Electronic Supplementary Material (ESI) for CrystEngComm.

Optical properties of metal organic networks from distributed atomic polarizabilities

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Supporting Information

Table S1. The main bonding distances (in Å) of the optimized crystal structures of species **1**

Metal	M-$N_{equatorial}$	M-$O_{equatorial}$	M-O_{apical}
Mn	2.042	1.990	2.077
Co	1.951	1.913	2.215
Ni	1.903	1.870	2.553
Cu	2.018	1.969	2.323
Zn	2.094	2.066	2.027

Table S2. The optimized crystal structure of species **1** in space group $P2_12_12_1$.

1-Co

Unit cell (Å) a = 10.97820, b = 8.682629; c = 8.454156
Fractional coordinates

Co	0.39274814	0.33160388	-0.27246396
O	-0.47395274	0.44369374	-0.36279288
O	-0.34997388	0.45673407	0.42802252
O	0.37695389	0.46973510	-0.09787043
O	0.25100228	-0.45408562	0.09355642
N	0.42210603	0.18339770	-0.44149396
N	0.26807181	0.21308899	-0.16183214
C	0.42713222	0.29210265	0.28441435
C	-0.49976138	0.25373120	0.43317866
C	0.19541344	0.32190185	-0.06333484
C	0.13205960	0.24451218	0.07600892
C	0.27907141	0.45575662	-0.01490970
C	-0.43594455	0.39523795	-0.49729756
H	0.46873599	0.09008876	-0.39852883
H	0.34194145	0.14277004	-0.48662131
H	0.21321513	0.15525117	-0.24062959
H	0.30564459	0.13019196	-0.08976587
H	-0.42685774	0.17304754	0.40336790
H	0.12745597	0.37387919	-0.14178391
H	0.40121839	0.18605463	0.22290649
H	0.34461509	0.35660109	0.31252181
H	0.48184774	0.36199858	0.20376787
H	0.19682441	0.17866633	0.14689846
H	0.08966561	0.33199842	0.15035380
H	0.06210423	0.16546989	0.03313534

1-Ni:

Unit cell (Å) a = 10.92757 b = 8.782542 c = 8.566947

Ni	0.40407077	0.31777362	-0.26888593
O	-0.46868091	0.43121563	-0.35848813
O	-0.35006594	0.45271824	0.43050085
O	0.38712941	0.45610940	-0.10524389
O	0.25917107	-0.46803819	0.08370092
N	0.42708868	0.17771949	-0.43531687
N	0.27691935	0.20629735	-0.16836854
C	0.42294652	0.28810716	0.29555561
C	-0.49850584	0.24866205	0.43754765
C	0.20180124	0.31728758	-0.07773033
C	0.12916342	0.24541005	0.05434453
C	0.28716147	0.44523638	-0.02407275
C	-0.43352650	0.38773364	-0.49446809
H	0.47600806	0.08502999	-0.39652594
H	0.34530912	0.13797464	-0.47665266
H	0.22292181	0.14887958	-0.24736176
H	0.31182296	0.12521845	-0.09387950
H	-0.42607397	0.16891893	0.40441205
H	0.13990535	0.37104583	-0.16182183
H	0.39569843	0.18407730	0.23414357
H	0.34085528	0.35042674	0.32998614
H	0.47456756	0.35932330	0.21438977
H	0.18951607	0.18749643	0.13695909
H	0.07843956	0.33340129	0.11672752
H	0.06445008	0.16214422	0.00856699

1-Cu

Unit cell (Å) a = 11.32534 b = 8.647134 c = 8.512780

Cu	0.39265306	0.32658408	-0.27761784
O	-0.47100942	0.44030963	-0.36474719
O	-0.34974267	0.45236590	0.42910768
O	0.38151695	0.46208915	-0.09325833
O	0.25645872	-0.45914217	0.09198648
N	0.42647755	0.17606523	-0.45263871
N	0.26663132	0.20609368	-0.16243421
C	0.43272758	0.29669329	0.28184417
C	-0.49677895	0.25141768	0.42800480
C	0.20068739	0.31827263	-0.06389690
C	0.13877823	0.24357477	0.07614443
C	0.28459125	0.45012032	-0.01492979
C	-0.43415514	0.39154133	-0.49815229
H	0.47201563	0.08404532	-0.40710366
H	0.34916136	0.13584398	-0.49869501
H	0.21313658	0.15160099	-0.24286723
H	0.30448395	0.12252893	-0.09289382
H	-0.42603476	0.17142135	0.39578740
H	0.13524681	0.37336953	-0.14038053
H	0.40500818	0.19288961	0.21794786
H	0.35423818	0.36338817	0.31290586
H	0.48669054	0.36713024	0.20314580
H	0.20102384	0.17599697	0.14610374
H	0.09971186	0.33300210	0.14999603
H	0.06868215	0.16655174	0.03573039

1-Zn

Unit cell (Å) a = 11.55892 b = 8.566973 c = 8.488868

Zn	0.37227409	0.33559851	-0.29947854
O	-0.47843674	0.44480648	-0.37005112
O	-0.35189349	0.45480554	0.43082070
O	0.37737130	0.45897120	-0.08871009
O	0.25714313	-0.45741150	0.09641446
N	0.42851410	0.17152787	-0.46432744
N	0.25911292	0.20326146	-0.15915638
C	0.43820741	0.29948189	0.27418774
C	-0.49446585	0.25146917	0.42156378
C	0.19924239	0.31506290	-0.05449698
C	0.14387170	0.23915705	0.09030810
C	0.28387833	0.44792887	-0.01131465
C	-0.43678428	0.39443415	-0.49979416
H	0.47535965	0.08599957	-0.40950502
H	0.35989883	0.11887091	0.48211430
H	0.20349645	0.14621588	-0.23388002
H	0.30175934	0.12092027	-0.09296686
H	-0.42342667	0.17371392	0.38927667
H	0.13147572	0.37189167	-0.12438740
H	0.41149150	0.19597229	0.20769980
H	0.36085778	0.36627340	0.30493680
H	0.49161551	0.37213343	0.19741468
H	0.20679145	0.16701658	0.15284986
H	0.11024898	0.32800611	0.16991895
H	0.07176030	0.16505630	0.05407077

Table S3. The refractive index of **1-Cu**, calculated at B3LYP/cc-pVDZ level. See Figure S1 for the description of the clusters

Type of Calculation	n_a	n_b	n_c	n_{iso}
SBU and Oriented gas model				
Square planar	1.446	1.364	1.514	1.441
Square pyramidal	1.416	1.371	1.476	1.421
Dimer	1.414	1.380	1.487	1.427
Trimer	1.419	1.379	1.491	1.43
Cluster with H_2O and NH_3	1.435	1.385	1.495	1.438
Cluster with alanine	1.446	1.383	1.493	1.441
SBU in PCM and Oriented gas model				
Square planar	1.611	1.452	1.74	1.601
Square pyramidal	1.569	1.487	1.663	1.573
SBU and Lorentz correction				
Square planar	1.647	1.486	1.808	1.647
PBC[(1)]	1.538	1.472	1.569	1.526

(1) One diffused function of Cu was removed to avoid divergence.

Table S4. The refractive index of **2-Ni**, calculated at B3LYP/cc-pVDZ level with various spin polarization and field corrections options.

Type of Calculation	n_1	n_2	n_3
SBU and Oriented gas model			
Square planar S(Ni)=0	1.610	1.391	1.404
Octahedral S(Ni)=0	1.576	1.382	1.389
Square planar S(Ni)=1	1.586	1.388	1.388
Octahedral S(Ni)=1	1.569	1.369	1.367
SBU in PCM and Oriented gas model			
Square planar S(Ni)=0	2.075	1.535	1.561
Octahedral S(Ni)=0	1.998	1.536	1.531
Square planar S(Ni)=1			
Octahedral S(Ni)=1	1.955	1.507	1.491
SBU and Lorentz correction			
Square planar S(Ni)=0	2.095	1.535	1.561
Square planar S(Ni)=1	2.017	1.529	1.530
PBC			
S(Ni)=1	1.676	1.542	1.527

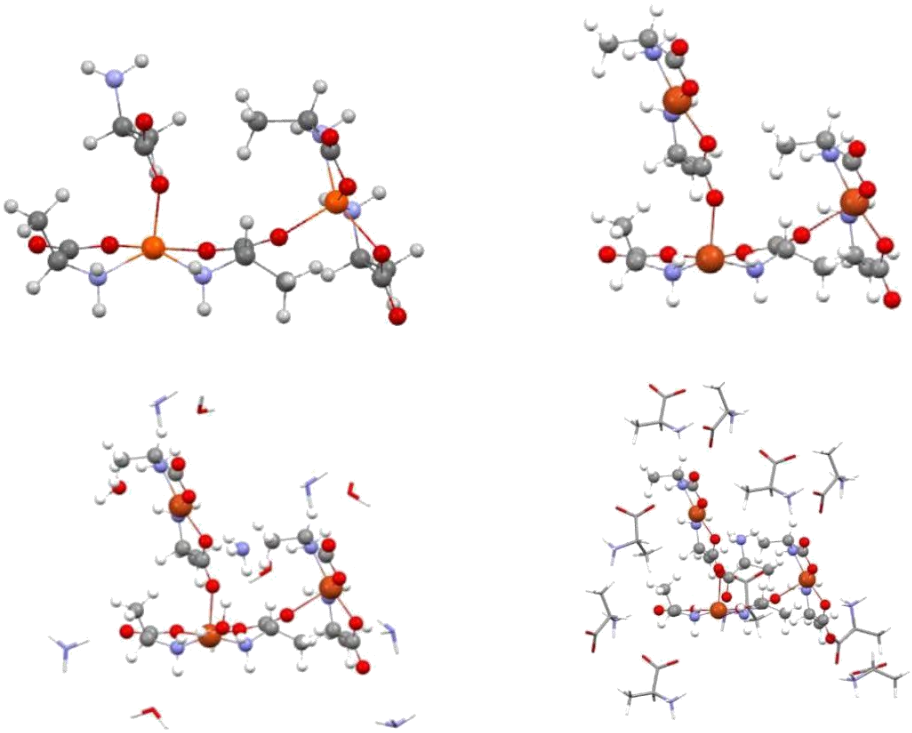

Figure S1. The clusters used for the calculations reported in Table S3. Top left: a dimeric unit; top right: a trimeric unit; Bottom left trimeric unit with H_2O and NH_3 molecules saturating the hydrogen bond sites; d) Bottom right, trimeric unit with alanine saturating the hydrogen bond sites.

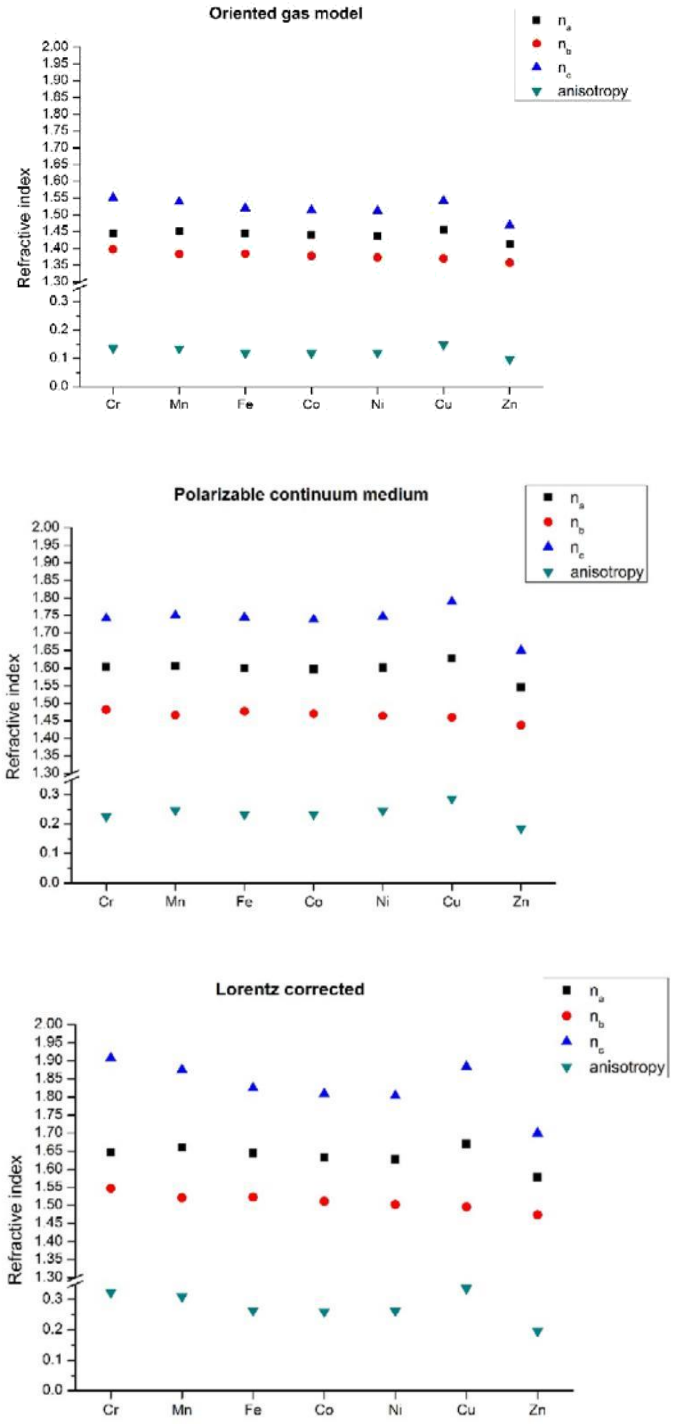

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Figure S2. Refractive indices for structures 1.Top: oriented gas model polarizabilities calculated using the square planar SBU; centre: the same SBU in a PCM based on the average dielectric function of the crystal; bottom: with a Lorentz correction. a, b and c are the refractive index components along the three crystallographic directions and the anisotropy is calculated as Δ 0.5 3 , where , , are the eigenvalues of the optic indicatrix (coinciding with , , only in orthogonal crystal systems, as species **1**).

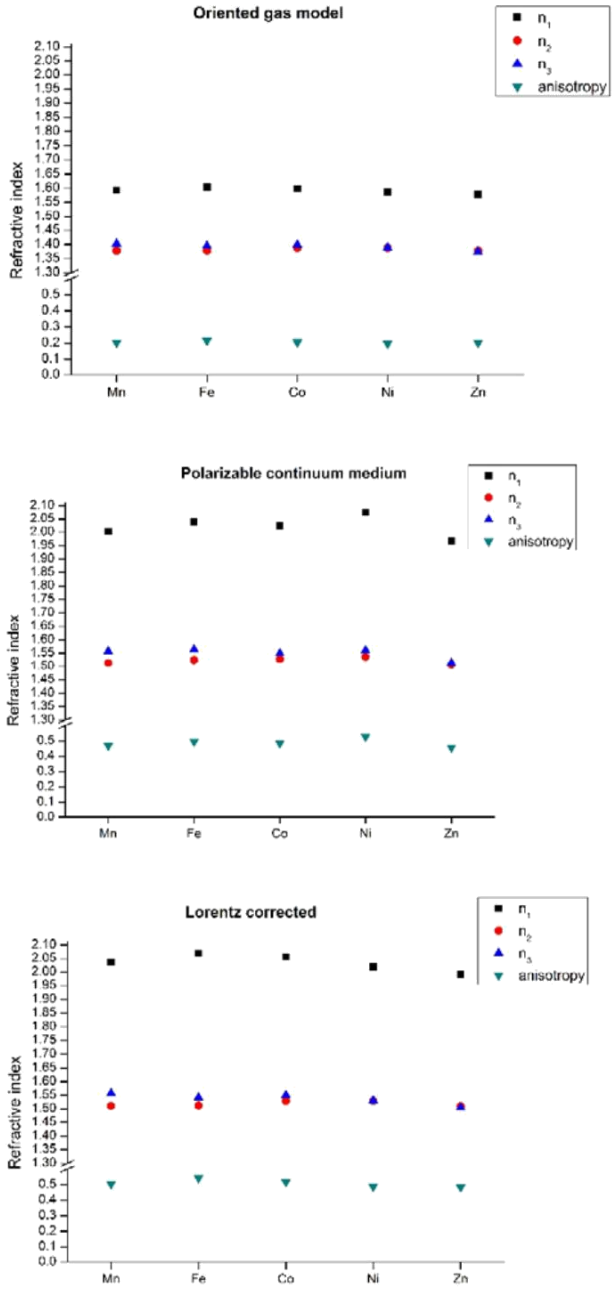

Figure S2. Refractive indices for structures 2.Top: oriented gas model polarizabilities calculated using the square planar SBU; centre: the same SBU in a PCM based on the average dielectric function of the crystal; bottom: with a Lorentz correction. a, b and c are the refractive index components along the three crystallographic directions and the anisotropy is calculated as Δ 0.5 3 , where , , are the eigenvalues of the optic indicatrix (coinciding with , , only in orthogonal crystal systems, as species **1**).