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Fixed Distance Photoinduced Electron Transfer between Fe and Zn Porphyrins Encapsulated within the Zn HKUST-1 Metal Organic Framework

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An attractive strategy for the development of photocatalytic metal organic framework (MOF) materials is to co-encapsulate a photoactive electron donor with a catalytic electron acceptor within the MOF. Here we report the co-encapsulation of both Zn(II) tetrakis(tetra 4-sulphonatophenyl)porphyrin (Zn4SP) and Fe(III) tetrakis (tetra 4-sulphonatophenyl) porphyrin (Fe4SP) into an HKUST-1 (Zn) MOF and demonstrate photoinduced electron transfer (ET) between the co-encapsulated guest. Photo-excitation of the Zn4SP results in fixed-distance inter-molecular ET between the encapsulated ^{3}Zn4SP and the Fe(III)4SP as evident by the reduction in the encapsulated ^{3}Zn4SP lifetime from 890 μs (k_{obs} $1.1x10^3$ s^{-1}) to 83 μs (k_{obs} = $1.2x10^4$ s^{-1}) in the presence of Fe4SP giving a k_{ET} ~ $1.1x10^4$ s^{-1}. The data are consistent with ET taking place between encapsulated porphyrins that are two cages apart in distance with a reorganizational energy of ~1.65 eV, β = 1.25 and ΔG^0 = -0.97 eV (within a semi-classical Marcus theory framework).

Electron transfer (ET) reactions are fundamental to nearly all chemical and biological processes including, but certainly not limited to, cellular respiration, photosynthesis, photovoltaics, and both homogeneous and heterogeneous catalysis.[1-4] In the case of biological systems these reactions involve either inter- or intra-molecular ET typically between metal centers either embedded within the same protein complex or belonging to distinct proteins forming a catalytic complex. In the case of catalysts, similar inter- and intra-molecular ET can take place between donor and acceptor components of the catalytic system. The rates of both inter- and intra-molecular ET systems can be described by the semi-classical Marcus equation:

$$k_{ET} \sim k_o \exp(-\beta(d-R_o))\exp(-(\Delta G°+\lambda)2/4\lambda RT) \qquad (1)$$

where k_o is the rate constant associated with barrier-less ET, typically on the order of a molecular vibration (~10^{13} s^{-1}), R_o is the van der Waals contact distance between the donor and acceptor, β is an empirically determined electronic coupling factor, d is the donor acceptor distance, λ is the total reorganizational energy (inner sphere plus outer sphere) and ΔG° is the reaction driving force.[2] In solution, both intra- and inter-molecular ET can take place with appreciable rates (ns to ms) over relatively long distances (tens of Å) facilitated by electronic coupling between donor and acceptor.

Figure 1: Diagram illustrating both intra-molecular (Cytochrome c Oxidase) and inter-molecular (Cytochrome c: Cytochrome c Peroxidase non-covalent complex) and biomimetic inter-cavity ET in an HKUST-1 Metal Organic Framework.

Porphyrin based donor-acceptor ET systems are of particular importance due to their prevalence in essential biological processes including photosynthesis and catalysis as well as the fact the closed shell metalloporphyrins exhibit relatively long lived singlet and triplet states allows for ET reactions between porphyrins to be photo-initiated. To date a wide variety of porphyrin based donor acceptor systems have been designed to probe fundamental aspects of ET as well as to facilitate long range charge separation including prophryin donor-acceptor complexes contained within solid state matrices.[5] A variety of solid matrices have been utilized in order to immobilize porphyrin donor acceptor pairs including clays, zeolites, mesoporous silicates and nanotubes. Immobilization of donor-acceptors within solid matrices also has significant effects upon the ET rates and mechanisms effecting electronic state localization, phonon coupling, enhancement of weak interactions, and less efficient vibrational relaxation.

Of specific interest in the area of porphyrin based ET is the mimicry of the catalytic diversity of heme containing enzymes in the development of homogeneous and heterogeneous catalysts.[6-15] An attractive target for heme biomimetic systems are metal organic framework (MOF) materials that contain polyhedral cages.[16,17] Polyhedral MOFs share common structural features with heme proteins including large pockets which can accommodate the catalytic metalloporphyrin as well as channels which connect the bulk solvent to the various interior cages within the MOF. In addition, both the topology and the structural versatility of the MOF can be tuned through application of the molecular building blocks approach (MBB) in which metal-ligand clusters form building units providing a wide array of three dimensional topologies. Coupling the three dimensional structure with the ability to functionalize the organic ligand component of the MBB affords enormous flexibility in catalytic tuneability.

The prototypical MOF, HKUST-1, formed through the assembly of benzene-1,3,5-tricarboxylate anions and either copper(II)[18] or zinc(II)[19] cations, contain several features that are attractive towards heme biomimetic chemistry including three structurally distinct polyhedral cages capable of entrapping guest molecules (Fig. 1). The HKUST-1 framework has now been shown to selectively encapsulate metallo-porphyrins including Fe(III)tetrakis(4-sulphonatophenyl)porphyrin (Fe4SP), Mn(III)tetrakis(4-sulphonatophenyl)porphyrin (Mn4SP) and Zn(II) tetrakis(4-methylpyridyl)porphyrin (ZnT4MPyP) within the octahedral cage while the remaining cavities allow small molecules to reach the active site for catalysis much like channels in heme proteins.[20,21] More importantly, the porphyrin encapsulated HKUST-1 materials demonstrate crystallographically resolved, although disordered, porphyrin macrocycles in the cages reminiscent of heme pockets as well as heme protein-like catalytic peroxidase activity.

As part of our on-going efforts to develop heme biomimetic MOF materials we have examined photo-induced inter-cavity ET between the excited triplet state Zn4SP and co-encapsulated Fe4SP. Crsytalline Zn4SP@HKUST-1 (Zn) and Zn4SP:Fe4SP@HKUST-1 (Zn) materials were prepared through a 'ship-in-a-bottle' approach as described previously (see the supplementary materials for synthesis and X-ray characterization).[18] The ability to co-encapsulate both Zn4SP and Fe4SP into the HKUST-1 (Zn) is demonstrated optically in Fig. S1 of the supplementary materials. Interestingly, for all mass ratios used in the synthesis of Zn4SP:Fe4SP@HKUST-1 (Zn) the Fe4SP displayed the highest loading, relative to Zn4SP (1:1, 1:2 and 2:1 Fe4SP:Zn4SP by mass gave 1.1:1, 1.6:1 and 3.5:1 molar ratios, respectively). The total porphyrin loading (porphyrin complexes per octahedral cavity) has been previously estimated to be ~ 60% as.[20]

Figure 2: Top: Single wavelength transient absorption of the triplet state decay of Zn4SP@HKUST-1 (Zn) suspended in ethanol (red trace) and solubilized in H_2O (black trace) monitored at 420 nm (Soret bleach and recovery). Bottom: Triplet-Triplet absorption decay of Zn4SP@HKUST-1 (Zn) with varying amounts co-encapsulated Fe4SP suspended in ethanol.

In the absence of Fe4SP, the ^{3}Zn4SP@HUKUST-1 (Zn) decays with a rate constant of 1.1×10^{3} s^{-1} which is approximately a factor of two larger than that observed for the ^{3}Zn4SP in solution (536 s^{-1}) (Fig. 2, Top Panel). Porphyrin out-of-plane distortions have been suggested to enhance the coupling between the triplet excited and singlet ground states thus facilitating non-radiative decay and decreasing the triplet state lifetime.[21] It is possible that encapsulation of the porphyrin results in distortions from planarity although the crystallographic resolution and disorder precludes definitive identification of porphyrin distortions. Interestingly, the corresponding ^{3}ZnTMPyP@HKUST-1 (Zn) decay rate is three times slower than that observed for ZnTMPyP in solution which was attributed to the HKUST-1 (Zn) cavity actually damping low frequency out-of-plane porphyrin vibrational modes.[21] However, ZnTMPyP also exhibits coupling between the porphyrins S1 state and a charge transfer state localized on the peripheral pyridyl groups (absent in the Zn4SP) that is influenced by the angle of the pyridyl groups and the porphyrin plane and possibly porphyrin planarity.[19] It is likely that the charge transfer state in the ZnTMPyP also modulates the electronic coupling between the T_1 to S_0 states through the spin orbit coupling matrix element.

In the presence of co-encapsulated Fe4SP the rate of ^{3}Zn4SP decay rate is further increased (Fig. 3, Bottom) due to either an enhancement of the non-radiative decay pathway of ^{3}Zn4SP to the singlet ground state induced by the presence of Fe4SP in neighbouring cavities or inter-cavity ET from the ^{3}Zn4SP to the ground state Fe4SP. The favourability of inter-cavity ET can be evaluated using a Rhem-Weller[22] analysis:

$$\Delta G_{ET} = e[E_D^{o} - E_A^{o}] - \Delta E^{*} + w \qquad (2)$$

where E_D^{o} is the reduction potential of the donor, E_A^{o} is the reduction potential of the acceptor, ΔE^{*} is the energy of the excited singlet or triplet state and w is the work required to bring together the donor and acceptor within the ET distance (0 in this case as the ET is fixed distance within the MOF cavities). As the X-ray crystal structure reveals a very hydrophobic pocket associated with porphyrin binding the E^{o} values used to estimate the ΔG^{o} values are for Zn(II) tetraphenyl porphyrin (ZnTPP) and Fe(III) tetraphenyl porphyrin (FeTPP) in organic solvents. Using an E^{o} of -0.49 V for the Fe(III)TPP -> Fe(II)TPP (CH_2Cl_2/TBAH)[23] and 0.51V for the Zn(II)TPP -> Zn(II)$TPP^{+\bullet}$ [24] as well as the excited state properties of Zn4SP[25] the ΔG^{o} associated with ET between the singlet and triplet state Zn4SP and ground state Fe4SP within the HKUST-1 (Zn) are found to be -25 kcal mol^{-1} and -14 kcal mol^{-1}, respectively. The corresponding rate constant for inter-cavity ET between ^{3}Zn4SP and Fe4SP is derived from:

$$[^{3}\mathrm{Zn4SP}]\text{----}[\mathrm{Fe(III)4SP}] \xrightarrow{k_{ET}} [\mathrm{Zn4SP}^{+\bullet}]\text{----}[\mathrm{Fe(II)4SP}] \qquad (3)$$

$$[^{3}\mathrm{Zn4SP}]\text{----}[\mathrm{Fe(III)4SP}] \xrightarrow{k_{T}} [\mathrm{Zn4SP}]\text{----}[\mathrm{Fe(II)4SP}] \qquad (4)$$

where (3) is ET between co-encapsulated ^{3}Zn4SP and Fe(III)4SP and (4) is the triplet state decay of encapsulated ^{3}Zn4SP that are too far from co-encapsulated Fe4SP for productive ET to take place. The observed triplet decay rate is given by:

$$-d[^3Zn4SP]/dt = k_{obs}[^3Zn4SP] = (k_T + k_{ET})[^3Zn4SP] \quad (5)$$

$$k_{ET} = k_{obs} - k_T \quad (6).$$

where k_T is the triplet decay rate constant of Zn4SP@HKSUT-1 (Zn) ($1.1x10^3$ s^{-1}) and k_{obs} is the decay rate constant of the Zn4SP:Fe4SP@HKSUT-1 (Zn) with the highest Fe4SP:Zn4SP ratio
($1.2x10^4$ s^{-1}). The k_{ET} is found to be $1.1x10^4$ s^{-1}.

Figure 3: Plots of calculated k_{ET} versus λ for differing β values using d = 29 Å , k_0 = $1x10^{13}$ s^{-1}, R_0 = 9.7 Å (for Fe4SP/Zn4SP), ΔG° = -0.61 eV (-14 kcal mol^{-1}) and T = 300K. The line designates the observed k_{ET} of 11,000 s^{-1}.

Semi-classical Marcus theory can provide important insights into the photoinduced ET process (Fig. 3). Three sets of parameters could give rise to the observed rate constants (the solid dots in Fig. 3): λ = 1.2 eV, β = 1.25, d=29 Å; λ = 1.75 eV, β = 1. 5, d=29 Å; λ = 2.35 eV, β = 1.75, d=29 Å. For all three parameter sets the distance giving rise to the ~11,000 s^{-1} rate constant is 29 Å which corresponds to donor-acceptor pairs that are separated by one empty cavity (Fig. 4). That is, of the randomly distributed Zn4SP and Fe4SP within the pores of the HKUST-1 (Zn) framework the transient absorption is only probing the population of Zn4SP and Fe4SP that are within 29 Å. The parameter sets with λ = 1.2 eV and β = 1.25 and λ = 1.75 eV and β = 1.5 are within the range of values observed for a variety of fixed distance inter-molecular ET between porphyrins.[21] The λ of 2.35 eV represents considerable structural reorganization that is not likely to occur in the confined space of the octahedral cavities of the MOF.

Figure 4: Diagram illustrating the possible ET distances between encapsulated porphyrins within the octahedral cavities of HKUST-1 (Zn). Top- From X-ray data, porphyrin loading but with fractional occupancies. Bottom- Diagram illustrating the actual random distribution of porphyrin complexes within the framework. Dotted circle indicates distances giving rise to ^{3}Zn4SP to Fe4SP ET while the solid circle indicates the distance for ^{1}Zn4SP to Fe4SP ET. The red and green symbols represent positions of randomly encapsulated Zn4SP and Fe4SP.

Photoinduced ET between ^{1}Zn4SP and Fe4SP can also take place (but at much shorter distances) due to the favourable ΔG° value. Although the fluorescence lifetime and steady state emission data do not display significant changes upon Fe4SP co-encapsulation photoinduced ET from the ^{1}Zn4SP to Fe4SP may still occur but with very low probability due to the low occupancy of the porphyrins within the octahedral cavities (Fig. S2 and S3, supplementary material).

Previous studies from our laboratory of inter-cavity ET between Ru(II)tris(2,2'-bipyridine) and Co(II)tris(2,2'-bipyridine) encapsulated within a polyhedral Zn(II)-trimesic acid MOF, USF2 gave a value of λ only slightly lower than the porphyrin system (1.25 eV) reflecting limited structural reorganization of the redox products.[24] In the case of the Zn4SP:Fe4SP@HKUST-1(Zn) system the slightly higher value of λ may arise from restrictions in $Zn4SP^{+\bullet}$ and/or Fe(II)4SP deformations upon change in redox state resulting in an increase in the inner sphere λ.

Conclusions

The results presented here demonstrate intercavity photoinduced electron transfer between ^{3}Zn4SP and Fe4SP co-encapsulated within a HKUST-1(Zn) MOF with a rate constant of 11,000 s^{-1}. Interestingly, despite a favourable ΔG^0, no ET occurs between the ^{1}Zn4SP and Fe4SP most likely due to the large distance between Zn4SP and Fe4SP complexes within the HKUST-1(Zn) framework. The results are also consistent with ET taking place between ^{3}Zn4SP and Fe4SP that are separated by one octahedral cavity (i.e., non-adjacent cavities) and occurs from a pyrole edge associated with a Zn4SP to the pyrole edge associated with a Fe4SP.

Notes and references

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†Electronic Supplementary Information (ESI) available: [Synthethic procedures and spectroscopic details]. See DOI: 10.1039/c000000x/

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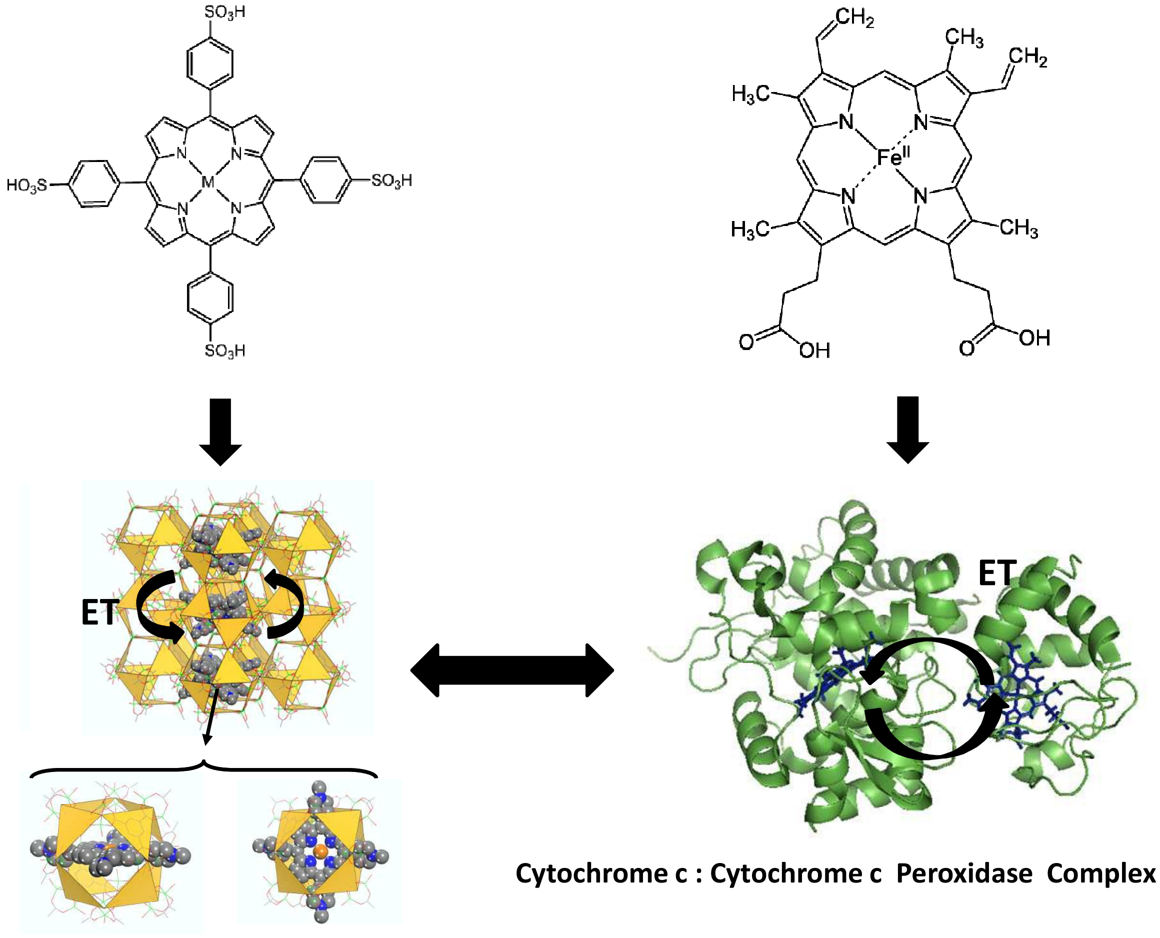
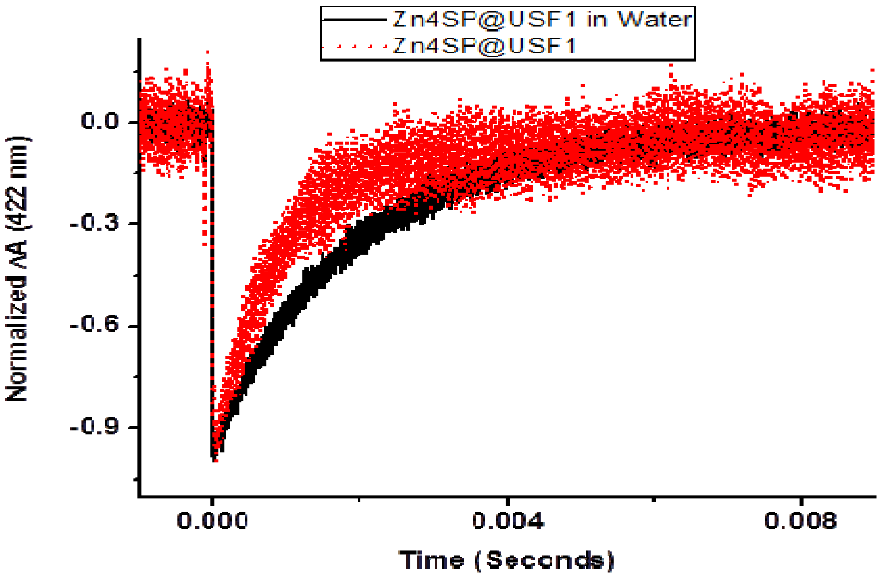
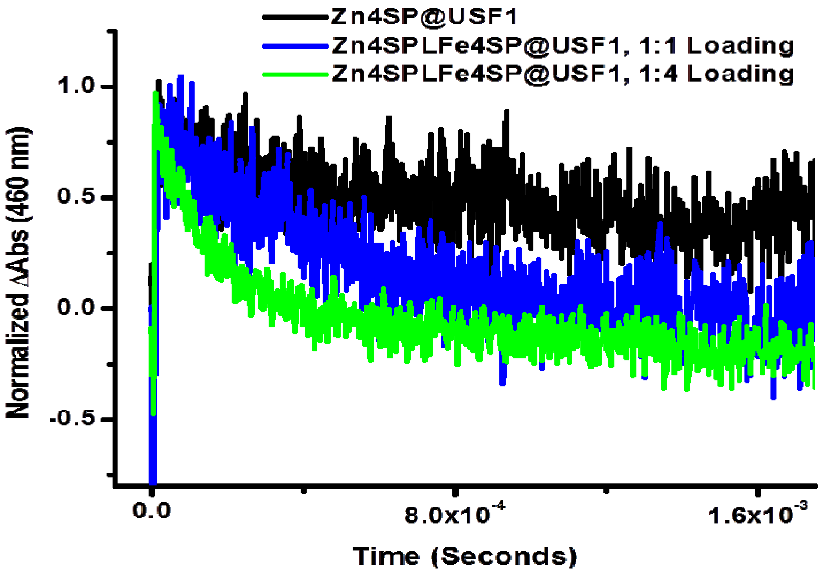
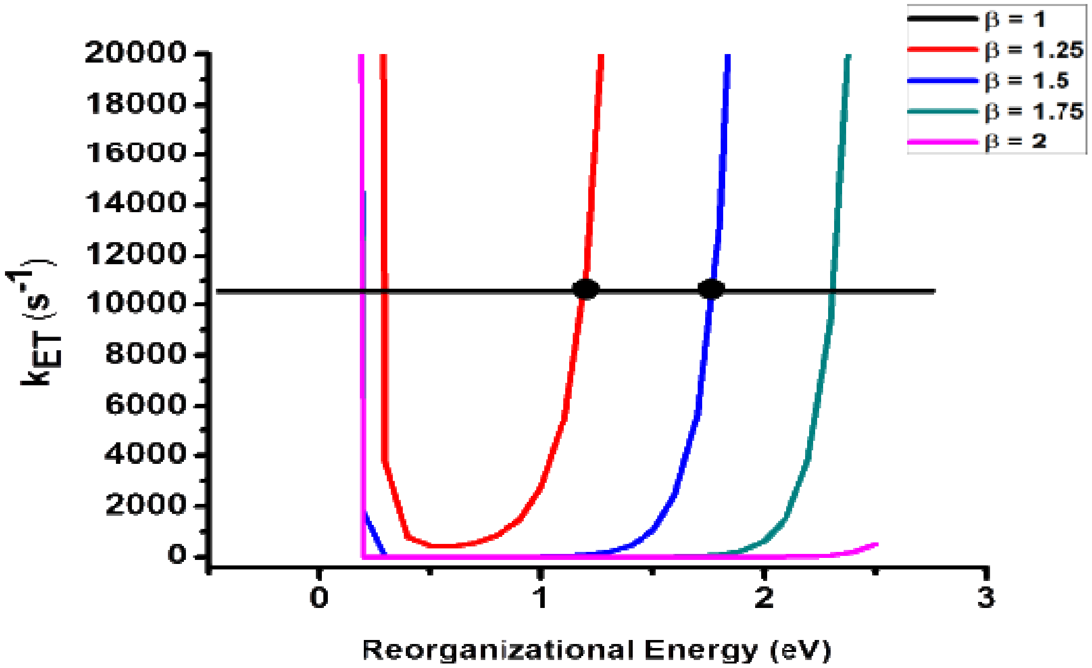


Zn4SP-Fe4SP HKSUT-1

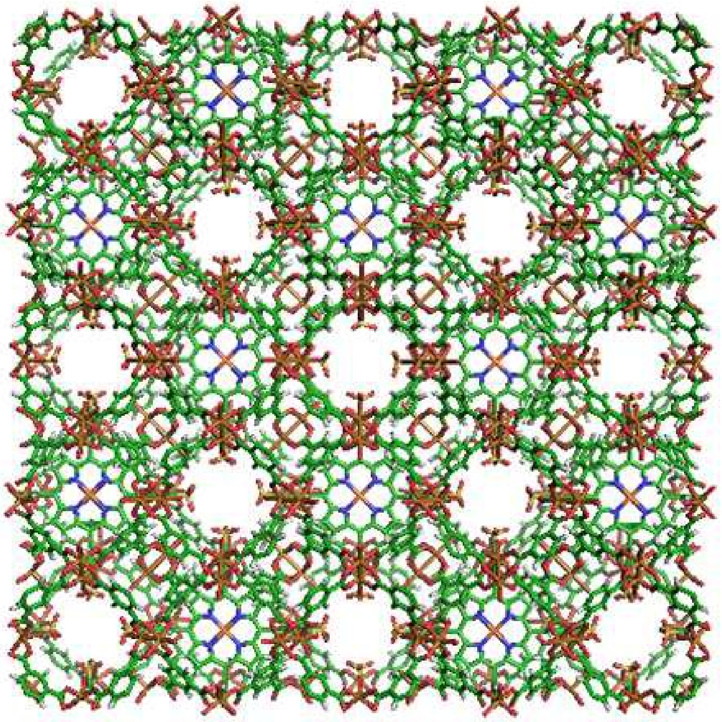
Cytochrome c : Cytochrome c Peroxidase Complex

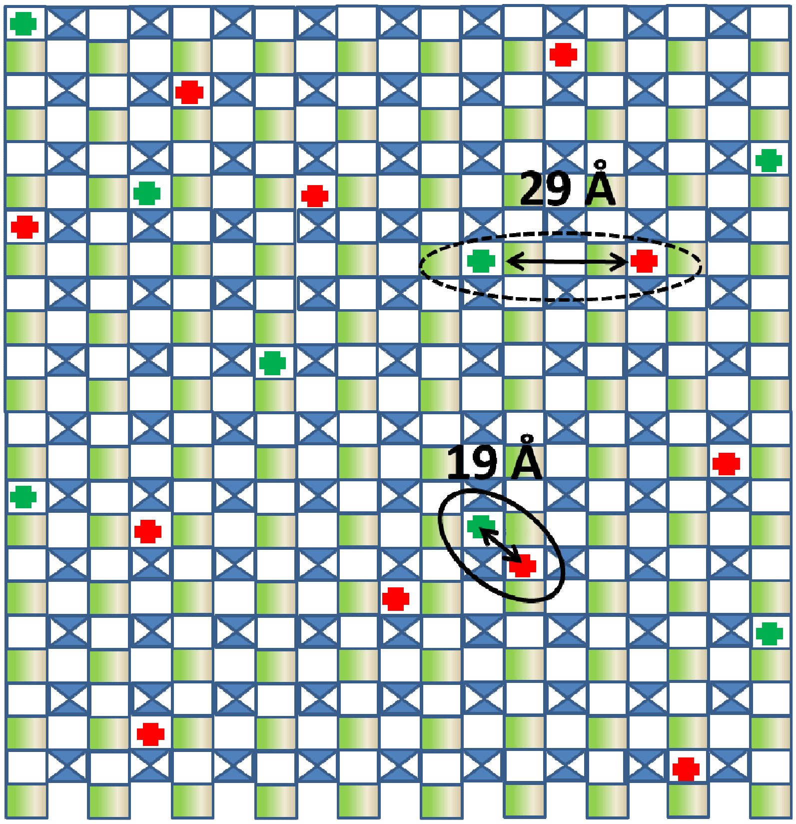

Zn4SP@USF1 in Water
Zn4SP@USF1
Normalized ΔA (422 nm)
0.0
-0.3
-0.6
-0.9
0.000
0.004
0.008
Time (Seconds)

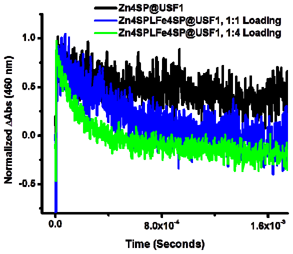

Zn4SP@USF1
Zn4SPLFe4SP@USF1, 1:1 Loading
Zn4SPLFe4SP@USF1, 1:4 Loading
Normalized ΔAbs (460 nm)
1.0
0.5
0.0
-0.5
0.0
8.0x10⁻⁴
1.6x10⁻³
Time (Seconds)

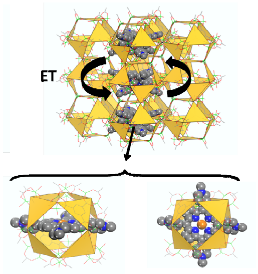


β = 1
β = 1.25
β = 1.5
β = 1.75
β = 2
k_{ET} (s^{-1})
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
0
1
2
3
Reorganizational Energy (eV)




29 Å
19 Å





Zn4SP-Fe4SP HKSUT-1