Supplementary Information

Table S1 Labelling convention throughout the Figures, Tables and Text. Diverse labelling systems have been adopted in the original reports/CCDC archives of the structures listed in Table 1, which, for the sake of comparative description have been uniformly overlaid by our own system throughout the Figures, Tables and text. These correspond to those of the utilized original reports as follows; associated transformations are not included; the relevant associations of the anions to the ligands of cation 3 are given **bold** in parentheses. The 'polarity' of cation 1 (relative to the short axis) is opposite those of cations 2, 3.

M/X (/S) [Ref]	Cu/BF_4 ($Pna2_1$) [1]	Cu/BF_4 ($P2_12_12_1$) [6]	Cu/ClO_4 [2f]	Ag/BF_4 [3]	Ag/ClO_4*	Ag/PF_6*	Cu/PF_6/MeCN*,†
Metal atoms (Cu/Ag)							
1	1	2	2	1	3	1	1
2	3	1	1	2	2	2	3
3	2	2	3	2	1	3	2
Anions (central B/P/Cl atom)							
B	3 (B)	1 (B)	3 (Cl)	1 (B)	3 (Cl)	3 (P)	2 (P)
C	1	2	1	3	1	1	3
D	2	3	2	2	2	2	(2)
Coordinated acetonitrile ligands (denoted by N); relativities wrt *b* are shown as U,D							
1A	12	7	8	4	321	131	13
1B	9	6	5	3	341	121	11
1C	11	5	6	2	331	141	12
1D	10	8	7	1	311	111	14
2A	1	10	11	10	221	231	24
2B	3	11	12	11	211	221	22
2C	2	12	10	9	241	241	21
2D	4	9	9	12	231	211	23
3A	6	3	3	7	111	321	32
3B	8(**3**)	1(**3**)	1(**2**)	5(**1**)	121(**3**)	341(**3**)	31(**2**)
3C	7(**2**)	2(**1**)	4(**1**)	8(**3**)	141(**1**)	331(**1**)	33(**3**)
3D	5(**1**)	4(**2**)	1(**3**)	6(**2**)	131(**2**)	311(**2**)	34(**1**)

*This work; †the third cation here does not overlay the B ligand in projection down the short axis, but is displaced so as to accommodate the additional solvent molecule, and thus lies between cations 2 and 3 (Figs. 1(d), 3(iii)).

Table S2. Approaches within the clusters (C-H...N < 2.85 Å; C-H...M < 3.25 Å). For the published structures, labelling corresponds to those of the CCDC cif files.

A…B	d(A…B) / Å	Transformation (B)
$[Cu(NCMe)_4][BF_4]$ (*Pna*2_1)		
N(3)...H(19)	2.80	-
N(4)...H(19)	2.69	-
N(4)...H(28)	2.78	1–x, 1–y, ½+z
N(6)...H(27)	2.64	1–x, 1–y, ½+z
Cu(1)...H(19)	3.20	-
Cu(2)...H(21)	3.20	1–x, 1–y, –½+z
Cu(3)...H(27)	3.00	1–x,1 –y, ½+z
$[Cu(NCMe)_4][BF_4]$ ($P2_12_12_1$)		
N(3)…H(18)	2.64	1–x, ½+y, ½–z
N(4)...H(32)	2.79	-
N(9)...H(4)	2.79	-
Cu(1)..H(18)	3.22	½–x, 1+y, ½–z
Cu(2)...H(6)	3.06	1–x, –½+y, ½–z
$[Cu(NCMe)_4][ClO_4]$		
N(3)...H(13)	2.67	-
Cu(1)...H(13)	3.13	-
Cu(2)...H(10)	2.98	-
$[Ag(NCMe)_4][BF_4]$		
N(5)...H(32)	2.83	–½+x, ½–y, z
N(7)...H(7)	2.69	–x, 1–y, –½+z
N(12)...H(23)	2.82	½+x, ½–y, z
Ag(1)...H(24)	3.21	-
$[Ag(NCMe)_4][ClO_4]$		
N(111)...H(34C)	2.67	½+x, 3/2–y, z
N(121)...H(21A)	2.79	3/2–x, –½+y, ½+z
N(231)...H(31B)	2.82	1–x, 1–y, –½+z
Ag(3)...H(14A)	3.09	–½+x, 3/2–y, z
$[Ag(NCMe)_4][PF_6]$		

N(111)...H(33C)	2.83	-
N(211)...H(33B)	2.78	-
N(221)...H(33B)	2.84	-
Ag(2)...H(33B)	2.94	-
$[Cu(NCMe)_4][PF_6](MeCN)$		
N(22)...H(36C)	2.65	2–x, ½+y, 3/2–z
Cu(1)...H(36B)	2.99	2–x, ½+y,3/2–z

Table S3. Approaches between clusters (C,N... C,N < 3.50 Å, C-H...N < 2.85 Å; C-H...M < 3.25 Å, H...H < 2.55 Å). For the published structures, labelling corresponds to those of the CCDC cif files.

A…B	**d(A…B) / Å**	**Transformation (B)**
$[Cu(NCMe)_4][BF_4]$ (*Pna*2_1)		
N(2)...C(23)	3.396(9)	x, –1+y, z
N(3)...C(23)	3.426(10)	x ,–1+y, z
N(9)...C(1)	3.433(9)	-
N(11)...C(1)	3.306(7)	-
N(11)...C(10)	3.363(8)	3/2–x, ½+y, ½+z
C(5)...C(23)	3.445(10)	x, –1+y, z
C(10)...C(21)	3.422(10)	3/2–x, –½+y, ½+z
N(2)...H(36)	2.81	x, 1+y, z
N(8)...H(8)	2.84	-
N(10)...H(20)	2.89	1-x, 1–y, ½+z
Cu(1)...H(23)	3.13	–½+x, ½–y, z
Cu(1)...H(36)	3.20	x, –1+y, z
Cu(2)...H(3)	3.08	-
$[Cu(NCMe)_4][BF_4]$ (*P*$2_1 2_1 2_1$)		
N(5)...C(19)	3.274(5)	-
N(6)...C(19)	3.424(5)	-
N(11)...C(13)	3.434(5)	–1+x, y, z
N(12)...C(13)	3.363(6)	–1+x, y, z
C(13)...C(21)	3.453(6)	1+x, y, z
N(3)...H(26)	2.61	½–x, 1–y, ½+z

N(5)...H(10)	2.74	½+x, ½–y, 1–z
Cu(1)...H(26)	3.02	½–x, 3/2–y, –z
Cu(2)...H(10)	3.03	½+x, ½–y,1–z
Cu(3)...H(3)	3.14	½–x, 1–y, –½+z
Cu(3)...H(20)	3.19	–1+x, y, z
H(23)...H(25)	2.44	–x, –½+y, ½–z

$[Cu(NCMe)_4][ClO_4]$

N(5)...C(21)	3.413(5)	1–x, 1–y, ½+z
N(6)...C(21)	3.305(4)	1–x, 1–y, ½+z
N(10)...C(15)	3.373(4)	1–x, –y, –½+z
N(12)...C(15)	3.416(5)	1–x, –y, –½+z
C(15)...C(23)	3.457(5)	1–x, –y, –½+z
N(2)...H(26)	2.84	½+x, ½–y, z
N(6)... H(5)	2.64	–½+x, ½–y, z
N(7)... H(5)	2.73	–½+x, ½–y, z
Cu(1)...H(26)	3.20	½+x, ½–y, z
Cu(2)...H(5)	2.94	–½+x, ½–y, z
Cu(2)...H(33)	3.04	1–x, 1–y, ½+z
Cu(3)...H(22)	3.14	1–x, –y, –½+z
Cu(3)...H(2)	3.19	–½+x, ½–y, z

$[Ag(NCMe)_4][BF_4]$

N(2)...N(10)	3.467(4)	–½+x, ½–y, z
N(2)…C(19)	3.324(4)	–½+x, ½–y, z
N(7)…C(4)	3.446(5)	-
N(9) ...C(7)	3.362(4)	½+x, 3/2–y, z
N(11)…C(7)	3.495(4)	–½+z, 3/2–y, z
N(12)…C(16)	3.421(4)	½+x, ½–y, z
N(5)…H(21)	2.86	x, –1+y, z
N(7)…H(35)	2.80	-
Ag(1)...H(30)	3.13	
Ag(3)...H(12)	3.23	
Ag(3)...H(15)	3.15	

$[Ag(NCMe)_4][ClO_4]$

N(211)...C(321)	3.478(4)	x, –1+y, z
N(241) ...C(321)	3.335(3)	x, –1+y, z

N(331) ...C(221)	3.299(3)	-
N(111)...H(23C)	2.76	1–x, 1–y, ½+z
N(111)...H(33A)	2.85	3/2–x, ½+y, ½+z
N(241)...H(12C)	2.82	1–x, 1–y, –½+z
N(331)...H(13A)	2.67	-
Ag(2)...H(12B)	3.23	1–x, 1–y, –½+z
Ag(2)...H(32C)	3.15	x, –1+y, z
Ag(3)...H(13A)	2.97	-
Ag(3)...H(22A)	3.12	-

$[Ag(NCMe)_4][PF_6]$

N(121)...C(231)	3.391(4)	–x, –½+y, ½–z
N(141)...C(231)	3.346(4)	–x, –½+y, ½–z
N(141)...C(312)	3.404(5)	½–x, 1–y, –½-z
N(221)...C(131)	3.392(4)	1–x, ½+y, ½–z
N(241)...C(131)	3.305(4)	1–x, ½+y, ½–z
N(241)...H(13A)	2.83	1–x, ½+y, ½–z
N(241)...H(34B)	2.83	½–x, 1–y, –½+z
Ag(1)...H(23A)	3.19	–x, –½+y, ½–z
Ag(1)...H(31C)	3.03	½–x, 1–y, –½+z
Ag(2)...H(13A)	3.06	1–x, ½+y, ½–z
H(12B)...H(34A)	2.54	–½+x, ½–y, 1–z
H(22A)...H(32B)	2.48	1+x, y, z

$[Cu(NCMe)_4][PF_6]$ (MeCN)

N(22)...C(27)	3.324(3)	½+x, 3/2–y, 1–z
C(17)...C(25)	3.493(3)	-
C(14)...C(37)	3.447(3)	–½+x, 3/2–y, 2–z
C(23)...C(27)	3.307(3)	½+x, 3/2–y, 1–z
N(22)...H(36C)	2.65	2–x, ½+y, 3/2–z
N(32)...H(14B)	2.83	½+x, 3/2–y, 2–z
N(34)...H(34A)	2.89	–1+x, y, z
Cu(2)...H(28B)	3.06	½+x, 3/2–y, 1–z

Interactions with the solvent:

N(41)...C(34)	3.427(3)	x–1, y, z
N(41)...C(37)	3.417(3)	x–1, y, z
N(51)...C(11)	3.468(3)	2–x, –½+y, 3/2–z

N(51)...C(62)	3.490(4)	2–x, –½+y, 3/2–z
N(61)...C(13)	3.244(3)	-
N(61)...C(21)	3.310(3)	2–x, –½+y, 3/2–z
N(41)...H(14B)	2.77	–½+x, 3/2–y, 2–z
N(41)...H(32A)	2.85	–½+x,3 /2–y, 2–z
N(51)...H(26C)	2.66	-

Table S4. Hydrogen bonds between clusters and anions (d(H...O,F) < 2.6 Å). For the published structures, labelling corresponds to those of the CCDC cif files.

C-H...O,F	d(H…O,F) / Å	d(C…O,F) / Å	Transformation (O,F)
$[Cu(NCMe)_4][BF_4]$ (*Pna*2_1)			
C(2)--H(1)..F(8)	2.55	3.493(10)	-
C(2) --H(2) ..F(11)	2.48	3.311(9)	–½+x, 3/2–y, z
C(4) --H(5) ..F(3)	2.40	3.324(9)	-
C(4) --H(6) ..F(9)	2.45	3.330(11)	–½+x, ½–y, z
C(8) --H(11) ..F(11)	2.59	3.364(10)	–½+x, ½–y, z
C(10)--H(13)..F(4)	2.53	3.426(10)	1–x, –y, ½+z
C(10)--H(14)..F(10)	2.45	3.273(9)	3/2–x, –½+y, ½+z
C(10)--H(14)..F(9)	2.58	3.489(9)	3/2–x, –½+y, ½+z
C(12) --H(18) ..F(10)	2.57	3.389(12)	-
C(14)--H(20)..F(5)	2.57	3.292(8)	-
C(24)--H(34)..F(7)	2.54	3.425(12)	1–x, 2–y, –½+z
$[Cu(NCMe)_4][BF_4]$ (*P*$2_1$$2_1$$2_1$)			
C(6) --H(9)..F(6)	2.57	3.341(7)	-
C(8) --H(10)..F(8)	2.57	3.436(2)	–½+x, ½–y, 1–z
C(8) --H(11)..F(6)	2.36	3.255(5)	–½+x, ½–y, 1–z
C(8) --H(12)..F(8)	2.45	3.426(6)	–1+x, y, z
C(14)--H(19)..F(5)	2.42	3.359(6)	½+x, ½–y, 1–z
C(16)--H(23)..F(5)	2.37	3.119(6)	–½+x, ½–y, 1–z
C(20)--H(28)..F(2)	2.56	3.409(5)	-
C(20)--H(29)..F(9)	2.53	3.327(6)	3/2–x, 1–y, –½+z
C(22)-H(31)...F(3)	2.56	3.273(1)	–1+x, y, z
C(24)--H(34)..F(11)	2.41	3.195(6)	1–x, –½+y, ½–z
C(24)--H(35)..F(12)	2.48	3.349(6)	½–x, 1–y, –½+z

$[Cu(NCMe)_4][ClO_4]$

C(2)-H(3)..O(6)	2.60	3.277(5)	-
C(4)-H(4)..O(5)	2.47	3.339(5)	3/2–x, –½+y, ½+z
C(4)-H(6)..O(9)	2.51	3.444(6)	3/2–x, –½+y, ½+z
C(6)-H(9)..O(5)	2.59	3.392(7)	-
C(8)-H(12)..O(2)	2.60	3.216(5)	-
C(10)-H(14)..O(7)	2.57	3.403(5)	3/2–x, –½+y, ½+z
C(16)-H(23)..O(1)	2.59	3.464(6)	x, –1+y, z
C(18)-H(25)..O(8)	2.51	3.348(6)	–½+x, ½–y, z
C(20)-H(29)..O(4)	2.43	3.254(6)	1–x, 1–y, –½+z
C(20)-H(30)..O(10)	2.35	3.254(6)	–½+x, ½–y, z
C(22)-H(31)..O(3)	2.56	3.506(5)	-
C(22)-H(32)..O(8)	2.55	3.385(5)	–½+x, 3/2–y, z
C(24)-H(36)..O(9)	2.57	3.413(6)	-

$[Ag(NCMe)_4][BF_4]$

C(2)-H(2)..F(8)	2.52	3.207(4)	½–x, –½+y, –½+z
C(8)-H(10)..F(8)	2.47	3.352(5)	½–x, ½+y, –½+z
C(12)-H(16)..F(7)	2.57	3.466(6)	x, –1+y, –1+z
C(12)-H(18)..F(4)	2.50	3.292(4)	x, y, –1+z
C(18)-H(25)..F(1)	2.52	3.377(4)	½–x, ½+y, –½+z
C(18)-H(27)..F(6)	2.32	3.268(5)	½–x, –½+y, –½+z
C(20)-H(28)..F(10)	2.56	3.436(5)	x, –1+y, z

$[Ag(NCMe)_4](ClO_4)$

C(132)-H(13B)..O(24)	2.52	3.473(4)	-
C(132)-H(13C)..O(32)	2.44	3.340(3)	-
C(242)-H(24A)..O(34)	2.52	3.349(4)	–½+x, ½–y, z
C(242)-H(24B)..O(22)	2.31	3.250(4)	–½+x, ½–y, z
C(312)-H(31A)..O(12)	2.57	3.480(4)	–½+x, ½–y, z
C(322)-H(32A)..O(23)	2.57	3.371(4)	x, 1+y, z

$[Ag(NCMe)_4][PF_6]$ (disordered anions, all components)

C(122)-H(12C)..F(13')	2.44	3.269(9)	-
C(132)-H(13B)..F(16')	2.30	3.244(11)	1+x, y, z
C(132)-H(13C)..F(26')	2.40	3.297(9)	1+x, y, z
C(142)-H(14A)..F(24')	2.52	3.298(9)	½+x, ½–y, –z

C(142)-H(14B)..F(23)	2.51	3.192(8)	-
C(142)-H(14C)..F(12)	2.54	3.267(6)	–x, –½+y, ½–z
C(211)-H(21B)..F(36)	2.40	3.386(3)	1+x, y, z
C(222)-H(22B)..F(23')	2.36	3.318(11)	–x, ½+y, ½–z
C(242)-H(24A)..F(32)	2.39	3.354(3)	½+x, 3/2–y, –z
C(242)-H(24C)..F(11)	2.50	3.295(6)	–x, ½+y, ½–z
C(312)-H(31A)..F(24)	2.59	3.399(6)	–½–x, 1–y, ½+z
C(312)-H(31B)..F(24)	2.59	3.071(7)	–x, ½+y, ½–z
C(312)-H(31B)..F(26')	2.41	3.144(8)	½–x, 1–y, ½+z
C(322)-H(32B)..F(14)	2.42	3.091(6)	-
C(322)-H(32C)..F(25')	2.47	3.168(12)	–½–x, 1–y, ½+z
C(342)-H(34A)..F(33)	2.55	3.533(7)	–x, –½+y, ½–z
C(342)-H(34A)..F(34)	2.50	3.205(9)	–x, –½+y, ½-z
C(342)-H(34A)..F(35')	2.54	3.196(10)	–x, –½+y, ½–z
C(342)-H(34A)..F(36')	2.35	3.202(11)	–x, –½+y, ½–z
C(342)-H(34B)..F(31)	2.41	3.347(7)	–½–x, 1–y, ½+z
C(342)-H(34C)..F(35)	2.45	3.235(6)	½–x, 1–y, ½+z

$[Cu(NCMe)_4][PF_6](MeCN)$ (disordered anions; major components)

C(12)--H(12C)..F(31)	2.53	3.416(3)	-
C(14)--H(14A)..F(15A)	2.59	3.553(5)	1–x, ½+y, 3/2–z
C(14)--H(14C)..F(24A)	2.37	3.191(4)	-
C(16)--H(16A)..F(16A)	2.35	3.330(5)	2–x, ½+y, 3/2–z
C(16)--H(16B)..F(36A)	2.24	3.189(4)	1+x, y, z
C(16)--H(16C)..F(24A)	2.52	3.482(4)	1+x, y, z
C(18)--H(18B)..F(25A)	2.49	3.264(4)	-
C(22)--H(22A)..F(15A)	2.60	3.550(5)	1+x, y, z
C(24)--H(24A)..F(34A)	2.54	3.060(5)	1+x, y, z
C(28)--H(28A)..F(11)	2.39	3.326(3)	-
C(28)--H(28C)..F(32)	2.54	3.498(3)	-
C(28)--H(28A)..F(35A)	2.60	3.127(4)	-
C(34)--H(34B)..F(22)	2.42	3.306(4)	1+x, y, z
C(34)--H(34C)..F31)	2.59	3.194(3)	2–x, –½+y, 3/2–z
C(38)--H(38C)..F(21)	2.58	3.529(3)	½+x, 3/2–y, 2–z
Interactions with the solvent:			
C(42)--H(42B)..F(23A)	2.48	3.266(5)	½+x, 3/2–y, 2–z
C(62)--H(62A)..F(16A)	2.53	3.320(4)	1–x, ½+y, 3/2–z

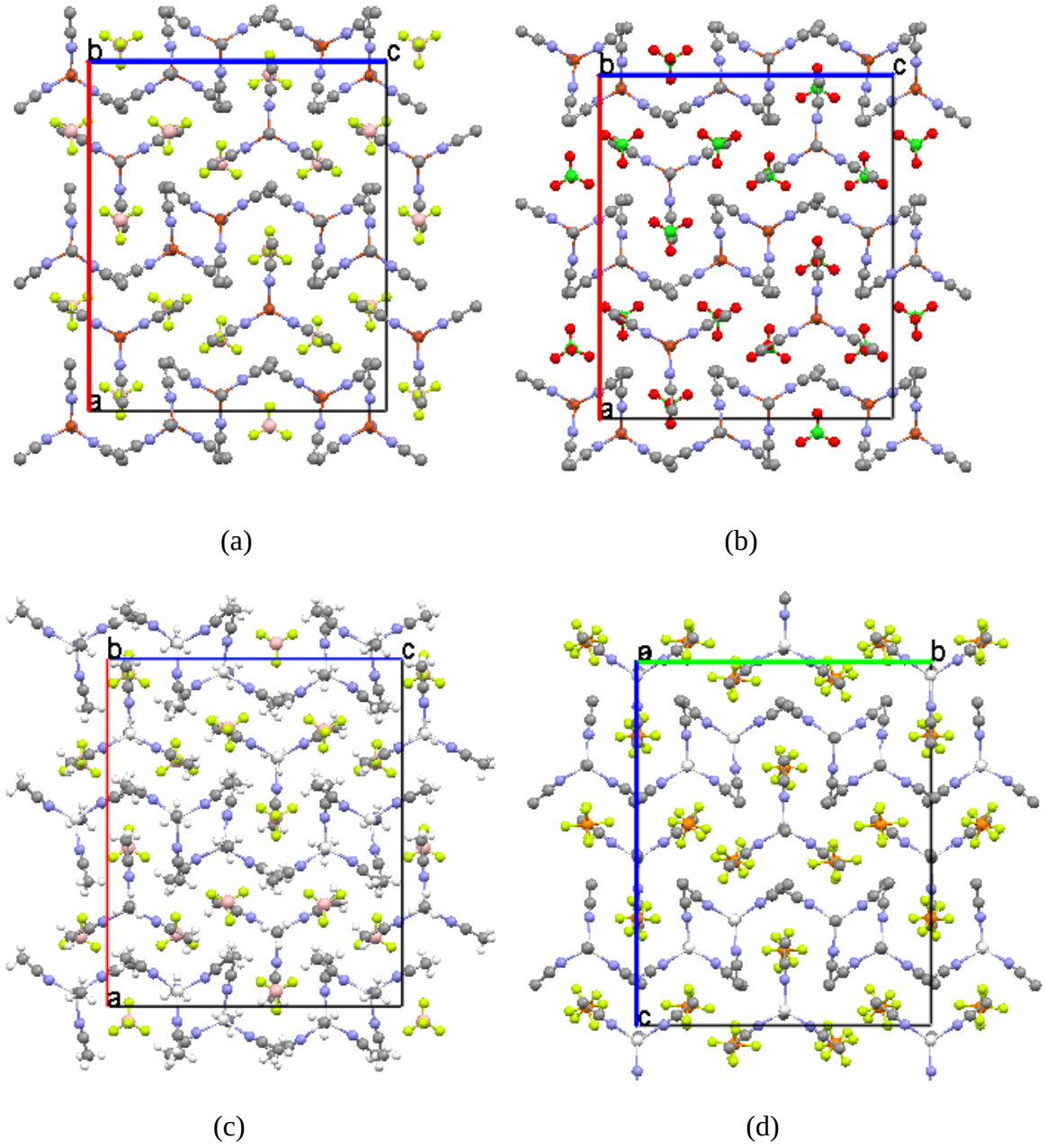


Fig. S1. Crystal packing diagrams (red, green and blue lines indicate *a*, *b*, *c* cell axes respectively) projected down the shortest axis (*ca* 8.3-8.6 Å in all cases). (a) $[Cu(NCMe)_4][BF_4]$ ($Pna2_1$), (b) $[Cu(NCMe)_4][ClO_4]$ ($Pna2_1$), (c) $[Ag(NCMe)_4][BF_4]$ ($Pna2_1$), (d) $[Ag(NCMe)_4][PF_6]$ ($P2_12_12_1$).

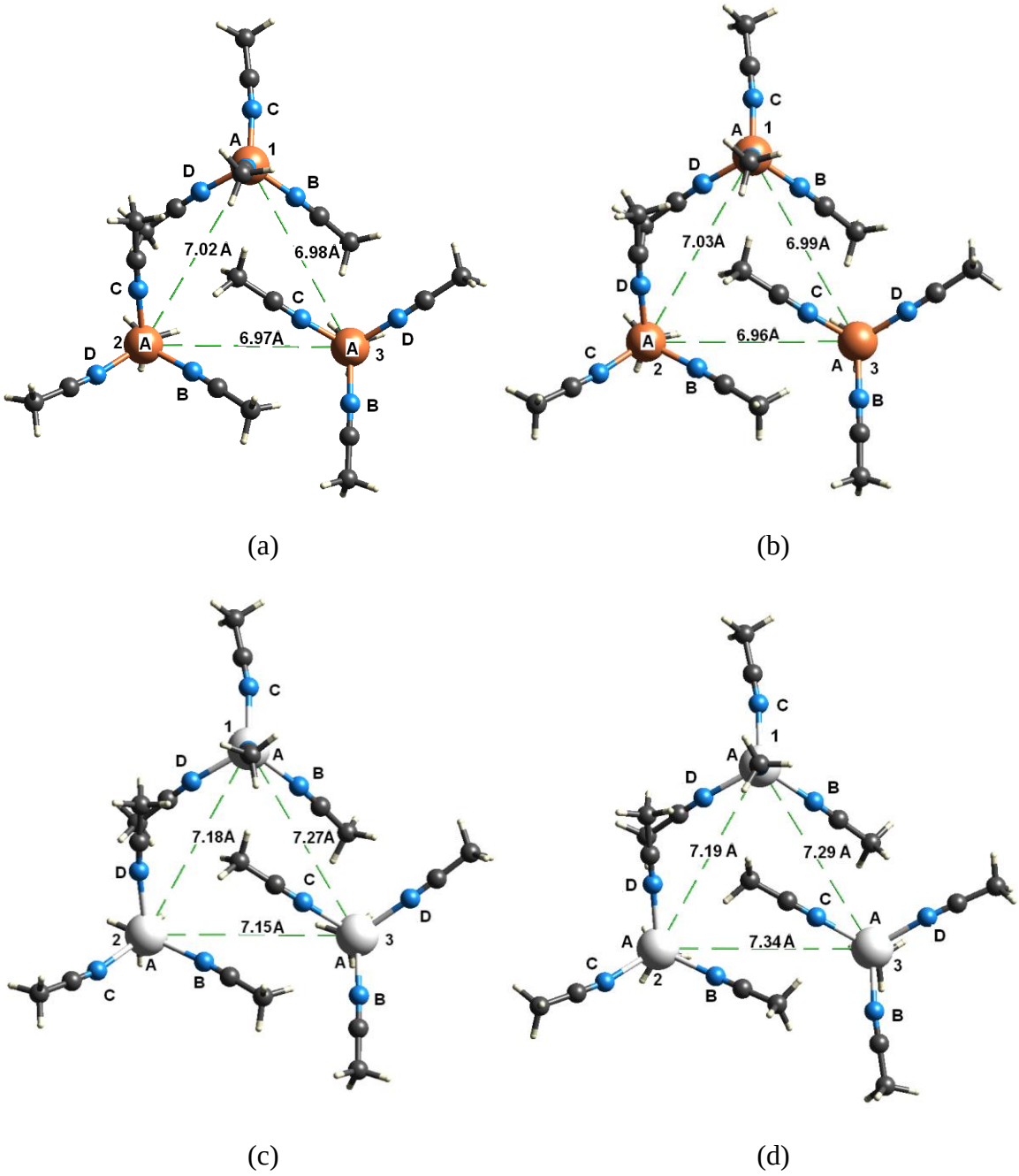
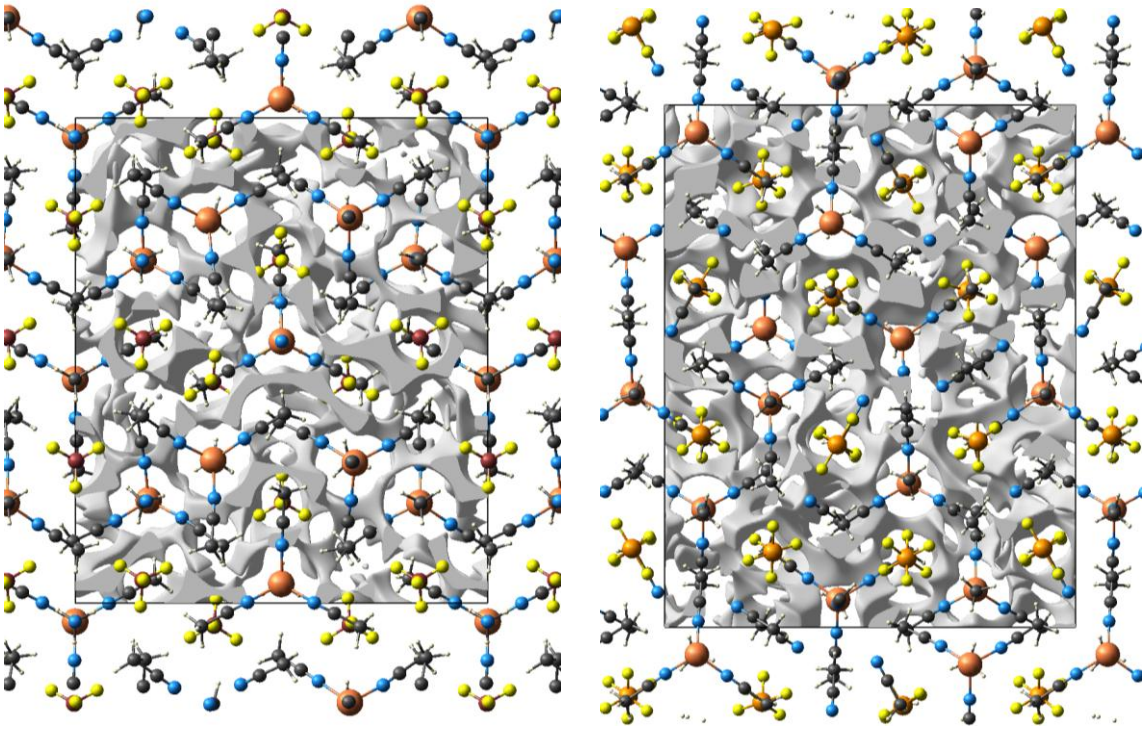
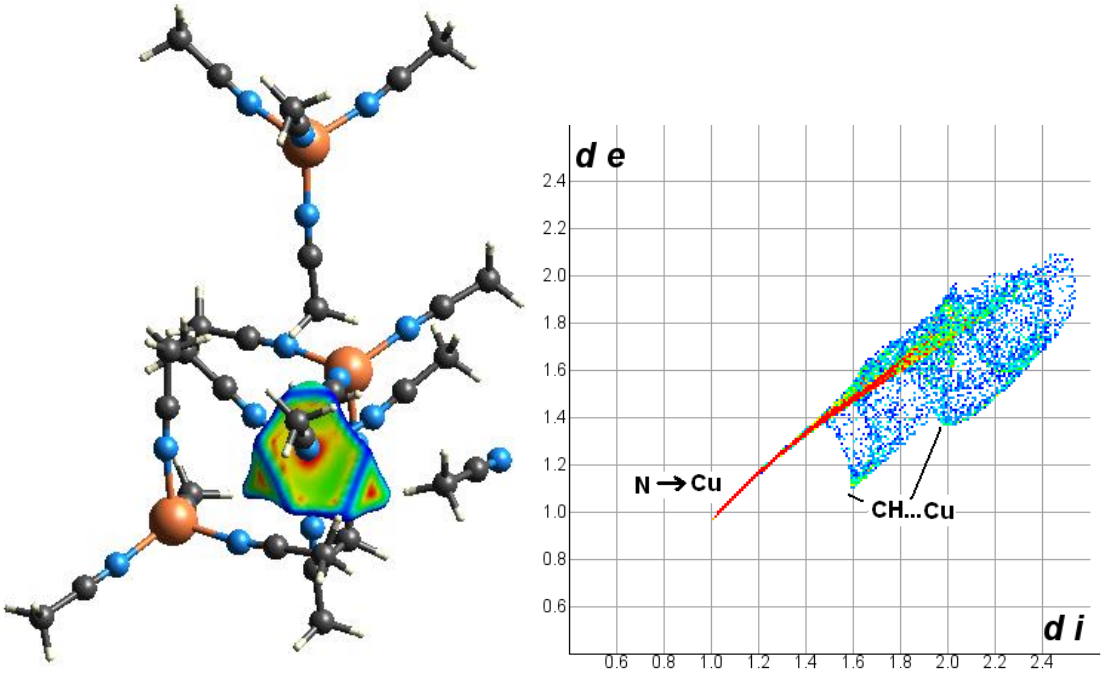


Fig. S2. Relevant clusters of three independent cations (suitably transformed) showing intermetallic distances (see also Table 2), (For labelling, see caption of Fig. 2.), for (a) $[Cu(NCMe)_4][BF_4]$ ($Pna2_1$), (b) $[Cu(NCMe)_4][ClO_4]$ ($Pna2_1$), (c) $[Ag(NCMe)_4][BF_4]$ ($Pna2_1$), (d) $[Ag(NCMe)_4][PF_6]$ ($P2_12_12_1$).



(a) (b)

Fig. S3 The crystal voids in the unit cells of (a) $Cu(NCMe)_4][BF_4]$ ($P2_12_12_1$) and (b) $Cu(NCMe)_4][PF_6](MeCN)$ projected down the short axes. The percentages of voids in the unit cells (all cases) are given in Table 2.



(a) (b)

Fig. S4 (a) Atomic Hirshfeld surface of Cu3 in $[Cu(NCMe)_4][PF_6](MeCN)$ ($P2_12_12_1$) with the descriptor 'curvedness' mapped onto the surface. (b) Corresponding fingerprint plot for Cu3.

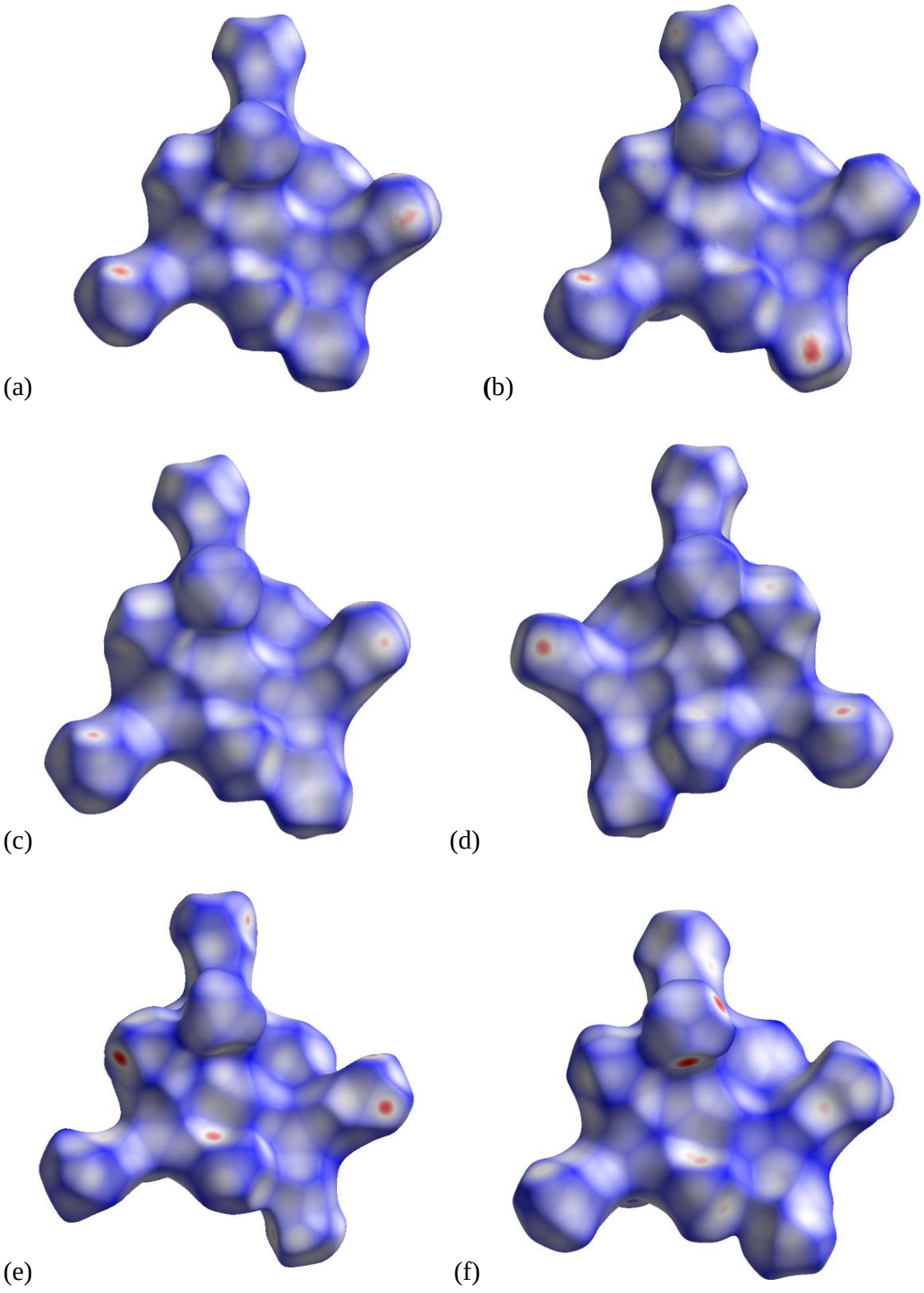


Fig. S5. Hirshfeld Surfaces with the descriptor 'd_{norm}' mapped onto them for the trinuclear cationic arrays of (a) $[Cu(NCMe)_4][BF_4]$ ($Pna2_1$), (b) $[Cu(NCMe)_4][BF_4]$ ($P2_12_12_1$), (c) $[Ag(NCMe)_4][BF_4]$ ($Pna2_1$), (d) $[Ag(NCMe)_4][ClO_4]$ ($Pna2_1$), (e) $[Ag(NCMe)_4][PF_6]$ ($P2_12_12_1$) and (f) $[Cu(NCMe)_4][PF_6](MeCN)$ ($P2_12_12_1$).