Supplementary Information

Figures

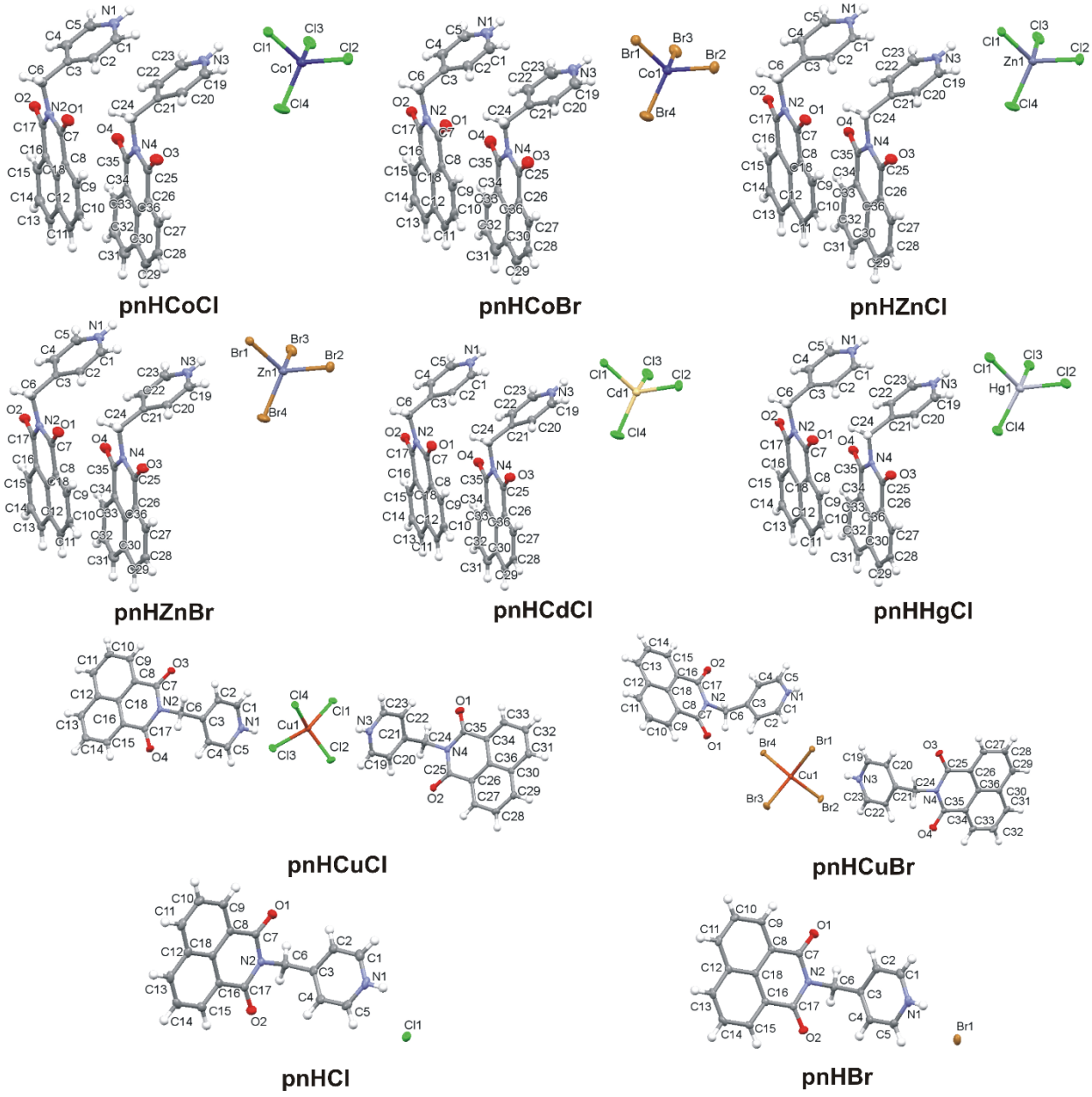


Fig. S1 Asymmetric units of structures **pnHCoCl**, **pnHCoBr**, **pnHZnCl**, **pnHZnBr**, **pnHCdCl** and **pnHHgCl**, **pnHCuCl**, **pnHCuBr**, **pnHCl** and **pnHBr**, illustrating the atomic numbering scheme. Ellipsoids are drawn at the 50% probability level.

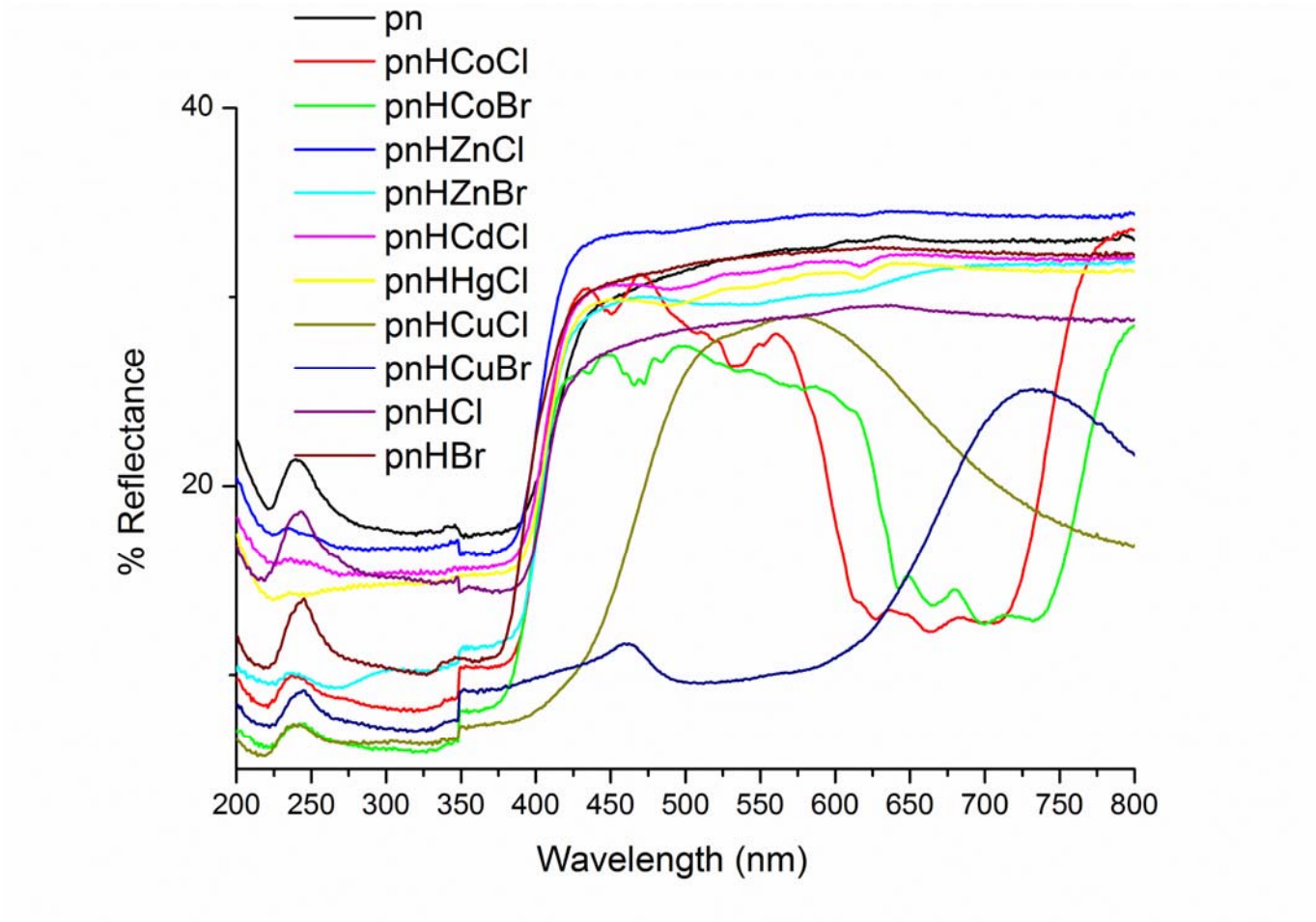


Fig. S2 Diffuse reflectance spectra of all compounds.

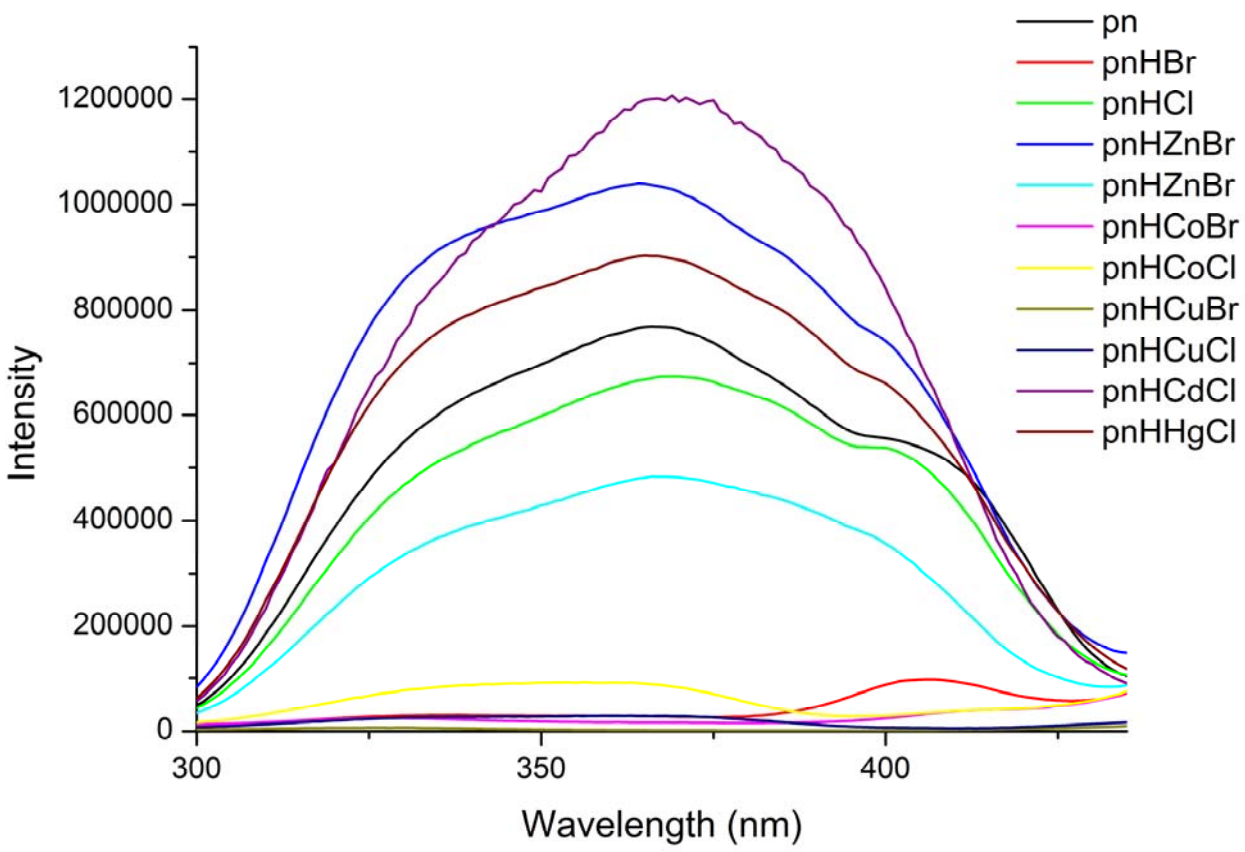


Fig. S3 Fluorescence excitation spectra of all compounds.

Tables

Table S1 Crystallographic parameters and refinement results for compounds **pnHCoCl, pnHCoBr, pnHZnCl, pnHZnBr** and **pnHCdCl**.

Structure	**pnHCoCl**	**pnHCoBr**	**pnHZnCl**	**pnHZnBr**	**pnHCdCl**
Empirical formula	$2[C_{18}H_{13}N_2O_2]^+$ $[CoCl_4]^{2-}$	$2[C_{18}H_{13}N_2O_2]^+$ $[CoBr_4]^{2-}$	$2[C_{18}H_{13}N_2O_2]^+$ $[ZnCl_4]^{2-}$	$2[C_{18}H_{13}N_2O_2]^+$ $[ZnBr_4]^{2-}$	$2[C_{18}H_{13}N_2O_2]^+$ $[CdCl_4]^{2-}$
Formula weight/ $g.mol^{-1}$	779.34	957.18	784.79	963.62	832.81
Temperature/ K	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength/ Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions a/Å	7.8831(4)	7.933(2)	7.9049(10)	7.9152(3)	7.8678(7)
b/Å	14.6869(8)	14.728(4)	14.7046(18	14.7377(6)	14.7568(13)
c/Å	14.5239(8)	14.966(5)	14.5448(19	14.9796(6)	14.8082(13)
α/°	102.504(2)	102.650(10)	102.479(6)	102.5410(10)	102.750(4)
β/°	100.890(2)	100.863(9)	100.932(6)	100.9130(10)	100.866(4)
γ/°	92.406(2)	93.145(9)	92.276(6)	93.4390(10)	93.071(4)
Volume/ $Å^3$	1606.07(15)	1667.0(9)	1615.0(4)	1665.52(11)	1638.7(3)
Z	2	2	2	2	2
Density (calculated)/ Mg/m^3	1.612	1.907	1.616	1.921	1.688
Absorption coefficient/ mm^{-1}	0.917	5.357	1.141	5.584	1.041
F(000)	794	938	800	944	836
Crystal size/ mm^3	0.033 x 0.082 x 0.152	0.020 x 0.121 x 0.287	0.086 x 0.121 x 0.321	0.020 x 0.180 x 0.300	0.030 x 0.060 x 0.500
Theta range for data collection/ °	2.267 to 26.373	2.238 to 26.372	2.263 to 26.369	2.236 to 26.372	2.250 to 26.372
Reflections collected	67905	49749	50580	58279	49156
Independent reflections	6564 [R(int) = 0.0575]	6816 [R(int) = 0.1014]	6344 [R(int) = 0.0448]	6807 [R(int) = 0.0466]	6718 [R(int) = 0.0873]
Completeness to ϑ (%)	99	100	97	100	99
Max. and min. transmission	0.7468 and 0.6281	0.7454 and 0.5937	0.6528 and 0.7454	0.7462 and 0.5506	0.9281 and 0.7438
Data / restraints / parameters	6564 / 132 / 442	6816 / 132 / 442	6344 / 132 / 442	6807 / 132 / 442	6718 / 132 / 442
Goodness-of-fit on F^2	1.031	1.033	1.180	1.064	1.025
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0398, wR2 = 0.0917	R1 = 0.0459,wR2 = 0.1175	R1 = 0.0746, wR2 = 0.1830	R1 = 0.0300, wR2 = 0.0780	R1 = 0.0365, wR2 = 0.0698
R indices (all data)	R1 = 0.0561, wR2 = 0.1003	R1 = 0.0820, wR2 = 0.1300	R1 = 0.0927, wR2 = 0.1830	R1 = 0.0366,wR2 = 0.0817	R1 = 0.0622, wR2 = 0.0771
Largest diff. peak and hole/ $e.Å^{-3}$	0.627 and -0.412	1.158 and -0.592	2.06 and -0.72	1.196 and -0.475	0.577 and -0.538

Table S1 continued Crystallographic parameters and refinement data for structures **pnHHgCl, pnHCuCl, pnHCuBr, pnHCl** and **pnHBr.**

Structure	**pnHHgCl**	**pnHCuCl**	**pnHCuBr**	**pnHCl**	**pnHBr**
Empirical formula	$2[C_{18}H_{13}N_2O_2]^+ [HgCl_4]^{2-}$	$2[C_{18}H_{13}N_2O_2]^+ [CuCl_4]^{2-}$	$2[C_{18}H_{13}N_2O_2]^+ [CuBr_4]^{2-}$	$[C_{18}H_{13}N_2O_2]^+ Cl^-$	$[C_{18}H_{13}N_2O_2]^+ Br^-$
Formula weight/ $g.mol^{-1}$	921.00	783.95	961.76	324.75	369.21
Temperature/ K	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength/ Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
Unit cell dimensions					
a/Å	7.8598(4)	7.7660(6)	7.6700(4)	7.3112(7)	13.5398(16)
b/Å	14.7496(9)	55.312(4)	7.6942(5)	7.7033(7)	7.7569(9)
c/Å	14.7874(8)	7.4689(5)	28.2690(19)	13.0401(12)	15.2010(17)
α/°	102.704(2)	90	87.564(3)	79.183(3)	90.
β/°	101.054(2)	91.983(2)	89.895(2)	86.649(3)	112.641(3)
γ/°	93.104(2)	90	89.559(2)	88.692(3)	90.
Volume/ $Å^3$	1632.97(16)	3206.4(4)	1666.72(18)	720.09(12)	1473.5(3)
Z	2	4	2	2	4
Density (calculated)/ Mg/m^3	1.873	1.624	1.916	1.883	1.664
Absorption coefficient/ mm^{-1}	5.089	1.064	5.498	0.277	2.801
F(000)	900	1596	942	942	744
Crystal size/ mm^3	0.063 x 0.079 x 0.144	0.031 x 0.182 x 0.535	0.054 x 0.208 x 0.319	0.120 0.450 0.580	0.48 x 0.44 x 0.44
Theta range for data collection/ °	2.252 to 26.371	2.209 to 26.451	2.65 to 28.27	2.69 to 26.58	2.57 to 26.52
Reflections collected	56440	75027	52474	20729	41090
Independent reflections	6690 [R(int) = 0.0505]	6614 [R(int) = 0.0542]	8321 [R(int) = 0.0668]	3005 [R(int) = 0.0420]	3052 [R(int) = 0.0527]
Completeness to ϑ (%)	99	99.9	99.4	99.6	99.8
Max. and min. transmission	0.7467 and 0.6202	0.5213 and 0.7446	0.7452 and 0.5489	0.8620 and 0.8086	0.3720 and 0.3466
Data / restraints / parameters	6690 / 132 / 442	6614 / 0 / 490	8321 / 132 / 446	3005 / 0 / 260	3052 / 0 / 261
Goodness-of-fit on F^2	1.047	1.264	1.052	1.069	1.043
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0489, wR2 = 0.1053	R1 = 0.0696, wR2 = 0.1212	R1 = 0.0550, wR2 = 0.1310	R1 = 0.0338, wR2 = 0.0795	R1 = 0.0208, wR2 = 0.0542
R indices (all data)	R1 = 0.0558, wR2 = 0.1066	R1 = 0.0919, wR2 = 0.1267	R1 = 0.0717, wR2 = 0.1372	R1 = 0.0478, wR2 = 0.0850	R1 = 0.0233, wR2 = 0.0554
Largest diff. peak and hole/ $e.Å^{-3}$	5.861 and -7.375	0.56 and -0.58	1.754 and -1.150	0.274 and -0.237	0.342 and -0.333

Table S2 Selected bond lengths, angles and torsion angles in the isostructural series (Å,°).

	pnHCoCl	**pnHCoBr**	**pnHZnCl**	**pnHZnBr**	**pnHCdCl**	**pnHHgCl**
M-X(1) (Å)	2.2970(7)	2.4307(10)	2.3079(14)	2.4351(4)	2.4929(8)	2.5485(6)
M-X(2) (Å)	2.2893(7)	2.4299(9)	2.2928(14)	2.4366(4)	2.4797(8)	2.5205(7)
M-X(3) (Å)	2.2819(7)	2.4124(11)	2.2910(15)	2.4137(5)	2.4669(8)	2.4875(7)
M-X(4) (Å)	2.2323(8)	2.3742(11)	2.2230(16)	2.3664(5)	2.4019(9)	2.3920(8)
X(1)-M-X(2) (°)	108.58(3)	106.64(4)	107.74(5)	106.207(16)	106.59(3)	104.31(2)
X(1)-M-X(3) (°)	109.50(3)	112.30(3)	108.71(5)	115.151(16)	110.12(3)	109.13(2)
X(1)-M-X(4) (°)	107.83(3)	106.97(3)	108.43(6)	107.925(18)	106.94(3)	105.98(3)
X(2)-M-X(3) (°)	103.37(3)	103.97(3)	103.50(5)	103.981(16)	99.68(3)	98.09(2)
X(2)-M-X(4) (°)	115.37(3)	115.65(4)	115.50(6)	115.349(18)	119.12(3)	120.54(3)
X(3)-M-X(4) (°)	112.04(3)	111.35(4)	112.65(7)	112.088(19)	113.99(3)	117.79(3)
N(2)-C(6)-C(3) (°)	111.7(2)	111.4(4)	111.8(4)	111.9(2)	111.5(2)	111.6(2)
N(2)-C(6)-C(3)-C(4) (°)*	100.7(3)	100.5(5)	101.3(5)	97.7(3)	100.1(3)	99.8(7)
Angle between aromatic planes (Cation 1)(°)	61.76(6)	60.1(1)	61.6(1)	60.28(7)	60.69(7)	61.1(1)
N(4)-C(24)-C(21) (°)	112.95(19)	112.6(4)	112.8(4)	112.9(2)	112.9(2)	113.23(19)
N(4)-C(24)-C(21)-C(22) (°)*	89.8(3)	93.6(6)	90.5(6)	92.6(3)	90.3(3)	90.2(7)
Angle between aromatic planes (Cation 2)(°)	56.87(6)	57.7(1)	56.5(1)	57.32 (7)	57.26(7)	57.1(1)

* These torsion angles correspond to the N-C-C-ϕ torsion angle defined by Sarma *et al.*[5]

Table S3 Strong hydrogen bonding parameters [Å, ˚] for all the structures.

Structure	D-H···A (Å)	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	∠ (DHA) (˚)	Symmetry Operator
pnHCoCl	N(1)-H(1N)...Cl(2)^{i}	0.93(3)	2.69(3)	3.376(2)	131(2)	i: -x+2,-y+1,-z
	N(1)-H(1N)...Cl(3)i	0.93(3)	2.38(3)	3.134(2)	138(2)	
	N(3)-H(3N)...Cl(1)	0.90(3)	2.50(3)	3.195(2)	134(2)	
	N(3)-H(3N)...Cl(1)^{i}	0.90(3)	2.60(3)	3.263(2)	131(2)	
pnHCoBr	N(1)-H(1N)...Br(2)^{i}	0.94(6)	2.71(6)	3.441(4)	135(5)	i: -x+2,-y+1,-z
	N(1)-H(1N)...Br(3)^{i}	0.94(6)	2.67(6)	3.379(5)	133(5)	
	N(3)-H(3N)...Br(1)	1.05(6)	2.60(6)	3.390(5)	132(4)	
	N(3)-H(3N)...Br(1)^{i}	1.05(6)	2.58(6)	3.363(4)	131(4)	
pnHZnCl	N(1)-H(1N)...Cl(2)^{i}	0.86	2.76	3.392(5)	131.6	i: -x+2,-y+1,-z
	N(1)-H(1N)...Cl(3)i	0.86	2.43	3.140(5)	140.7	
	N(3)-H(3N)...Cl(1)	0.86	2.52	3.199(5)	136.4	
	N(3)-H(3N)...Cl(1)^{i}	0.86	2.66	3.268(5)	128.8	
pnHZnBr	N(1)-H(1N)...Br(2)^{i}	0.88(4)	2.76(4)	3.435(2)	134(3)	i: -x+2,-y+1,-z
	N(1)-H(1N)...Br(3)^{i}	0.88(4)	2.67(4)	3.365(3)	136(3)	
	N(3)-H(3N)...Br(1)	0.90(4)	2.71(4)	3.391(3)	133(3)	
	N(3)-H(3N)...Br(1)^{i}	0.90(4)	2.66(4)	3.363(3)	135(3)	
pnHCdCl	N(1)-H(1N)...Cl(2)^{i}	0.85(3)	2.79(3)	3.389(3)	129(3)	i: -x+2,-y+1,-z
	N(1)-H(1N)...Cl(3)^{i}	0.85(3)	2.48(3)	3.178(3)	139(3)	
	N(3)-H(3N)...Cl(1)	0.84(3)	2.55(3)	3.229(3)	138(3)	
	N(3)-H(3N)...Cl(1)^{i}	0.84(3)	2.67(3)	3.272(3)	130(3)	
pnHHgCl	N(1)-H(1N)...Cl(2)^{i}	0.87(8)	2.73(8)	3.352(6)	129(6)	i: -x+2,-y+1,-z
	N(1)-H(1N)...Cl(3)^{i}	0.87(8)	2.48(8)	3.183(6)	137(7)	
	N(3)-H(3N)...Cl(1)	0.88(9)	2.54(9)	3.216(6)	134(7)	
	N(3)-H(3N)...Cl(1)^{i}	0.88(9)	2.60(9)	3.259(6)	132(7)	
pnHCuCl	N(1)-H(1N)… Cl(3)	0.94(6)	2.27(6)	3.132(4)	153(5)	
	N(1)-H(1N)...Cl(4)	0.94(6)	2.68(5)	3.303(4)	124(4)	
	N(3)-H(3N)…Cl(1)	0.78(5)	2.43(5)	3.114(4)	147(5)	
	N(3)-H(3N)…Cl2	0.78(5)	2.71(5)	3.295(4)	133(5)	
pnHCuBr	N(1)-H(1N)...Br(4)^{i}	0.64(9)	2.81(9)	3.392(7)	153(10)	i: x,y-1,z
	N(1)-H(1N)...Br(3)^{i}	0.64(9)	3.01(9)	3.458(6)	130(9)	
	N(3)-H(3N)...Br(1)	0.93(8)	2.71(7)	3.373(6)	129(6)	
	N(3)-H(3N)...Br(2)	0.93(8)	2.62(8)	3.357(6)	136(6)	
pnHCl	N(1)-H(1N)...Cl(1)	0.88(2)	2.53(2)	3.1868(15)	131.9(16)	i: -x,-y+2,-z+2
	N(1)-H(1N)...Cl(1)^{i}	0.88(2)	2.61(2)	3.2328(15)	128.9(16)	
pnHBr	N(1)-H(1N)...Br(1)	0.87(3)	2.41(3)	3.1940(15)	151(2)	

Hydrogen bonding definition: Strong hydrogen bonding donors and acceptors, d_{min}(D...A = R(D)+R(A) - 0.50 Å; d_{max}(D...A) = R(D)+R(A), D-H...A > 120.0˚ (Default definition in Mercury[14])

Table S4 Isostructurality parameters

Structures		Π	ε	A	I_v (%)
pnHCoCl	**pnHCoBr**	0.01407	0.01248	0.58142	94.2
pnHCoCl	**pnHZnCl**	0.00165	0.00185	0.49425	99.0
pnHCoCl	**pnHZnBr**	0.01424	0.01218	0.71771	93.6
pnHCoCl	**pnHCdCl**	0.00880	0.00672	0.86979	95.6
pnHCoCl	**pnHHgCl**	0.00776	0.00555	1.07544	95.2
pnHCoBr	**pnHZnCl**	0.01240	0.01061	0.74211	93.8
pnHCoBr	**pnHZnBr**	0.00016	0.00029	6.78038	98.1
pnHCoBr	**pnHCdCl**	0.00538	0.00543	0.47040	96.4
pnHCoBr	**pnHHgCl**	0.00625	0.00689	0.46043	95.2
pnHZnCl	**pnHZnBr**	0.01256	0.01031	0.91397	93.4
pnHZnCl	**pnHCdCl**	0.00714	0.00485	1.35944	95.2
pnHZnCl	**pnHHgCl**	0.00610	0.00369	1.81357	94.9
pnHZnBr	**pnHCdCl**	0.00538	0.00543	0.64835	96.5
pnHZnBr	**pnHHgCl**	0.00642	0.00660	0.56377	96.1
pnHCdCl	**pnHHgCl**	0.00102	0.00116	1.07361	98.7

Table S5 Selected bond lengths, angles and torsion angles in structures **pnHCuCl**, **pnHCuBr**, **pnHCl** and **pnHBr** (Å,°).

	pnHCuCl	**pnHCuBr**	**pnHCl**	**pnHBr**
M-X(1) (Å)	2.2485(13)	2.3684(11)	-	-
M-X(2) (Å)	2.2408(13)	2.4074(11)	-	-
M-X(3) (Å)	2.2534(13)	2.3946(11)	-	-
M-X(4) (Å)	2.2444(12)	2.4065(11)	-	-
X(4)-M-X(3) (°)	94.31(5)	98.14(4)	-	-
X(4)-M-X(2) (°)	145.79(5)	134.63(4)	-	-
X(3)-M-X(2) (°)	95.51(5)	98.02(4)	-	-
X(4)-M-X(1) (°)	94.86(5)	98.92(4)	-	-
X(3)-M-X(1) (°)	146.07(5)	136.34(5)	-	-
X(2)-M-X(1) (°)	95.01(5)	97.91(4)	-	-
N(2)-C(6)-C(3) (°)	110.4(4)	111.3(6)	111.61(13)	112.45(12)
N(2)-C(6)-C(3)-C(4) (°)	87.2(5)	-96.4(8)	81.73(18)	96.08(17)
Angle between aromatic planes (°)	70.0(3)	62.3(2)		
N(4)-C(24)-C(21) (°)	110.9(4)	112.2(5)	-	-
N(4)-C(24)-C(21)-C(22) (°)	89.7(5)	85.3(8)	-	-
Angle between aromatic planes (°)	71.7(3)	63.2(2)		

Table S6 Fluorescence excitation wavelengths of all compounds.

Structure	Fluorescence Excitation wavelength (nm)
pn	366
pnHCoCl	356
pnHCoBr	328
pnHZnCl	364
pnHZnBr	366
pnHCdCl	365
pnHHgCl	365
pnHCuCl	360
pnHCuBr	326
pnHCl	368
pnHBr	406

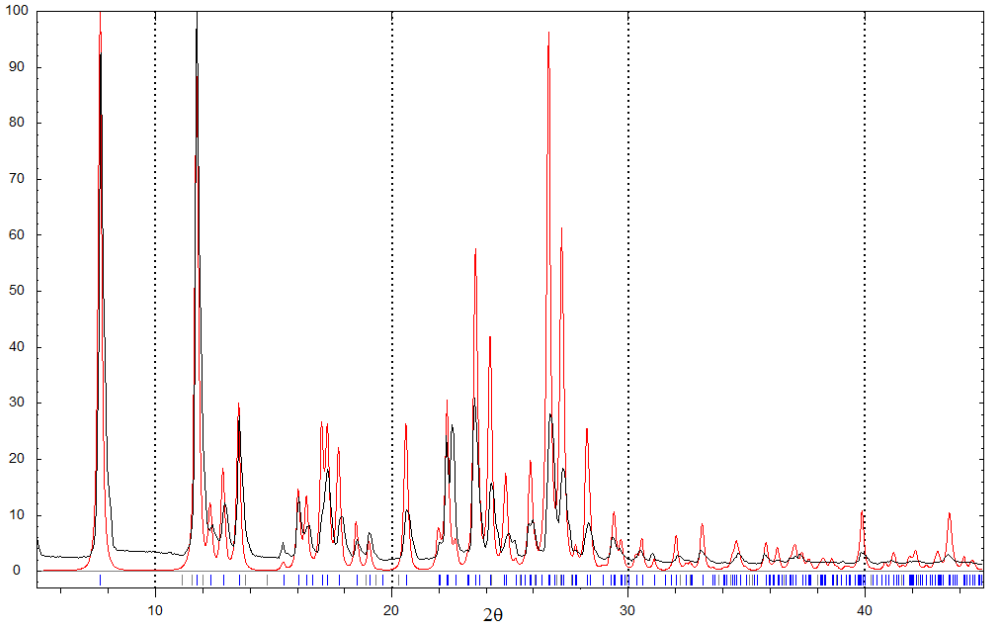
Calculated and Experimental Powder Patterns

Experimental powder X-ray patterns of the bulk samples were compared with powder patterns calculated from the single crystal structures determined in the study, or from the structures reported in the CSD, in order to determine if the single crystal is representative of the bulk sample.

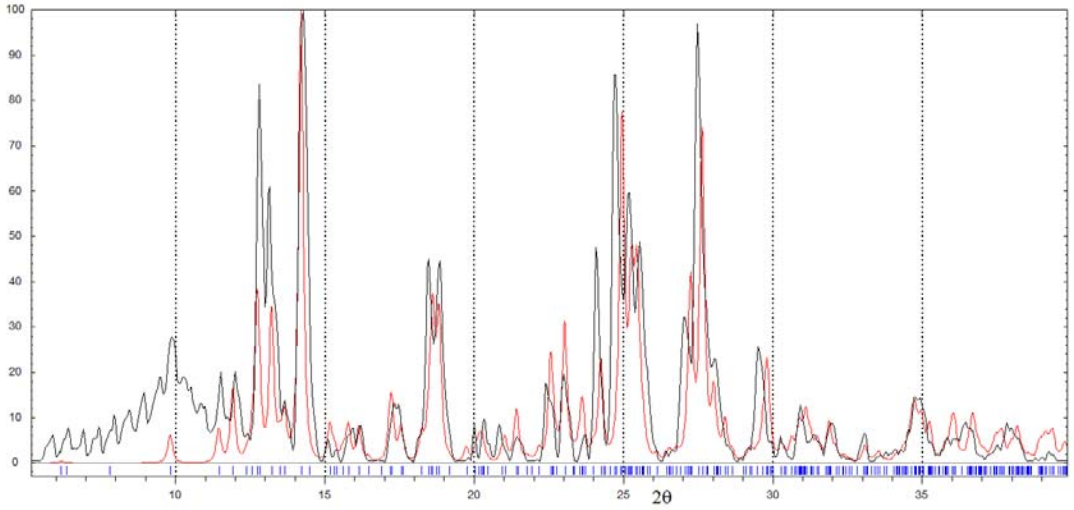
The experimental powder patterns are shown in black and the calculated patterns are given in red.

The experimental powder patterns were not collected for compounds containing Cd or Hg salts, thus for compounds **pnHCdCl** and **pnHHgCl** respectively, due to the toxicity of these metals.

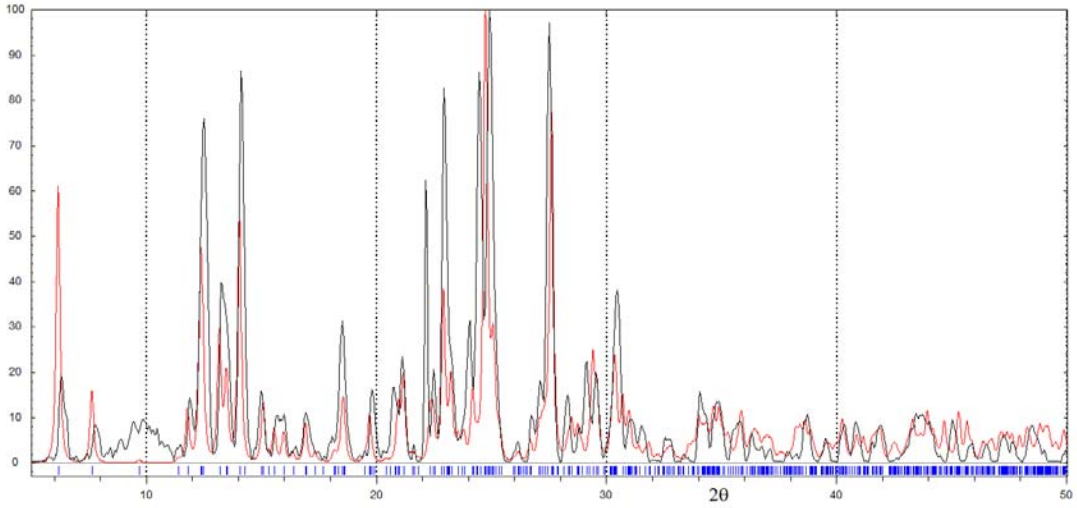
1. N-(4-picolyl) 1, 8-naphthalimide (**pn**) compared with single crystal structure WEZDAH in literature.



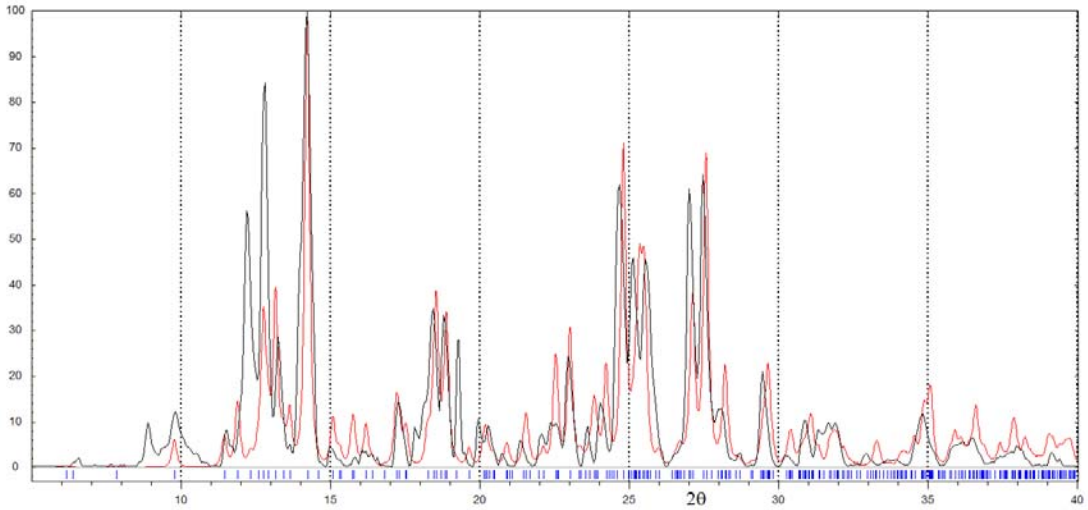
2. pnHCoCl



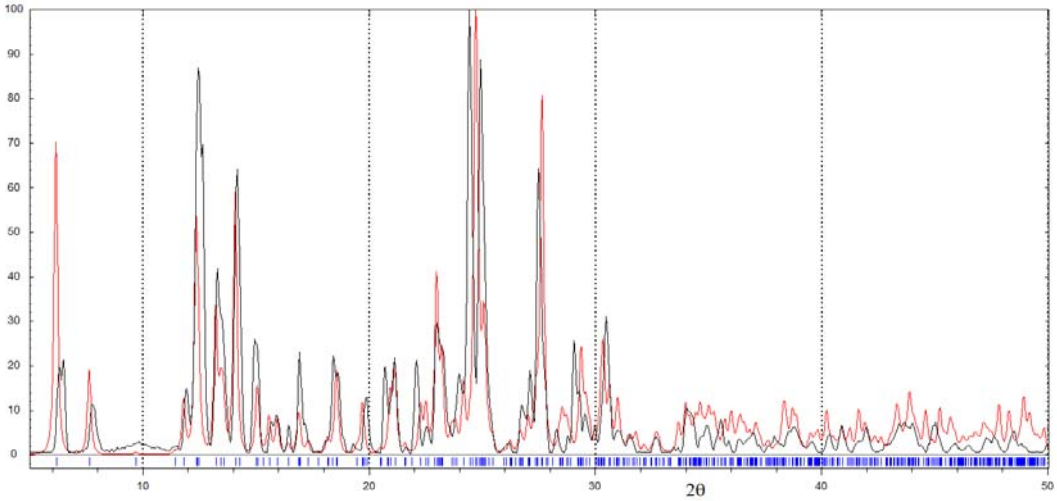
3. pnHCoBr



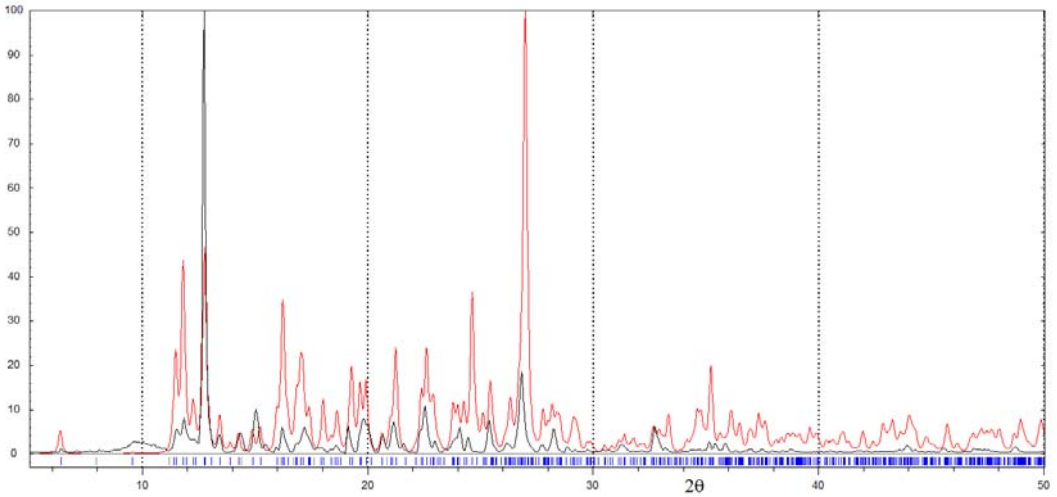
4. pnHZnCl



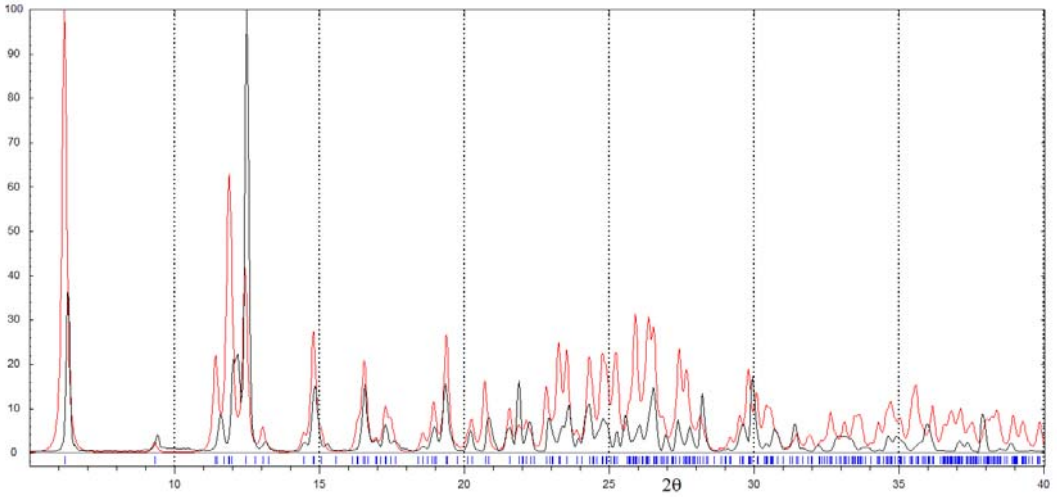
5. **pnHZnBr**



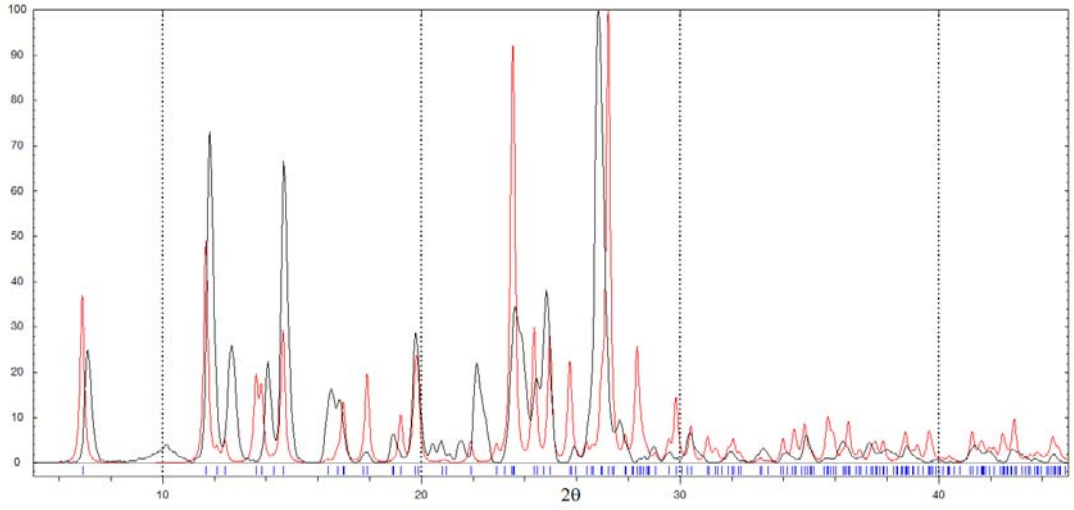
6. **pnHCuCl**



7. **pnHCuBr**



8. pnHCl



9. **pnHBr**