Supporting Information

From a Binary to a Quaternary Cocrystal: An Unusual Supramolecular Synthon

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Author Contributions

M.P. Conceptualization: Supporting; Data curation: Lead; Formal analysis: Equal; Investigation: Lead; Methodology: Lead; Resources: Lead; Software: Lead; Validation: Equal; Visualization: Lead; Writing - Original Draft: Supporting; Writing - Review & Editing: Supporting.

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S1: General Information.

RES, **TMP**, **PHE** and **PYR** were procured from Sigma Aldrich and were used without further purification.

Resorcinol (**RES**)

Pyrene (**PYR**)

Tetramethylpyrazine (**TMP**)

Phenazine (**PHE**)

S2: Crystallization Experiments. Solvent assisted grinding procedure was followed for the synthesis of the multi-component molecular solids. Stoichiometric amount of the solids were taken in a mortar along with a few drops of a solvent. The mixture was then ground with a pestle to get a homogeneous mixture and the process was repeated several times. Then solid mixture was then dissolved in different solvents and kept for crystallization.

(a) *Resorcinol.Phenazine* (**RES.PHE**): A 1:1 mixture of resorcinol and phenazine along with 2-3 drops of methanol was ground in a mortar with a pestle for 15 minutes. Diffraction quality block shaped yellow crystals were obtained from tetrahydrofuran (THF) at room temperature after 3-4 days.

(b) *Resorcinol.Phenazine.Pyrene* (**RES.PHE.PYR**): A 1:1:1 mixture of resorcinol, phenazine and pyrene along with 2-3 drops of methanol was ground in a mortar with a pestle for 15 minutes. Diffraction quality block shaped yellow crystals were obtained from tetrahydrofuran (THF) at room temperature after 3-4 days.

(c) *Resorcinol.Tetramethylpyrazine.Pyrene* (**RES.TMP.PYR**): An equimolecular mixture of resorcinol, tetramethylpyrazine and pyrene was taken in a mortar along with 2-3 drops of methanol and ground with a pestle for 15 minutes. Diffraction quality block shaped yellow crystals were obtained from a mixture of nitromethane and benzene (1:1) at room temperature after 3-4 days.

(d) *Resorcinol.Phenazine.Tetramethylpyrazine.Pyrene* (**RES.PHE.TMP.PYR**): A 2:2:2:1 mixture of resorcinol, phenazine, tetramethylpyrazine and pyrene along with 2-3 drops of methanol was ground in a mortar with a pestle for 20 minutes. From a mixture of nitromethane and benzene (1:1), initially yellow crystals of **RES.PHE** were formed and then slowly diffraction quality block shaped red crystals were grown on the surface of **RES.PHE** binary cocrystals.

S3: SCXRD experiment.

Single crystal X-ray diffraction (SCXRD) data of all the cocrystals were collected on a Rigaku Mercury 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromator Mo K α radiation at 293K with an attached low temperature gas spray cooler. The data were processed with the Rigaku CrystalClear 2.0 software.^{1,2} Structure solution and refinements were executed using SHELX-2013³ implemented in the WinGX suite.⁴ All the nonhydrogen elements were refined anisotropically and hydrogen atoms were refined isotropically. Mercury version 3.8 was used for molecular representations and packing diagrams. Crystallographic data are given in the Supporting Information, (S4). Structural data are available at CCDC 1903868-1903871.

1. *Crystal Clear-SM Expert 2.0 rc14*; Rigaku Corporation: Tokyo, Japan, **2009**.
2. J. Pflugrath, *Acta Crystallogr. Sect. D* **1999**, 55, 1718-1725.
3. G. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, 64, 112-122.
4. L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, 32, 837-838.

S4: Crystallographic Table.

Compound	RES.PHE	RES.TMP.PYR	RES.PHE.PYR	RES.PHE.TMP.PYR
Formula	C ₁₅ H ₁₁ N ₂ O	C ₄₄ H ₄₆ N ₄ O ₄	C ₃₄ H ₂₄ N ₂ O ₂	C ₆₄ H ₅₂ N ₄ O ₄
F. W. (g/mol)	235.26	694.85	492.55	941.09
Crystal system	monoclinic	triclinic	triclinic	monoclinic
Space group	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P2</i> ₁ / <i>c</i>
T (K)	293 (2)	293 (2)	293 (2)	100 (2)
<i>a</i> (Å)	14.277(16)	8.806(5)	9.501(7)	17.323(7)
<i>b</i> (Å)	11.427(12)	10.222(5)	10.979(8)	14.591(6)
<i>c</i> (Å)	14.480(16)	11.441(6)	11.882(8)	18.265(8)
α (°)	90	65.821(15)	79.326(19)	90
β (°)	102.729(13)	80.09(2)	87.396(16)	90.146(7)
γ (°)	90	83.61(2)	89.378(18)	90
<i>V</i> (Å ³)	2304(4)	924.6(9)	1216.7(15)	4617(3)
<i>Z</i>	8	1	2	4
ρ_{calc} (g/cm ³)	1.356	1.248	1.344	1.354
θ range	2.305, 27.500	1.970, 27.498	1.746, 27.496	1.175, 27.500
<i>F</i> (000)	984	370	516	1984
μ (mm ⁻¹)	0.087	0.080	0.084	0.085
<i>R</i> _I [<i>I</i> > 2 σ (<i>I</i>)]	0.0674	0.0613	0.0653	0.0640
<i>wR</i> ₂	0.2190	0.2087	0.2156	0.1903
G.O.F.	1.121	1.092	1.089	1.153
CCDC no.	1903869	1903868	1903870	1903871

S5: Face indexing images.

Compound	Crystal Image	Indexed Faces
RES.PHE		
RES.PHE.TMP.PYR		

S6: Thickness measurement of the LSAMs.

RES.PHE: The thickness of the LSAM (10.988 Å) is the distance between the centroids of the two **PHE** molecules.

RES.PHE.TMP.PYR: The thickness of the LSAM (11.039 Å) is the distance between the centroids of the **TMP** and **PYR** molecules.

RES.PHE.PYR: The thickness of the LSAM (11.155 Å) is the distance between the centroids of the **PHE** and **PYR** molecules.

RES.TMP.PYR: The thickness of the LSAM (11.316 Å) is measured in two steps. First, we measured the distance between the centroid of the **TMP** and its orthogonal projection point on the **PYR** molecule (7.754 Å) (since the **PYR** molecule is slightly offset to one side with respect to the **TMP** molecules) and then we add the average perpendicular distance of the two **PYR** molecules in a pyrene diad (3.562 Å), obtained from CSD analysis (S7), to it. Since the **PYR** molecules are offset in the pyrene diads, considering the perpendicular distance of the two **PYR** molecules is more authentic for the thickness calculation than the centroid-centroid distance.

S7: CSD analysis.

A search of the CSD was performed with the ConQuest version 1.23. The analysis covered both organic and inorganic compounds with non-ionic and unsubstituted **PYR** molecules in the unit cell. A total of 11 hits were obtained where two **PYR** molecules formed a sandwich-type diad and these pyrene diads possessed a very close resemblance in molecular structure. The informations obtained from these structures (11 published and 2 new structures) were used to calculate the thickness of the LSAMs.

Sr No.	CSD Code	Perpendicular distance between two Pyrene molecules (d_p) in Å	Centroid-Centroid distance between two Pyrene molecules (d_c) in Å
1	GUQPOZ	3.450	3.873
2	PYRENE	3.533	3.953
3	PYRENE10	3.452	3.872
4	QOWTUR	3.430	3.933
5	RACSAP	3.595	4.065
6	YUFHIS	3.513	3.821
7	BAYWEE	3.615	4.438
8	CETROJ	3.490	3.878
9	PILNAB	3.520	4.208
10	PILNEF	3.640	4.374
11	ZAWPUL	3.974	3.962
12	RES.PHE.PYR	3.562	3.861
13	RES.PHE.TMP.PYR	3.565	3.699
		Average 3.562	Average 3.870

d_c vs. d_p plot shows a close structural similarity among the sandwich-type pyrene diads