Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Modulating magnetic behavior of Fe-MOF-74 by high electron affinity of the guest molecule

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The orbital overlap in the intrachain superexchange in Figure 4

On the basis of PROCAR data from VASP, where it includes the spd- and site projected wave function character in each of energy bands, we estimate the degrees of orbital overlaps between the target d orbitals (Fe1–$d_{x^2-y^2}$ and d_{z^2}, Fe2–d_{yz}, and Fe3–$d_{x^2-y^2}$) and p_σ orbitals of O^{br}. In this analysis, we approximate that if one of the target d orbitals is mixed with one of the p_σ orbitals of O^{br}, both of those orbitals have higher atomic orbital (AO) coefficients at the same energy band. That is, by multiplying the AO coefficients for the target d orbitals of Fe by the AO coefficients for the p_σ orbitals of O^{br} in all energy bands, we estimate the relative degree of orbital overlaps of p_σ orbitals with Fe2–d_{yz} vs. Fe1– or Fe3–e_g. From Table SI 1, it is clearly seen that these p_σ orbitals overlapping with the e_g orbtials ($d_{x^2-y^2}$ and d_{z^2}) of Fe1 and Fe3 are much more pronounced than the overlapping with the d_{yz} orbital of Fe2, due to the σ bonding directions, supporting our interpretations based on the GKA rules. We note that the reason for the non-zero overlap values in Table S1 for Fe2–d_{yz} (despite the geometric near-orthogonality) is due to the limitation of the present approximate analysis which does not include the phase information, however, it does provide the relative degree of orbital overlaps between the p_σ orbitals of O^{br} and Fe2–d_{yz} vs. Fe1– or Fe3–e_g.

$O^{br}–p_\sigma$	
Fe2–d_{yz}	Fe1– or Fe3–e_g
0.18	0.44

Table SI 1. Approximate relative degrees of orbital overlaps of O^{br}-p_σ with Fe2-d_{yz} vs. Fe1- or Fe3-e_g. Values in this table are an averaged value for all the p_σ orbitals of O^{br} in Figure 4.