General application of mechanochemistry to templated solid-state reactivity: rapid and solvent-free access to crystalline supermolecules.

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Supplementary data

- Figure S1. Experiments involving resorcinol (res) and *trans*-1,2-bis(4-pyridyl)ethylene (4,4'- bpe).
- Figure S2. Experiments involving 5-methoxyresorcinol (5-OMe-res) and 4,4'-bpe.
- Figure S3. Experiments involving 5-cyanoresorcinol (5-CN-res) and 4,4'-bpe.
- Figure S4. Experiments involving 4,6-dichlororesorcinol (4,6-diCl-res) and 4,4'-bpe.
- Figure S5. Experiments involving res and *trans*-1,2-bis(2-pyridyl)ethylene (2,2'-bpe).
- Figure S6. Experiments involving 4-chlororesorcinol (4-Cl-res) and *trans*-1-(2-pyridyl)-2-(4-pyridyl)ethylene (2,4'-bpe).

Figure S7. Experiments involving 1,8-bis(4-pyridyl)naphthalene (**DPN**) and fumaric acid (**fum**).

Figure S8. Experiments involving 2,3-bis(4-methylenethiopyridyl)naphthalene (2,3-nap) and fum.

Figure S9. ¹H-NMR spectrum of ground dry mixture of res and 4,4'-bpe after UV-irradiation.

Figure S10. Cell constants for (5-CN-res)·(4,4'-bpe) and (4,6-diCl-res)·(4,4'-bpe).

Fig. S1. Powder X-ray diffraction pattern of (a) simulated pattern from single-crystal structure of (res)·(4,4'-bpe), (b) ground dry mixture of res + 4,4'-bpe (1 hr), (c) ground dry mixture of res + 4,4'-bpe (45 min), (d) ground dry mixture of res + 4,4'-bpe (30 min), (e) ground dry mixture of res + 4,4'-bpe (15 min), (f) ground dry mixture of res + 4,4'-bpe (3 min), (g) 4,4'-bpe, (h) res.







Fig. S3. Powder X-ray diffraction pattern of (a) simulated pattern from single-crystal structure of (**5-CN-res)**·(**4**,**4**'-**bpe**) and (b) ground dry mixture of **5-CN-res** + **4**,**4**'-**bpe** (15 min).



Fig. S4. Powder X-ray diffraction pattern of (a) simulated pattern from single-crystal structure of (**4,6-diCl-res**)·(**4,4'-bpe**) and (b) ground dry mixture of **4,6-diCl-res** + **4,4'-bpe** (15 min).



Fig. S5. Powder X-ray diffraction pattern of (a) simulated pattern from single-crystal structure of (res)·(2,2'-bpe) and (b) ground dry mixture of res + 2,2'-bpe (15 min).







Fig. S7. Powder X-ray diffraction pattern of (a) simulated pattern from single-crystal structure of $(DPN)\cdot(fum)$, (b) ground dry mixture of DPN + fum (1hr), (c) ground dry mixture of DPN + fum with EtOAc (10 min), (d) fum, and (e) DPN.



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Fig. S8. Powder X-ray diffraction pattern of (a) simulated pattern from single-crystal structure of (2,3-nap)·(fum), (b) ground dry mixture of 2,3-nap + fum (1hr), (c) ground dry mixture of 2,3-nap + fum with EtOAc (10 min), (d) fum, and (e) 2,3-nap.



Fig. S9. ¹H-NMR spectrum of ground (3 min.) dry mixture of **res** and **4,4-bpe** after UV-irradiation.



Fig. S10. Cell constants for (5-CN-res)·(4,4'-bpe) and (4,6-diCl-res)·(4,4'-bpe).

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(5-CN-res)·(4,4'-bpe):
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a = 7.643(5) b = 9.198(5) c = 24.120(5) alpha = 85.24(1) beta = 89.50(1) gamma = 73.43(1)space group = P -1

(4,6-diCl-res)·(4,4'-bpe):

a = 8.5991(10) b = 11.8300(13) c = 16.6872(18) beta = 99.119(5) space group = P 21/n

Structure details will be reported at a later date.