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Shape and size mimicry in the design of ternary molecular solids: Towards a robust strategy for crystal engineering

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Supplementary Information

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Experimental Section

Single crystal X-ray diffraction

Single crystal X-ray data for all crystals were collected on a Rigaku Mercury375/M CCD (XtaLAB mini) diffractometer using graphite monochromated Mo-Kα radiation at 150 K and the data were processed with Rigaku Crystal clear software[1]. Structure solution and refinement were performed using SHELX-97[2] using the WinGX suite[3]. Refinement of coordinates and anisotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. Mercury version 2.3 was used for molecular representations and packing diagrams.

1. CrystalClear 2.0, Rigaku Corporation, Tokyo, Japan.
2. G**.** M**.** Sheldrick, SHELXTL V5.1; Madison, WI, 1998.
3. L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837–838.

Crystallization

Orcinol : 4,4'-bipyridine **(1)**. Both the compounds were taken in 1:1 ratio and ground together in a mortar and with a pestle for ten minutes. Then the powder obtained was dissolved in MeOH. Crystals were obtained by slow evaporation of solvent after 2-3 days. The same co-crystal was obtained when orcinol and 4,4′-bipyridine were taken in 1: 2 ratios and ground in a mortar. In that case crystal was obtained from 1,4-dioxane by slow evaporation.

Orcinol : 4,4'-bipyridine **(2).** An equimolar mixture of orcinol and 4,4′-bipyridine was ground with 2-3 drops of EtOH (solvent drop grinding). The ground sample was dissolved in a minimum amount of MeCN and crystals of the 2:3 cocrystal, suitable for X-ray diffraction, were obtained after four days.

2-Methylresorcinol : 4,4′-bipyridine **(3).** An equimolar mixture of 2-methylresorcinol and 4,4′-bipyridine were ground with 2-3 drops of EtOH. The ground sample was dissolved in the minimum amount of 1:1 DMSO–$CHCl_3$ and crystals of the 2:3 compound, suitable for X-ray diffraction, were obtained after five days.

Orcinol : 4,4′-bipyridine: phenazine **(4).** Orcinol, 4,4′-bipyridine and phenazine were taken in 2:2:1 ratio and ground in a mortar after addition of few drops of MeOH by solvent drop grinding method. The powder obtained was then dissolved in a series of solvents. Yellow colored crystals were obtained from MeOH after three days.

Orcinol : 4,4′-bipyridine : acridine **(5).** Orcinol, 4,4′-bipyridine and acridine were taken in 2:2:1 ratio and ground in a mortar after addition of few drops of MeOH. The powder obtained was then dissolved in a series of solvents. Pale yellow colored crystals were obtained from MeCN and MeOH after 3 days.

Orcinol : 4,4′-bipyridine : anthracene **(6).** Orcinol, 4,4′-bipyridine and acridine were taken in 2:2:1 ratio and ground in a mortar after addition of few drops of MeOH. The powder obtained was then dissolved in a series of solvents. Crystals were obtained from THF after 3 days by slow evaporation of solvent.

Orcinol :4,4′-bipyridine : 2,2′-bithiophene **(7).** A 2:2:1 molar mixture of orcinol, 4,4′-bipyridine and 2,2′-bithiophene were ground with 2-3 drops of EtOH. Then the ground sample was dissolved in a minimum amount of ^{i}PrOH and crystals of the 2:2:1 compound, suitable for X-ray diffraction, were obtained after four days.

2-Methylresorcinol : 4,4′-bipyridine : biphenyl **(8).** 2:2:1 Molar equivalents of 2-methylresorcinol, 4,4′-bipyridine and biphenyl were ground with 2-3 drops of EtOH. Then the ground sample was dissolved in a minimum amount of 1,4-dioxane and crystals of the 2:2:1 compound, suitable for X-ray diffraction, were obtained after seven days.

2-Methylresorcinol : 4,4′-bipyridine : biphenyl **(9).** 2:1:1 Molar equivalents of 2-methylresorcinol, 4,4′-bipyridine and biphenyl were ground with 2-3 drops of EtOH. The ground sample was dissolved in a minimum amount of 1,4-dioxane and crystals of the 2:1:1, compound, suitable for X-ray diffraction, were obtained after six days.

2-Methylresorcinol : 4,4′-bipyridine : 2,2′-bithiophene **(10).** A 2:2:1 mixture of 2-methylresorcinol, 4,4′-bipyridine and 2,2′-bithiophene was ground with 2-3 drops of EtOH. Then the ground sample was dissolved in a minimum amount of ^{i}PrOH and crystals of the 2:2:1 ternary compound, suitable for X-ray diffraction, were obtained after 4 days.

2-Methylresorcinol : 4,4′-bipyridine : 2,2′-bithiophene **(11).** 2:1:1 Molar equivalents of 2-methylresorcinol, 4,4′-bipyridine and 2,2-'bithiophene were ground with a few drops of EtOH. The ground sample was dissolved in a minimum amount of MeCN and crystals of the 2:1:1 compound, suitable for X-ray diffraction, were obtained after 3 days.

2-Methylresorcinol : 4,4′-bipyridine : pyrene **(12).** A 2:2:1 mixture of 2-methylresorcinol, 4,4′-bipyridine and pyrene was ground with 2-3 drops of EtOH. The ground sample was dissolved in a minimum amount of MeOH and crystals of the 4:3:2 compound, suitable for X-ray diffraction, were obtained after 6 days.

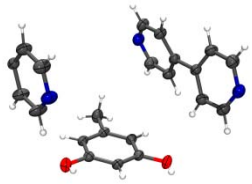
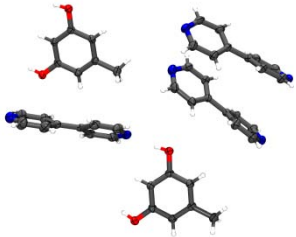
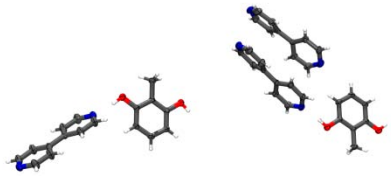
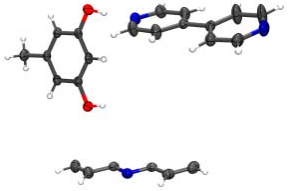
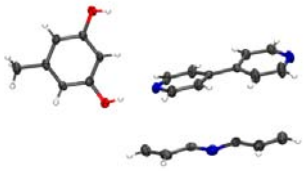
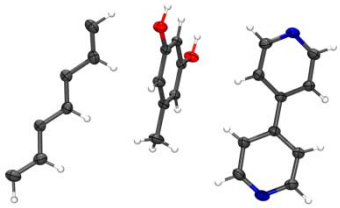
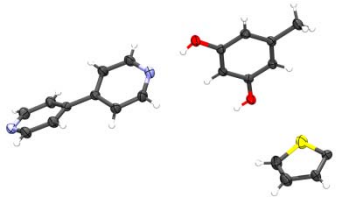
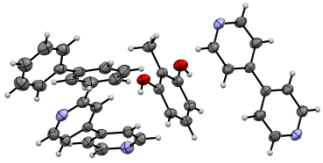
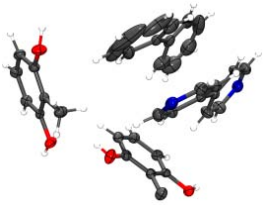
2-Methylresorcinol : 4,4′-bipyridine : phenazine **(13).** 2-Methylresorcinol, 4,4′-bipyridine and phenazine were taken in 2:2:1 ratio and ground in a mortar after addition of a few drops of MeOH. The powder obtained was then dissolved in a series of solvents. Crystals were obtained from THF after 2 days by slow evaporation of the solvent.

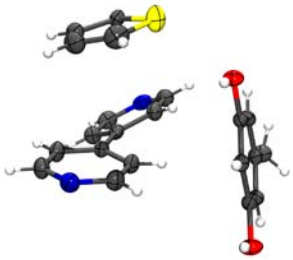
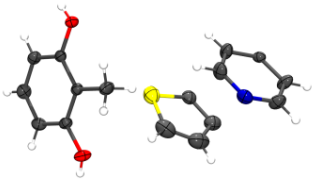
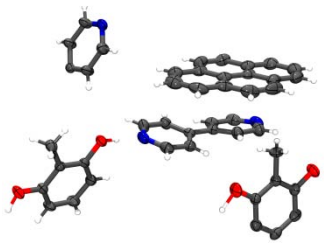
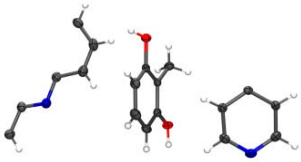
2. Crystallographic information

	1	**2**	**3**	**4**	**5**	**6**
	Orcinol : 4,4'-bipyridine	Orcinol : 4,4'-bipyridine	2-Methylresorcinol : 4,4'-bipyridine	Orcinol : 4,4'-bipyridine : phenazine	Orcinol : 4,4'-bipyridine : acridine	Orcinol : 4,4'-bipyridine : anthracene
Formula	$(C_{10}H_8N_2)_3 \cdot (C_7H_8O_2)_2$	$(C_{10}H_8N_2)_3 \cdot (C_7H_8O_2)_2$	$(C_{10}H_8N_2)_3 \cdot (C_7H_8O_2)_2$	$(C_{12}H_8N_2) \cdot (C_{10}H_8N_2)_2 \cdot (C_7H_8O_2)_2$	$(C_{13}H_9N) \cdot (C_{10}H_8N_2)_2 \cdot (C_7H_8O_2)_2$	$(C_{14}H_{10}) \cdot (C_{10}H_8N_2)_2 \cdot (C_7H_8O_2)_2$
Formula weight	716.82	716.82	716.82	740.84	739.85	738.86
Crystal System	Triclinic	Orthorhombic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.8290(18)	9.346(6)	7.4790(15)	9.4283(10)	9.3265(7)	9.2102(9)
b (Å)	10.079(2)	23.250(15)	14.911(3)	10.1821(10)	10.3739(8)	10.4824(11)
c (Å)	12.092(2)	33.59(2)	18.243(4)	11.1549(11)	11.1923(8)	11.2645(11)
α (°)	67.68(3)	90	110.11(3)	69.876(5)	68.503(5)	68.340(5)
β (°)	77.45(3)	90	90.79(3)	86.613(6)	86.581(6)	88.208(6)
γ (°)	69.16(3)	90	102.61(3)	69.427(5)	69.849(5)	70.827(5)
V (Å^{-3})	926.1(4)	7299(8)	1855.6(7)	939.04(17)	943.12(13)	949.65(17)
Z	1	8	2	1	1	1
ρ_{calc} *(gcm^{-3})*	1.285	1.305	1.283	1.310	1.304	1.292
F(000)	378	3024	756	390	390	390
μ(mm)	0.084	0.085	0.084	0.085	0.085	0.083
Temp(K)	150	150(2)	150 (2)	150	150	150
Total ref.	9829	55276	19860	9968	10093	10154
Unique ref.	4209	8337	8511	4305	4319	4345
Observed ref. (I > 2σ(I))	2926	6722	5557	3306	3679	3653
R	0.0653	0.0996	0.0736	0.0510	0.0509	0.0427
wR2	0.2191	0.2708	0.2365	0.1291	0.1471	0.1188
S	1.10	1.186	1.046	1.04	1.08	1.07
CCDC No.	836446	836451	836442	836450	836448	836449

	7	**8**	**9**	**10**	**11**	**12**	**13**
	Orcinol : 4,4'-bipyridine : *2,2*'-bithiophene	2-Methylresorcinol : 4,4'-bipyridine : biphenyl	2-Methylresorcinol : 4,4'-bipyridine : biphenyl	2-Methylresorcinol : 4,4'-bipyridine : 2,2'-bithiophene	2-Methylresorcinol : 4,4'-bipyridine : 2,2'-bithiophene	2-Methylresorcinol : 4,4'-bipyridine : pyrene	2-Methylresorcinol : 4,4'-bipyridine : phenazine
Formula	$(C_{10}H_8N_2)\cdot(C_7H_8O_2)\cdot(C_8H_6S_2)_{0.5}$	$(C_{12}H_{10})\cdot(C_{10}H_8N_2)_2\cdot(C_7H_8O_2)_2$	$(C_{12}H_{10})\cdot(C_{10}H_8N_2)\cdot(C_7H_8O_2)_2$	$(C_{10}H_8N_2)\cdot(C_7H_8O_2)\cdot(C_8H_4S_2)_{0.5}$	$(C_{10}H_8N_2)\cdot(C_7H_8O_2)_2\cdot(C_8H_4S_2)$	$(C_{16}H_{10})_2\cdot(C_{10}H_8N_2)_3\cdot(C_7H_8O_2)_4$	$(C_{12}H_8N_2)\cdot(C_{10}H_8N_2)\cdot(C_7H_8O_2)_2$
Formula weight	363.45	714.84	558.65	362.44	570.72	1241.40	584.66
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	9.3357(12)	26.380(5)	7.737(4)	7.4470(15)	7.827(6)	7.509(6)	7.6576(9)
b (Å)	12.3050(14)	7.5320(15)	19.791(10)	9.4240(19)	18.987(14)	8.755(6)	19.710(2)
c (Å)	17.910(2)	19.030(4)	9.508(5)	14.075(3)	11.956(6)	24.70(2)	11.6365(12)
α (°)	90	90	90	72.08(3)	90	91.768(12)	90
β (°)	116.558(7)	101.93(3)	95.170(7)	76.66(3)	126.99(3)	96.793(14)	125.572(7)
γ (°)	90	90	90	89.64(3)	90	93.035(13)	90
V (Å^{-3})	1840.3(4)	3699.5(13)	1450.0(13)	912.3(4)	1419.2(18)	1609(2)	1428.6(3)
Z	4	4	2	2	2	1	2
ρ_{calc} (gcm^{-3})	1.312	1.283	1.280	1.319	1.336	1.281	1.359
F(000)	764	1512	592	380	600	652	616
μ(mm)	0.193	0.083	0.083	0.195	0.228	0.081	0.090
Temp(K)	150(2)	150 (2)	150 (2)	150 (2)	150 (2)	150 (2)	150
Total ref.	19129	18432	15099	9717	14493	17140	14793
Unique ref.	4212	4281	6630	4166	3250	7370	3280
Observed ref. (I > 2σ(I))	3744	2962	6082	3373	2807	4555	2732
R	0.0579	0.0878	0.0570	0.0605	0.0543	0.0677	0.0420
wR2	0.1682	0.2559	0.1620	0.2001	0.1730	0.2283	0.1023
S	1.067	1.169	1.054	1.107	1.053	1.079	1.05
CCDC No.	836452	836443	836592	836441	836445	836444	836447

3. ORTEP Diagrams (only the asymmetric unit is shown)

		
Orcinol : 4,4'-bipyridine **(1)**	Orcinol : 4,4'-bipyridine **(2)**	2-Methylresorcinol : 4,4'-bipyridine **(3)**
		
Orcinol : 4,4'-bipyridine : phenazine **(4)**	Orcinol : 4,4'-bipyridine : acridine **(5)**	Orcinol : 4,4'-bipyridine : anthracene **(6)**
		
Orcinol : 4,4'-bipyridine : 2,2′-bithiophene **(7)**	2-Methylresorcinol : 4,4'-bipyridine : biphenyl **(8)**	2-Methylresorcinol : 4,4'-bipyridine : biphenyl **(9)**

		
2-Methylresorcinol : 4,4'-bipyridine : 2,2′-bithiophene **(10)**	2-Methylresorcinol : 4,4'-bipyridine : 2,2′-bithiophene **(11)**	2-Methylresorcinol : 4,4'-bipyridine : pyrene **(12)**
		
2-Methylresorcinol : 4,4'-bipyridine : phenazine **(13)**		