Electronic Supporting Information

for

Redefining the preferences of five-membered chelate rings: insights from the Cambridge Structural Database and theoretical calculations

Maryam Bazargan[a], Masoud Mirzaei[a,*], Antonio Franconetti,[b] Antonio Frontera[b,*]

[a] *Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, 917751436, Mashhad, Iran E-mail: mirzaeesh@um.ac.ir and mirzaei487@yahoo.com*

[b] *Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, Palma de Mallorca, Baleares E-07122, Spain E-mail: toni.frontera@uib.es*

Index

H																**He**
Li 15 13 9	**Be** -- -- 1				**Cr** 118 2.06 79.66							**B** 2 27 --	**C**	**N**	**O**	**F**	**Ne**
Na 30 6 4	**Mg** 30 7 8											**Al** 1 6 4	**Si** 24 28 --	**P**	**S**	**Cl**	**Ar**
K 18 3 8	**Ca** 30 13 5	**Sc** 3 4 --	**Ti** 4 28 --	**V** 136 152 3	**Cr** 113 137 121	**Mn** 762 677 84	**Fe** 355 298 26	**Co** 745 554 969	**Ni** 556 560 493	**Cu** 2082 1992 732	**Zn** 740 639 143	**Ga** 16 19 9	**Ge** 11 16 5	**As** 1 5 --	**Se** -- 2 --	**Br**	**Kr**
Rb 4 -- 3	**Sr** 24 5 5	**Y** 37 15 4	**Zr** 2 9 --	**Nb** 3 12 --	**Mo** 116 162 30	**Tc** 10 15 6	**Ru** 284 1568 98	**Rh** 39 101 37	**Pd** 135 415 233	**Ag** 78 115 7	**Cd** 609 439 78	**In** 39 55 16	**Sn** 57 48 3	**Sb** 14 14 1	**Te** -- 2 --	**I**	**Xe**
Cs	**Ba** 30 8 11	**La** 122 31 16	**Hf** -- 1 --	**Ta** -- 1 --	**W** 25 81 11	**Re** 111 256 13	**Os** 43 144 18	**Ir** 37 99 23	**Pt** 101 394 318	**Au** 10 20 8	**Hg** 24 39 11	**Tl** 12 7 3	**Pb** 210 114 20	**Bi** 52 32 --	**Po**	**At**	**Rn**
Fr	**Ra**	**Ac**	**Rf**	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**	**Nh**	**Fl**	**Mc**	**Lv**	**Ts**	**Og**
			Ce 58 12 8	**Pr** 88 31 7	**Nd** 112 38 10	**Pm**	**Sm** 112 42 13	**Eu** 253 77 10	**Gd** 94 35 8	**Tb** 143 43 1	**Dy** 107 51 9	**Ho** 50 16 6	**Er** 75 30 5	**Tm** 19 9 4	**Yb** 77 31 3	**Lu** 12 16 --
			Th -- 10 --	**Pa**	**U** 38 67 --	**Np** 2 14 --	**Pu** -- 4 --	**Am** -- 1 --	**Cm**	**Bk**	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**

The frequency of the structures with *phen* backbone and Cr as a central metal
The frequency of the structures with *bpy* backbone
The frequency of the structures with *en* backbone

Fig. S1: Frequency of metal complexes with *phen*/*bpy*/*en* ligands in red/green/blue, respectively.

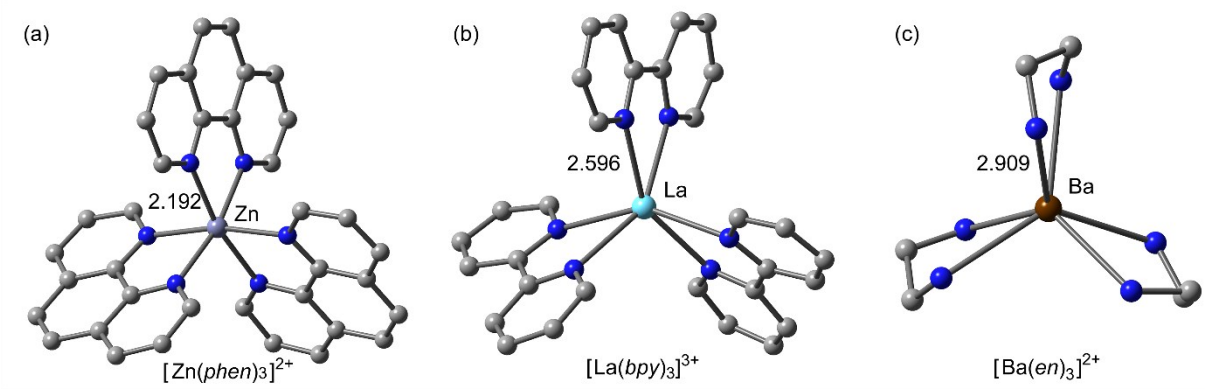

Fig S2. BP86-D3/def2-TZVP optimized structures of three representative complexes (Distances in Å). H-atoms omitted for clarity.

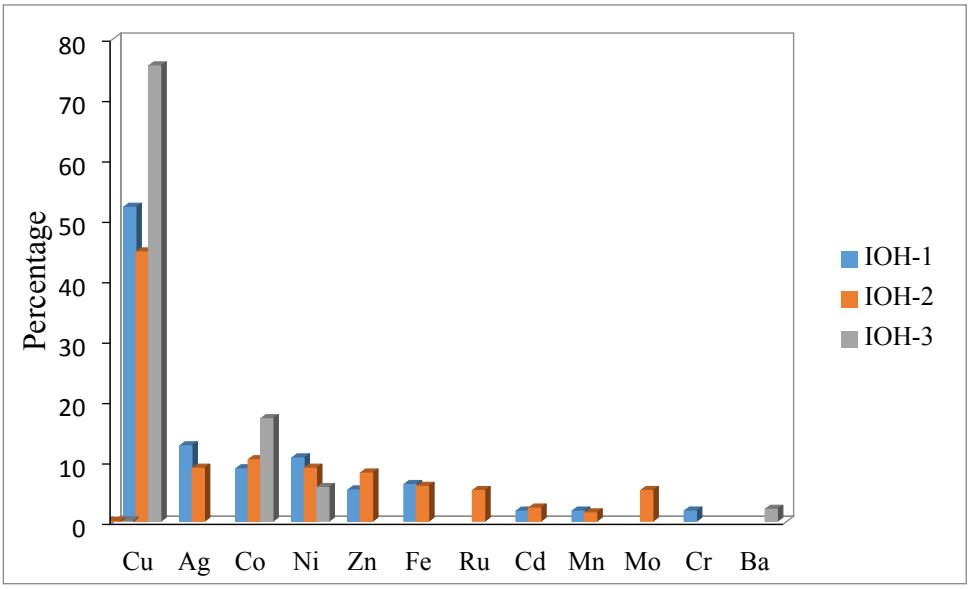

Fig. S3. Categorization of all IOH-1–3 based on central metal in the MOCs.

Theoretical methods

The optimization of the complexes was carried out using the TURBOMOLE software (version 7.0) [S1] at the PB86-D3/def2-TZVP level of theory. The minimum nature of the complexes was confirmed by frequency calculations. The complexation energies reported in Table 2 were computed by calculating the difference between the energies of isolated monomers and their assembly.

[S1] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, Chem. Phys. Lett. 162 (1989) 165-169.