Supporting Information for

Re-Examining the Electronic Structure of Fluorescent Tetra-Silver Cluster in Zeolite

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Geometry Optimization of $[Ag_4^{2+}][H_2O]_4$ in the Zeolite Cage

Our caged $[Ag_4^{2+}][H_2O]_4$ model is obtained by placing the constrained-optimized complex at the center of the cage, with both the isolated complex and the resulting superstructure having an essentially tetrahedral symmetry. This approach is adopted to reflect the experimental structure proposed in ref 13 of the main text. We note that, the constrained-optimized complex is not a minimum on its potential energy surface, with imaginary frequencies correspond to reorientations of the water molecules (Fig. S1); some of these motions lead to them drifting away from the center of the Ag_3 faces.
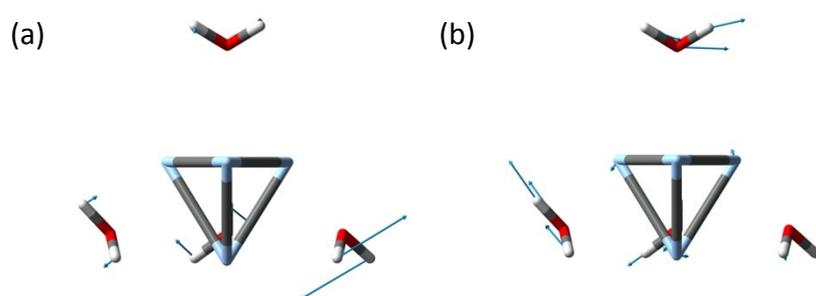
Fig. S1 Displacement vectors for selected imaginary vibrational modes for $[Ag_4^{2+}][H_2O]_4$ that correspond essentially to (a) rotation of a water molecule, and (b) drifting of water molecules away from the centers of the Ag_3 faces.

As noted in ref 13, when one allows the $[Ag_4^{2+}][H_2O]_4$ moiety in the cage to fully optimize, the resulting structure (Fig. 1b in the main text) corresponds to an off-center silver cluster plus a separate four-water cluster. We also find such a structure in our own optimization of $[Ag_4^{2+}][H_2O]_4$ inside the cage. Thus, we have modified our strategy to only allow the water molecules to be optimized. To better reflect the cluster complex in a zeolite, we put the caged structure inside a continuum cavity with an optimal radius of 7.8 Å. While the exact dielectric constant of the zeolitic environment is not known, it is likely to be moderately large (see, for example, E. İZCİ, A. İZCİ, *Turkey J. Chem.*, 2007, **31**, 523; W. Zhou, K. S. Zhao, *J. Phys. Chem. C*, 2008, **112**, 15015). In our computations, we use a value of 20.

The structure that we have obtained in this manner has the water molecules dislocated slightly from the Ag_3 face centers. The imaginary modes for this system are associated mainly with the relaxation of the constrained cage, while those for the dislocation of water molecules are no longer present. Optimization of the entire $[Ag_4^{2+}][H_2O]_4$ moiety within the continuum-

encapsulated cage does not lead to a segregated structure like the one in ref 13 of the main text. Thus, the inclusion of an appropriate environment for the $[Ag_4^{2+}][H_2O]_4$ complex stabilizes its structure.

The slight dislocation of water molecules introduces asymmetry to the system. In the calculated UV/vis spectrum, we see a narrowing of the relevant singlet–triplet gap for intersystem crossing (Fig. S2). Specifically, the initial unoptimized structure has a gap of 0.57 eV (Table 1 in the main text), whereas the value for the cluster–continuum-optimized structure is 0.32 eV. While the latter value is notably smaller, it is still considerably larger than the ones with randomly substituted cage-Al atoms (Table 1 in the main text). It is also noteworthy that the value of 0.32 eV is still larger than our estimated upper limit for an effective intersystem crossing (see section "Fundamentals of the Electronic Transitions" in the main text).
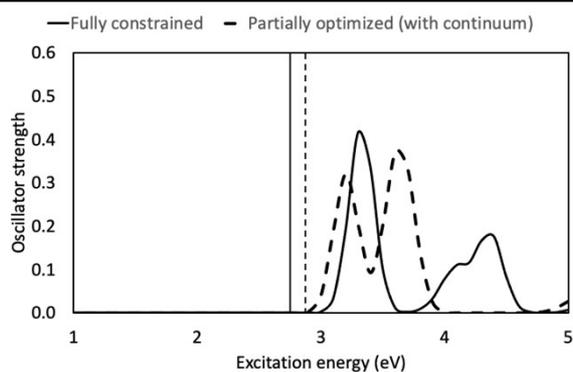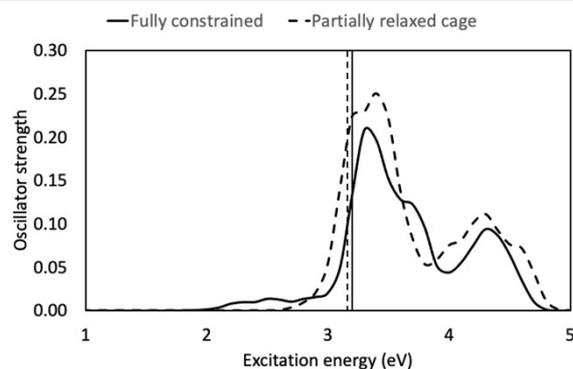

Fig. S2 Calculated UV/vis spectra for $[Ag_4^{2+}][H_2O]_4$ cluster in the Si_{24} cage with no structural relaxation, versus that for an analogue in a dielectric continuum and with relaxation of the core. The corresponding vertical lines indicate lower-energy triplet excited state energies that are closest to the singlet absorption maxima.

Partial Structural Relaxation for Al-Substituted Cages

The structure that we adopted from ref 13 in the main text is based on LTA zeolite, with the geometry being essentially identical to the known experimental structure. This experimentally determined structure corresponds to a mixed Si/Al material with a 1:1 ratio. Thus, the cage structure that we use would seem suitable for accommodating both Si and Al atoms in an average manner. To probe the effect of structural relaxation on the relevant orbital energies involved in the absorption and emission, for a water complex in a $Si_{22}Al_2$ cage (system 5 in Table 1 of the main text), we have optimized the AlO_3H moieties while constraining the rest of the structure. The singlet and ISC triplet energies for this system are 3.19 and 3.17 eV, respectively, which deviate only slightly from the corresponding values without structural relaxation (3.24 and 3.21 eV, respectively). Fig. S3 illustrates this in a pictorial manner. Major absorption features remain upon partial structural relaxation. The ISC-relevant triplet states for the two systems are close in energy and, importantly, they both are close to the absorption maxima.
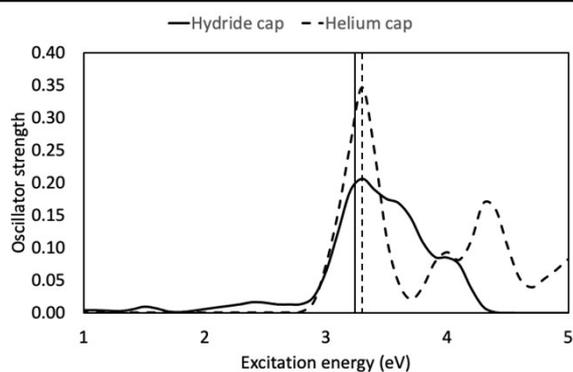

Fig. S3 Calculated UV/vis spectra for $[Ag_4^{2+}][H_2O]_4$ cluster in a $Si_{22}Al_2$ cage with no structural relaxation upon Al substitution versus an analogue with relaxation of the AlO_3H moieties. The corresponding vertical lines indicate lower-energy triplet excited state energies that are closest to the singlet absorption maxima.

The Effect of Charge for the $Si_{12}Al_{12}$ System

The $[Ag_4^{2+}][H_2O]_4$-in-$Si_{12}Al_{12}$ system that we present in the main text, which resembles the experimental composition of the material, has an overall charge of −10. Such a substantial charge on the system may raise the question of whether it would lead to dubious results. An intuitive strategy to investigate the effect of the large charge on the electronic structure is to remove the capping hydrides from the Al atoms, which would then result in a moderate overall charge of +2. However, the absence of capping groups for Al creates holes that in turn leads to spurious electronic transitions. Thus, instead of removing the capping hydrides, we replace them with isoelectronic and neutral helium atoms. The effect of such a change on the major features in the relevant electronic structures is of little qualitative consequence (Fig. S4). Notably, the major absorption maxima in both cases are ~3.3 eV, and both of the relevant triplet excited states situate close to these peaks.
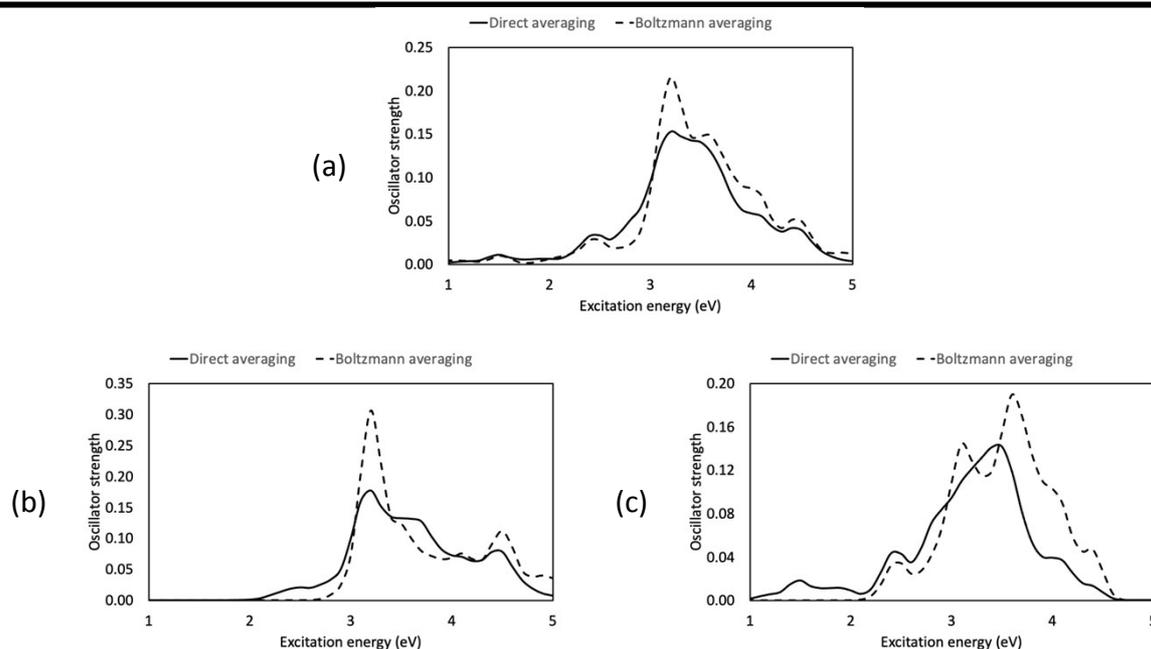

Fig. S4 Calculated UV/vis spectra for $[Ag_4^{2+}][H_2O]_4$ cluster in a $Si_{12}Al_{12}$ cage with all-hydrogen caps and with helium caps for the Al atoms. The corresponding vertical lines indicate lower-energy triplet excited state energies that are closest to the singlet absorption maxima.

**Simulated Spectrum Taking Relative Energies into Account**

Fig. 5 in the main text employs direct averaging of relevant spectra. Some of systems used in the averaging are structural isomers and their energies are thus directly comparable. In such cases, an alternative would be to use Boltzmann averaging for subsets of isomeric systems, together with direct averaging of the resulting Boltzmann-averaged spectra. We have obtained a different spectrum by this means (Fig. S5). The two composite spectra show similar qualitative features, with the Boltzmann averaged one showing a sharper maximum, which is related to the lowered weight for some component spectra. We note that, however, the relative energies used for determining the Boltzmann weights are for the gas-phase model systems. It is unclear how well they reflect the relative stability (and concentration) in the actual material. In passing, we note that the precise identification of Al locations in zeolites is yet to be completely resolved and it corresponds to an active field of research (see, for example, D. E. Perea, I. Arslan, J. Liu, Z. Ristanović, L. Kovarik, B. W. Arey, J. A. Lercher, S. R. Bare, B. M. Weckhuysen, *Nat. Commun.*, 2015, **6**, 7589).

Fig. S5 Calculated UV/vis spectra for (a) the average of the spectra for all asymmetric models ($5 \times Si_{22}Al_2$, $5 \times Si_{20}Al_4$, $1 \times Si_{12}Al_{12}$), with averaging accomplished either directly, i.e., with equal weight for all component spectra, or by Boltzmann weighting where applicable, as well as the corresponding component spectra for the sets of (b) $Si_{22}Al_2$ and (c) $Si_{20}Al_4$ models.

The "Metastable" [Ag$_4{}^{2+}$][CO]$_4$ Cluster

We note in the "Models with Alternative Ligands" section of the main text that the [Ag$_4{}^{2+}$][CO]$_4$ cluster (with CO binding through its carbon atom) is thermodynamically less stable than Ag$_4{}^{2+}$ + 4 CO by a substantial amount. Nonetheless, this cluster represents a local minimum from our constrained optimization, which implies a barrier towards ligand dissociation. We have further examined this aspect by scanning the distance between the Ag$_3$ faces and the CO ligands, while allowing the Ag–Ag and C–O distances to relax. The energy profile obtained at the optimization (B3LYP) level (Fig. S6) indeed shows a moderate barrier of 35 kJ mol^{-1} towards dissociation.
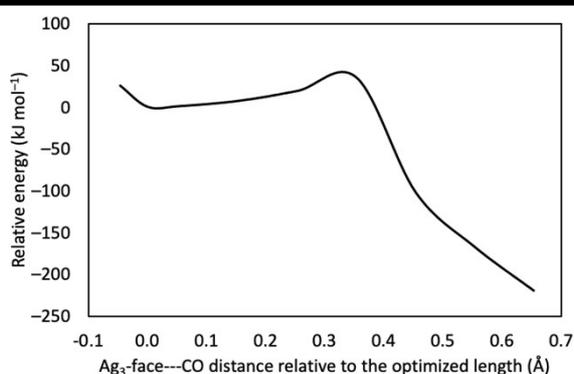
Fig. S6 Energy profile for the [Ag$_4{}^{2+}$][CO]$_4$ cluster with CO binding through its carbon atom.