Supporting Materials

C–H...X (X = F, Cl, Br, I) versus π-stacking in the crystal packing of compounds containing the {M(tpy)X$_3$} motif

Catherine E. Housecroft* and Edwin C. Constable

Table S1. Crystallographic cell dimensions for the compounds in Table 1 of the manuscript.

CSD Refcode	Space group	Temp. / K[a]	*a* / Å	*b* / Å	*c* / Å	α / °	β / °	γ / °
QQQCBD	$P2_1/c$	295	8.346	14.063	14.172	90	111.08	90
TPYGAC	$P2_1/c$	295	8.324	14.12	14.223	90	110.77	90
TPYGAC01	$P2_1/n$	123	8.2492	14.177	13.7119	90	104.217	90
TERPIN	$P2_1/c$	295	8.582	14.155	14.36	90	109.32	90
TERPIN01	$P2_1/n$	103	8.4662	14.113	14.1329	90	106.253	90
TERPIN02	$P2_1/n$	293	8.5764	14.1465	14.0909	90	105.818	90
TERPTL	$P2_1/c$	295	8.637	14.198	14.43	90	108.62	90
KEZZOH	$P2_1/n$	100	8.5434	13.9045	14.0175	90	106.779	90
PAXVAM	$P2_1/n$	223	8.3949	14.291	13.693	90	105.318	90
HUJKIG	$P2_1/n$	160	8.256	14.0522	13.6961	90	104.912	90
HUJKIG02	$P2_1/n$	100	8.2732	14.113	13.787	90	104.987	90
CUBQEV	$P2_1/n$	295	8.3834	14.101	14.734	90	104.68	90
BONRAY	$P2_1/n$	120	8.2641	14.0199	13.6468	90	105.073	90
WOLDOQ	$P2_1/n$	173	8.3436	14.0986	13.7754	90	104.868	90
LOBXAD	$P2_1/n$	123	8.3602	14.5133	13.9874	90	104.967	90
RARVIT	$P2_1/n$	120	8.4851	14.3395	13.9396	90	106.309	90
BONREC	$P2_1/n$	120	8.4381	14.3627	13.9568	90	106.42	90

[a] Temperature of X-ray diffraction data collection.

Table S2. C–H3/H4/H5...Cl_{ax} interactions in isostructural octahedral [M(tpy)X_3] compounds, X = Cl or Br. The interactions are defined in Figure 3b in the manuscript.

REFCODE **Space Group**	**M**	**X**	**Within a chain:**[a] **C–H…X_{ax};** **C…X_{ax}/Å;** **∠C–H3/3'…X_{eq}/°**	**Between chains:**[b] **C–H…X_{ax};** **C…X_{ax}/Å;** **∠C–H3/3'…X_{eq}/°**	**Between sets of chains:**[c] **C–H…X_{ax};** **C…X_{ax}/Å;** **∠C–H3/3'…X_{eq}/°**	**Ref.**
TPYGAC01 $P2_1/n$	Ga	Cl	2.775, 2.797; 3.664(2), 3.717(2); 138.7, 142.1	2.759, 2.931, 2.592; 3.455(2), 3.545(2), 3.633(2); 123.4, 113.5, 157.3	2.687, 3.008; 3.424(2), 3.565(2); 124.6, 112.3	[**Error! Bookmark not defined.**]
TERPIN01 $P2_1/n$	In	Cl	2.717, 2.837; 3.625(3), 3.806(2); 140.7, 148.2	2.665, 3.082, 2.644; 3.431(2), 3.613(3), 3.632(3); 126.9, 111.9, 147.9	2.644, 3.297; 3.484(3), 3.780(3); 133.5, 108.1	[**Error! Bookmark not defined.**]
TERPIN02 $P2_1/n$	In	Cl	2.769, 2.880; 3.662(4), 3.836(3); 130.1, 146.6	2.680, 3.169, 2.682; 3.469(3), 3.701(4), 3.658(4); 128.9, 111.0, 148.9	2.671, 3.276; 3.490(4), 3.769(3); 131.6, 108.7	[**Error! Bookmark not defined.**]
KEZZOH $P2_1/n$	Sc	Cl	2.701, 2.854; 3.617(7), 3.804(6); 141.4, 145.8	2.662, 3.113, 2.639; 3.631(7), 3.641(7), 3.413(6); 127.5, 110.6, 147.9	2.629, 3.276; 3.458(6), 3.751(7); 132.4, 107.6	[**Error! Bookmark not defined.**]
PAXVAM $P2_1/n$	Mn	Cl	2.881, 2.864; 3.690(2), 3.805(2); 131.2, 144.7	2.725, 3.201, 2.701; 3.497(2), 3.723(3), 3.708(3); 127.6, 110.4, 153.5	2.785, 3.118; 3.511(2), 3.660(2); 124.0, 111.5	[**Error! Bookmark not defined.**]
HUJKIG $P2_1/n$	Fe	Cl	2.751, 2.807; 3.634(2), 3.730(2); 138.0, 142.5	2.700, 2.986, 2.590; 3.423(2), 3.563(2), 3.618(2); 123.4, 113.5, 157.3	2.680, 3.037; 3.426(2), 3.585(2); 125.3, 111.7	[**Error! Bookmark not defined.**]
HUJKIG02 $P2_1/n$	Fe	Cl	2.759, 2.812; 3.643(2), 3.737(2); 138.1, 142.7	2.709, 2.987, 2.596; 3.428(2), 3.564(2), 3.625(2); 123.1, 113.5, 157.5	2.687, 3.052; 3.435(2), 3.598(2); 125.5, 111.6	[**Error! Bookmark not defined.**]
CUBQEV $P2_1/n$	Ru	Cl	2.82, 3.04; 3.76(1), 3.76(1); 124.3, 144.6	2.82, 3.16, 2.79; 3.49(1), 3.63(1), 3.78(1); 119.6, 106.8, 152.2	2.74, 3.33; 3.58(1), 3.80(1); 133.6, 107.4	[**Error! Bookmark not defined.**]
BONRAY $P2_1/n$	Ir	Cl	2.767, 2.782; 3.698(4), 3.705(3); 143.3, 142.4	2.782, 2.878, 2.604; 3.452(3), 3.509(4), 3.638(4); 119.6, 117.0, 158.2	2.682, 2.992; 3.420(4), 3.559(4); 124.6, 112.8	[**Error! Bookmark not defined.**]
WOLDOQ $P2_1/n$	Os	Cl	2.787, 2.850; 3.691(4), 3.736(4); 140.2, 138.5	2.642, 3.064, 2.672; 3.465(4), 3.581(4), 3.665(4); 131.8, 109.7, 151.3	2.695, 3.089; 3.470(4), 3.584(4); 127.7, 108.4	[**Error! Bookmark not defined.**]
LOBXAD $P2_1/n$	Ga	Br	2.892, 2.970; 3.857(2), 3.838(3); 147.7, 136.9	2.806, 3.158, 2.682; 3.580(3), 3.743(3), 3.745(3); 127.9, 114.8, 165.0	2.843, 3.018; 3.575(3), 3.651(3); 124.5, 117.5	[**Error! Bookmark not defined.**]
RARVIT $P2_1/n$	Cr	Br	2.910, 2.927; 3.862(2), 3.828(3); 146.1, 140.3	2.805, 3.166, 2.731; 3.576(3), 3.750(3), 3.775(3); 127.7, 114.4, 160.6	2.833, 3.058; 3.573(3), 3.671(3); 125.1, 116.1	[**Error! Bookmark not defined.**]
BONREC $P2_1/n$	Ir	Br	2.94, 2.96; 3.87(2), 3.88(2); 142.0, 143.0	2.81, 3.13, 2.74; 3.58(2), 3.75(2), 3.79(2); 127.6, 116.2, 162.2	2.86, 2.99; 3.60(2), 3.66(2); 125.1, 119.9	[**Error! Bookmark not defined.**]

[a]Green hashed lines in Figure 3b/3c; [b]red hashed lines in Figure 3b/3c; [b]blue hashed lines in Figure 3b/3c.