

## *Supporting Information*

### **Inter-ligand delocalisations in transition metal complexes containing multiple non-innocent ligands**

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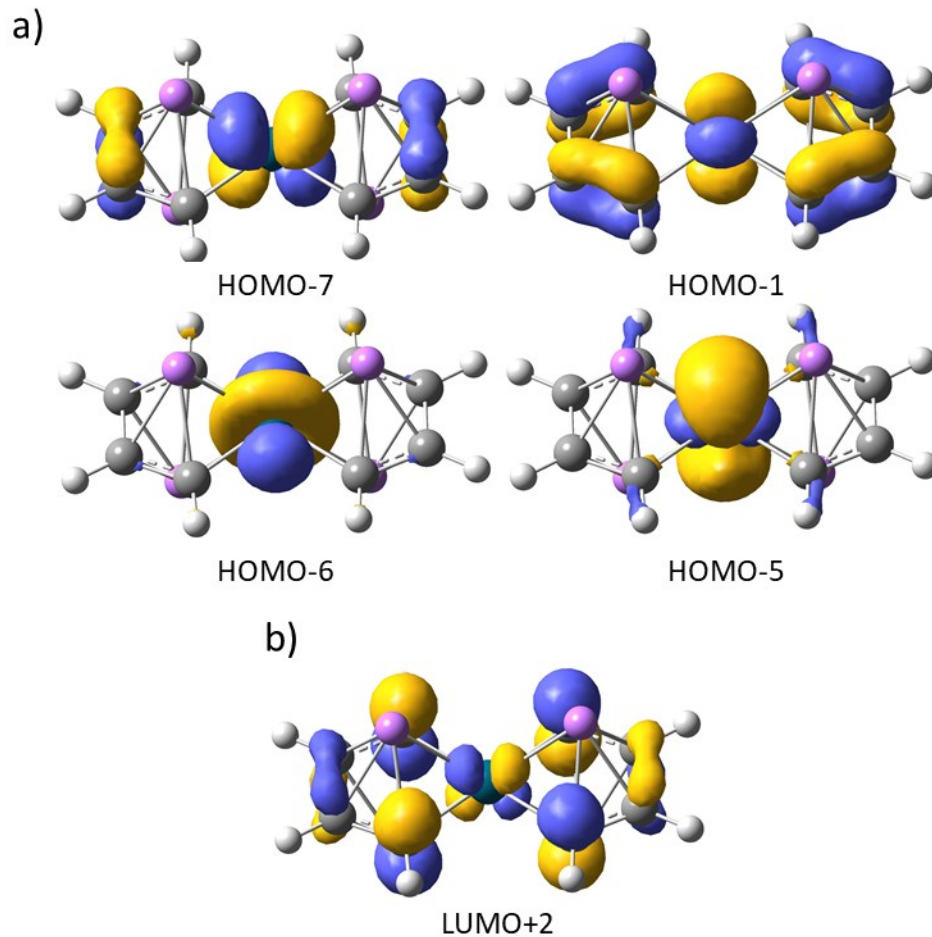
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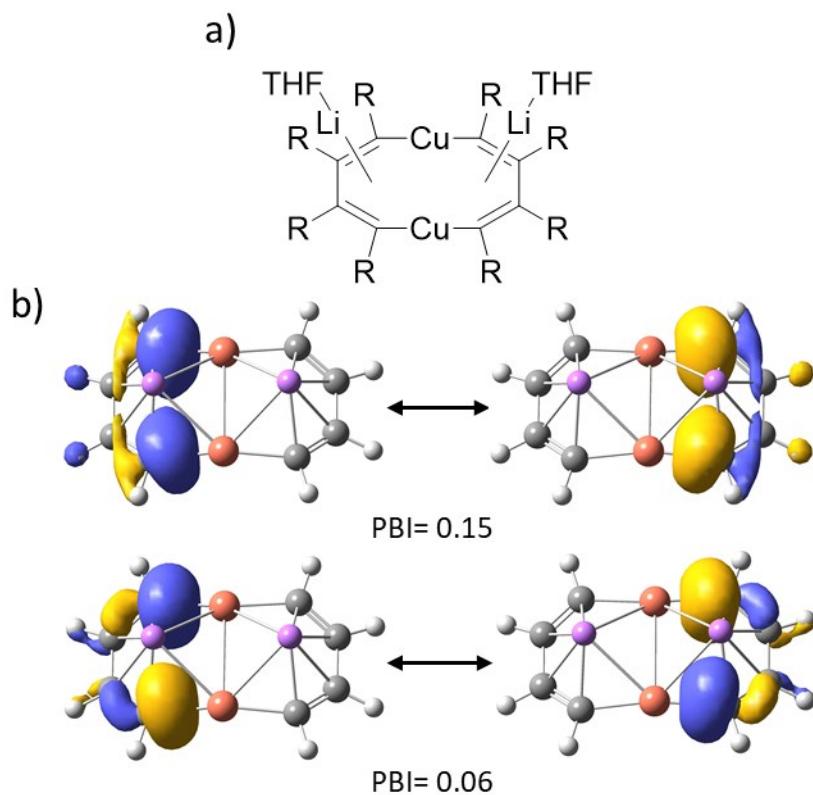
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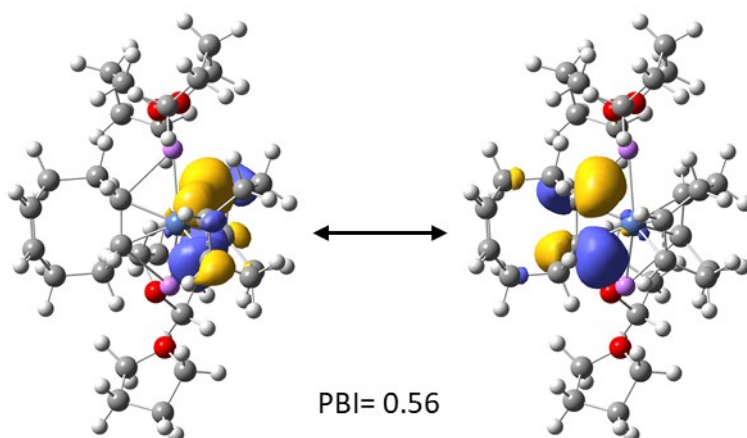
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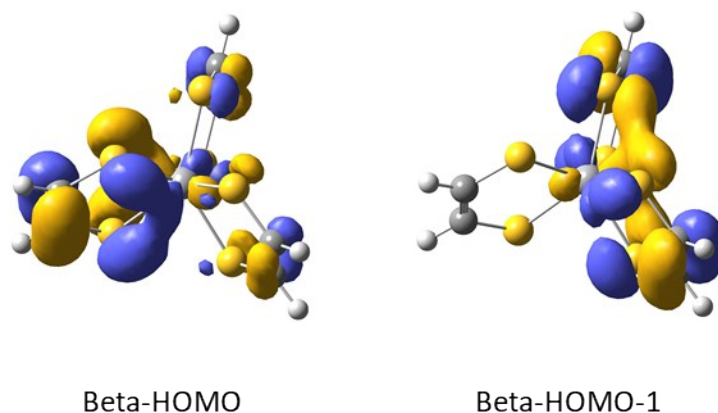
**Fig. S1.** Selected molecular orbitals (MOs) calculated for the model tetralithio spiroaromatic palladole **1'**. a) The 4 MOs associated to the  $d^8$  configuration of the palladium(II) centre. b) The unoccupied MO associated to the out-of-phase combination of the two  $\pi_3$  orbitals of the two  $C_4R_4$  units. Because this orbital is unoccupied while the in-phase combination is occupied, there is a “remote inter-ligand delocalisation” between the two  $C_4R_4$  ligands. Isovalue: 0.05



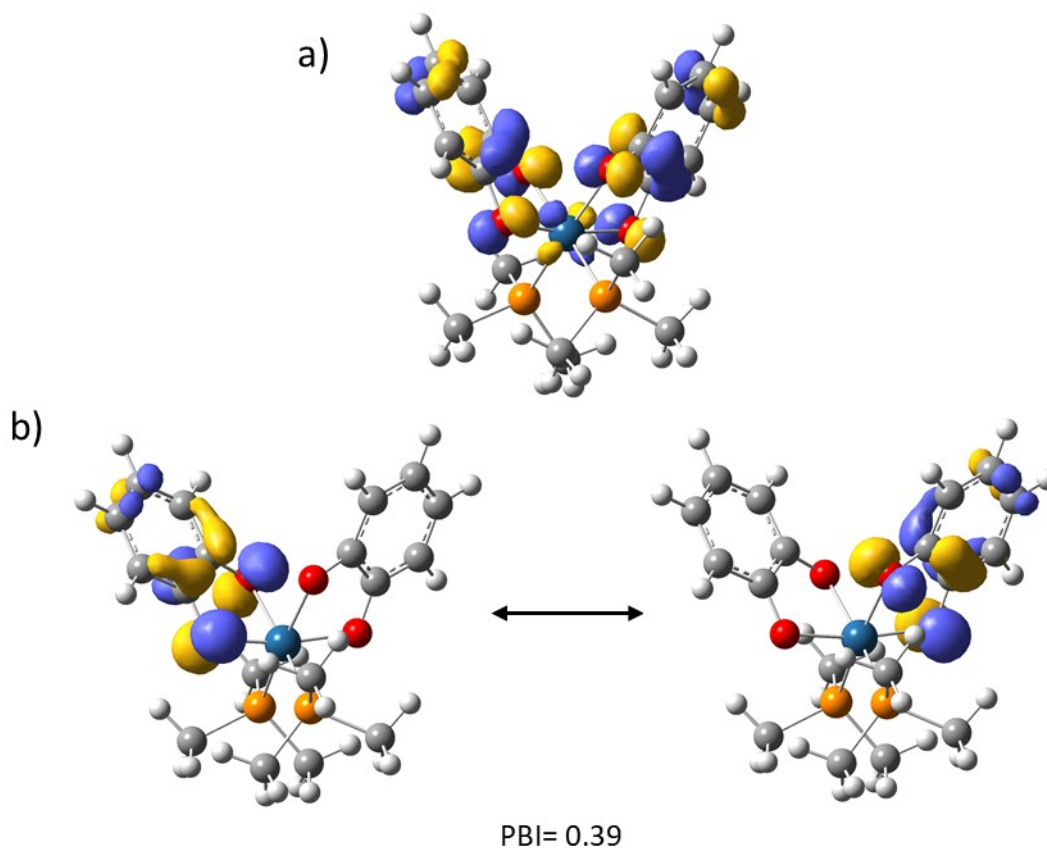
**Fig. S2.** Analysis of the dicupra[10]annulene complex with two as opposed to four Li cations in the dicupra[10]annulene (**2**). a) Structure of the complex. b) Dominant PIO pairs for the complex. Note that the PBI of this top PIO pair is merely 0.15, much smaller than the case shown in Figure 3 (the case with four Li cations). The top PIO pair is also of  $\sigma$  character, in contrast to the one with  $\pi$  character in Figure 3. These indicate the absence of “remote inter-ligand delocalisation” in this case. Isovalue: 0.05



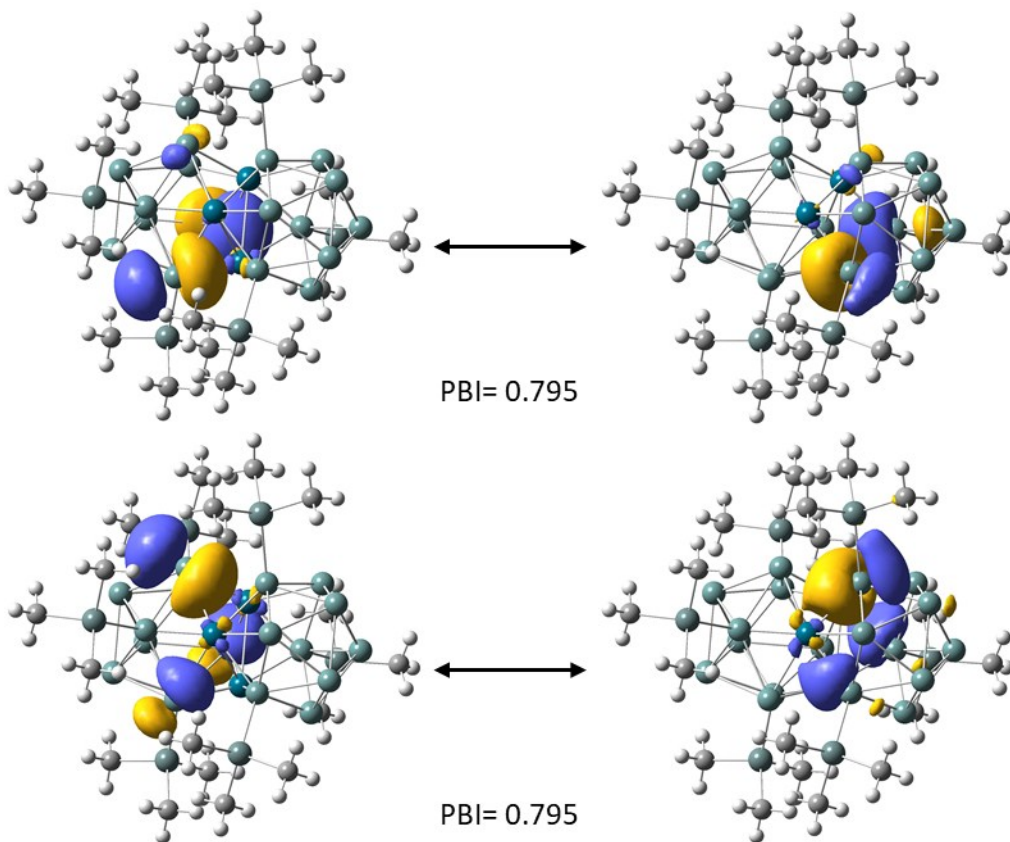
**Fig. S3.** PIO analysis of  $[\text{Ni}(\text{COD})_2]^{2-}$  (**3**). The large PBI indicates the presence of a remote inter-ligand delocalisation between the two COD ligands. Isovalue: 0.05



**Fig. S4.** Frontier beta-MOs calculated for tris(dithiolene)vanadium(IV) (**4**). Note their close resemblance to the alpha-MO counterparts (Fig 5d). Isovalue: 0.05



**Fig. S5.** a) The HOMO calculated for the simplified  $\text{Os}(\text{PPh}_3)_2(\text{Q})_2$  model ( $\text{Q} = 3,5\text{-di-tert-butyl-1,2-quinone}$ ) (All of the substituents on the phosphines are modeled by  $\text{CH}_3$  while those on quinone are replaced by H). Isovalue: 0.05 b) The PIO pair representing the “remote inter-ligand delocalisation” between the two quinone ligands. Isovalue: 0.065



**Fig. S6.** The PIO pairs representing the “remote inter-ligand delocalisation” between the two  $\text{Ge}_9\text{R}_3$  cages. Isovalue: 0.035

**Table S1.** Singlet-Triplet gap of selected complexes

Complex	Singlet Energy (Hartree)	Triplet Energy (Hartree)	Gap (kcal/mol)
<b>1</b>	-466.5594	-466.4970	39.1
<b>2</b>	-732.1841	-732.1306	33.6
Os(PPh <sub>3</sub> ) <sub>2</sub> (Q) <sub>2</sub>	-1774.6788	-1774.6615	10.8