CORA Cork Open Research Archive
Cartlann Taighde Oscailte Chorcaí

Title	Ligand design for long-range magnetic order in metal-organic frameworks
Authors	Tiana, Davide;Hendon, Christopher H.;Walsh, Aron
Publication date	2014-09-23
Original Citation	Tiana, D., Hendon, C. H. and Walsh, A. (2014) 'Ligand design for long-range magnetic order in metal-organic frameworks', Chemical Communications, 50(90), pp. 13990-13993. doi: 10.1039/c4cc06433j
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://pubs.rsc.org/en/content/articlepdf/2014/cc/c4cc06433j - 10.1039/c4cc06433j
Rights	© The Royal Society of Chemistry 2014. This article is licensed under a Creative Commons Attribution 3.0 Unported Licence - https://creativecommons.org/licenses/by/3.0/
Download date	2026-11-15 15:35:46
Item downloaded from	https://hdl.handle.net/10468/6419

UCC
University College Cork, Ireland
Coláiste na hOllscoile Corcaigh

Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2014

Supporting information for:

Ligand design for long-range magnetic order in metal-organic frameworks

Davide Tiana, Christopher H. Hendon, and Aron Walsh*

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

E-mail: a.walsh@bath.ac.uk

Electronic Supporting Information

Tetrahedral and octahedral Mn coordination

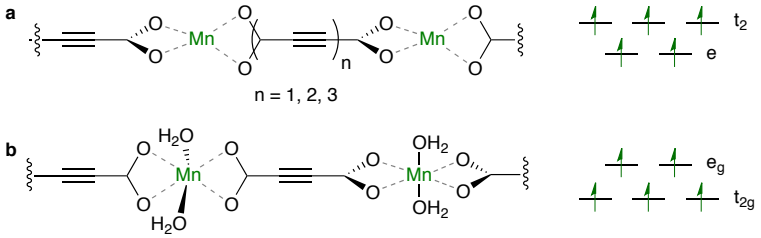


Figure S1: Schematic structures and ligand field splitting for Mn polymers with (a) tetrahedral and (b) octahedral coordination. The associated relaxed structure parameters are given in the tables below.

*To whom correspondence should be addressed

Convergence of calculations

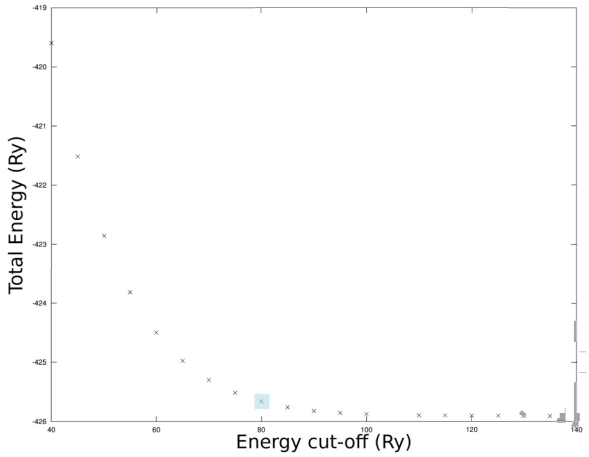


Figure S2: Plane-wave cut-off convergence for the norm-conserving pseudopotential with the PBEsol exchange correlation functional. A value of 80 Ry has been used in our production runs.

Table S1: Difference in energy (in meV) between the AFM and FM states for system **I** using different pseudopotentials and functionals. Note that in Quantum Espresso, a stress tensor is not calculated for hybrid functionals. Thus, for a better comparison, only the atomic positions have been optimized keeping the volume fixed at the PBE*sol* level. PBE*sol* so = PBE*sol* with the inclusion of relativistic spin-orbit coupling. nc = norm conserving pseudopotential, PAW = projector augmented wave. An energy cut-off 80 Ry is used throughout.

Functional	Type	Pseudopotential	ΔE
PBE*sol*	GGA	nc	22
PBE*sol* so	GGA	nc	22
PBE*sol*	GGA	PAW	18
HSE06	HYBRID	nc	17
PZ	LDA	nc	21

Super-exchange decay with distance

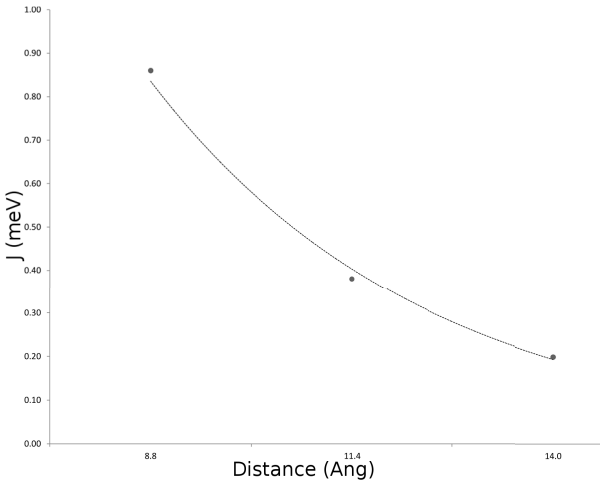


Figure S3: Exponential decay of the exchange energy vs d(M-M). $R^2 = 0.998$.

Frontier electronic orbitals

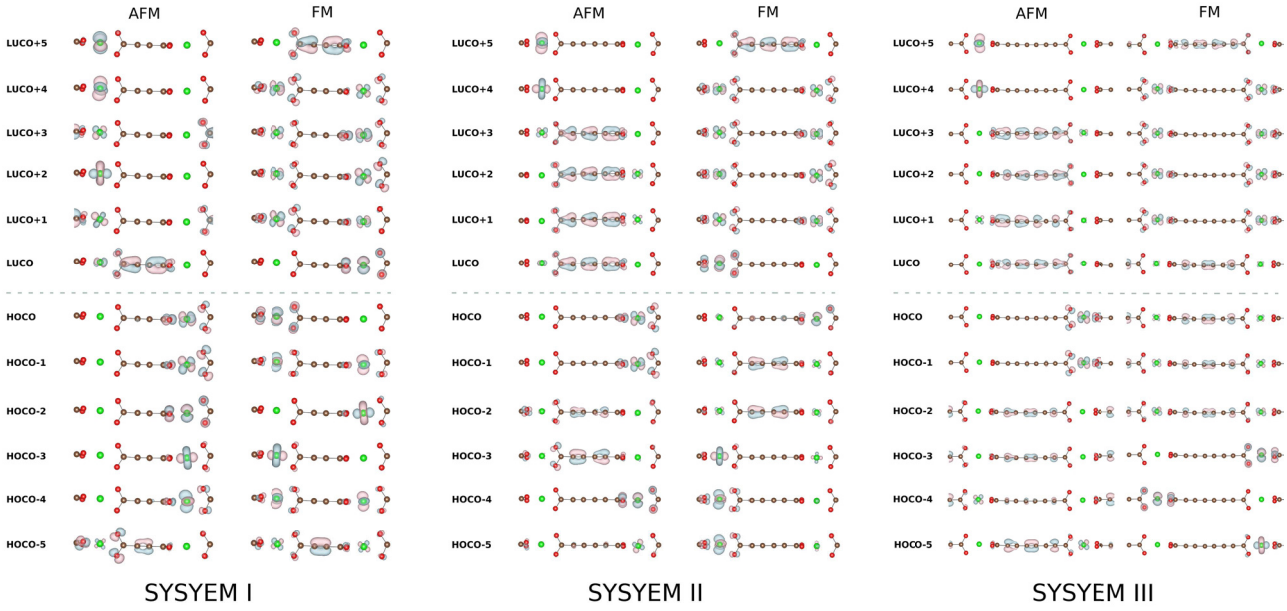


Figure S4: Frontier orbitals for the AFM and FM states for systems **I** (left), **II** (middle) and **III** (right). Isovalue = 5 e-3 au. O = red, C = brown, Mn = green.

Optimized geometry

Table S2: Lattice parameters and fractional coordinates for system **I** in its AFM state. Lattice vectors in Å, cell angles in °

$\mathbf{a} = \mathbf{b}$	10.0000 Å		
$\mathbf{c}$	17.5056 Å		
$\alpha = \beta = \gamma$	90°		
C1	-0.020978	-0.006136	0.212666
C2	-0.025580	-0.005139	0.281807
C3	-0.013423	-0.001992	0.132394
C4	-0.027533	-0.003304	0.362204
O1	0.097757	-0.031712	0.099732
O2	-0.116999	0.033066	0.093885
O3	-0.023875	-0.114758	0.398729
O4	-0.031748	0.109738	0.396989
Mn1	-0.024033	-0.000558	0.497627
C5	0.005325	0.021946	0.712497
C6	0.012114	0.025347	0.781465
C7	-0.004476	0.013206	0.632393
C8	0.011931	0.021827	0.861899
O5	-0.121190	0.003856	0.601949
O6	-0.002672	-0.092192	0.894736
O7	0.023949	0.130655	0.900236
O8	0.102528	0.014012	0.591907
Mn2	0.002602	0.012241	-0.002705

Table S3: Lattice parameters and fractional coordinates for system **I** in its FM state. Lattice vectors in Å, cell angles in °

$\mathbf{a} = \mathbf{b}$	10.0000 Å		
$\mathbf{c}$	17.5056 Å		
$\alpha = \beta = \gamma$	90°		
C1	-0.020978	-0.006136	0.212666
C2	-0.025580	-0.005139	0.281807
C3	-0.013423	-0.001992	0.132394
C4	-0.027533	-0.003304	0.362204
O1	0.097757	-0.031712	0.099732
O2	-0.116999	0.033066	0.093885
O3	-0.023875	-0.114758	0.398729
O4	-0.031748	0.109738	0.396989
Mn1	-0.024033	-0.000558	0.497627
C5	0.005325	0.021946	0.712497
C6	0.012114	0.025347	0.781465
C7	-0.004476	0.013206	0.632393
C8	0.011931	0.021827	0.861899
O5	-0.121190	0.003856	0.601949
O6	-0.002672	-0.092192	0.894736
O7	0.023949	0.130655	0.900236
O8	0.102528	0.014012	0.591907
Mn2	0.002602	0.012241	-0.002705

Table S4: Lattice parameters and fractional coordinates for system **II** in its AFM state. Lattice vector in Å, cell angles in °

a = **b**	10.0000 Å		
c	22.7203 Å		
$\alpha = \beta = \gamma$	90°		
C1	-0.011873	-0.010740	0.169030
C2	-0.011832	-0.010446	0.222726
C3	-0.008980	-0.007792	0.107133
C4	-0.011699	-0.009795	0.281317
O1	0.101136	-0.034733	0.080345
O2	-0.115465	0.022630	0.078314
O3	-0.005773	-0.120901	0.424759
O4	-0.023338	0.102513	0.424915
Mn1	-0.018379	-0.009943	0.502112
C5	-0.004190	-0.008710	0.669040
C6	-0.001638	-0.006688	0.722795
C7	-0.008803	-0.009425	0.607190
C8	0.000558	-0.000681	0.896977
O5	-0.123064	-0.014757	0.581137
O6	-0.020992	-0.110677	0.924750
O7	0.021382	0.109301	0.924921
O8	0.100723	-0.004430	0.577608
Mn2	-0.001354	-0.000489	0.002112
C9	-0.011530	-0.008904	0.335048
C10	-0.013430	-0.008989	0.396949
C11	0.000052	-0.004100	0.781318
C12	0.000988	-0.001243	0.835042

Table S5: Lattice parameters and fractional coordinates for system **II** in its FM state. Lattice vectors in Å, cell angles in °

$\mathbf{a} = \mathbf{b}$	10.0000 Å		
$\mathbf{c}$	22.7202 Å		
$\alpha = \beta = \gamma$	90°		
C1	-0.012460	-0.011390	0.168803
C2	-0.012122	-0.010554	0.222555
C3	-0.009488	-0.008388	0.106852
C4	-0.011737	-0.009613	0.281145
O1	0.100518	-0.036025	0.080047
O2	-0.115506	0.023149	0.077946
O3	-0.005459	-0.120908	0.424563
O4	-0.023316	0.102602	0.424763
Mn1	-0.018118	-0.009876	0.501912
C5	-0.004149	-0.008975	0.668955
C6	-0.001534	-0.007026	0.722692
C7	-0.008725	-0.009489	0.607015
C8	0.000504	-0.000506	0.896989
O5	-0.122993	-0.014751	0.580919
O6	-0.020897	-0.110231	0.924996
O7	0.021517	0.109808	0.924705
O8	0.100859	-0.004377	0.577478
Mn2	-0.000702	0.001084	0.001975
C9	-0.011292	-0.008744	0.334902
C10	-0.013228	-0.008918	0.396832
C11	0.000056	-0.004414	0.781291
C12	0.000772	-0.001458	0.835015

Table S6: Lattice parameters and fractional coordinates for system **III** in its AFM state. Lattice vectors in Å, cell angles in °

a = **b**	10.0000 Å		
c	27.9026 Å		
$\alpha = \beta = \gamma$	90°		
C1	-0.002081	0.005747	0.578061
C2	-0.002918	0.006526	0.628539
C3	-0.003081	0.007100	0.672467
C4	-0.003299	0.007125	0.719951
C5	-0.003277	0.006623	0.764105
C6	-0.001770	0.005480	0.811588
C7	0.001342	0.004160	0.855515
C8	0.003654	0.002485	0.905997
O1	-0.024152	0.114977	0.554917
O2	0.020999	-0.104379	0.555494
O3	-0.107270	0.001437	0.929408
O4	0.116581	0.002132	0.928314
O5	0.106058	0.015759	0.428020
C9	-0.007016	0.007106	0.406071
C10	-0.010286	0.009457	0.355617
C11	-0.012345	0.009966	0.311685
C12	-0.013731	0.009483	0.264188
C13	-0.014194	0.007417	0.220039
C14	-0.012924	0.004800	0.172553
C15	-0.010576	0.002155	0.128617
O6	0.013615	-0.110165	0.055727
C16	-0.003729	0.001056	0.078170
O7	-0.014307	0.111816	0.054894
O8	-0.116934	-0.003953	0.429814
Mn1	-0.000970	0.003549	0.492058
Mn2	0.007512	0.000040	-0.007893

Table S7: Lattice parameters and fractional coordinates for system **III** in its FM state. Lattice vectors in Å, cell angles in °

a = **b**	10.0000 Å		
c	27.9066 Å		
$\alpha = \beta = \gamma$	90°		
C1	-0.002095	0.005751	0.578068
C2	-0.002914	0.006532	0.628547
C3	-0.003067	0.007101	0.672466
C4	-0.003285	0.007125	0.719950
C5	-0.003282	0.006621	0.764102
C6	-0.001785	0.005481	0.811591
C7	0.001336	0.004160	0.855500
C8	0.003668	0.002477	0.905988
O1	-0.024181	0.115015	0.554948
O2	0.020998	-0.104419	0.555523
O3	-0.107296	0.001445	0.929372
O4	0.116632	0.002107	0.928281
O5	0.106095	0.015775	0.427994
C9	-0.007022	0.007116	0.406075
C10	-0.010287	0.009448	0.355611
C11	-0.012341	0.009968	0.311690
C12	-0.013720	0.009489	0.264187
C13	-0.014185	0.007415	0.220046
C14	-0.012923	0.004798	0.172547
C15	-0.010578	0.002161	0.128630
O6	0.013627	-0.110209	0.055756
C16	-0.003734	0.001044	0.078173
O7	-0.014325	0.111844	0.054918
O8	-0.116976	-0.003940	0.429790
Mn1	-0.000963	0.003537	0.492062
Mn2	0.007505	0.000057	-0.007897

Table S8: Lattice parameters and fractional coordinates for Mn polymer with octahedral coordination in its AFM state. Lattice vectors in Å, cell angles in °

$\mathbf{a} = \mathbf{b}$	10.0000 Å		
$\mathbf{c}$	17.45604 Å		
$\alpha = \beta = \gamma$	90°		
Mn1	0.501168	0.450545	0.466432
Mn2	0.000000	0.450545	0.466432
O1	0.000000	0.450545	0.237338
O2	0.000000	0.450545	0.695526
O3	0.501168	0.222091	0.466432
O4	0.501168	0.679000	0.466432
O5	0.101222	0.337195	0.466432
O6	0.901115	0.563896	0.466432
O7	0.901115	0.337195	0.466432
O8	0.101222	0.563896	0.466432
O9	0.399482	0.450545	0.353232
O10	0.602855	0.450545	0.579632
O11	0.602855	0.450545	0.353232
O12	0.399482	0.450545	0.579632
H1	0.455872	0.736006	0.466432
H2	0.546465	0.165084	0.466432
H3	0.546465	0.736006	0.466432
H4	0.455872	0.165084	0.466432
H5	0.000000	0.371462	0.752490
H6	0.000000	0.529628	0.180374
H7	0.000000	0.529628	0.752490
H8	0.000000	0.371462	0.180374
C1	0.135691	0.450545	0.466432
C2	0.866646	0.450545	0.466432
C3	0.637526	0.450545	0.466432
C4	0.364811	0.450545	0.466432
C5	0.215662	0.450545	0.466432
C6	0.786675	0.450545	0.466432
C7	0.284892	0.450545	0.466432
C8	0.717445	0.450545	0.466432

Table S9: Lattice parameters and fractional coordinates for Mn polymer with octahedral coordination in its FM state. Lattice vectors in Å, cell angles in °

$\mathbf{a} = \mathbf{b}$	10.0000 Å		
$\mathbf{c}$	17.50554 Å		
$\alpha = \beta = \gamma$	90°		
Mn1	0.500000	0.450545	0.466432
Mn2	0.000000	0.450545	0.466432
O1	0.000000	0.450545	0.237338
O2	0.000000	0.450545	0.695526
O3	0.500000	0.222162	0.466432
O4	0.500000	0.678929	0.466432
O5	0.101121	0.337135	0.466432
O6	0.898879	0.563956	0.466432
O7	0.898879	0.337135	0.466432
O8	0.101121	0.563956	0.466432
O9	0.398416	0.450545	0.353202
O10	0.601584	0.450545	0.579662
O11	0.601584	0.450545	0.353202
O12	0.398416	0.450545	0.579662
H1	0.454817	0.736070	0.466432
H2	0.545183	0.165020	0.466432
H3	0.545183	0.736070	0.466432
H4	0.454817	0.165020	0.466432
H5	0.000000	0.371495	0.752456
H6	0.000000	0.529596	0.180408
H7	0.000000	0.529596	0.752456
H8	0.000000	0.371495	0.180408
C1	0.135408	0.450545	0.466432
C2	0.864591	0.450545	0.466432
C3	0.636034	0.450545	0.466432
C4	0.363966	0.450545	0.466432
C5	0.215172	0.450545	0.466432
C6	0.784828	0.450545	0.466432
C7	0.284212	0.450545	0.466432
C8	0.715788	0.450545	0.466432