Electronic Supplementary Material (ESI) for CrystEngComm.

Solvent induced conformational polymorphism

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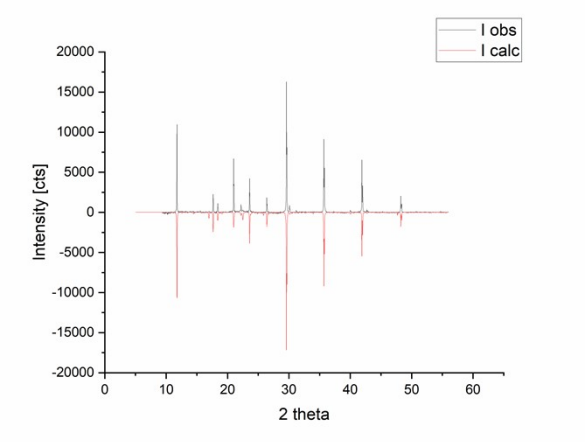
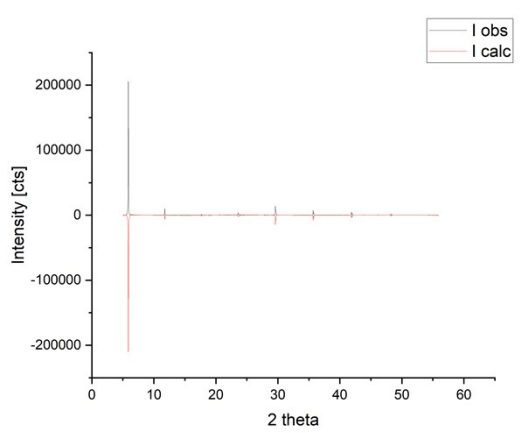
Supplementary

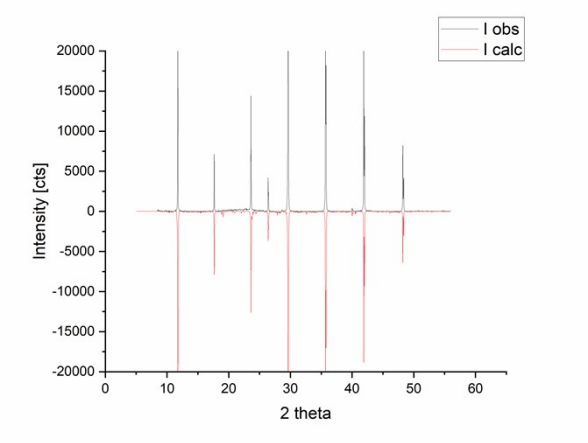
Synthesis of 2,5-Bis(3-bromophenyl)furan. A solution of sodium nitrite (6.38 g, 92.5 mmol) in H_2O (14 ml) was added dropwise to the stirred mixture of 3-bromoaniline 14.4 g (83.7 mmol), concentrated HCl (36%, 0.3 mol, 30 ml), and H_2O (15 ml) at a temperature below +5°C. The cold solution was filtrated and the diazonium salt was slowly added to a vigorously stirred solution of 2-furoic acid (4.6 g, 41.0 mmol) and $CuCl_2 \cdot 2H_2O$ (1.0 g, 5.9 mmol) in acetone (70 ml) at the room temperature. The rate of addition was controlled by the nitrogen and carbon dioxide evolution (3–4 bubbles/sec, 0.5–1 h). At the end of the reaction, after the evolution of nitrogen and carbon dioxide ceased, water (200 ml) was added, extracted with CH_2Cl_2, washed with 10% K_2CO_3 (2×200 ml), and H_2O (3×200 ml), and the organic layers were dried with anhyd. Na_2SO_4 concentrated and purified by column chromatography (eluent hexane). Yield 23% (3.56 g).



A) EtOH Form α%; β43%



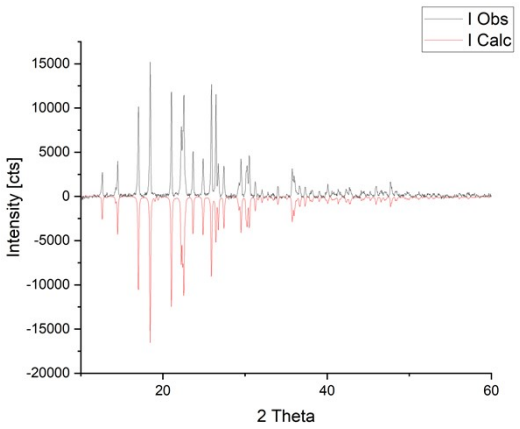
B) ACN form β



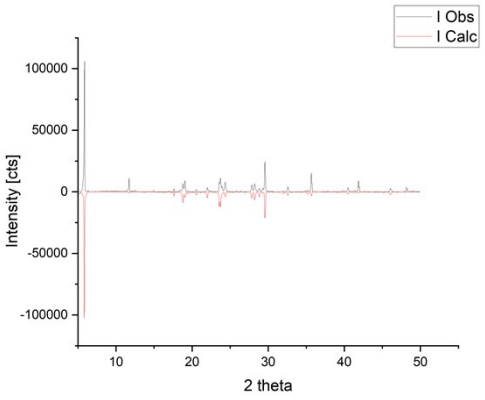
C) EtOH Form α 7%; β 93%

S. Figure 1. PXRDs of fast crystallization on glass from **A)** & **C)** ethanol; **B)** acetonitrile. Grey-Intensity observed, red-intensity calculated from the structural data.

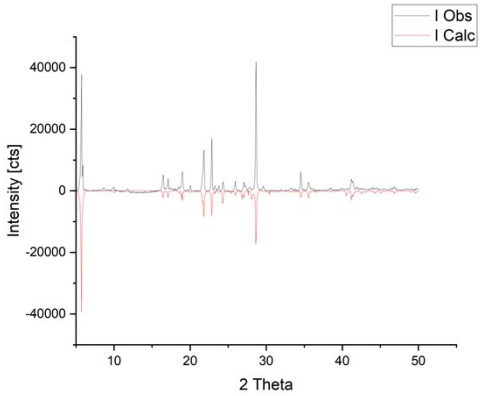
α



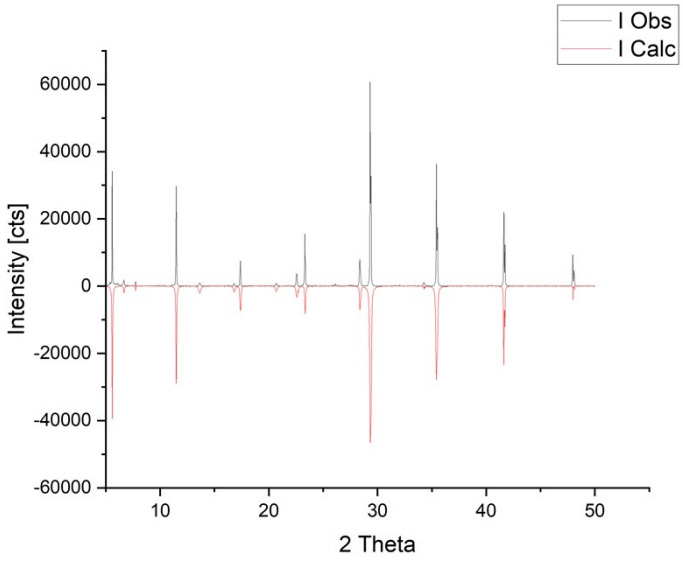
β



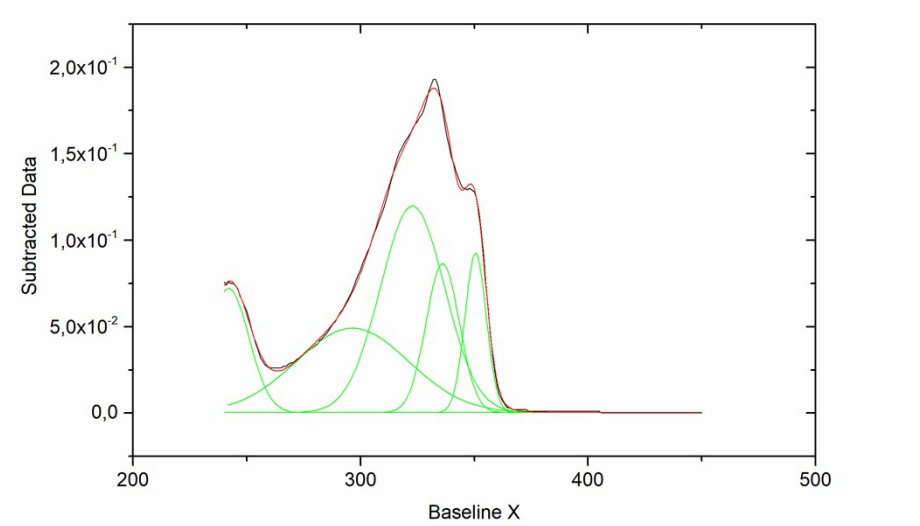
γ



S. Figure 2. The PXRD of the polymorphs structures of the **MBPF**. Grey-intensity observed, red-intensity calculated from the structural data.



S. Figure 3. PXRD of the sample after crystallization from the vapor. The diffractograms indicates presents of forms β and γ with dominant phase γ.



Fitting Results

Peak Index	Peak Type	Area Intg	FWHM	Max Height	Center Grvty	Area IntgP
1	Gaussian	0,94668	20,97637	0,07173	242,0516	8,73709
2	Gaussian	2,99134	58,27469	0,04877	296,43641	27,6077
3	Gaussian	4,23335	33,31587	0,11937	322,82795	39,07049
4	Gaussian	1,57976	17,25641	0,086	336,1115	14,57996
5	Gaussian	1,08403	11,05644	0,09211	350,59085	10,00475

S. Figure 4. UV-Vis spectra of the **MBPF** from chloroform and its decomposition. The component at 322 and 336 nm correspond to monomers. The component at 350 nm corresponds to dimers.

S. Table 1. Crystal17 calculations of the crystal net energies for studied polymorphs using different basis sets and structure optimization.

E_{total} [kJ]	$E_{mol\ D}$ [kJ]	$E_{mol\ noD}$ [kJ]	$E_{mol\ cpc}$ [kJ]	BSSE [kJ]	Form

DZVP

-61302025,59	-15325134,36	-15324947,36	-15325136,74	189,3832338	α
Z	4				
$E_{coh\ Bartolomeo}$ = **-372,0361295**					
$E_{coh+BSSE}$ = **-182,6528956**					
-61302905,8	-15325283,45	-15325097	-15325360,46	263,4596354	β
Z	4				
$E_{coh\ Bartolomeo}$ = **-442,9998668**					
$E_{coh+BSSE}$ = **-179,5402314**					
-61302027,08	-15325132,4	-15324945,71	-15325139,42	193,711696	γ
Z	4				
$E_{coh\ Bartolomeo}$ = **-374,367502**					
$E_{coh+BSSE}$ = **-180,6558059**					

TZVP

-61317490,65	-15329049,25	-15328862,24	-15329010,12	147,878497	α
Z	4				
$E_{coh\ Bartolomeo}$ = **-323,4132546**					
$E_{coh+BSSE}$ = **-175,5347576**					
-61318075,1	-15329194,42	-15329007,97	-15329161,45	153,4765996	β
Z	4				
$E_{coh\ Bartolomeo}$ = **-324,3599133**					
$E_{coh+BSSE}$ = **-170,8833137**					
-61317491,03	-15329047,6	-15328860,91	-15329011,07	150,1674073	γ
Z	4				
$E_{coh\ Bartolomeo}$ = **-325,1592254**					
$E_{coh+BSSE}$ = **-174,9918181**					

Optimization - TZVP

-61321672,73	-15329761,33	-15329576,05	-15328988,26	-587,7957436	α
Z	4				
$E_{coh\ Bartolomeo}$ = **-656,8497117**					
$E_{coh+BSSE}$ = **-1244,645455**					
-61321725,09	-15329761,78	-15329576,72	-1,53E+07	-584,321125	β
Z	4				
$E_{coh\ Bartolomeo}$ = **-669,4925044**					
$E_{coh+BSSE}$ = **-1253,813629**					
-61321729,37	-15329761,77	-15329576,77	-15329011,08	-565,695114	γ
Z	4				
$E_{coh\ Bartolomeo}$ = **-670,5760767**					
$E_{coh+BSSE}$ = **-1236,27119**					