Crystal 1



**Fig. S8.1** Torsion angle of Crystal 2



**Fig. S8.3** Torsion angle of Crystal 3



**Fig. S8.4** Torsion angle of Crystal 4

## S9. UV & PL spectrum

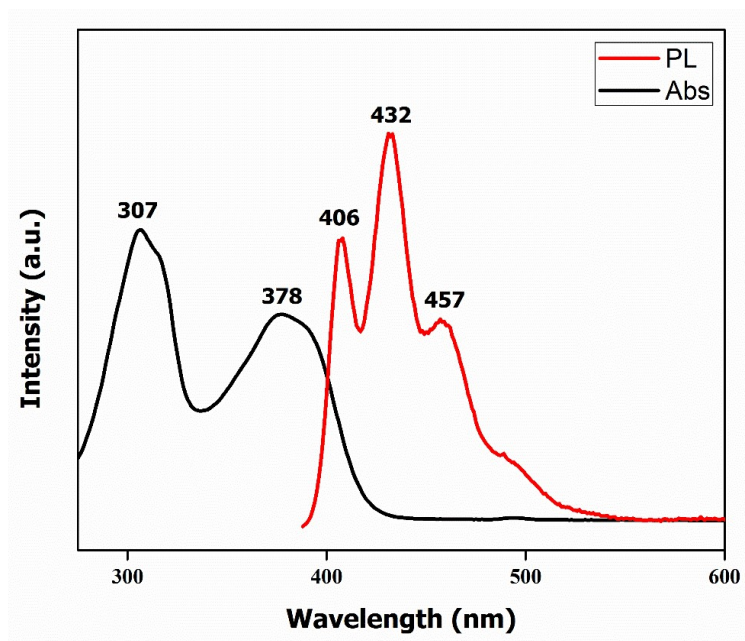


Fig. S9.1 UV and PL Spectrum of crystal 1.

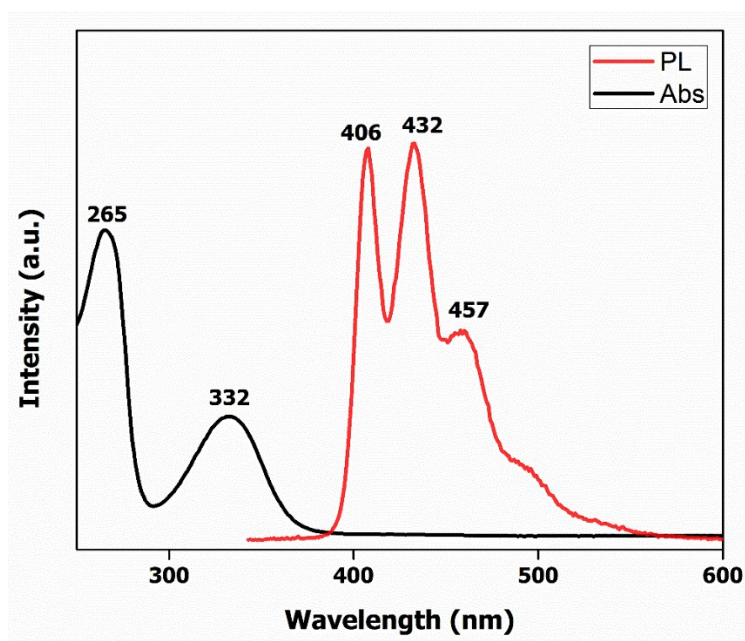


Fig. S9.2 UV and PL Spectrum of crystal 2.

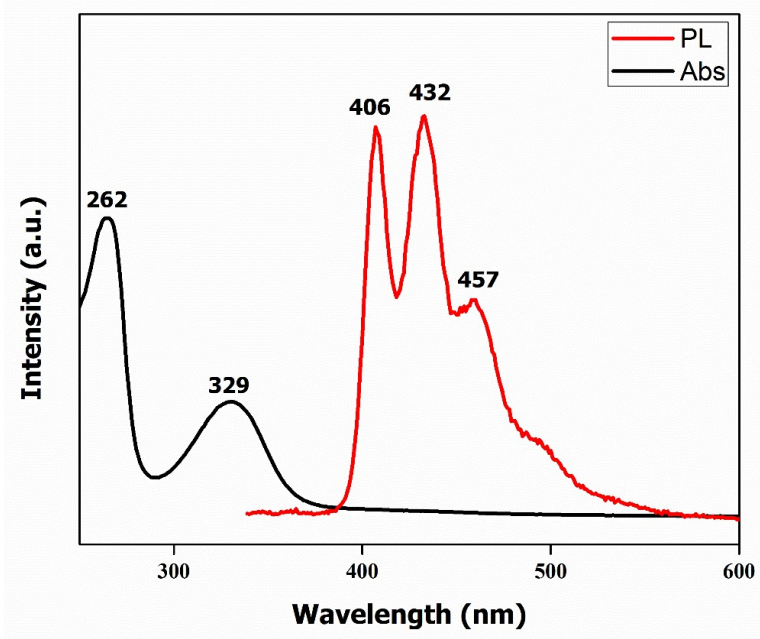


Fig. S9.3 UV and PL Spectrum of crystal 3.

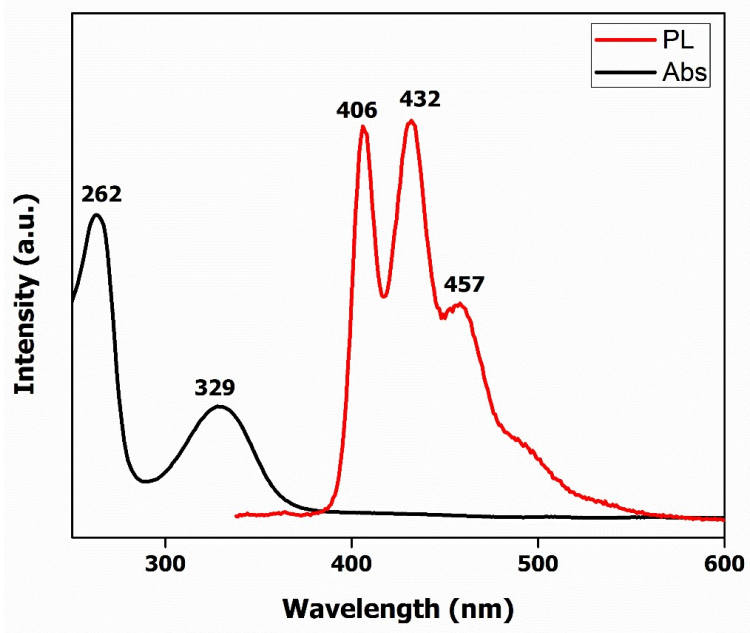


Fig. S9.4 UV and PL Spectrum of crystal 4.

### S10. Fluorescence Microscopy images

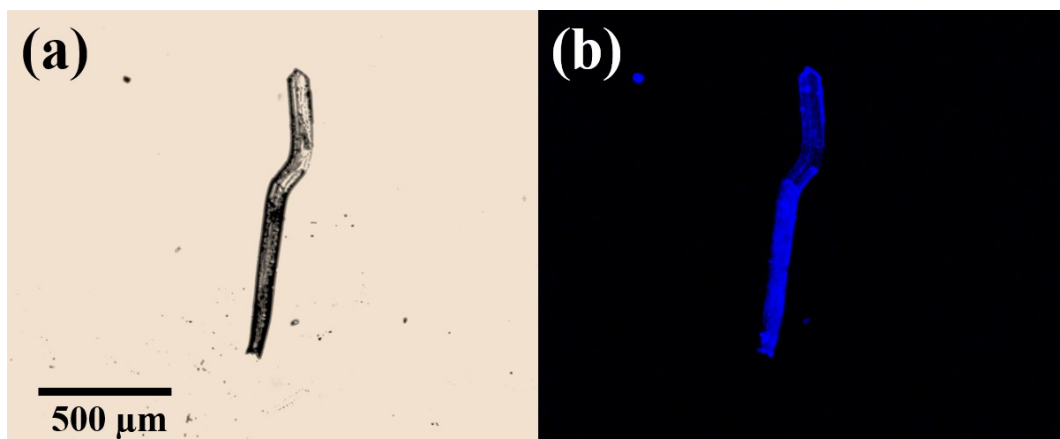


Fig. S10.1 Fluorescence microscopy image of Crystal 1 (a) in Brightfield (b) 342-378 nm.

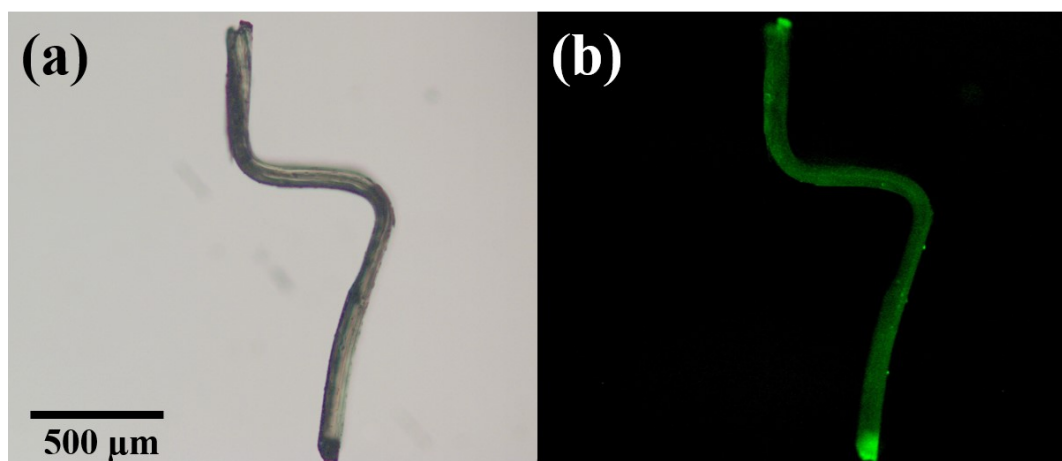
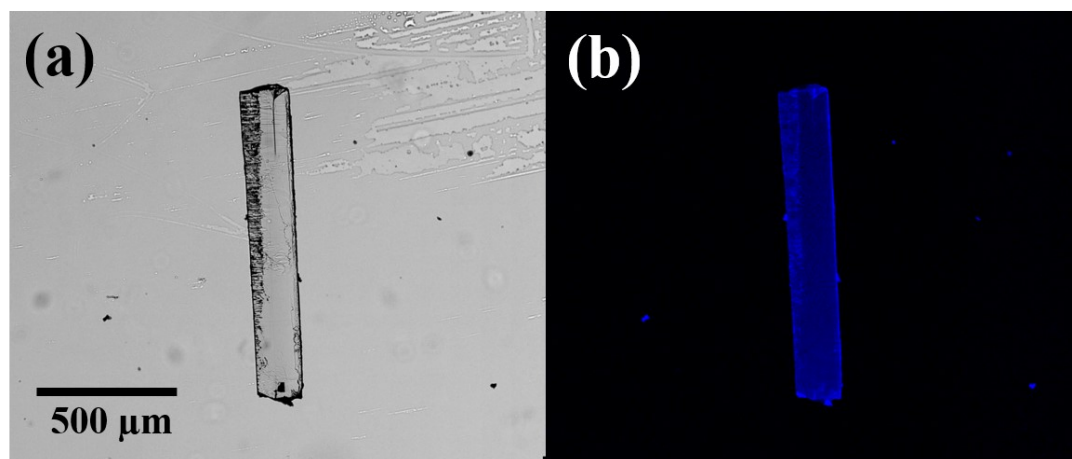
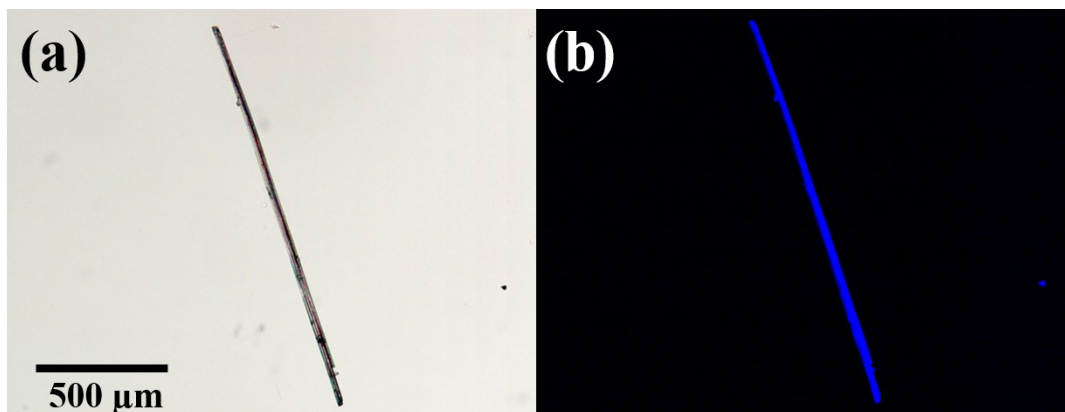


Fig. S10.2 Fluorescence microscopy image of Crystal 2 (a) in Brightfield (b) 452-488 nm.



**Fig. S10.3** Fluorescence microscopy image of Crystal **3** (a) in Brightfield (b) 342-378 nm.



**Fig. S10.4** Fluorescence microscopy image of Crystal **4** (a) in Brightfield (b) 342-378 nm.

### S11. References

- 1 A. K. Saini, K. Natarajan and S. M. Mobin, *Chem. Commun.*, 2017, **53**, 9870–9873.
- 2 S. Yang, H. Kou, H. Wang, K. Cheng and J. Wang, *New J. Chem.*, 2010, **34**, 313–317.
- 3 M. J. Turner, S. P. Thomas, M. W. Shi, D. Jayatilaka and M. A. Spackman, *Chem. Commun.*, 2015, **51**, 3735–3738.
- 4 P. R. Spackman, M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, D. Jayatilaka and M. A. Spackman, *J Appl Crystallogr*, 2021, **54**, 1006–1011.