SUPLEMENTARY INFORMATION

Structural and Physico-Chemical Characterization of Hybrid Materials Based on Globular Quinuclidinum Cations Derivatives and Tetrachloridocobaltate(II) Anions

Cantia Belloso-Casuso,[a,b,c] Imanol de Pedro,[*a] Laura Canadillas-Delgado,[b] Garikoitz Beobide,[d,e] Manuel Sánchez-Andújar,[f] Javier Gárcia Ben,[f] Julian Walker,[g] Palmerina González Izquierdo, [a] Israel Cano,[h] Jesus Rodríguez Fernández [a] and Oscar Fabelo[*b]

[a] CITIMAC, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander.

[b] Institut Laue-Langevin, BP 156X, F-38042 Grenoble Cedex, France.

[c] Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), 28049 Madrid, Spain

[d] Departamento de Química Organica e Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, E-48080, Bilbao, Spain.

[e] Basque Ctr Mat Applicat & Nanostruct, BCMat, UPV EHU Sci Pk, Leioa 48940, Spain.

[f] QuiMolMat Group, Department of Chemistry, Faculty of Science and Advanced Scientific Research Center (CICA), Zapateira, University of A Coruna, 15071 A Coruna, Spain.

[g] Department of Materials Science and Engineering, Norwegian University of Science and Technology, NO-7491Trondheim, Norway

[h] Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040 Madrid, Spain

Content

Scheme 1: View of the chemical structure of the organic. Color codes: brown, carbon; red, oxygen; light blue, nitrogen; pink, hydrogen,

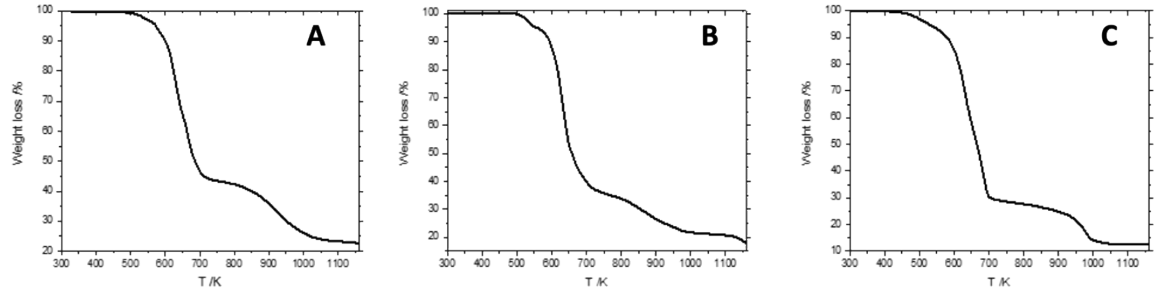

Fig. S1. TGA analysis for compounds **A**, **B** and **C.**

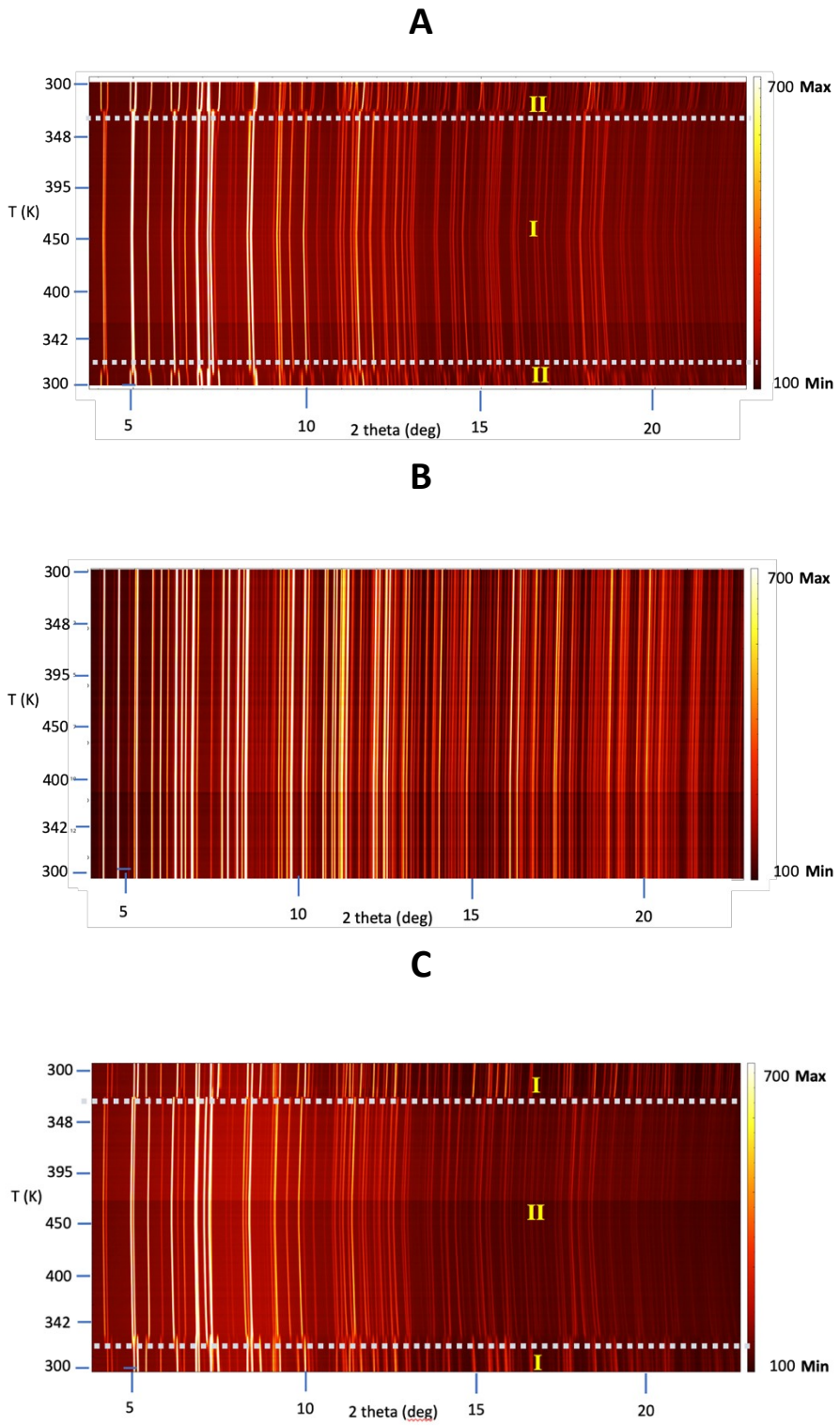

Fig. S2. 2D view of SC-XRPD data of compound **A, B** and **C** from RT to 450 K upon a heating cooling mode showing the crystal phase transitions from phase **II** to **I**.

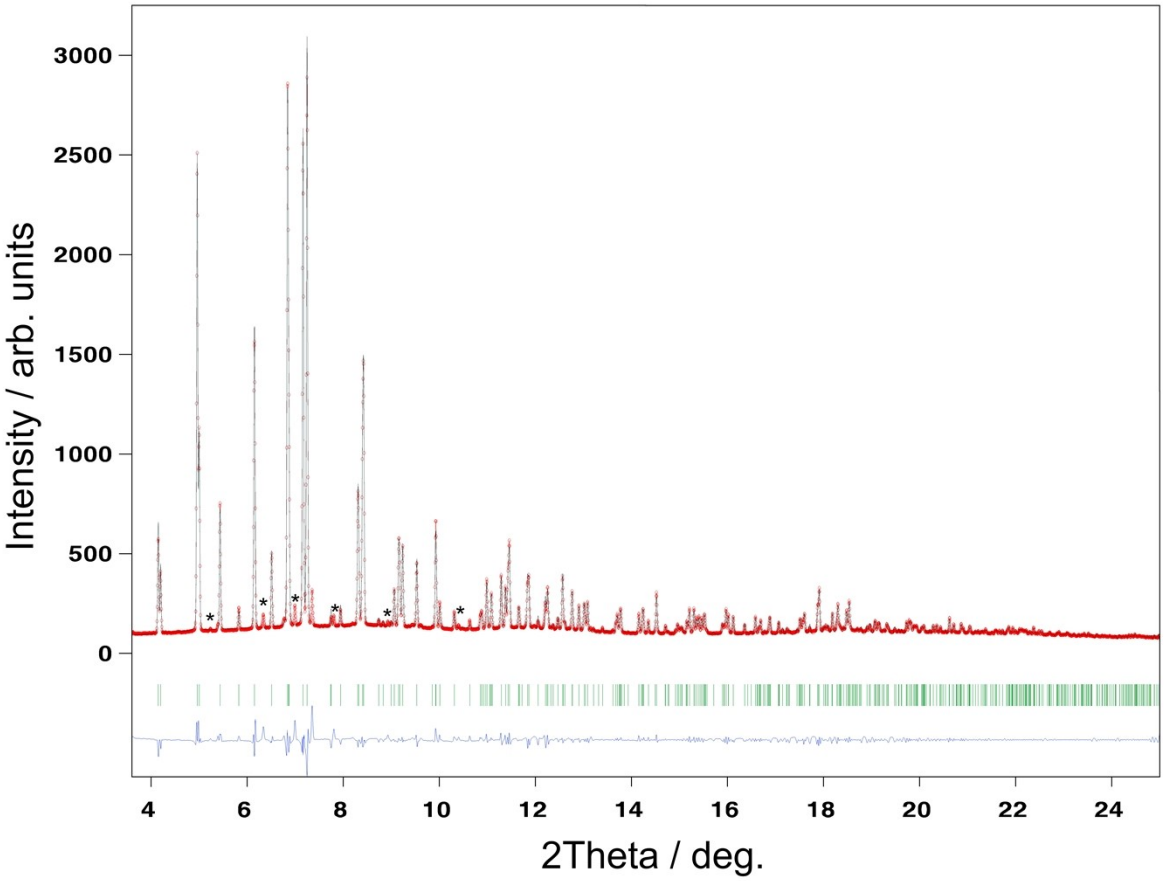

Fig. S3. Rietveld refinement of compound **A** at 400 K. The main impurity peaks are highlighted with an asterisk symbol.

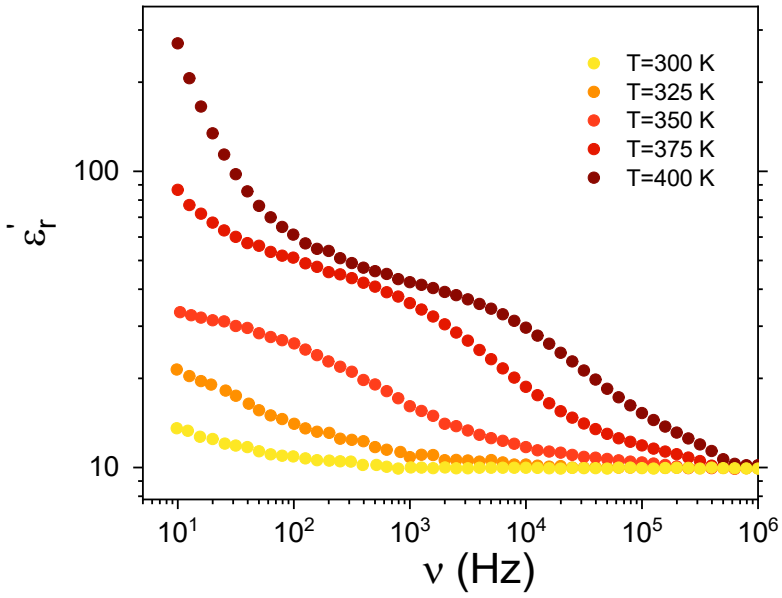

Fig. S4 Frequency dependence of the ε'_r values of **B** at different temperatures

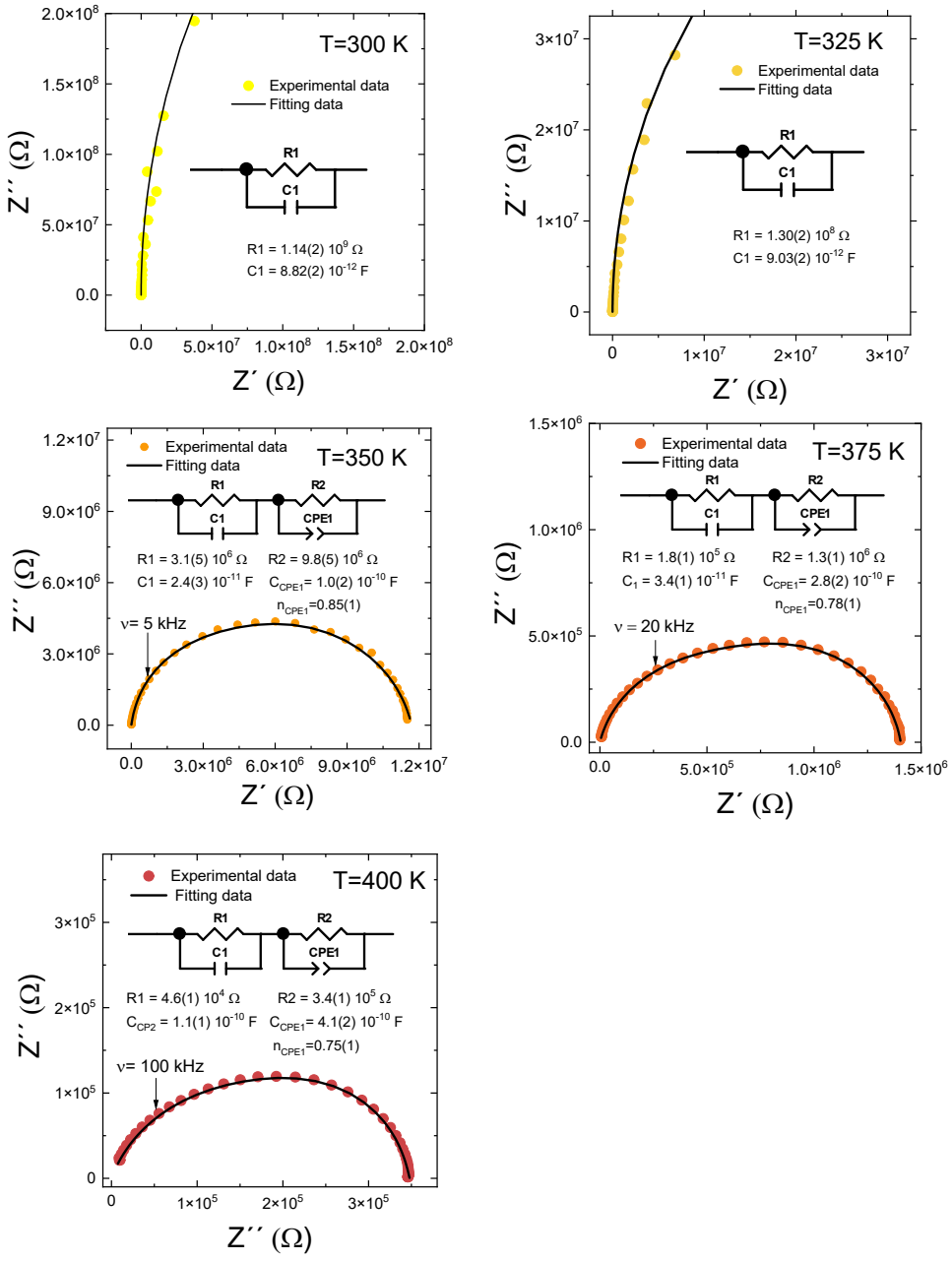

Fig. S5. Impedance complex plane plots and equivalent circuits obtained for compound **B** at different temperatures.

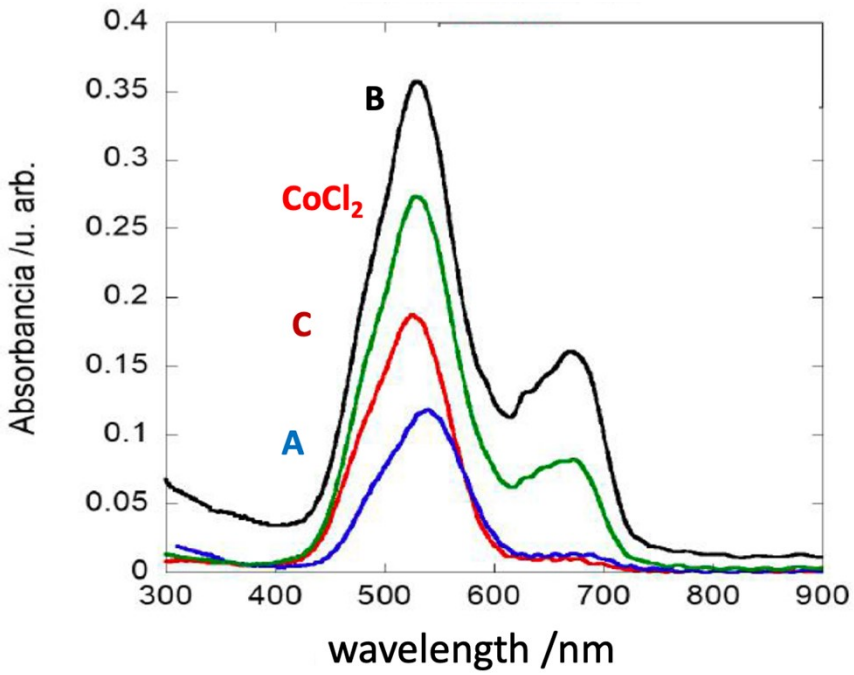

Fig.S6. UV spectrum of **A**, **B**, **C** and $CoCl_2$ compounds

Table S1. Crystallographic data and refinement details of SCXRD of **A** at 400 K.

	A
Cryst. Syst.	orthorhombic
Space group	*P n m a*
a (Å)	12.69091(6)
b (Å)	9.63357(4)
c (Å)	16.43013(8)
α(°)	90
β (°)	90
γ(°)	90
V (Å^3)	2008.728(17)
Z	4
λ (Å)	0.601840
Temperature (K)	400(2)
Number of points	4994
2theta range min	0.03400
2theta range max	26.14904
R factor (%)	4.8311
wR factor (%)	6.7023
Number reflns	623
Number parameters	74

Table S2. Crystallographic data and refinement details of SCXRD of compounds **A**, **B** and **C** at 100 K.

	A	**B**	**C**
Formula	$C_{14}H_{28}N_2CoCl_4$	$C_7H_{16}N_2CoCl_4$	$C_{42}H_{84}N_6O_6Co_3Cl_{12}$
M (g mol^{-1})	425.11	328.95	1371.34
Cryst. Syst.	monoclinic	monoclinic	orthorhombic
Space group	*P* $2_1/n$	*P* c	*P* 2_1 2_1 2_1
a (Å)	9.4413(3)	6.4979(4)	9.5314(12)
b (Å)	12.1521(5)	16.0144(10)	15.705(2)
c (Å)	16.2434(7)	12.9534(8)	38.490(5)
α(º)	90	90	90
β (º)	93.5690(10)	91.907(2)	90
γ(º)	90	90	90
V (Å^3)	1860.02(13)	1347.18(14)	5761.6(12)
Z	4	4	4
ρ_{calc} (g·cm^{-3})	1.518	1.711	1.581
Colour	purple	purple	purple
F(000)	884	708	2844
μ (cm^{-1})	7.70	10.44	122.03
θ range	1.65 to 23.63º	1.00 to 23.78	2.30 to 72.64
HKL range	-13<=h<=13, -17<=k<=17, -22<=l<=23	-9<=h<=9, -23<=k<=23, -18<=l<=18	-11<=h<=11, -19<=k<=19, -47<=l<=38
Meas./indep. refl.	18631/5664	27640/8005	50126/11022
$R_{eqv.}$	0.0723	0.01134	0.0841
Obs. refl. [I > 2σ(I)]	4430	4125	9067
R, Rw	0.0434, 0.0989	0.0650, 0.0296	0.0968, 0.2780
R, Rw(all)	0.0602, 0.1095	0.0645, 0.9286	0.1156, 0.3031
of (S)	1.062	1.325	1.151
Parameters	190	253	623
Máx./min. $\Delta\rho$ (e Å^{-3})	0.491/-0.612	1.560/-0.484	1.746/-0.923
λ (Å)	0.56086	0.56086	1.54178
Temperature (K)	100(2)	100(2)	100(2)

Table S3. Main bond lengths (Å) and angles (º) obtained from crystallographic data and refinement details of SCXRD of **A**, **B** and **C** compounds at 300 K.

Compound A Bond lengths (Å)	
Co1-Cl1	2.2546(16)
Co1-Cl3	2.2803(15)
Co1-Cl4	2.2673(17)
Co1-Cl2	2.2810(16)

Compound A Bond angles (°)	
Cl1-Co1-Cl4	113.26(7)
Cl4-Co1-Cl3	106.81(6)
Cl4-Co1-Cl2	112.86(7)
Cl1-Co1-Cl3	110.31(7)
Cl1-Co1-Cl2	105.75(7)
Cl3-Co1-Cl2	107.75(6)

Compound B Bond lengths (Å)	
Co1-Cl1	2.274(2)
Co1-Cl2	2.2784(16)
Co1-Cl3	2.2865(3)
Co1-Cl4	2.260(3)
Co2-Cl5	2.287(3)
Co2-Cl6	2.274(2)
Co2-Cl7	2.2741(16)
Co2-Cl8	2.259(3)

Compound B Bond angles (°)	
Cl1-Co1-Cl2	108.13(7)
Cl1-Co1-Cl3	111.71(9)
Cl1-Co1-Cl4	103.38(9)
Cl2-Co1-Cl3	114.96(8)
Cl2-Co1-Cl4	107.01(7)
Cl3-Co1-Cl4	111.67(8)
Cl5-Co2-Cl6	111.24(10)
Cl5-Co2-Cl7	109.08(8)
Cl5-Co2-Cl8	104.41(9)
Cl6-Co2-Cl7	106.95(8)
Cl6-Co2-Cl8	110.31(7)
Cl7-Co2-Cl8	114.79(6)

Compound C Bond lengths (Å)	
Co1-Cl2	2.2576(13)
Co1-Cl1	2.2857(19)
Co1-Cl3	2.2640(13)
Co1-Cl4	2.3000(19)

Compound C Bond angles (°)	
Cl2-Co1-Cl3	113.94(5)
Cl3-Co1-Cl1	108.06(8)
Cl3-Co1-Cl4	111.67(8)
Cl2-Co1-Cl1	110.61(8)
Cl2-Co1-Cl4	105.70(8)
Cl1-Co1-Cl4	106.64(7)

Table S4. Main bond lengths (Å) and angles (º) obtained from crystallographic data and refinement details of SCXRD of **A**, **B** and **C** compounds at 100 K.

Compound A Bond lengths (Å)	
Co1-Cl1	2.2707(7)
Co1-Cl3	2.2785(7)
Co1-Cl2	2.2742(7)
Co1-Cl4	2.2901(7)

Compound A Bond angles (°)	
Cl1-Co1-Cl2	111.45(3)
Cl2-Co1-Cl3	105.91(3)
Cl2-Co1-Cl4	108.36(3)
Cl1-Co1-Cl3	113.87(3)
Cl1-Co1-Cl4	103.95(3)
Cl3-Co1-Cl4	113.31(3)

Compound B Bond lengths (Å)	
Co1-Cl1	2.280(3)
Co1-Cl2	2.2804(11)
Co1-Cl3	2.260(3)
Co1-Cl4	2.256(5)
Co2-Cl5	2.300(2)
Co2-Cl6	2.2765(11)
Co2-Cl7	2.275(4)
Co2-Cl8	2.276(3)

Cl6-Co2-Cl8	107.06(8)
Cl7-Co2-Cl8	114.79(6)

Compound B Bond angles (°)	
Cl1-Co1-Cl2	107.74(8)
Cl1-Co1-Cl3	112.07(14)
Cl1-Co1-Cl4	103.61(12)
Cl2-Co1-Cl3	106.61(8)
Cl2-Co1-Cl4	115.81(10)
Cl3-Co1-Cl4	111.67(8)
Cl5-Co2-Cl6	108.90(9)
Cl5-Co2-Cl7	112.12(19)
Cl5-Co2-Cl8	110.68(16)
Cl6-Co2-Cl7	110.28(14)

Compound C Bond lengths (Å)]			
Co1-Cl4	2.262(3)	Co1-Cl3	2.266(3)
Co1-Cl1	2.298(3)	Co1-Cl2	2.303(3)
Co2-Cl6	2.265(3)	Co2-Cl7	2.261(3)
Co2-Cl5	2.294(3)	Co2-Cl8	2.314(3)
Co3-Cl12	2.261(3)	Co3-Cl11	2.260(3)
Co3-Cl10	2.288(3)	Co3-Cl9	2.312(3)

Compound C Bond angles (°)			
Cl4-Co1-Cl3	113.88(11)	Cl4-Co1-Cl1	109.46(10)
Cl3-Co1-Cl1	109.16(11)	Cl4-Co1-Cl2	106.57(11)
Cl3-Co1-Cl2	111.06(11)	Cl1-Co1-Cl2	106.42(11)
Cl6-Co2-Cl7	113.37(11)	Cl6-Co2-Cl5	108.00(12)
Cl7-Co2-Cl5	110.36(12)	Cl6-Co2-Cl8	113.62(11)
Cl7-Co2-Cl8	105.67(11)	Cl5-Co2-Cl8	105.55(12)
Cl12-Co3-Cl11	114.40(11)	Cl12-Co3-Cl9	111.86(11)
Cl11-Co3-Cl9	104.29(11)	Cl10-Co3-Cl9	107.13(12)

Table S5. Crystallographic data and refinement details of SCXRD of **C** compounds at 400 K.

	C
Formula	$C_{42}H_{83}N_6O_6Co_6Cl_{12}$
M (g mol^{-1})	1370.33
Cryst. Syst.	orthorhombic
Space group	*P n m a*
a (Å)	12.8461(13)
b (Å)	9.8389(9)
c (Å)	16.5685(18)
α(°)	90
β (°)	90
γ(°)	90
V (Å^3)	2094.1(4)
Z	4
ρ_{calc} (g·cm^{-3})	1.54178
Colour	
F(000)	2840
μ (cm^{-1})	335.74
θ range	4.36 to 43.93
HKL range	-9<=h<=11, -8<=k<=5, -12<=l<=14
Meas./indep. refl.	3290/822
$R_{eqv.}$	0.0554
Obs. refl. [I > 2σ(I)]	253
R, Rw	0.2051, 0.4573
R, Rw(all)	0.2599, 0.4828
Gof (S)	1.047
Parameters	40
Máx./min. $\Delta\rho$ (e Å^{-3})	0.558/-0.971
λ (Å)	1.54178
Temperature (K)	400(2)