Electronic Supplementary Material (ESI) for ChemComm.

Using Structural Modularity in Cocrystals to Engineer Properties: Elasticity

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Supporting Information

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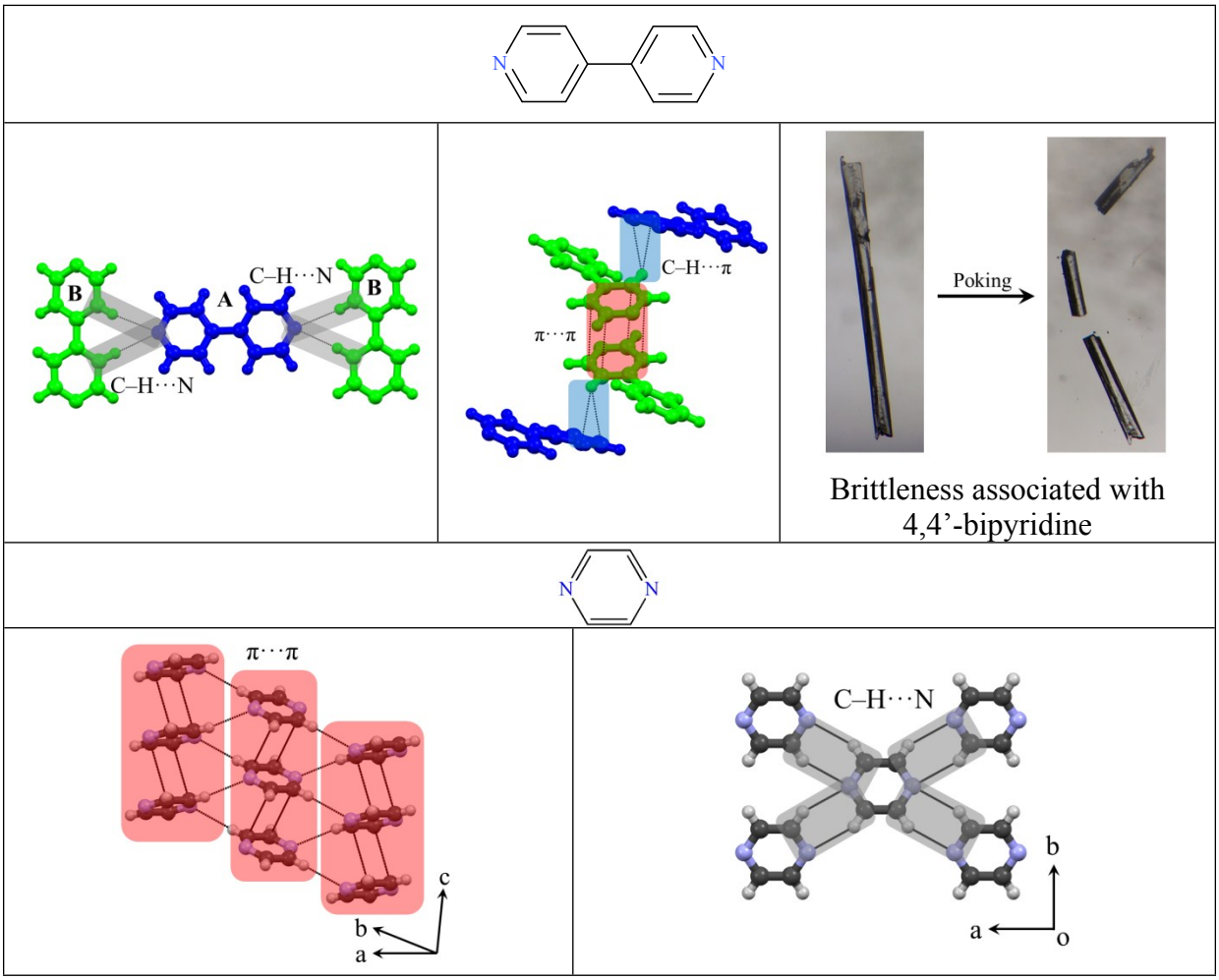
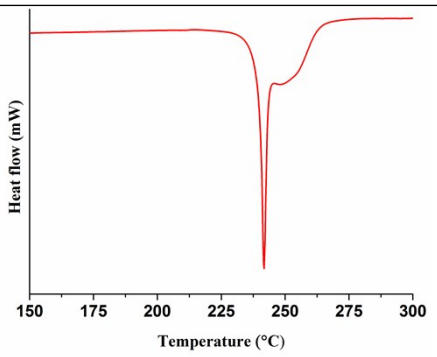
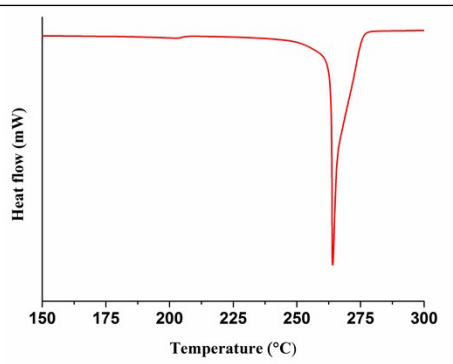
S1: Some representative synthons in brittle 4, 4'-bipyridine and pyrazine



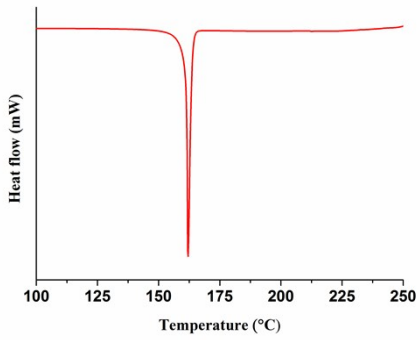
S2: DSC diagrams and melting points of the cocrystals E1-E5



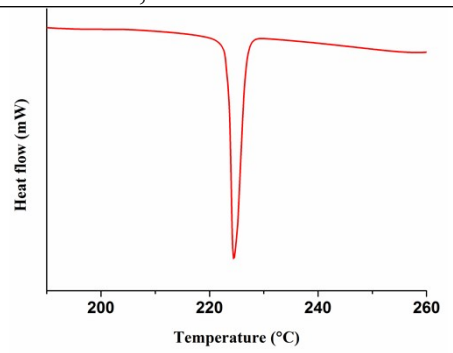
E1, MP= 241.74 °C



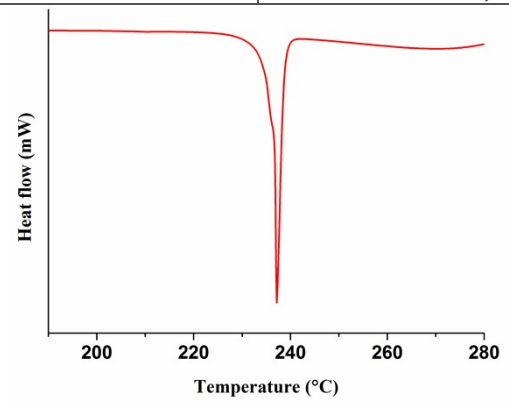
E2, MP= 264.01 °C



E3, MP= 162.06 °C



E4, MP= 224.4 °C



E5, MP= 237.15 °C

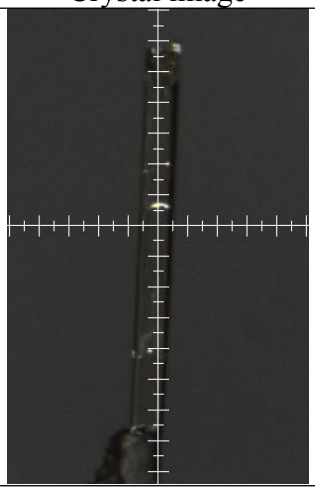
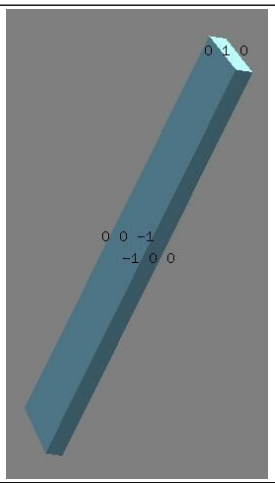
S3: SCXRD experiment

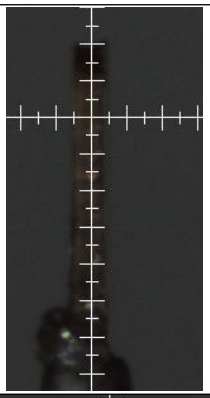
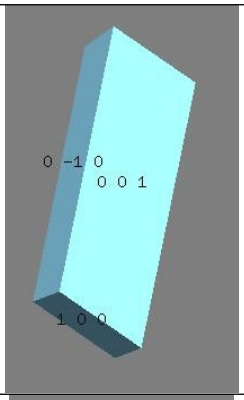
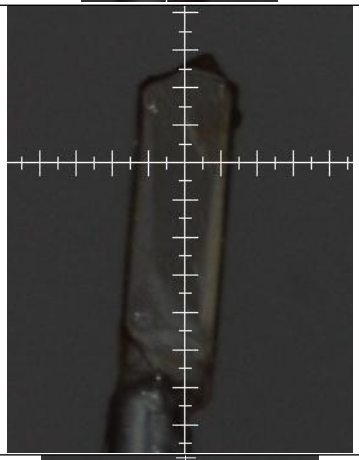
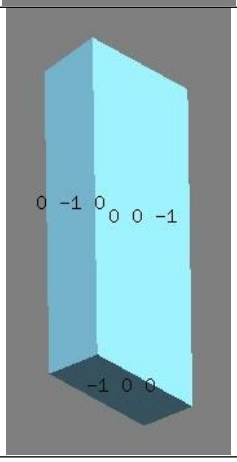
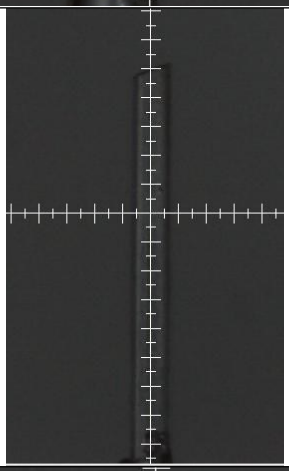
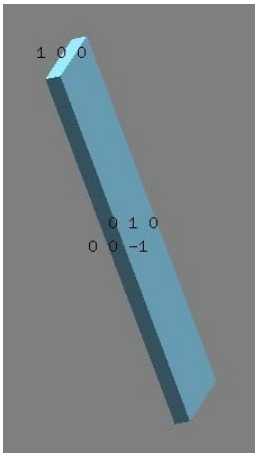
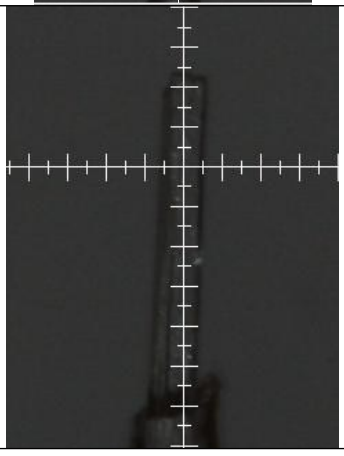
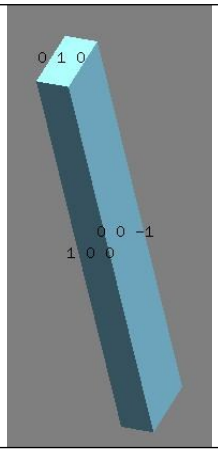
Single crystal x-ray data (SCXRD) were collected on a Rigaku Mercury 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromatic Mo Kα radiation, with a Rigaku low temperature gas spray cooler. Data were processed with the Rigaku *CrystalClear 2.0* software.[1,2] Structure solution and refinements were performed using SHELX97[3] implemented in the WinGXsuite.[4]

S4: Crystallographic information table

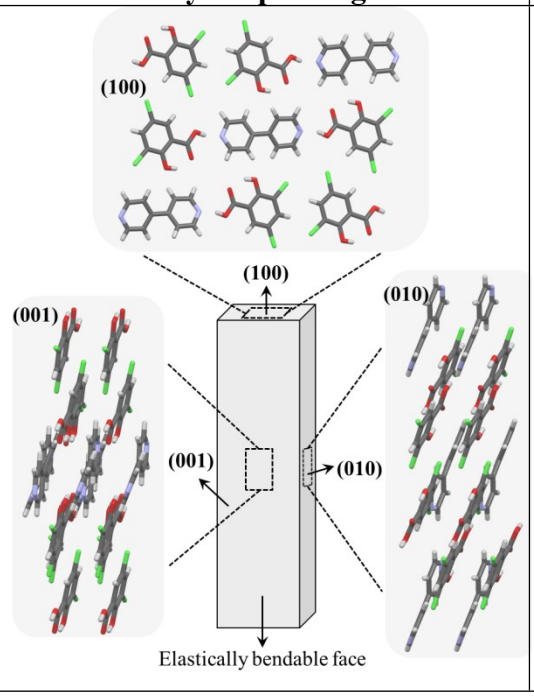
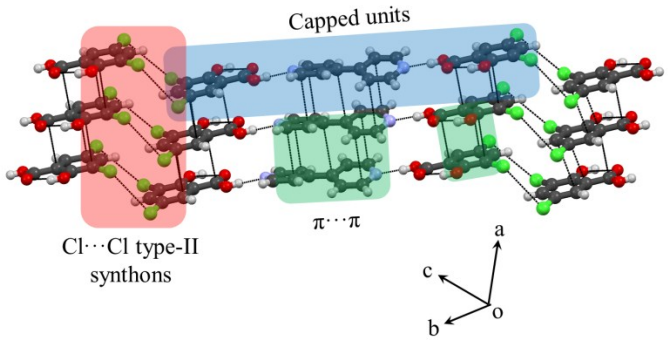
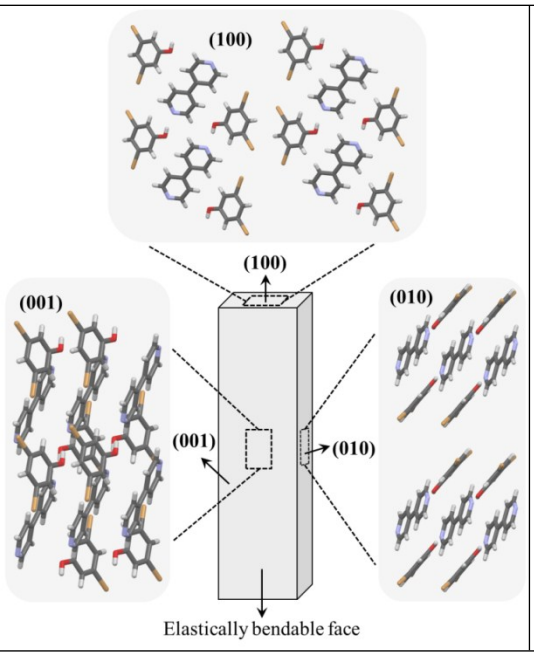
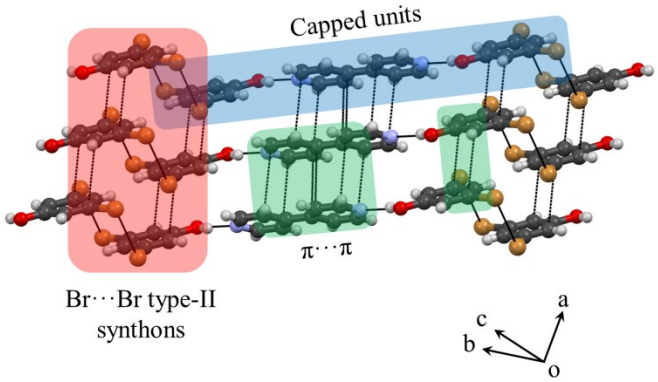
Compounds	**E1**	**E2**	**E3**	**E4**	**E5**
Formula	$0.5(C_{10}H_8N_2)$, $C_7H_4I_2O_3$	$C_{10}H_8N_2$, $2(C_7H_4Cl_2O_3)$	$0.5(C_{10}H_8N_2)$, $C_6H_4Br_2O$	$0.5(C_4H_4N_2)$, $C_7H_4Cl_2O_3$	$0.5(C_4H_4N_2)$, $C_7H_4I_2O_3$
Formula weight	467.99	570.19	329.985	247.05	429.95
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*□	*P*□	*P*□	*C*2/*c*
a (Å)	17.60(3)	3.795(9)	4.183(3)	3.803(5)	27.78(3)
b (Å)	4.372(6)	14.70(3)	8.769(7)	10.407(12)	4.706(4)
c (Å)	34.30(5)	21.40(5)	15.366(12)	13.414(16)	17.566(16)
α (°)	90	80.70(5)	94.10(3)	68.67(4)	90
β (°)	97.444(15)	89.35(6)	95.78(3)	85.89(4)	96.051(8)
γ (°)	90	89.09(5)	99.68(3)	80.72(4)	90
V (Å^3)	2617(6)	1178(5)	550.5(7)	488.0(11)	2284(4)
Z	8	2	1	2	8
ρ_{calc} (g/cm^3)	2.375	1.608	1.991	1.681	2.501
F(000)	1736.0	580.0	318.0	250.0	1576.0
Temp. (K)	173 K	173 K	173 K	173 K	293 K
R_1	0.0666	0.0975	0.0560	0.0450	0.0416
wR_2	0.2193	0.2997	0.1890	0.1535	0.1531
Goodness-of fit	1.117	1.098	1.150	1.164	1.178
CCDC No.	1472664	1472665	1472666	1472667	1472668

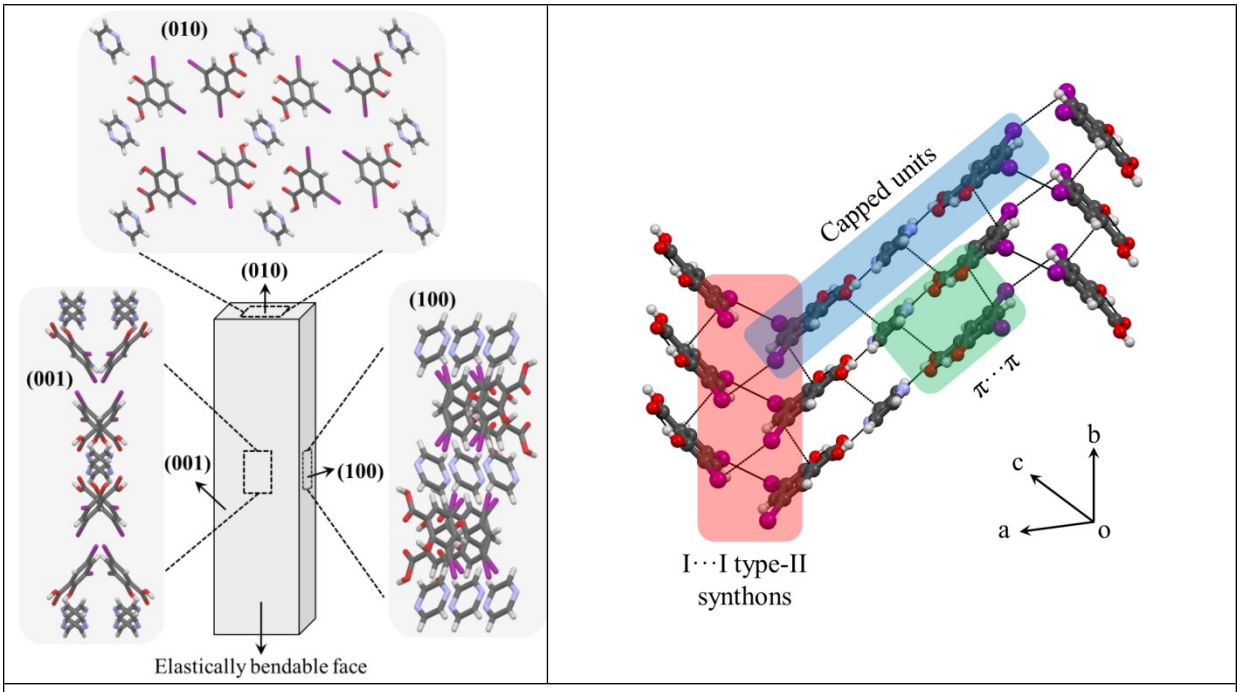
S5: Face indexing images of elastic cocrystals E1-E5

Cocrystal	Crystal image	Indexed faces
E1		

E2		 0 -1 0 0 0 1 1 0 0
E3		 0 -1 0 0 0 -1 -1 0 0
E4		 1 0 0 0 1 0 0 0 -1
E5		 0 1 0 0 0 -1 1 0 0

S6: Crystal packing and some significant synthons in E1-E5

Crystal packing	Significant interactions
	
E2	
	
E3	



E5

S7: Crystal structure description of E2-E5

The 1:2 bipyridine–3,5-dichlorosalicylic acid cocrystal **E2** crystallizes in the *P*□ space group with *Z'*=1. The acid···pyridine (1.74 Å; 1.75 Å) contact based capped units are arranged along the *a*-axis via π···π (3.47 Å) interactions to form the columns (ESI, S6). The Cl···Cl (3.68 Å, θ_1= 85.6°, θ_2=128.6°; 3.88 Å, θ_1= 86.6°, θ_2=127.6°) type-II halogen bonds connect the columns to generate parallel chains along [01□]. These parallel chains are linked through C–H···O (2.69 Å; 2.80 Å), C–H···Cl (3.04 Å; 3.02 Å) and C–Cl···O (3.30 Å) interactions. This molecular organisation in **E2** is similar to that in **E1**.

The 1:2 cocrystal **E3** is composed of 4,4'-bipyridine and 3,5-dibromophenol (*P*□, *Z'*=0.5). The phenol···pyridine (1.92 Å) synthons result in capped units which stack (3.55 Å) along the *a*-axis (see ESI). These stacked columns form Br···Br (4.00 Å, θ_1= 77.2°, θ_2= 121.8°; 3.56 Å, θ_1= 113.4°, θ_2= 169.5°) type-II halogen bonds along [001] and [010]. There are also exist some supportive C–H···O (2.79 Å) interactions. The similar structural pattern of this cocrystal suggests that phenols too might be good candidates in capping based design.

The 1:2 base-acid cocrystal **E4** crystallizes in the triclinic space group *P*□ with *Z'*=0.5 (Figure 6). Each pyrazine molecule is capped with the acid at both ends (1.88 Å) and the capped units are organised through π···π (3.37 Å) interactions along the *a*-axis to form stacked columns which are interconnected via dimeric Cl···Cl (3.6 Å, θ_1= 88.5°, θ_2= 124.6°) type-II halogen bonds along the [012] direction, generating infinite parallel chains. Adjacent chains are connected with C–H···O (2.42 Å), C–H···Cl (2.87

Å) and C–Cl···O (3.30 Å) interactions. The packing is very similar to the earlier cocrystals and demonstrates the generality of the design strategy.

In the 1:2 cocrystal **E5** (*C*2/*c*, *Z'*=0.5) similar capping is seen (acid···pyridine, 1.79 Å; ESI, S6). The π···π stacked columns of capped units (3.16 Å) are directed along the unique axis *b*. The halogen bonds (4.00 Å, 74°, 153°) along [201] connect neighbouring columns leading to parallel tapes which associate with C–H···O (2.57 Å) and C–I···O (3.58 Å) interactions. The structure is isotropic. In summary, the similar molecular arrangements in all cocrystals, **E1** to **E5**, which is according to the design strategy outlined in the main paper is very encouraging for a targeted property like elasticity.

References

1. Crystal Clear 2.0 (Rigaku Corporation: Tokyo).

2. J. Pflugrath, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 1999, **55**, 1718–1725.

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**, 837–838.