## Supporting Information:

# Probing Solute-Solvent Interactions of Transition Metal Complexes Using L-Edge Absorption Spectroscopy 

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## I. EXPERIMENTAL METHODS

## A. Data acquisition and data treatment

By comparison of the transmitted intensity $I(E)$ to the intensity of the direct beam $I_{0}(E)$, the X-ray absorption $A(E)$ is determined via $A(E)=-\log _{10}\left[I(E) / I_{0}(E)\right]$. The raw absorption signal is displayed in Figure S 1 as the energy-dependent optical density (OD) and as an average of multiple scans for $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$ in water (10 scans), ethanol (50 scans) and DMSO (8 scans).

To isolate spectral intensity originating from core-excitations into bound states of $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$, background originating from two different sources has to be subtracted. Absorption by the solvent is estimated to decrease with a linear slope throughout the measured energy window. Additionally, two edge-jumps have to be modeled that result from continuum excitations at the $\mathrm{L}_{3}$ and $\mathrm{L}_{2}$-edge, respectively. We follow the procedure by Cho et al. [1], where both edge-jumps are modeled with an arctangent, which is centered at the respective edge $\left(\mathrm{E}_{L_{3}}=710 \mathrm{eV}\right.$ and $\left.\mathrm{E}_{L_{2}}=722.5 \mathrm{eV}\right)$ and has a width derived from the core-hole lifetime broadening ( $\mathrm{w}_{L_{3}}=0.2 \mathrm{eV}$ and $\mathrm{w}_{L_{2}}=0.4 \mathrm{eV}$ ). This amounts to the overall fit function with the variables $\mathrm{y}_{0}, \mathrm{a}, \mathrm{h}_{L_{3}}, \mathrm{~h}_{L_{2}}$ :

$$
\begin{align*}
f(E) & =y_{0}+a \cdot E+h_{L_{3}} \cdot\left(\arctan \left(w_{L_{3}} \cdot\left(E-E_{L_{3}}\right)\right)+1.5\right) / 3  \tag{S1}\\
& +h_{L_{2}} \cdot\left(\arctan \left(w_{L_{2}} \cdot\left(E-E_{L_{2}}\right)\right)+1.5\right) / 3
\end{align*}
$$

To estimate the error associated with the background subtraction, we have to consider that the spectral regions, where bound excitations are present (703-716eV, 718-730 eV), are excluded from the fit. As the error should be biggest in those areas and smallest in the linear parts of the spectra, we use the ratio of the overall height of the two edge-jumps $\left(\mathrm{h}_{L_{3}}+\mathrm{h}_{L_{2}}\right)$ and the maximum of the absorption signal to define a percentage-wise error associated with every point in the spectra. This gives an estimated error of 0.15 for water, 0.32 for ethanol and 0.31 for DMSO at each point of the individual spectra.


Figure S 1: Averaged absorption signal of $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$ (a) water, (b) ethanol and (c) DMSO before background subtraction. The fit of the background is additionally shown and consists of a linear function modeling the background from the solvent on top of two arctangents modeling the two edge jumps resulting from the respective $L_{3}$ and $L_{2}$ continuum excitations.

## B. Estimating the thickness of the liquid leaf

The sample thickness was determined by comparing the transmitted intensity before the Fe L-edge absorption onset at 700 eV to tabulated values [2] of the pure solvent. This was done separately for all individual scans allowing for the determination of an error in terms of the standard deviation. This amounts to a thickness of $(2.5463 \pm 0.0089) \mu \mathrm{m}$ in water, $(4.242 \pm 0.088) \mu \mathrm{m}$ in ethanol and $(3.30 \pm 0.18) \mu \mathrm{m}$ DMSO.

## C. Determination of the sample concentration

The concentration of $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$ in water amounts to $(58 \pm 1) \mathrm{mMol}$ as determined during preparation of the sample solution. The error results from the measuring inaccuracy of sample weight and water volume. To determine the concentration of $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$ in EtOH and DMSO, optical absorption spectra of the samples were recorded and scaled to the low-energy MLCT band of the reference spectra displayed in the main text. These spectra were recorded on carefully prepared solutions with measurement uncertainties on the order of $\mu \mathrm{Mol}$ for the sample concentration. This procedure yielded sample concentrations of 88 mMol in DMSO and 9.4 mMol in ethanol used for the X-ray absorption measurements. After ion-exchange, these samples were directly dissolved from the rotary evaporation flask into the target solvent by using an ultrasonic bath. We assume that this procedure yields a small fraction of oxidized $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{1-}$ causing the pre-peak at 705.6 eV visible for the spectra in ethanol and DMSO (compare Figure 1 in the main article and as well as Figure S1) similar to what has been observed by Penfold et al. [3] for ferrocyanide dissolved in ethylene glycol. To account for these uncertainties, we therefore estimate the error of the concentration from the relative height of the pre-peak with respect to the main absorption line to be $10 \%$ for $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$ in EtOH and DMSO.

## D. Spectra normalization and total the L-edge absorption

The energy-dependent absorption coefficient $\epsilon$ is defined as

$$
\begin{equation*}
\epsilon=-\log _{10}\left(\frac{I(E)}{I_{0}}\right) / c d \tag{S2}
\end{equation*}
$$

with sample concentration c and thickness d. After background-subtraction, the spectra displayed in Figure S1 are therefore normalized by sample concentration and thickness to yield the spectra depicted in Figure 2 of the main article, which are then independent of experimental parameters. For the total L-edge absorption, all entries of the spectra are summarized and the error of the total absorption is calculated using Gaussian error propagation.

## II. DETAILS OF THE MOLECULAR DYNAMICS SIMULATIONS

Initially, we generated a cubic box of length 3.4 nm comprising the $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$ complex, two $\mathrm{K}^{+}$counterions and the remaining of the space was filled with solvent molecules by using the gmx_solvate tool from the Gromacs package [4]. For water 1270 molecules were included, for ethanol 362 and for dimethyl sulfoxide (DMSO) 270. All calculations used periodic boundary conditions, the temperature was controlled by a modified Berendsen thermostat ( 0.1 ps time-constant) and in NPT runs the Parrinello-Rahman pressure-coupling ( 2 ps time-constant) was used. For the calculation of the Coulomb and van der Waals term a cut-off of 1.4 nm was employed, while long-range electrostatics were treated via the particle mesh Ewald (PME) procedure. The energy of the initially generated system was minimized, and subsequently the box was equilibrated in two steps: first an NVT equilibration at T $=298 \mathrm{~K}$ was run for $500 \mathrm{ps}(\Delta t=0.5 \mathrm{fs})$, followed by an NPT equilibration at $\mathrm{T}=298$ K and $\mathrm{P}=1$ bar, which was also run for $500 \mathrm{ps}(\Delta t=0.5 \mathrm{fs})$. The coordinates of the complex were constrained to the center of the box throughout the equilibration. Finally, a production NPT run of $10 \mathrm{~ns}(\Delta t=0.2 \mathrm{fs}, \mathrm{T}=298 \mathrm{~K}$ and $\mathrm{P}=1 \mathrm{bar})$ was performed from which snapshots were collected every 1 ps . The final run was used for analysis of the radial distribution functions and for sampling configurations for the spectral calculations.

## A. Force field parametrization for $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$

We have followed the protocol adopted by Prampollini et al. [5] in their study of the ferrous and ferric hexacyanide ions, which employs the Joyce program [6] for deriving forcefield (FF) parameters from quantum chemical calculations. The FF used for describing the intramolecular interactions is given as

$$
\begin{align*}
V_{\text {intra }} & =\sum_{i=0}^{N_{b}} \frac{1}{2} k_{r}^{(i)}\left(r^{(i)}-r_{0}^{(i)}\right)^{2}+\sum_{j=0}^{N_{\theta}} \frac{1}{2} k_{\theta}^{(j)}\left(\theta^{(j)}-\theta_{0}^{(j)}\right)^{2}  \tag{S3}\\
& +\sum_{k=0}^{N_{\phi}} \frac{1}{2} k_{\phi}^{(k)}\left(\phi^{(k)}-\phi_{0}^{(k)}\right)^{2},
\end{align*}
$$

where the first term describes bond stretchings, with $r_{0}^{(i)}$ and $k_{r}^{(i)}$ being the equilibrium distance and force constant for the $i-t h$ bond, respectively. The second term describes angular deformations (bending vibrations) with the equilibrium angle and force constant
of the $j$ - th coordinate being $\theta_{0}^{(j)}$ and $k_{\theta}^{(j)}$, respectively. Finally, the last term describes the improper dihedrals via the equilibrium angle $\phi_{0}^{(k)}$ and force constant $k_{\phi}^{(k)}$ for each k -th mode. Since the system under study is fairly rigid, we do not use any "soft" dihedrals in the FF.

The intermolecular interactions between molecules A and B are modeled by the standard combination of the Coulomb and Lennard-Jones potentials

$$
\begin{equation*}
V_{\text {inter }}=\sum_{i=1}^{N_{A}} \sum_{j=1}^{N_{B}} 4 \epsilon_{i j}\left[\left(\frac{\sigma_{i j}}{r_{i j}}\right)^{12}-\left(\frac{\sigma_{i j}}{r_{i j}}\right)^{6}\right]+f \frac{q_{i} q_{j}}{r_{i j}} \tag{S4}
\end{equation*}
$$

where $i$ and $j$ denote atoms belonging to molecules A and $\mathrm{B}, f=e^{2} / 4 \pi \varepsilon_{0}, q_{i}$ and $q_{j}$ are the charges of the atoms, and $r_{i j}$ is their internuclear distance. For the Lennard-Jones potentials the parameters $\sigma_{i j}$ and $\epsilon_{i j}$ are obtained via the following combination rules for each pair: $\sigma_{i j}=\left(\sigma_{i i} \sigma_{j j}\right)^{1 / 2}, \epsilon_{i j}=\left(\epsilon_{i i} \epsilon_{j j}\right)^{1 / 2}$.

Table S1: Optimized cartesian coordinates of $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$.

| atom | $\mathrm{x}(\AA)$ | $\mathrm{y}(\AA)$ | $\mathrm{z}(\AA)$ | atom | $\mathrm{x}(\AA)$ | $\mathrm{y}(\AA)$ | $\mathrm{z}(\AA)$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Fe | -0.00002 | 0.00000 | 1.09376 | C | -0.00001 | 0.72809 | -1.65339 |
| C | 1.98389 | 0.00000 | 1.07393 | C | -0.00001 | -0.72809 | -1.65339 |
| C | -1.98392 | 0.00000 | 1.07396 | C | -0.00001 | 1.51617 | -2.80555 |
| C | 0.00000 | 1.42841 | 2.42411 | C | 0.00000 | -1.51617 | -2.80555 |
| C | 0.00000 | -1.42841 | 2.42411 | C | 0.00001 | 2.89346 | -2.69171 |
| N | 3.13787 | 0.00000 | 0.91930 | C | 0.00001 | -2.89346 | -2.69171 |
| N | -3.13790 | 0.00001 | 0.91934 | H | 0.00000 | 2.99553 | 0.70423 |
| N | 0.00001 | 2.36446 | 3.11778 | H | 0.00000 | -2.99553 | 0.70423 |
| N | 0.00001 | -2.36446 | 3.11778 | H | 0.00003 | 4.52364 | -1.26659 |
| N | -0.00001 | 1.27853 | -0.41358 | H | 0.00003 | -4.52364 | -1.26659 |
| N | -0.00001 | -1.27853 | -0.41358 | H | 0.00001 | 3.52029 | -3.57574 |
| C | 0.00000 | 2.61829 | -0.30995 | H | 0.00002 | -3.52029 | -3.57574 |
| C | 0.00000 | -2.61830 | -0.30995 | H | -0.00001 | 1.04715 | -3.77991 |
| C | 0.00001 | 3.45086 | -1.41284 | H | -0.00001 | -1.04715 | -3.77991 |
| C | 0.00001 | -3.45086 | -1.41285 |  |  |  |  |

The gas-phase structure was optimized at the level of theory described in the main text and is shown in Table S1. The optimization was followed by a normal-mode analysis calcu-
lation which yielded only real frequencies. The computed Hessian was then used as input for the Joyce program to derive the intramolecular FF parameters.

For describing the electrostatic interactions charges were derived by using the Chelpg fitting procedure via the Multiwfn [7] program based on calculations carried out with Orca, at the level of theory described in the main text. The van der Waals radii used for the derivation of the Chelpg charges were: $2.1 \AA$ for $\mathrm{Fe}, 1.7 \AA$ for $\mathrm{C}, 1.5 \AA$ for N and $1.2 \AA$ for H.

The set of non-bonded parameters is shown in Table S 2 while the derived set of intramolecular FF parameters is displayed in Table S3. The labelling of the atoms used to describe the interactions is shown in Figure S 2 .


Figure S 2: Atomic labels used in the force-field specification.

Table S2: Non-bonded parameters for $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$

|  | $\mathrm{q}(e)$ | $\sigma(\mathrm{nm})$ | $\epsilon\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ |
| :---: | :---: | :---: | :---: |
| FE | -1.304 | 0.2594 | 0.0544 |
| CZ1 | 0.402 | 0.3650 | 0.6276 |
| NZ1 | -0.835 | 0.3200 | 0.7113 |
| CZ2 | 0.456 | 0.3650 | 0.6276 |
| NZ2 | -0.855 | 0.3200 | 0.7113 |
| NC | 0.413 | 0.3250 | 0.7110 |
| CA1 | -0.238 | 0.3550 | 0.2930 |
| CA2 | -0.098 | 0.3550 | 0.2930 |
| CA3 | 0.019 | 0.3550 | 0.2930 |
| CA4 | -0.179 | 0.3550 | 0.2930 |
| CA5 | -0.082 | 0.3550 | 0.2930 |
| HA1 | 0.200 | 0.2420 | 0.1260 |
| HA2 | 0.138 | 0.2420 | 0.1260 |
| HA3 | 0.143 | 0.2420 | 0.1260 |
| HA4 | 0.168 | 0.2420 | 0.1260 |

Table S3: Derived intramolecular force field parameters for $\left[\mathrm{Fe}(\mathrm{bpy})(\mathrm{CN})_{4}\right]^{2-}$, describing bond stretching, angular deformation and improper dihedrals.


## III. HYDROGEN BOND (HB) ANALYSIS

Based on the MD simulations, we carried out an analysis of the HB interactions between the solute and the protic solvents (water and ethanol). This was done with the $g m x r d f$ and gmx hbond tools of the Gromacs package. The HBs were defined by the following criteria: $r_{N-O}<3.0 \AA$ and $\angle N H O<20^{\circ}$, similar to previous studies $[3,5]$.


Figure S 3: Total and partial N-H pair correlation functions for the CN ligands in water (a) and ethanol (d). Distribution of N - O distances involved in hydrogen bonding for water (b) and ethanol (e). Distribution of $\angle N O H$ angles involved in Hydrogen bonding in water (c) and ethanol (f). The inset in panel (f) shows the definition of the distances and angle.

As can be seen from Figure S3, the solvation shell structure differs slightly between the axial CN ligands (denoted NZ1 as in Figure S2) when compared to the in-plane CN ligands (NZ2). This is reflected by the higher number of HBs per ligand $\left(n_{H B}\right)$ shown in Table. S4.

A visual representation of the distribution of water molecules in the first solvation shell around the cyanide ligands can be seen in Figure S4, where the mass-weighted density function for the atoms of the water molecules is shown.

In summary, the complex experiences a number of HBs between $2.13-2.95$ per cyanide in water, while in ethanol the number of HBs lies within $1.38-2.22$ per cyanide. The N-H

Table S4: Hydrogen bonding parameters extracted from the MD simulations in water and ethanol. The $r_{N H}$ distance is obtained from the maximum of the $g_{N H}(r)$ pair-correlation function. The number of $\mathrm{HBs}\left(n_{H B}\right)$ is defined via the N and the water OH bond for

$$
\angle N H O<20^{\circ} \text { and } r_{N O}<3.0 \AA .
$$

| water | $r_{N-H}$ | $r_{N-O}(\AA)$ | $\angle N O H\left({ }^{\circ}\right)$ | $\mathrm{n}_{H B}$ |
| :--- | :--- | :--- | :--- | :--- |
| Total | 1.68 | $2.75 \pm 0.11$ | $9.36 \pm 4.64$ | $2.54 \pm 0.41$ |
| NZ1 | 1.68 | $2.76 \pm 0.11$ | $9.34 \pm 4.64$ | $2.68 \pm 0.54$ |
| NZ2 | 1.70 | $2.74 \pm 0.11$ | $9.39 \pm 4.63$ | $2.40 \pm 0.56$ |
| EtOH | $r_{N-H}$ | $r_{N-O}(\AA)$ | $\angle N O H\left({ }^{\circ}\right)$ | $\mathrm{n}_{H B}$ |
| Total | 1.80 | $2.77 \pm 0.11$ | $9.25 \pm 4.57$ | $1.80 \pm 0.42$ |
| NZ1 | 1.78 | $2.77 \pm 0.11$ | $9.17 \pm 4.55$ | $2.00 \pm 0.50$ |
| NZ2 | 1.76 | $2.76 \pm 0.11$ | $9.34 \pm 4.59$ | $1.60 \pm 0.54$ |



Figure S 4: Mass-weighted density function of oxygen atoms (red surface, isovalue $=0.86$ ) and hydrogen atoms (white surface, isovalue $=0.12$ ) of the water molecules around the complex. Plot constructed from the MD data with the VMD volmap plugin.
distances of HBs in ethanol are slightly longer than in water by $\sim 0.1 \AA$. In both solvents, the axial ligands experience a slightly higher number of HBs on average. Further details are shown in Table. S4.

## IV. EXCHANGE AND CORRELATION FUNCTIONAL DEPENDENCE

Figure $S 5$ (a) shows the tests carried out for the $\mathrm{L}_{2,3}$-edge XAS in gas-phase and using CPCM in DMSO. Qualitatively compatible results are obtained with all the global-hybrids considered: M06, PBE0 and B3LYP. However, the relative intensity and energy of the $\pi^{*}$ peak with respect to the $e_{g}$ transition is sensitive to the amount of Hartree-Fock (HF) exchange of the functional, the higher the fraction of HF exchange the lower the intensity of the $\pi^{*}$ peak and the larger the energy spacing with respect to the main $e_{g}$ peak.


Figure S 5: Dependence of the the (a) $\mathrm{L}_{2,3}$-edge and (b) UV-Vis spectral calculations on the choice of the exchange and correlation functional used in the TD-DFT calculations.

Still, all functionals predict the relative intensity of this peak to be higher in DMSO than in gas-phase. The agreement is, however, far worse in the absence of HF exchange, as seen by the qualitatively disparaging behavior of the pure M06L functional.

Looking at panel (b) for the results for the UV-Vis spectrum, all global-hybrids performed similarly once again. In contrast, the range-corrected CAM-B3LYP functional performed
worse than the global-hybrid functionals considered here. Such failures of CAM-B3LYP have been reported before [8].

We deemed the quality of the results to be slightly better with the M06 functional for both the XAS and UV-Vis spectra and therefore this functional was chosen for the production calculations in the article.


Figure S 6: (a) UV-Vis spectra for the complex in water and DMSO considering 50 samples, and including or excluding explicit HB interactions with water. (b) $\mathrm{L}_{2,3}$ edge spectra in water and DMSO considering 50 samples, and including or excluding explicit HB interactions with water. (c) UV-Vis spectra in water and DMSO considering a single optimized structure with CPCM. (d) $\mathrm{L}_{2,3}$ edge spectra in water and DMSO considering a single optimized structure with CPCM.

## V. THE ROLE OF HYDROGEN BONDING ON THE SPECTRA

Figure S6 displays a comparison between different levels of approximation in accounting for the solvation effects in water. It can be seen that the inclusion of the first solvation shell around the cyanide ligands is crucial for reproducing the solvatochromic shift of the MLCT band as well as the increase in intensity of the $\pi^{*}$ feature in the $\mathrm{L}_{2,3}$ spectrum.

## VI. CDA: FRAGMENT ORBITAL DECOMPOSITION ANALYSIS

Figure S 7 shows the selected orbitals of the idealized solvation model, which are discussed in the main text and used to analyze the different contributions to the metal-ligand bond. It should be noted, that within the $\mathrm{C}_{2 v}$ point group $\sigma$ and $\pi$ ligand orbitals are allowed to mix, which complicates the analysis. Furthermore, there is strong mixing of the orbitals of the complex with those of the surrounding waters, which poses an obstacle to a definite one-to-one comparison between the orbitals of the gas-phase and solvated case. The only exception are the metal-dominant $t_{2 g}$-like orbitals that are well defined in both, the isolated and the solvated complex.

The system was divided into 4 fragments: The $\mathrm{Fe}^{2+}$ cation, the $4 \mathrm{CN}^{-}$ligands, the 2-2'-bipyridine ligand, and finally the 11 water molecules. The system belongs to the $\mathrm{C}_{2 v}$ point group, however, we use an approximate Oh labelling for the Fe orbitals. Since the CDA procedure is based on the Mulliken partition for deriving populations, it can lead to unreliable results for large basis sets, especially if diffuse functions are present. Therefore, we carried out the analysis with the smaller, closely related def2-SV(P) basis set, instead of the previously adopted larger def2-TZVP(-f).

Tables S5, S6 and S7 show the decomposition of the orbitals selected in Figure S7 in terms of the relevant orbitals of the metal center and the cyanide ligands. Furthermore, for the solvated case, the total fraction of water orbitals is also shown.


Figure S 7: Selected Kohn-Sham orbitals for analyzing the solvation effect on the bonding channels between the cyanide ligands and the metal center. Orbitals are grouped as being metal-dominant (Fe $t_{2 g}$-like) and ligand dominant ( $\sigma$ - and $\pi$-like) and are also classified by their respective irreducible representation. All orbitals were plotted with a 0.03 isovalue.

Table S5: Fragment orbital populations (\%) from the decomposition of the $t_{2 g}$-like orbitals of the complex in terms of the orbitals of $\mathrm{Fe}^{2+}, \mathrm{CN}^{-}$, bpy and water.

| gas | orbital | $\epsilon_{i}(\mathrm{eV})$ | $\mathrm{Fe} t_{2 g}$ | $\mathrm{Fe} e_{g}$ | $\mathrm{CN}^{-} \sigma$ | $\mathrm{CN}^{-} \pi$ | $\mathrm{CN}^{-} \pi^{*}$ | bpy $\pi^{*}$ |  |
| :--- | :---: | :---: | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  | $79 / 36-\mathrm{A} 1$ | 1.238 | 80.70 | 0.00 | 0.00 | 10.62 | 3.78 | 0.00 |  |
|  | $80 / ~ 13-\mathrm{B} 2$ | 1.391 | 64.73 | 0.00 | 2.31 | 10.19 | 4.14 | 16.07 |  |
|  | $81 /$ | $6-\mathrm{A} 2$ | 1.441 | 77.86 | 0.00 | 0.00 | 12.16 | 4.69 | 2.84 |
| solvated | orbital | $\epsilon_{i}(\mathrm{eV})$ | $\mathrm{Fe} t_{2 g}$ | $\mathrm{Fe} e_{g}$ | $\mathrm{CN}^{-} \sigma$ | $\mathrm{CN}^{-} \pi$ | $\mathrm{CN}^{-} \pi^{*}$ | bpy $\pi^{*}$ | water |
|  | $134 / 53-\mathrm{A} 1$ | -1.176 | 83.15 | 0.00 | 0.00 | 6.07 | 5.90 | 0.00 | 0.00 |
|  | $135 / 28-\mathrm{B} 2$ | -0.999 | 72.57 | 0.00 | 0.00 | 8.25 | 5.42 | 8.17 | 0.00 |
|  | $136 / 17-\mathrm{A} 2$ | -0.944 | 79.52 | 0.00 | 0.00 | 8.14 | 5.89 | 1.57 | 0.00 |

Table S6: Fragment orbital populations (\%) from the decomposition of the $\sigma$-like orbitals of the complex in terms of the orbitals of $\mathrm{Fe}^{2+}, \mathrm{CN}^{-}$and water.

| gas | orbital | $\epsilon_{i}(\mathrm{eV})$ | $\mathrm{Fe} t_{2 g}$ | $\mathrm{Fe} e_{g}$ | $\mathrm{CN}^{-} \sigma$ | $\mathrm{CN}^{-} \pi$ | $\mathrm{CN}^{-} \pi^{*}$ |  |
| :--- | :---: | :---: | :--- | :--- | :--- | :--- | :--- | :--- |
|  | $60 / 30-\mathrm{A} 1$ | -3.301 | 0.00 | 17.53 | 55.77 | 0.00 | 0.00 |  |
|  | $70 / 33-\mathrm{A} 1$ | -1.330 | 0.00 | 5.82 | 85.00 | 0.00 | 0.00 |  |
|  | $76 / 35-\mathrm{A} 1$ | -0.573 | 0.00 | 6.16 | 49.31 | 36.63 | 0.00 |  |
|  | $59 / 22-\mathrm{B} 1$ | -3.507 | 0.00 | 17.46 | 42.10 | 1.01 | 0.00 |  |
|  | $77 / 26-\mathrm{B} 1$ | -0.374 | 0.00 | 6.99 | 62.19 | 22.56 | 0.00 |  |
| solvated | orbital | $\epsilon_{i}(\mathrm{eV})$ | $\mathrm{Fe} t_{2 g}$ | $\mathrm{Fe} e_{g}$ | $\mathrm{CN}^{-} \sigma$ | $\mathrm{CN}^{-} \pi$ | $\mathrm{CN}^{-} \pi^{*}$ | water |
|  | $92 / 41-\mathrm{A} 1$ | -6.332 | 0.00 | 4.25 | 51.81 | 0.00 | 0.00 | 37.75 |
|  | $115 / 48-\mathrm{A} 1$ | -3.720 | 0.00 | 9.65 | 54.22 | 18.10 | 0.00 | 11.03 |
|  | $126 / 51-\mathrm{A} 1$ | -3.101 | 0.00 | 3.71 | 24.41 | 38.17 | 0.00 | 25.52 |
|  | $91 / 29-\mathrm{B} 1$ | -6.459 | 0.00 | 5.66 | 65.19 | 0.00 | 0.00 | 21.59 |
|  | $121 / 35-\mathrm{B} 1$ | -3.319 | 0.00 | 2.54 | 26.95 | 6.41 | 0.00 | 57.38 |

Table S7: Fragment orbital populations (\%) from the decomposition of the $\pi$-like orbitals of the complex in terms of the orbitals of $\mathrm{Fe}^{2+}, \mathrm{CN}^{-}$, bpy and water.

| gas | orbital | $\epsilon_{i}(\mathrm{eV})$ | $\mathrm{Fe} t_{2 g}$ | $\mathrm{Fe} e_{g}$ | $\mathrm{CN}^{-} \sigma$ | $\mathrm{CN}^{-} \pi$ | $\mathrm{CN}^{-} \pi^{*}$ | bpy $\pi$ |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
|  | $69 / 32-\mathrm{A} 1$ | -1.430 | 8.66 | 0.00 | 3.63 | 81.77 | 0.00 | 0.00 |  |
|  | $72 / 34-\mathrm{A} 1$ | -1.197 | 1.80 | 4.70 | 28.50 | 60.88 | 0.00 | 0.00 |  |
|  | $63 / 2-\mathrm{A} 2$ | -3.220 | 2.49 | 0.00 | 0.00 | 3.70 | 0.00 | 91.85 |  |
|  | $68 / 4-\mathrm{A} 2$ | -1.475 | 7.02 | 0.00 | 0.00 | 77.55 | 1.04 | 13.51 |  |
|  | $75 / 5-\mathrm{A} 2$ | -0.650 | 0.00 | 0.00 | 0.00 | 98.97 | 0.00 | 0.00 |  |
| solvated | $67 / 10-\mathrm{B} 2$ | -1.551 | 6.88 | 0.00 | 8.25 | 79.79 | 1.02 | 0.00 |  |
|  | $73 / 11-\mathrm{B} 2$ | -0.923 | 0.00 | 0.00 | 8.08 | 81.38 | 0.00 | 2.82 |  |
|  | $71 / 24-\mathrm{B} 1$ | -1.263 | 0.00 | 2.42 | 21.26 | 71.64 | 0.00 | 0.00 |  |
|  | $74 / 25-\mathrm{B} 1$ | -0.802 | 0.00 | 0.00 | 0.00 | 95.90 | 0.00 | 0.00 |  |
|  | $103 / 45-\mathrm{A} 1$ | -5.019 | 2.06 | 0.00 | 3.70 | 46.03 | 0.00 | 0.00 | 40.14 |
|  | $116 / 49-\mathrm{A} 1$ | -3.564 | 3.60 | 0.00 | 5.54 | 28.99 | 0.00 | 0.00 | 55.31 |
|  | $102 / 9-\mathrm{A} 2$ | -5.075 | 4.38 | 0.00 | 0.00 | 16.40 | 0.00 | 75.68 | 0.00 |
|  | $107 / 10-\mathrm{A} 2$ | -4.371 | 0.00 | 0.00 | 0.00 | 56.87 | 0.00 | 19.05 | 18.76 |
|  | $117 / 12-\mathrm{A} 2$ | -3.557 | 0.00 | 0.00 | 0.00 | 55.05 | 0.00 | 12.24 | 30.21 |
|  | $106 / 21-\mathrm{B} 2$ | -4.466 | 2.07 | 0.00 | 12.18 | 59.59 | 0.00 | 4.50 | 18.45 |
|  | $118 / 23-\mathrm{B} 2$ | -3.515 | 0.00 | 0.00 | 0.00 | 73.13 | 0.00 | 5.89 | 16.29 |
|  | $108 / 32-\mathrm{B} 1$ | -4.314 | 0.00 | 1.30 | 9.50 | 42.45 | 0.00 | 0.00 | 41.07 |
|  | $114 / 34-\mathrm{B} 1$ | -3.742 | 0.00 | 0.00 | 2.87 | 73.01 | 0.00 | 0.00 | 18.16 |

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