DNA is a unique nanoscale material that enables the design and synthesis of nanoscale structures of prescribed shape and functionality via programmable self-assembly. Angstrom-level control over the location and orientation of programmed Watson-Crick basepairs offers the ability to scaffold and spatially organize optically active materials to yield novel optical and photonic properties. Here, we present two distinct strategies for designing and synthesizing DNA-based photonic materials, and emphasize the roles of computational modeling in this process. First, we use computational modeling to design mechanically stiff nanoscale DNA “molds” that have user-specified three-dimensional cavities with a nucleating gold seed, which grows in solution to fill and replicate the cavity. We demonstrate the capability of producing nanoparticulates of various shapes and materials that exhibit plasmonic properties that are consistent with electromagnetism simulations. In silico design of stiff molds of nearly arbitrary geometric cavities with resulting optical properties that are prescribed a priori enable a property-by-design framework for producing inorganic particles with prescribed functional properties. Second, we use DNA to program the scaffolding of chromophores into complex three-dimensional assemblies, enabling controlled energy transfer at the nanoscale. This strategy is inspired by nature, where cells use organized assemblies of chromophores to capture photons and funnel the resulting excitons toward the reaction center where they are converted to chemical energy. In particular, the close-packing of chromophores results in the emergence of quantum coherences that strongly affect exciton transport across the complex. Using Förster energy transfer modeling, as well as a hybrid molecular dynamics and quantum mechanical approach, we demonstrate how emergent excitonic and light-harvesting properties of diverse DNA-dye assemblies can be elucidated.

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2Interdisciplinary Life Sciences program, Purdue University, West Lafayette, IN, USA, 3Argonne National Laboratory, Lemont, IL, USA, 4Physics, Purdue University, West Lafayette, IN, USA, 5Research Center for Nanoscale Structure Matter, South Federal University, West Lafayette, IN, USA. Technology to convert Solar energy into fuel is being developed to search for alternate energy sources. This includes electrochemical cells based on artificial water splitting catalysts. By studying their water splitting mechanism we can hope to optimize the energy conversion process and also learn more natural water splitting complexes like Photosystem II. In this study, we analyzed two reported single site Ruthenium based catalysts, \([\text{Ru}^{II}(\text{bpy})(\text{tpy})\text{Cl}]^{+}\) and \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\), using EPR and X-Ray Spectroscopy characterization. We found that \([\text{Ru}^{II}(\text{bpy})(\text{tpy})\text{Cl}]^{+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\). We also found that \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\). We also found that \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\). We also found that \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\). We also found that \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\). We also found that \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\). We also found that \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\). We also found that \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is not a catalyst and that its oxidation past \([\text{Ru}^{III}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) is impeded by a lack of electron transfer. Using EPR and K-edge EXAFS, we also show that the \(\text{Ru}=\text{O}\) distance measured after adding Ce IV is more consistent with its assignment as \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{2+}\) intermediate and not with \([\text{Ru}^{IV}(\text{bpy})(\text{tpy})\text{Cl}]^{3+}\).