Supporting Information

Anisotropic charge-transfer effect in the asymmetric $Fe(CN)_5NO$ octahedron of sodium nitroprusside: a soft x-ray absorption spectroscopy study

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We describe the detailed method of making the MOs. For simplicity, no Coulomb interaction on C, N, and O atoms is taken into account. The parameters ($pd\pi$) and ($pp\pi$) can be calculated according to the relations of ($pd\pi$)/($pd\sigma$) = –1.0/2.2 and ($pp\pi$)/($pp\sigma$) = –1.0/4.0, respectively. This method gives the energy levels with the bonding- and antibonding-type characters. In all symmetries, the bonding-type MOs are occupied. Figures S1(a) and S1(b) schematically show the MO that hybridizes with the Fe 3*d*(*xy*) and 3*d*(*yz*) [or 3*d*(*zx*)] orbitals. It is noted that the ligand orbitals along the *z*-axis do not contribute to the hybridization between the Fe 3*d*(*xy*) orbital and the MO.

In Fig. S1(a), the MO is composed of the C and N 2*p* orbitals. The transfer integrals for C-C and C-N ($(pp\sigma)_{CC}$ and $(pp\sigma)_{CN}$), and the one-electron C and N 2*p* levels (ε_C and ε_N) were used to define the MO energy levels. The MO wave functions are

$$\Phi_{P,i} = \sum_j c_{ij}\varphi_j \quad \text{(S1)}$$

where φ_j represents the C 2*p* and/or N 2*p* wave functions and the coefficient c_{ij} is expressed as a function of the transfer integrals and the one-electron levels. The hybridization strengths between the Fe 3*d* orbital and the MOs could be derived from combining the coefficient c_{ij} in the MO wave functions with the transfer integral for Fe-C, which is expressed as

$$V_i = \sum_k c_{ik}v_k \quad \text{(S2)}$$

Here, the value v_k is proportional to $(pd\pi)_C$ and the transfer integral for Fe-N is not included in Eq. (S2). The Fe 3*d*(x^2–y^2) orbital does not hybridize with the NO ligand, either. Thus, the parameters used in Fig. S1(a) were also used to define the MO energy levels. The hybridization strengths between the Fe 3*d*(x^2–y^2) orbital and the MOs could be derived from combining the MO wave functions with the transfer integral for Fe-C, $(pd\sigma)_C$.

Same methods could be applicable to MOs that include the NO ligand as shown in Fig. S1(b). Not only the parameters used in Fig. S1(a) but also the transfer integrals for N'-C and N-O ($(pp\sigma)_{N'C}$ and $(pp\sigma)_{NO}$), and the one-electron O 2*p* level (ε_O) were used to define the MO energy levels and the coefficient c_{ij} in Eq. (S1). In Fig. S1(b), φ_j in Eq. (S1) represents the C 2*p*, N 2*p*, and/or O 2*p* wave functions. The hybridization strengths between the Fe 3*d* orbital and the MOs could be derived from combining the coefficient c_{ij} in the MO wave functions with the transfer integral for Fe-C and Fe-N, $(pd\pi)_C$ and $(pd\pi)_N$. Similarly, the Fe 3*d*($3z^2$–r^2) orbital hybridize with the NO ligand. Thus, the parameters used in Fig. S1(b) were also used to define the MO energy levels. The hybridization strengths between the Fe 3*d*($3z^2$–r^2) orbital and the MOs could be derived from combining the MO wave functions with the transfer integral for Fe-C and Fe-N', $(pd\sigma)_C$ and $(pd\sigma)_N$.

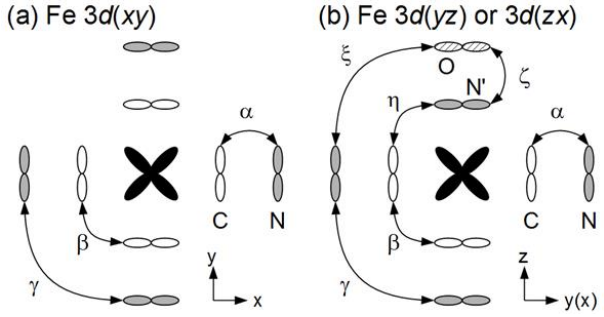

FIG. S1 Molecular orbitals hybridized with (a) Fe 3*d*(*xy*) orbital and (b) Fe 3*d*(*yz*) or 3*d*(*zx*) orbital. Here, $\alpha = (pp\pi)_{CN}$, $\beta = -((pp\sigma)_{CC}-(pp\pi)_{CC})/2$, $\gamma = 0$, $\zeta = (pp\pi)_{NO}$, $\eta = -((pp\sigma)_{NC}-(pp\pi)_{NC})/2$, and $\xi = 0$. The N atom in the NO ligand is expressed as N'.