Supporting information

Combinatorial crystal synthesis of ternary solids based on 2-methylresorcinol

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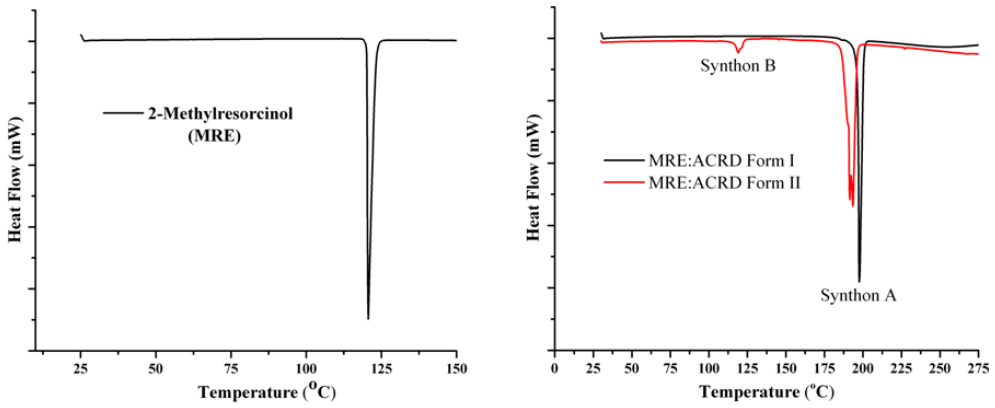
1. Characterization techniques

(a) Single crystal X-ray diffraction

Single crystal x-ray data for all crystals were collected on a *Rigaku Mercury 375/M CCD (XtaLAB mini)* diffractometer using graphite monochromator Mo-Kα radiation at 150 K and were processed with *Rigaku crystal clear software.*[1] Structure solution and refinement were performed using SHELX-2013[2] embedded in the WinGX suite.[3] Refinement of coordinates and isotropic thermal parameters of non-hydrogen atoms were carried out by the full-matrix least-squares method. Mercury version 3.5 was used for molecular representations and packing diagrams.[4] Acidic hydrogen atoms, especially in MRE, were located by difference Fourier maps while in other cases also at the calculated positions in the riding model.

1. CrystalClear 2.0, *Rigaku Corporation*, Tokyo, Japan.
2. G. M. Sheldrick, *ActaCrystallogr., Sect. C,* 2015, **71**, 3-8.
3. L. J. Farrugia, *J. Appl. Crystallogr.* 1999, **32**, 837.
4. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.,* 2006, **39**, 453.

(b) Differential Scanning Calorimetry (DSC)



DSC profile of MRE (left). Thermal behaviour of 1:1 and 1:2 MRE:ACR crystal forms (right). Note the high temperature phase transition in metastable form II.

2. Crystallization Details:

a) *2-Methylresorcinol* **(1)**: Colorless diffraction quality crystals were obtained from chloroform.

b) *2-Methylresorcinol:2,2'-bipyridine* **(2)**: Liquid assisted grinding was performed on a 1:1 mixture of the precursor compounds with THF as a solvent. Colorless diffraction quality crystals were obtained in 2-3 days from benzene.

c) *2-Methylresorcinol:4-phenylpyridine* **(3)**: An equimolar mixture of 2-methylresorcinol and 4-phenylpyridine was ground with 2-3 drops of THF (liquid assisted grinding). Colorless diffraction quality crystals were obtained from acetone or benzene after 2-3 days.

d) *2-Methylresorcinol:1,10-phenanthroline* **(4)**: An equimolar mixture of 2-methylresorcinol and 1,10-phenanthroline was ground with 2-3 drops of THF. Colorless diffraction quality crystals were obtained from benzene or acetonitrile after 2-3 days.

e) *2-Methylresorcinol:7,8-benzoquinoline* **(5)**: Both compounds were taken in 1:1 ratio and ground together with 2-3 drops of THF in a mortar and with a pestle for ten minutes. Purple colored diffraction quality crystals were obtained from benzene after 4 days.

f) *2-Methylresorcinol:4-aminopyridine* **(6)**: An equimolar mixture of 2-methylresorcinol and 4-aminopyridine was ground in a mortar with a pestle for ten minutes with 2-3 drops of methanol. Light brown color diffraction quality crystals were obtained after 4 days from chloroform.

g) *2-Methylresorcinol:4-dimethylaminopyridine* **(7)**: Both the compounds were taken in 1:1 ratio and ground together with 2-3 drops of methanol in a mortar with a pestle for ten minutes. Light brown color diffraction quality crystals were obtained after 4-5 days from chloroform.

h) *2-Methylresorcinol:quinoxaline* **(8)**: Liquid assisted grinding was performed with THF as a solvent. Light brown color diffraction quality crystals were obtained after 4 days from benzene at 5^{o}C.

i) *2-Methylresorcinol:2,3-dimethylquinoxaline* **(9):** An equimolar mixture of 2-methylresorcinol and 2,3-dimethylquinoxaline was ground in a mortar with a pestle for ten minutes with 2-3 drops of methanol. Light green color diffraction quality crystals were obtained from nitromethane.

j) *2-Methylresorcinol:tetramethylpyrazine* **(10)**: 1:2 mixture of 2-methylresorcinol and tetramethylpyrazine was ground in a mortar with a pestle for ten minutes with 2-3 drops of THF. Colorless diffraction quality crystals were obtained after 4 days from benzene.

k) *2-Methylresorcinol:1,2-bis(4-pyridyl)ethylene* **(11)**: Both compounds were taken in 1:1 ratio and ground together with 2-3 drops of THF in a mortar with a pestle for ten minutes. Orange color diffraction quality crystals were obtained from nitromethane.

l) *2-Methylresorcinol:1,2-bis(4-pyridyl)ethane* **(12)**: Both compounds were taken in 1:1 ratio and ground together with 2-3 drops of THF in a mortar with a pestle for 10-15 minutes. Colorless diffraction quality crystals of the 1:1 solid were obtained from nitromethane.

m) *2-Methylresorcinol:4,4'-azopyridine* **(13)**: Both compounds were taken in 1:1 ratio and ground together with 2-3 drops of THF in a mortar with a pestle for 10-15 minutes. Red color diffraction quality crystals were obtained from benzene.

n) *2-Methylresorcinol:phenazine* **(14)**: Both compounds were taken in 1:1 ratio and ground together with 2-3 drops of THF in a mortar with a pestle for 10-15 minutes. Green colored diffraction quality crystals were obtained from benzene.

o) *2-Methylresorcinol:acridine-Form I* **(15)**: Both compounds were taken in 1:1 ratio and ground together with 2-3 drops of THF in a mortar with a pestle for 10-15 minutes. Yellow colored diffraction quality crystals were obtained after 4-5 days from benzene.

p) *2-Methylresorcinol:acridine-Form II* **(16)**: Both compounds were taken in 1:1 ratio and ground together with 2-3 drops of THF in a mortar with a pestle for 10-15 minutes. Yellow colored diffraction quality crystals were obtained after 4 days from ethanol. Similar crystals could also be obtained by sublimation within 5 to 6 hours of a finely ground 1:2 stoichiometric mixture.

q) *2-Methylresorcinol:4-dimethylaminopyridine:Phenazine* **(17)**: An equimolar mixture of 2-methylresorcinol, 4-dimethylaminopyridine and phenazine was ground in a mortar with

a pestle for ten minutes with 2-3 drops of THF. Green colored diffraction quality crystals were obtained after 5 days from nitromethane.

r) *2-Methylresorcinol:4-dimethylaminopyridine:tetramethylpyrazine* **(18)**: An equimolar mixture of 2-methylresorcinol, 4-dimethylaminopyridine and tetramethylpyrazine was ground in a mortar with a pestle for ten minutes with 2-3 drops of THF. Colorless diffraction quality crystals were obtained after 5 days from a 1:1 solvent mixture of nitromethane and benzene.

s) *2-Methylresorcinol:4-phenylpyridine:tetramethylpyrazine* **(19)**: An equimolar mixture of 2-methylresorcinol, 4-phenylpyridine and tetramethylpyrazine was ground in a mortar with a pestle for ten minutes with 2-3 drops of THF. Colorless diffraction quality crystals were obtained after 5 days from nitromethane.

t) *2-Methylresorcinol:4-dimethylaminopyridine:2,3-dimethylquinoxaline* **(20)**: An equimolar mixture of 2-methylresorcinol, 4-dimethylaminopyridine and 2,3-dimethylquinoxaline was ground in a mortar with a pestle for ten minutes with 2-3 drops of THF. Colorless block shaped crystals were obtained after 4 days from nitromethane.

u) *2-Methylresorcinol: 1,10-phenanthroline: 4,4`-bipyridine* **(21):** An equimolar mixture of 2-methylresorcinol, 1,10-phenanthroline and 4,4`-bipyridine was ground in a mortar and pestle for ten minutes with 2-3 drops of THF. Colorless block shaped crystals were obtained after 5 days from nitromethane.

v) *2-Methylresorcinol: 1,10-phenanthroline: 4-phenylpyridine* **(22):** An equimolar mixture of 2-methylresorcinol, 1,10-phenanthroline and 4-phenylpyridine was ground in a mortar with a pestle for ten minutes with 2-3 drops of THF. Colorless block shaped crystals were obtained after 4 days from nitromethane.

3. Unsuccessful experimental efforts for the crystal synthesis of ternary solids:

	Compounds	Ratio	Crystallizing medium	Result
1	MRE: PHE:ACR	1:1:1	Chloroform	Binary (MRE:PHE)
2	MRE: PHE:ACR	1:1:1	Ethyl acetate	Binary (MRE:PHE)
3	MRE: PHE:ACR	2:1:1	Ethanol	Binary (MRE:PHE)
4	MRE: PHE:4PP	1:1:1	Nitromethane	Binary (MRE:PHE)
5	MRE: PHE:4PP	2:1:1	Nitromethane	Binary (MRE:PHE)

				Binary (MRE:4PP)
6	MRE: PHE:110PHE	2:1:1	Nitromethane	Binary (MRE:PHE)
7	MRE: PHE:4AP	1:1:1	Acetone	Binary (MRE:4AP)
8	MRE: PHE:4AP	1:1:1	Ethanol	Binary (MRE:4AP)
9	MRE: 110PHE:BZQL	1:1:1	Nitromethane	Binary (MRE:BZQL)
10	MRE: 110PHE:BZQL	1:1:1	Benzene	Binary (MRE:BZQL)
11	MRE:110PHE:4BP	1:1:1	Benzene	Binary (MRE:4BP)
12	MRE:110PHE:4PP	1:1:1	$CHCl_3$	Binary (MRE:110PHE)
13	MRE:110PHE:4PP	1:1:1	Benzene	Binary (MRE:110PHE)
14	MRE:110PHE:4DMAP	1:1:1	Nitromethane	Binary (MRE:4DMAP)
15	MRE:110PHE:4DMAP	1:1:1	EtOH	Binary (MRE:4DMAP)
16	MRE:110PHE:4AP	1:1:1	Acetonitrile	Binary (MRE:110PHE)
17	MRE:110PHE:4AP	1:1:1	Nitromethane	Binary (MRE:110PHE)
18	MRE:110PHE:4AP	1:1:1	Methanol	Binary (MRE:110PHE)
19	MRE: ACR:4PP	1:1:1	Nitromethane	Binary (MRE:ACR form I)
20	MRE: ACR:4PP	1:1:1	Nitromethane: Chloroform	Binary (MRE:ACR Form I)
21	MRE: ACR:4DMAP	1:1:1	Nitromethane	Binary (MRE:ACR form I)
22	MRE: ACR:4DMAP	2:1:1	Ethanol	Binary (MRE:ACR form II)
23	MRE: ACR:4DMAP	2:1:1	Nitromethane	Binary (MRE:4DMAP)
24	MRE: BZQL:4BAP	1:1:1	Nitromethane	Binary (MRE:4BP)
25	MRE: BZQL:4BAP	1:1:1	Benzene	Binary (MRE:4BP)

4. Crystallographic information

Compound	**1**	**2**	**3**	**4**	**5**	**6**
CCDC No.	1060872	1060873	1060874	1060875	1060876	1060877
Molecular Formula	$C_7H_8O_2$	$C_{17}H_{16}N_2O_2$	$C_{18}H_{17}N_1O_2$	$C_{19}H_{16}N_2O_2$	$C_{20}H_{17}N_1O_2$	$C_{12}H_{14}N_2O_2$
Formula Weight	124.13	280.32	279.33	304.34	303.35	218.25
Crystal System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$	*Pbca*	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	9.117(6)	7.6951(10)	11.3265(10)	7.900(4)	7.842(2)	7.986(5)
b (Å)	11.604(8)	20.299(2)	12.4430(11)	22.159(11)	21.894(4)	16.748(10)
c (Å)	18.108(12)	9.089(1)	21.1449(19)	8.964(5)	9.260(3)	8.276(5)
α (˚)	90	90	90	90	90	90

β (°)	92.885(8)	92.677(6)	90	106.540(5)	106.278(12)	90.474(8)
γ (°)	90	90	90	90	90	90
V (Å^3)	1913.0(2)	1418.2(3)	2980.1(5)	1504.3(14)	1526.1(7)	1106.9(12)
ρ_{calc} (g/cm^3)	1.293	1.313	1.245	1.344	1.320	1.310
F(000)	792	592	1184	640	640	464
μ. (mm^{-1})	0.094	0.087	0.081	0.088	0.083	0.091
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Total Reflns.	19457	14611	29717	15128	16018	11480
Unique Reflns.	4409	3239	3410	3448	3507	2534
Completeness (%)	99.8	99.8	99.8	99.6	99.8	99.8
R_{int}	0.081	0.099	0.079	0.093	0.165	0.092
R_1 (F^2)	0.0524	0.0522	0.0514	0.0484	0.0682	0.0488
wR_2(F^2)	0.1589	0.1697	0.1230	0.1492	0.2026	0.1559
GooF	1.14	1.11	1.16	1.10	1.15	1.13
2θ	54	54	54	54	54	54

Compound	**7**	**8**	**9**	**10**	**11**	**12**
CCDC No.	1060878	1060879	1060880	1060881	1060882	1060883
Molecular Formula	$C_{14}H_{18}N_2O_2$	$C_{22}H_{22}N_2O_4$	$C_{17}H_{18}N_2O_2$	$C_{15}H_{20}N_2O_2$	$C_{19}H_{18}N_2O_2$	$C_{19}H_{20}N_2O_2$
Formula Weight	246.30	378.42	282.33	260.33	306.35	308.37
Crystal System	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space Group	*P*2$_1$/*n*	*Cc*	*P*2$_1$/*n*	*Pbc*2$_1$	*P*2$_1$/*n*	*C*2/*c*
a (Å)	7.718(5)	20.478(4)	7.821(3)	9.0198(15)	17.8576(19)	8.139(2)
b (Å)	18.754(11)	7.1225(13)	22.849(8)	10.7769(18)	9.9354(10)	12.331(4)
c (Å)	9.201(6)	12.930(3)	8.387(3)	14.653(2)	18.732(2)	16.793(5)
α (°)	90	90.00	90.00	90	90	90

β (°)	96.278(8)	94.578(9)	91.286(15)	90	105.457(4)	98.031(13)
γ (°)	90	90.00	90.00	90	90	90
V (Å^3)	1323.8(14)	1879.9(7)	1498.4(9)	1424.4(4)	3203.3(6)	1668.9(8)
ρ_{calc} (g/cm^3)	1.236	1.337	1.252	1.214	1.270	1.227
F(000)	528	800.0	600.0	560	1296	656
μ. (mm^{-1})	0.084	0.093	0.083	0.081	0.083	0.080
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Total Reflns.	12859	9645	13123	14166	33416	7668
Unique Reflns.	3027	4273	3319	3257	7382	1915
Completeness (%)	99.7	99.0	97.3	100	99.9	99.1
R_{int}	0.111	0.100	0.113	0.079	0.112	0.109
R_1 (F^2)	0.0540	0.0652	0.0546	0.056	0.0796	0.0662
wR_2(F^2)	0.1560	0.1948	0.1691	0.1282	0.2461	0.2119
GooF	1.09	1.06	1.10	1.02	1.12	1.09
2θ	54	54	54	54	54	54

Compound	**13**	**14**	**15**	**16**	**17**	**18**
CCDC No.	1060884	1060885	1060886	1060887	1060888	1060889
Molecular Formula	$C_{17}H_{16}N_4O_2$	$C_{19}H_{16}N_2O_2$	$C_{20}H_{17}N_1O_2$	$C_{33}H_{26}N_2O_2$	$C_{33}H_{34}N_4O_4$	$C_{36}H_{48}N_6O_4$
Formula Weight	308.34	304.34	303.35	482.56	550.64	628.80
Crystal System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space Group	$P2_1/c$	$P2_1/n$	$P2_1/n$	P□	P□	P□
a (Å)	18.468(3)	7.656(7)	7.742(4)	9.097(17)	7.734(5)	7.7071(19)
b (Å)	7.2386(11)	22.46(2)	22.159(11)	12.117(19)	9.196(6)	8.9632(19)
c (Å)	11.831(2)	8.940(8)	9.100(5)	12.53(2)	20.844(14)	12.790(2)
α (°)	90	90	90	73.19(5)	101.370(15)	78.86(4)

β (°)	91.866(10)	91.516(14)	93.630(5)	81.98(5)	94.21(3)	79.56(4)
γ (°)	90	90	90	75.42(5)	96.022(17)	83.81(4)
V (Å^3)	1580.8(4)	1537.0(2)	1558.0(14)	1276(4)	1438.6(16)	850.1(3)
ρ_{calc} (g/cm^3)	1.296	1.315	1.293	1.256	1.271	1.228
F(000)	648	640	640	508	584	338
μ. (mm^{-1})	0.088	0.087	0.083	0.078	0.085	0.081
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Total Reflns.	16108	15342	15898	13607	15403	8736
Unique Reflns.	3628	3506	3558	5860	6586	3961
Completeness (%)	99.4	99.7	99.8	98.3	99.4	97.9
R_{int}	0.095	0.073	0.052	0.167	0.084	0.093
R_1 (F^2)	0.0663	0.0721	0.0503	0.1231	0.0729	0.0632
wR_2(F^2)	0.2005	0.2240	0.1623	0.3809	0.2307	0.2029
GooF	1.06	1.15	1.16	1.00	1.07	0.98
2θ	54	54	54	54	54	54

Compound	**19**	**20**	**21**	**22**
CCDC No.	1060890	1060891	1060870	1060871
Molecular Formula	$C_{22}H_{23}N_2O_2$	$C_{24}H_{28}N_4O_2$	$C_{29}H_{24}N_4O_2$	$C_{30}H_{25}N_3O_2$
Formula Weight	347.42	404.50	460.52	459.53
Crystal System	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	*P*□	*P*□	$P2_1/c$	$P2_1/c$
a (Å)	7.287(6)	7.635(5)	16.177(3)	16.337(13)
b (Å)	9.179(7)	9.055(8)	7.5746(13)	7.599(6)
c (Å)	14.419(11)	17.237(13)	19.698(4)	19.883(15)
α (°)	105.567(19)	96.22(3)	90	90

β (°)	90.12(3)	94.09(2)	107.485(9)	107.782(9)
γ (°)	93.375(19)	113.734(15)	90	90
V (Å^3)	927.3(13)	1075.8(14)	2302.2(8)	2350.4(3)
ρ_{calc} (g/cm^3)	1.244	1.249	1.329	1.299
F(000)	370.0	432.0	968.0	968.0
μ. (mm^{-1})	0.080	0.081	0.085	0.082
T (K)	150(2)	150(2)	150(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Total Reflns.	9785	10143	23137	24193
Unique Reflns.	4244	4226	5298	5409
Completeness (%)	98.8	99.6	99.2	99.9
R_{int}	0.094	0.113	0.104	0.158
R_1 (F^2)	0.0755	0.0586	0.0609	0.0974
wR_2(F^2)	0.2921	0.1865	0.1852	0.2727
GooF	0.95	1.02	1.21	1.14
2θ	54	52	54	54