Electronic Supplementary Material (ESI) for CrystEngComm

Supplementary information for

Changing Gears to Neutral in a Polymorph of One-Dimensional Arrays of Cogwheels Pairs of Molecular Rotors

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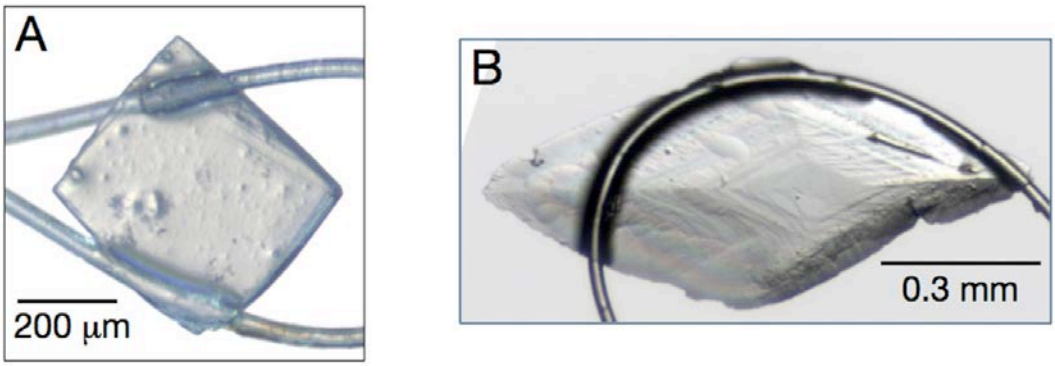

Chart 1. Crystal habits of (A) polymorph **1** and (B) polymorph **2**.

Crystallization procedures.

Polymorph 2. 10 mg of a polycrystalline sample of polymorph **1** are introduced in a 100 ml flask and 10 ml of acetonitrile (HPLC quality, Carlo Erba) are added; the suspension is heated to reflux (81°C); 2 ml increments of acetonitrile are then successively added and brought up to reflux until complete dissolution and a clear solution is obtained, requiring a total of 20 ml, that is reaching a concentration of 1.1 10^{-3} mol l^{-1}. The homogenous solution is maintained at reflux for one hour then the heating is switched off and the flask left to stand in the hot oil bath. The latter cools down to room temperature in *ca*. 9 hours when colorless diamond-shaped crystals (Chart 1B) are harvested.

Polymorph 1. 10 mg of a polycrystalline sample of polymorph **1**[9] are introduced in a 100 ml flask and 10 ml of acetonitrile (HPLC quality, Carlo Erba) are added; the suspension is heated to reflux (81°C); 2 ml increments of acetonitrile are then successively added and brought up to reflux until complete dissolution and a clear solution is obtained, requiring a total of 20 ml, that is reaching a concentration of 1.1 10^{-3} mol l^{-1}. The homogenous solution is maintained at reflux for one hour then the heating is switched off, the oil bath is removed, and the flask left to stand at room temperature. Crystals (Chart 1A) appear in the flask walls in *ca*. 2 hours.

Crystallization of polymorph 1 from polymorph 2.

10 mg of a diamond-shaped crystals of polymorph **2** are introduced in a 100 ml flask and 10 ml of acetonitrile (HPLC quality, Carlo Erba) are added; the suspension is heated to reflux (81°C); 2 ml increments of acetonitrile are then successively added and brought up to reflux until complete dissolution and a clear solution is obtained, requiring a total of 20 ml, that is reaching a concentration of 1.1 10^{-3} mol l^{-1}. The homogenous solution is maintained at reflux for one hour then the heating is switched off, the oil bath is removed, and the flask left to stand at room temperature yielding crystals characterized as polymorph **1** by their habits and unit cell determinations.

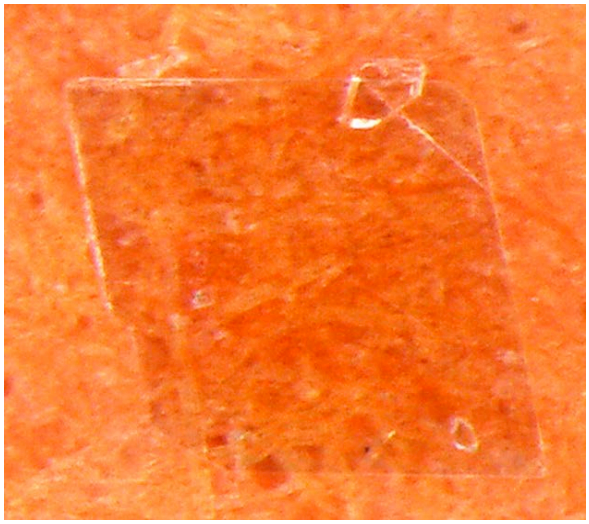

Figure S1. Crystal of polymorph **1** obtained from polymorph **2**.

Crystallographic data. A suitable crystal of polymorph **2** was coated with Paratone N oil, suspended in a small fiber loop and placed on a Bruker Kappa CCD diffractometer with a graphite monochromated MoKα (0.71073 Å) radiation. Data were collected at room temperature using a series of combinations of φ and ω scans. Data were processed using the EvalCCD program suite. Diffraction intensities were corrected for absorption by empirical method with the SADABS program. The structure was solved by a direct method and refined by a full-matrix least-squares method in an anisotropic approximation for all non-hydrogen atoms using the SHELX-97 programs. The H atoms were found by Fourier difference syntheses. Crystal data at 293 K: $C_{34}H_{32}N_2$, M_r = 468.62, monoclinic *C*2/*c*, *a* = 36.831(3), *b* = 6.1181(4), *c* = 12.2456(12) Å, *β* = 99.224(7)°, *V* = 2723.7(4) Å^3, *Z* = 4, *μ* = 0.66 cm^{-1}, $2\Theta_{max}$ = 54º, 22778 reflections measured, 2941 unique (R_{int} = 0.083), 1772 with $I > 2\sigma(I)$, 227 parameters refined, $R(F^2)$ = 0.0590, $wR(F^2)$ = 0.1181, GOF = 1.029. CCDC 965633.
For comparison, the 295 K data for the former[9] polymorph **1** reads: monoclinic *C*2/*c*, *a* = 31.539(6), *b* = 8.3673(8), *c* = 10.2441(9) Å, β = 97.164(8), *V* = 2682.3(6) Å^3, *Z* = 4.

Table S1. Geometry of C–H···N hydrogen bonds in polymorphs **1** and **2**.

Bond type	H···N distance, Å	C···N distance, Å	C–H···N angle, º
polymorph 1			
293 K	2.93	3.603(3)	130.4
polymorph 2			
293 K	2.59	3.434(4)	146.4

Computational details. Calculations were performed as described previously[9] using the hybrid M06-2X functional[11] and the 6-31G(d,p) basis set[12] as implemented in the Gaussian09 package.[13]

(11) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
(12) Hariharan, P. C.; Pople, J. A. *Theoret. Chimica Acta* **1973**, *28*, 213.
(13) Gaussian 09, Revision B1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr.; J. A., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

VT ^{1}H spin–lattice relaxation time (T_1) experiments. Experiments were carried out as described previously[7,8,9] on static crystalline samples at a ^{1}H Larmor frequencies of 55 MHz) and over a wide range of temperatures using a NMR spectrometer and probe built at Orsay.
As stated in the main text, the sample was composed of a batch of hand picked diamond-shaped crystals of polymorph **2** introduced one by one in a capillary. This procedure, however, do not prevent a residual error of introducing a small amount, of the order of 10%, of the other polymorph **1**. This small admixture of the NMR signal of this phase is source of error in the determination of T_1, therefore the T_1 values about room temperature are less accurate.

Second Harmonic Generation microscopy experiments. The SHG efficiency of one single crystal of each polymorph has been investigated by means of a SHG microscopy setup (Figure S2) which can provide 2-D mapping of the SHG signal of the crystals.The glass slide carrying the crystals was mounted on XYZ motorized stages (Newport) controlled by an 8 axes motion controller/ Driver (XPS, Newport). The laser source was a Ti:Sapphire (Tsunami, Spectra Physics), which is pumped by a 10 W solid-state laser (Millenia Xs, Spectra Physics). The laser system is tunable in the range 700 to 1080 nm and provides 120 fs duration laser pulses with 80 MHz repetition rate. Once the beam was collimated and expanded it was focused on the crystals by means of an x20 objective lens (N.A. 0.25) of an inverted, modified microscope (IX 71, Olympus). The angular deviation of the beam has been controlled by means of an X-Y scanner (Cambridge Technology), which is composed of two galvanometric mirrors. The SHG signal was filtered by means of a short-pass and a narrow bandpass filter (BG39, Schott and NT48-071, Edmund Optics respectively), and detected by a photon counter (C9744, Hamamatsu). The power/polarization of the beam, the amplitude of the galvanometric mirrors and the positioning of the sample were precisely adjusted by means of a homemade Labview program. The same program allows storing the signal for each position of the laser beam on the sample, providing finally the 2D-SHG images. The second order nonlinearity of the two crystals has been studied under the same experimental conditions. Specifically, the laser power has been adjusted to 90 mW, the

laser wavelength being tuned at 800 nm and a 200 μsec exposure time for each pixel has been utilized.

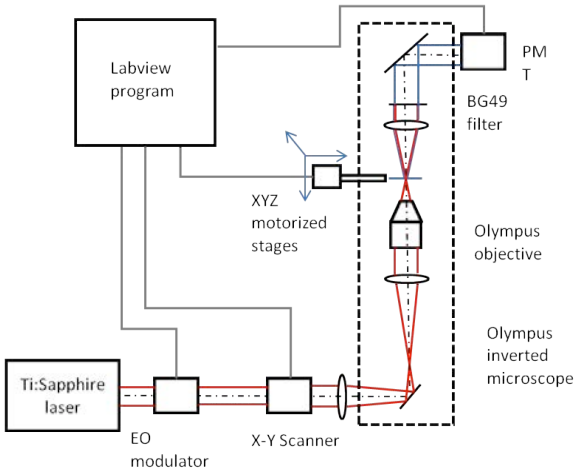

Figure S2. Experimental set up for SHG microscopy experiments.