Hot Hole Hopping in a Polyoxotitanate Cluster Terminated with Catechol Electron Donors

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Abstract

Fast hole hopping and in **Ti17cat4**, a 1 nm diameter molecular polyoxotitanate cluster bearing four catechol ligands (Ti₁₇(μ 4-O)₄(μ 3-O)₁₆(μ 2-O)₄(cat)₄(OPr^{*i*})₁₆), was investigated by ultrafast spectroscopy and quantum dynamics simulations. The catechol moieties coupled to the TiO₂ core of the cluster give rise to a charge transfer band, the excitation of which promotes an electron from the HOMO orbital of the ligand to the inorganic core, resulting in the formation of {cat^{+*},Ti³⁺}, a vibrationally hot polaronic exciton. Dynamic depolarization measurements indicate that within less than 100 fs the Franck-Condon polaronic state formed at the interface evolves into a fully charge-separated state and the injected electron delocalizes over the quasi conduction band of the cluster. The positive charge (hole) resulting from the injection does not remain static either. The initial hole hopping between the catechol sites occurs with the rate of ~5×10¹¹ s⁻¹ or more and competes with the intramolecular vibrational relaxation. Upon thermalization, the hopping slows down and continues at a rate of ~5×10¹⁰ s⁻¹. The experimentally observed rate of hole hopping agrees well with the results of quantum dynamics modeling of the wavepacket propagation.

Keywords: Polyxotitanate clusters, charge transfer, catechol, hole hopping, electron tunneling, QMD, depolarization spectroscopy, quantum dynamics.

Introduction

Monodisperse clusters containing multiple metal centers are of steadily growing interest because of their inherent relevance to catalysis¹⁻⁴ as well as their unique spectroscopic, optical and magnetic properties.⁵⁻⁸ Molecular oxometalates are of crucial importance in biological systems where they constitute the active centers of a number of enzymes, for example the widely studied Mn₄CaO₅ cluster⁹ in the oxygen evolving complex (OEC) of Photosystem II (PSII). Because of their size and composition, clusters are uniquely capable of reversibly accepting or donating more than one electron without undergoing a large structural rearrangement of their core or the immediate coordination sphere. Following the inspiration from the redox enzymes, these welldefined molecular "charge storage devices" can be creatively employed in artificial light-driven multi-electron catalysis.^{10,11} especially in the context solar production of fuels.^{12,13} The key initial event in all these applications is the photoinduced injection of a charge into the the core of cluster. Despite such importance, the literature on interfacial electron transfer in surface-modified molecular polyoxometalates has only recently begun to grow^{14,15} in contrast with the wealth of data on dye-sensitized nanoparticles of metal oxides. Similarly, the fundamental photophysics and unsubstituted the excited state behavior of molecular polyoxometalates remain underexplored.^{5,16,17}

In this paper, we present a combined transient absorption spectroscopy and quantum dynamics study of the charge injection, electron delocalization and hole migration in **Ti17cat4** $(Ti_{17}(\mu_4-O)_4(\mu_3-O)_{16}(\mu_2-O)_4(cat)_4(OPr^i)_{16})$, where cat = catecholate and OPrⁱ = isoproxide), a molecular cluster whose size and the complexity of electronic structure lies between mononuclear LMCT complexes such as the $[Ti(cat)_3]^{2-}$ and polydisperse dye-sensitized anatase which was studied in the form of thin mesoporous films, colloidal suspensions and individual nanoparticles

(Figure 1).¹⁸⁻²¹ The current work builds on the reported earlier investigation of confinement effects in **Ti17** (Ti₁₇(μ 4-O)₄(μ ₃-O)₁₆(μ ₂-O)₄(OPr^{*i*})₂₀), a cluster which can be viewed as the unsubstituted parent compound of **Ti17cat4**.^{5,22} Both systems belong to the growing family of polyoxotitanate clusters containing, thus far, 2 to 34 Ti centers which were synthesized over the past few years and whose X-ray structures have been solved²²⁻²⁴ thus greatly facilitating detailed exploration of their physical and chemical properties. The inorganic core of **Ti17cat4** and **Ti17** is identical, as shown in Figure 2. It consists 17 Ti and 24 O atoms and has the diameter of approximately 1.2 nm, i.e. markedly below the ~2 nm onset of quantum size effects predicted for TiO₂.²⁵ While all Ti surface sites in the parent **Ti17** cluster are terminated with aliphatic isopropoxide ligands with its electronic and optical properties are determined primarily by the TiO₂ core, **Ti17cat4** is bearing four electron donating catechol ligands.



Figure 1. From left to right: (a) the mononuclear $[Ti(cat)_3]^{2-}$ complex studied by Lian *et al.*¹⁸; (b) **Ti17cat4** polyoxotitanate cluster. In order to highlight the TiO₂ core, the isopropoxide ligands are represented as OH groups (color code: purple = C, green = Ti, red = O, white = H); (c) schematic representation of a dye-sensitized TiO₂ nanoparticle.

In terms of its electronic structure and spectroscopy, **Ti17cat4** is a molecular analogue of cat@TiO₂, a catechol modified colloidal TiO₂ and an archetype of a strongly coupled interfacial electron transfer (ET) system. Despite its small size, Ti17cat4 retains all salient features of cat@TiO₂, with the significant benefits of strictly monodisperse stoichiometry, well-characterized geometry and uniform ligand placement. In both cat@TiO₂ and in Ti17cat4 the mixing between the orbitals of the chemisorbed donor and the conduction band (CB) of the metal oxide substrate gives rise to a new electronic transition at energy that is lower than both the HOMO-LUMO gap of the donor and the band gap of the underlying semiconductor. The excitation of this long wavelength charge transfer (CT) band causes a direct injection of an electron from the HOMO of the donor into the semiconductor.²⁶⁻²⁹ In such strongly coupled systems, the distinct steps of the formation of a local excited state of the light-absorbing donor and the subsequent phonon-assisted electron tunneling are bypassed in a single photo-assisted electron transfer (ET) event that is instantaneous on the timescale of nuclear motion. Because the electron injection occurs in the Franck-Condon geometry of the system, cat@TiO₂ and similar strongly coupled assemblies are exceptionally well suited for experimental and theoretical investigations of the initial dynamics of interfacial charge separation and geminate electron-hole recombination.²⁶⁻³¹ The key finding reported here is that the hot hole formed upon the electron injection is not static, but migrates rapidly among the degenerate catechol sites of **Ti17cat4** at initial rates approaching 1×10^{12} s⁻¹. While the rates of the electron delocalization and hole hopping remain well separated, such unexpectedly rapid initial migration of the latter has implications for the charge recombination and the yield of charge carriers which can be harvested in a photocatalytic or photovoltaic application in clusters and sensitized nanoparticles. Of additional interest is the excellent agreement between

the results of the polarization dependent transient absorption experiments and theoretical modeling.



Figure 2. Structural models of the **Ti17cat4** (top left) and the **Ti17** cluster (top right) based on X-ray diffraction coordinates²² and rendered in Spartan.³² Color code: gray = isoproxide, catecholate = magenta, red = O. The single tetracoordinate Ti ion located at the center of both clusters and four Ti ions which are pentacoordinate in the **Ti17** prior to the isopropoxide-to-catecholate exchange leading to the **Ti17cat4** are highlighted in green. The corresponding solution UV-vis absorption spectra and schematic energy level diagrams are shown below the respective structures. The insets indicate the excitation wavelengths for each system.

Experimental

Synthesis: The synthesis, purification and structural characterization of the **Ti17cat4** polyoxotitanate clusters were described in detail in our previous work²² and references therein.

Pump-probe transient absorption spectroscopy in the visible and IR: 70 fs pulses at 795 nm were provided by a home-built 1.25 kHz multipass Ti:sapphire amplifier seeded by a Spectra-Physics Tsunami oscillator. The output of the amplifier was split to generate independently tunable pump and probe pulses. The pump beam (~25 fs, 3.5 mW, 370 nm) was produced by frequency doubling the output of the non-collinear optical parametric amplifier (Topas White, Light Conversion). The probe beam was delayed with respect to the pump using a computer-controlled delay stage and focused into a 2 mm sapphire plate to generate white light continuum. The white light was overlapped with the pump beam in a 10 mm fused silica cuvette containing the sample. The absorbance change for signal was collected by the detector (Thorlabs, DET110) and the monochromators (Oriel MS257 with 1200 lines grating). The relative polarization of the pump and probe beams was controlled using a wave plate. Samples for the transient absorption measurements were prepared by dissolving approximately 3 mg of solid **Ti17cat4** in 2 mL of dry solvent. After 30 minutes the clear solution was transferred into a standard quartz cuvette with an air-tight valve.

Raman microspectroscopy: Approximately 1 mg of the **Ti17** or **Ti17cat4** cluster was spread in an indentation in a clean brass cell and covered by a glass slide with vacuum oil along the edge to prevent air from entering the sample. The sample preparations were carried out in a glove box. Confocal Raman spectra were acquired using a Kaiser Optical Systems Raman Microprobe equipped with a 785 nm diode laser. A 100x oil immersion objective was used to focus approximately 6-10 mW of the single mode power within the sample volume of ~2 μ m³. The

spectral coverage ranged from 100 to 3450 cm⁻¹ and the resolution was 4 cm⁻¹. The spectra were acquired using 4 accumulations of 60 second exposure time each.

Computational Methods: The quantum dynamics simulations were based on a tight-binding extended-Hückel (EH) Hamiltonian, similarly to our previous work on polyoxotitanates.^{14,15} The EH Hamiltonian and resulting wavefunctions were computed using the program YAeHMOP³³ Briefly, an initial (at the moment of excitation) electronic wave packet $|\Psi(0)\rangle$, as described by initializing in the isolated molecular EH HOMO, which has a similar wavefunction to the hole, representing a hole formed by photooxidation of a catecholate adsorbate was evolved in time by integrating the time-dependent Schrödinger Equation 1.

$$i\hbar\partial\Psi/\partial t = E\Psi \tag{1}$$

To facilitate the integration, the initial wave packet was expanded in terms of the molecular orbitals /q> of **Ti17cat4** (Equation 2), i.e. just the HOMO, which in turn are written in terms of terms of the atomic orbital α on atom *i* (Equation 3).

$$|\Psi(0)\rangle = \Sigma_q C_q/q \rangle \tag{2}$$

$$|q\rangle = \sum_{i,\alpha} Q^{q}_{i\alpha} | i\alpha \rangle \tag{3}$$

Thus, the final wavefunction at time *t* is given in Equation 4.

$$|\Psi(t)\rangle = \sum_{q} C_{q} \exp(-iE_{q}t/\hbar)/q \rangle \tag{4}$$

The time-dependent occupancy of the photogenerated hole, i.e., the survival probability of the hole remaining on the adsorbate, $P_{MOL}(t)$, at at time *t*, is computed by Equation 5,

$$P_{MOL}(t) = |\Sigma_{i,\alpha}^{ADS} \Sigma_{j,\beta} B_i^*(t) B_j(t) S^{ij}|$$
(5)

where ADS indicates the adsorbate, S^{ij} is the overlap matrix element $\langle i\alpha | j\beta \rangle$ for atomic orbital α on atom *i* and atomic orbital β on atom *j*. In Equation 5, the wavefunction given in Equation 4 is projected onto the atomic orbitals of the adsorbate, α .

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The configuration of the cluster was obtained by relaxing the X-ray crystal structure²² by geometry optimization with density functional theory (DFT) at the B3LYP/LANL2DZ level, as implemented in the Jaguar software package.³⁴ To reduce the number of atoms in the computational model of the cluster, the isopropoxy ligands were replaced by hydroxyl ligands, although other Lewis base analogous such as methoxyl groups are in principle better mimics. In our particular case, however, binding of the Lewis base is onto Ti⁴⁺ which is d⁰ so there is little difference between the effect of the various different analogue groups. Four additional protons were adsorbed to the surface O²⁻ ions to neutralize the cluster. The resulting refined structure is in quantitative agreement with the X-ray model, indicating that structural changes due to temperature or solvation can be neglected due to the rigidity of the system. Simulations of the hole propagation dynamics were performed at this frozen geometry of the cluster in vacuum and did not include nuclear reorganization.

Results and Discussion

Structure, CT absorption and the ligand-core electronic coupling: The catechol ligands are arranged in a square around the center of **Ti17cat4** resulting in approximate four-fold overall symmetry of the complete assembly (Figure 2). From the crystallographic point of view, the spatial arrangement of the titanium and oxygen ions in **Ti17cat4** and **Ti17** corresponds most closely to brookite, the metastable and least common in nature phase of TiO₂. The Raman scattering spectra are consistent with this assignment.⁵ The spectrum of **Ti17** contains a characteristic progression of peaks at 644, 616 and 575 cm⁻¹ (in bulk brookite 635, 585 and 535 cm⁻¹). In **Ti17cat4** the overall appearance of the Raman peaks associated with the inorganic core of the cluster is very similar, but the origin of the sequence is shifted from 644 to 650 cm⁻¹.

The UV-vis absorption spectrum of **Ti17cat4** exhibits a prominent charge transfer band at 345 nm (Figure 2, left), which extends well into the visible range, rendering the solid compound bright red. The parent **Ti17** cluster which contains solely aliphatic isopropoxide ligands is colorless and the onset of the VB \rightarrow CB absorption of its TiO₂ core appears at ~300 nm (Figure 2, right). The charge transfer band in **Ti17cat4** is nearly identical with that observed in **cat@TiO2**. The CT absorption of the latter peaks at ~340 nm and has a similar shoulder at ~420 nm.^{27,28} The analogous $\pi \rightarrow 3d$ LMCT charge transfer band in the mononuclear [Ti(cat)₃]²⁻ complex has a maximum at 389 nm, with $\varepsilon_{max} = 9300$ M⁻¹cm⁻¹. The extinction coefficient of the CT band of **Ti17cat4** is approximately 1900 M⁻¹cm⁻¹ and its width 10300 cm⁻¹. These spectral parameters can be used to estimate the electronic coupling between the HOMO orbitals of the catechol ligands and the core of the cluster by applying the approximate Equation 6.

$$|V_{GE}| \approx 0.0205 \cdot (\varepsilon_{max} \cdot h \, v_{max} \cdot \Delta v_{1/2})^{1/2} / r_{GE} \tag{6}$$

which has been derived from the Mulliken-Hush theory by assuming Gaussian shape of the band and where $\Delta v_{I/2}$ is the FWHM of the CT band, v_{max} is the position of its maximum and r_{GE} is the effective displacement of the electron.³⁵ This approach yields $|V_{GE}| = 5160 \text{ cm}^{-1}$. Alternatively, one can view the total CT absorption cross section of **Ti17cat4** as a sum of separate CT transitions between each of the catechol moieties and the core of the cluster. In this case, the extinction coefficient of the CT band can be partitioned into four equal components of 475 M⁻¹cm⁻¹ per ligand. This approach, which seems more appropriate, yields $|V_{GE}| = 2580 \text{ cm}^{-1}$ for each catechol moiety. Even this lower value remains well within the strong coupling regime, with $|V_{GE}|$ exceeding both k_BT , as well as the frequency of the skeletal vibrations of ligand catechol and the phonon modes of the TiO₂ core, which are responsible for the bulk of the nuclear reorganization energy in this system.

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In calculating $|V_{GE}|$, we used $r_{GE} = 3$ Å, as determined by Nawrocka *et al.* in Stark spectroscopy experiments, which have shown that the CT transition in **cat@TiO**₂ is accompanied by a dipole moment change of 15.7 D.²⁸ The instantaneous charge separation distance of 3 Å deduced from the above $|\Delta \mu|_{CT}$ implies that at t = 0 the injected electron is localized on the Ti ion to which the donating catechol ligand is bound and only subsequently the wavepacket delocalizes over the available volume. The Stark effect measurements revealed also that the CT transition in $cat@TiO_2$ is accompanied by a reduction of polarizability, pointing to a tighter localization of charges in the incipient charge transfer state. This is consistent with the promotion of an electron from a delocalized π -orbital of catechol to a much more compact *d*-orbital of an individual Ti ion. These experimental results agree very well with the quantum mechanical modeling of electron injection into bulk TiO₂ performed by several groups.^{26,29,30} As we will see, the picture of a $\pi \rightarrow 3d$ interfacial polaronic exciton which undergoes rapid evolution into the fully charge-separated state through electron delocalization followed by slower hole relaxation applies also to **Ti17cat4**. Charge injection and hot hole hopping: In pump-probe experiments, excitation of the CT band of **Ti17cat4** with 370 nm light (indicated by the red arrow in Figure 2) leads to the appearance a broad and rather featureless transient absorption spectrum (Figure 3), the shape of which exhibits little response to the solvent. In acetonitrile, $\varepsilon = 36.6$, in which all measurements reported here were performed, the spectrum spans the entire probed range from 450 to 700 nm, nevertheless two discernible bands can be identified at ~450-530 and ~600-650 nm, respectively. The long

wavelength band originates from the electron injected into the metal oxide core of **Ti17cat4**, as determined in the prior work on the excess electron in **Ti17**.⁵ The short wavelength band is dominated by the absorbance of the hole, i.e. the radical cation of the oxidized catechol ligand.^{36,37} The formation of the charge separated state is complete within the ~100 fs temporal resolution of

our experiments. The decay of the broad spectrum is homogeneous, with only a hint of a dynamic blue shift at very early times, which is consistent with intramolecular vibrational relaxation (IVR). While in **Ti17** the precise location of the relaxed hole is not clear (most likely it is delocalized over the isopropoxide oxygens or the oxo bridges at the interface, or a combination of both), in **Ti17cat4** it is certain that the positive charge resides at one of the catechol units.



Figure 3. Transient absorption spectra of **Ti17cat4** in CH₃CN. The samples were excited at 370 nm, the white light probe polarization was set at the "magic angle" with respect to the pump. The shading indicates spectral regions dominated by the absorption of the injected electron (pink) and the cat^{+•} radical (blue).

In order to gain a better view of the excited state behavior of **Ti17cat4**, we turned to polarization dependent measurements which revealed a decidely more rich dynamics of the charge separated state than the broad and featureless magic angle spectra in Figure 3 would imply. The long wavelength, $\lambda > 550$ nm portion of the spectrum, which corresponds to the absorption of the

 e^{-} in the quasi-conduction band of the inorganic core of the cluster, shows no discernible dependence on the polarization of the probe pulse (Figure 4 and Table 1). In this wavelength range, transients collected with parallel and perpendicular probe polarization were perfectly superimposable except for the earliest times at 650 nm, showing that the depolarization of the absorption and hence the delocalization of the injected electron over the core of the cluster are much faster than the ~100 fs resolution of our experiments. This outcome is consistent with the picture of a band-like electronic structure of the TiO₂ core of the cluster, which was presented in the previous report on the unsubstituted **Ti17**.⁵ It also agrees very well with the experimental and theoretical literature on electron injection into bulk TiO₂.^{26,29,30}



Figure 4. Polarization dependent transient absorption profiles recorded for **Ti17cat4** in acetonitrile at 650 (left) and 750 nm (right).

The behavior of the $\lambda < 550$ nm region of the spectrum which is dominated by cat^{+•} is far more complex. Both the initial magnitude and the decay profiles respond strongly to the polarization of the probe pulse (Figure 5). At *t* = 0 the absorption at parallel probe polarization is 2-3 times higher than for crossed polarization, indicating that the hole remains localized on the parent ligand for a considerably longer time than it takes the electron to delocalize over the core of the cluster. The corresponding initial values of the polarization parameter R(t=0) are 0.47 and 0.25 at 495 and 530 nm, respectively. The lower value of *R* at 530 nm reflects a larger contribution from the instantaneously depolarized absorption of the injected electron which also absorbs light at this wavelength. The traces show rapid biphasic decay (Figure 5 and Table 1) and the depolarization appears to be complete by 15-20 ps after the excitation. Since rotational diffusion of a body as large as the **Ti17cat4** occurs with $\tau_{rot} > 200$ ps, the observed rapid depolarization dynamics is a signature of the hole hopping among the four degenerate catechols, with each hop between two adjacent sites changing the orientation of the transition dipole by +/- 90⁰.



Figure 5. Transient absorption profiles and corresponding R(t) depolarization traces (insets) recorded for **Ti17cat4** in acetonitrile at 495 (left) and 530 nm (right).

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It is unavoidable that the noise present in the individual A //(t) and $A_{\perp}(t)$ traces becomes exacerbated when polarization parameter R(t) is calculated using Equation 7.

$$R(t) = [A //(t) - A_{\perp}(t)]/[A //(t) + 2 \cdot A_{\perp}(t)]$$

$$\tag{7}$$

As a result, the analysis of R(t) profile was limited to as single exponential fit of the first 5 ps of the decay (Table 2 and the insets in Figure 5). Within this time window, the 495 nm data indicate that ~40% of the initial population depolarizes with the rate of 2.2 ± 0.8 ps, while the 530 nm traces return 2.5 ± 1.0 ps depolarization of ~50% of the population. Despite the substantial margin of error, the ~2 ps depolarization shows that the initial hole hopping in the charge separated (CS) state of **Til7cat4** is very fast and occurs at the same time scale as IVR and typical solvent reorganization dynamics.^{38,39} On the basis of the above relative amplitudes it appears that at least ~40% of the generated holes undergo a hop to an adjacent catechol site prior to thermalization.

Table 1. Kinetic parameters of the CT state of **Ti17cat4** retrieved at several probe wavelengths. For $\lambda \ge 650$ nm the averages of values obtained with || and \perp probe polarization.

| λ_{probe} and polarization | τ ₁ [ps] | A 1 | τ ₂ [ps] | \mathbf{A}_2 | τ3 [ps] | A 3 |
|---|---------------------|------------|---------------------|----------------|---------|------------|
| 495 nm | 1.42±0.48 | 0.40±0.09 | 9.03±2.7 | 0.60±0.17 | - | - |
| ⊥495 nm | 2.2±0.67 | 0.41±0.12 | 14.4±3.5 | 0.59±0.14 | - | - |
| 530 nm | 2.0±0.45 | 0.64±0.11 | 17.2±4.1 | 0.36±14 | - | - |
| ⊥530 nm | 3.1±0.52 | 0.62±0.15 | 29.5±8.7 | 0.38±12 | - | - |
| 650 nm | 1.28±0.73 | 0.64±0.13 | 15.6±4.2 | 0.25±0.13 | 240±34 | 0.11±0.04 |
| 750 nm | 1.1±0.44 | 0.53±0.11 | 24.0±5.3 | 0.35±0.1 | 221±10 | 0.12±0.06 |
| 850 nm | 1.71±0.19 | 0.52±0.08 | 15.9±4.9 | 0.20±0.02 | 294±45 | 0.28±0.04 |

| Wavelength [nm] | τ _{dep} [ps] | Α | $\mathbf{A}_{\mathbf{\infty}}$ |
|-----------------|-----------------------|-----------|--------------------------------|
| 495 | 2.2±0.8 | 0.42±0.17 | 0.58±0.23 |
| 530 | 2.5±1.0 | 0.40±0.14 | 0.60±0.32 |

Table 2. Depolarization time τ_{dep} obtained from single exponential fitting of the R(t) plots.

The rapid hot hole hopping among the equivalent catechol sites is fully corroborated by the results of quantum dynamics modeling of the relaxed structure with the X-ray diffraction crystal structure²² as the initial geometry, as described in the Computational Methods section. The final energy mismatch between the catechol sites in the optimized structure is within the range of ~ 5 meV. If one selects the highest energy site 1 (Figure 6) as a reference, the relative energies of a hole localized on the remaining catechol sites are -1.8, -5.4 and -2.5 meV for sites 2, 3 and 4, respectively. The energies of individual states localized on each catechol adsorbates are readily obtained from the projected density of states. The observed energy variation arises due to slight differences in the relaxed geometry of each catechol and its environment at the convergence cutoff of our calculations. This residual disorder most likely gives a much more realistic image of the catechol and isopropoxide ligands on surface of Ti17cat4 under ambient conditions than would a perfectly symmetric structure. In the context of this simulation, we take this energy distribution to represent a random, instantaneous snapshot of the fluctuating energy landscape of the cluster. Indeed, molecular dynamics modeling by this group and others has shown that electronic energy levels of adsorbates on the surface of TiO₂ fluctuate by at least a few tenths of an eV due to thermal motion (at room temperature $k_BT \approx 25$ meV).^{40,41}



Figure 6. Time-dependent occupancy of the photogenerated hole at each of the four catechol ligands during the first 40 ps of dynamics. The hole was initially localized on catechol **1**. Color code: green = Ti, red = O, blue = C, white = H.

The calculations reported here correspond to the low temperature, fully coherent limit. Under these conditions, the system has a rigid nuclear configuration and the hole propagation dynamics is determined by the electronic couplings between the nearly resonant sites. Within the Marcus theory description, this model corresponds to the limit where the reorganization energy λ is negligible and the hole transfer rate is given by Equation 8.

$$k \propto /V_{GE}/^2 \delta(\Delta G^*) \tag{8}$$

where in our approximation $\delta(\Delta G^{\sharp}) = 1$ when $\Delta G^{0} = 0$ (the δ function comes from taking the limit as the width or of the Gaussian that occurs in the usual Marcus expression with the width approaching zero) and the rate is determined by the strength of the electronic coupling $|V_{GE}|$ between two nearly resonant states. Figure 6 shows the oscillating population at each of the catechol sites during the simulation in which the hole was initially localized on catecholate with the highest energy, **1**. The population is transferred to the adjacent catechol moieties on short

picosecond time scale. The unequal degree of population transfer between each of the catechol ligands reflects the differences in the electronic coupling and in the energy mismatch for each pair of catechols. The calculated electronic coupling $|V_{GE}|$ between catechol 1 and catechol 2 is ~2.4 cm^{-1} , whereas the coupling between catechol 2 and catechol 3 is ~2.9 cm⁻¹. Even though the electronic coupling between sites 2 and 3 is stronger, very little population, <1%, appears to be transferred to catechol **3**. This behavior is consistent with the distance dependent attenuation of the superexchange interaction between the respective sites and the notable energy mismatch of ~ 3.6 meV between sites 2 and 3 leading to negligible occupancy of site 3. While the adjacent catechol moieties are only 6 Ti-O bonds away from one another and the edge-to-edge-distance is ~6.5 Å (~11 Å center-to-center), the shortest path linking the diagonal pairs of catechols involves 10 Ti-O bonds which span the ~11.4 Å edge-to-edge distance (16.2 Å center-to-center). Regardless of whether one takes the pathway approach or views the core of the cluster as electronically homogeneous, the coupling between the diagonal ligands is smaller than between the neighboring ones. The population of catechol 4 which is adjacent to catechol 1 remains rather low due to the large energy mismatch between these sites, even though they experience the largest electronic coupling as illustrated by the shortest period of oscillation, $\tau = 2.5$ ps). The time constant for the hole hop between two adjacent catechols taken to be $\frac{1}{2}$ of the oscillation period ranges from ~1.2 ps for sites 1 and 4 to ~ 2.1 ps for sites 1 and 2 and is in a remarkably good agreement with the depolarization measurements, given the simplicity of the model.

The above predictions of the frozen geometry model can be also used to estimate the rate of the thermalized hole hopping by substituting a reasonable value of the free energy of activation, ΔG^{\sharp} , in place of the δ function in Equation 8. The main component of the activation barrier for the hole hopping in **Ti17cat4** is the internal reorganization of the catechol ligand. DFT calculations at

the B3LYP level yield the cat \leftrightarrow cat^{+•} intramolecular reorganization energy of 1300 cm⁻¹ and, correspondingly, $\Delta G^{\dagger} = \lambda/4 = 325$ cm⁻¹ (at the limit of $\Delta G^{0} = 0$) for the catechol-to-catechol hole transfer. By taking this value and ignoring all other contributions to the overall reorganization energy, the upper limit for the rate of thermally assisted hole hopping in **Ti17cat4** is obtained. At T = 293 K the exponential factor $e^{-\Delta G^{\dagger} \hbar T}$ is ~0.2 and the corresponding thermal hopping rates are in the range of 1 – 1.6×10¹¹ s⁻¹. Additional components of λ (solvent relaxation and coupling to the phonon modes of the TiO₂ core of the cluster) will further reduce these rates. Interestingly, the calculated value of λ is very close to the frequencies of the in-plane skeletal modes of the aromatic ring of catechol. This suggests that the initial hot hole hopping in the 0-2 ps time window is associated with the population of these skeletal modes upon charge separation. Once the high frequency ring modes undergo IVR, only the slower, thermally assisted hoping is possible. Similar pronounced dependence of the electron transfer rate on the residual excess vibrational energy has been recently observed by this group for charge injection in dye-sensitized TiO₂ and electron hopping in dendritic electron donor-acceptor systems.^{42,43}

Sustained quantum beats with population exchange between adsorbates 1 and 2 are quite evident in Figure 6, while the occupancy of adsorbate 3 is negligible since it remains off-resonant relative to adsorbates 1 and 2 for the course of the dynamics. Unlike in the frozen geometry quantum dynamics simulation,⁴⁴ in the real cluster, the dephasing and IVR lead to rapid damping of such coherent population oscillations. Nevertheless, it is worthwhile to note that the four-fold symmetry of **Ti17cat4** influences the dephasing and the observable depolarization behavior. Since the transition dipoles of the neighboring catechol ligands are mutually orthogonal, each clockwise or counterclockwise hole hop between adjacent sites causes a complete 90⁰ switch of polarization. Each subsequent hop in any direction, fully restores the original polarization. As a result, the loss

of the polarization information in **Ti17cat4** occurs only because of the true dephasing of the hopping events, unlike in a system with randomly oriented transition dipoles, e.g. in a multichromophore polymer, in which every hop leads to a random change of polarization.



Figure 7. The depolarization profile R(t) of the 495 nm cat⁺⁺ band **Ti17cat4** computed on the basis of fitted kinetic parameters listed in Table 1 (green hatches) and the empirical triple exponential fit (red solid line). The likely location of the polarization switching hole hops is indicated.

Encouraged by the excellent agreement between the quantum dynamics modeling and the fast component of the experimentally observed depolarization dynamics, we decided to revisit the analysis of the latter. In order to circumvent the amplification of noise present in the experimental absorption decays, one can first fit the experimental A // (t) and $A_{\perp}(t)$ decay profiles and subsequently use the extracted kinetic parameters τ_i and A_i to calculate the evolution of R(t), rather

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than work directly with the raw A(t) traces. Naturally, this procedure must be viewed with caution, because the resulting R(t) plots are deceptively noise free, yet in reality they carry over all the errors associated with the original noisy data and therefore can be misleading. With this caveat in mind, in Figure 7 we show the R(t) trace calculated on the basis of the computed A //(t) and $A \perp (t)$ decays at 495 nm.

The computed R(t) exhibits an intriguing plateau in the 2-6 ps time window. Indeed, the corresponding change of slope can be seen in the same time window in the transient absorption profiles in Figure 5. The shape of the R(t) plot in Figure 7 cannot be reproduced by a single or double exponential function, however, it is mimicked exceedingly well by an empirical triple exponential fit with time constants $\tau_1 = 2.7$ ps (decay), $\tau_2 = 4.2$ ps (growth) and $\tau_3 = 18.8$ ps (decay). The fastest component agrees very well with the results of the direct fitting (Table 1 and Figure 5) and modeling (Figure 6). It corresponds to the first hop of the hot hole from the initially oxidized catechol. The somewhat slower 4.2 ps growth component gives rise to the plateau which is plausibly associated with the second hole hop, which, as discussed earlier, regardless of its clockwise or counter clockwise direction restores the polarization to the initial orientation and thus sharply slows down the observable depolarization, however, the slowing down of the underlying hole hopping dynamics is not nearly as dramatic. This is a significant point, because it means that the second hop does not need to be coherent in the strict sense in order to lead to the recurrence. Its impact on the apparent kinetics does not depend on the phase but merely only the relatively close rates of the first and second hop. The slowest, 18.8 ps depolarization component corresponds to the thermal hole hopping which continues as the system decays to the ground state. Importantly, this rate is broadly consistent with the approximate predictions of the thermal hopping based on the reorganization energy of the cat \leftrightarrow cat^{+•} exchange which, were discussed earlier.

Charge recombination: The decay of the charge-separated state of **Ti17cat4** is dominated a fast component, $k_1 \sim 8 \times 10^{11}$ s⁻¹, which is assigned to the geminate recombination of the nascent interfacial polarons. This process accounts for ~55% of the overall recombination and occurs at the same time scale as the initial hot hole hopping and the IVR (Figure 4, Table 1). Such high initial recombination in Ti17cat4 underscores the fact that rapid delocalization of the injected electrons in sensitized TiO_2 nanoparticles is more critical for the typically high yields of charge separation then the nuclear relaxation of the sensitizer. In the highly confined volume of the cluster, the electron cannot move far away from the hot hole which at t = 0 still retains the Franck-Condon geometry of neutral catechol in the ground state and only begins to evolve towards the relaxed structure of cat^{+•}, thus facilitating the geminate recombination. The remaining charge recombination in **Ti17cat4** is nonexponential and the retrieved time constants and relative amplitudes depend on the length of the data acquisition window which for practical reasons was limited to 300 ps. Approximately 20-35% of the charge separated states decay with the rate of k_2 ~ 5×10^{10} s⁻¹. This process most likely corresponds to the bulk-like recombination of delocalized electrons and thermally equilibrated holes, with the latter having already undergone 2-3 site-tosite hops. The final 10-20% of the population recombines with $k_3 \sim 4 \times 10^9$ s⁻¹. Such nonexponential recombination is typical of dye-sensitized colloidal TiO₂, in which the fast but minor geminate process is followed by the recombination of freely diffusing bulk conduction band electrons and finally by the broadly inhomogeneous disappearance of the electrons trapped by surface defects. Depending on the distribution of the trap depths, the latter rates span a very broad range from nanoseconds to milliseconds. Aside from the initial geminate (k_1) and the subsequent quasi-bulk recombination (k_2) , it is more difficult to explain the origin of multiexponential decay in the monodisperse and presumably trap-free **Ti17cat4** cluster. The core of the cluster is sufficiently

small for the injected electron to rapidly sample its entire volume, as evidenced by the observed <100 fs depolarization of the e^{-} absorption band. Such rapid sampling should lead to a homogeneous decay of the thermalized charge separated state. It is possible that a fraction of the long-lived electron-hole pairs undergoes intersystem crossing to the triplet state. The triplet electron-hole pairs may recombine at a slower rate because of the spin selection rules, which would be consistent with the large electron-hole exchange interaction deduced for the **Ti17** parent cluster in the previous study⁵ and the large singlet-triplet splittings postulated for excitons in small semiconductor nanoparticles.⁴⁵⁻⁴⁷



Figure 8. Proposed sequence of events following photoexcitation of the catechol \rightarrow TiO₂ charge transfer band in Ti17cat4.

Conclusions

Functionalized polyoxometalate clusters are excellent models of ultrafast charge injection and recombination and merit further spectroscopic investigations as well as full quantum dynamics simulations on the structure relaxed using DFT. The instantaneous electron injection and the lack of clear temporal separation between the subsequent relaxation processes provide a truly unique testing ground for theoretical modeling. The involvement of specific vibrational modes of the catechol ligand and the coupling to the phonon modes of the inorganic core are of particular interest. Because of the nanometer size of the TiO_2 core and the presence of a quasi-band structure, the clusters are much closer analogues of the catechol@TiO₂ and other dye@TiO₂ systems than the mononuclear [Ti(cat)₃]²⁻ complex.

The study of photoinduced electron transfer behavior in **Ti17cat4** revealed a highly dynamic system in which IVR, geminate charge recombination and hole hopping occur simultaneously and compete with each other, as illustrated schematically in Figure 8. Both experiments and simulations show that the initial hot hole hopping is very rapid and occurs at the time scale of 2 ps. At such early times after the charge separation the system retains some degree of vibrational excitation and it is not thermally equilibrated with the environment. More broadly, the observation of hot hole hopping in **Ti17cat4** adds to the growing body of evidence that electron transfer reactions occurring within ~10 ps of photoexcitation are rarely fully thermally equilibrated and may exhibit considerable departures from the predictions based on the standard Marcus theory and static ΔG^0 and λ parameters. Furthermore, the rapid hole hopping has significant implications for charge recombination in dye sensitized semiconductors, for which it is often assumed that the hole remains relatively static throughout the life span of the charge separated state.^{40-44,48}

The confinement of the injected electron in the small volume of the cluster and the lag between the electronic motion and the nuclear relaxation of the oxidized catechol lead to rapid recombination of a large fraction of the charge separated states. The reduced dielectric constant of the core in comparison with bulk TiO₂ may play an additional role in this regard.⁴⁵ Structural relaxation of the hole is essential for the stabilization of the charge separated state and to a great degree controls the course of the charge recombination in the cluster. In analogous sensitized TiO₂ nanoparticles and mesoporous films the same mismatch of the time scales is advantageous as it allows the electron to move far away from the point of injection so that the Coulomb and exchange

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interactions with the hole are heavily screened. As a result, the rate and the magnitude of the nuclear relaxation of the donor have a much smaller influence on the yield and survival of charge separated states in dye-sensitized nanoparticles.

Acknowledgement:

This research was supported by Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U. S. Department of Energy through Grant #DE-FG02-06ER15828 to P. P. Femtosecond laser instrumentation used to carry out this work was funded by National Science Foundation CRIF Grant #0342432 to P. P. V. S. B. would like to thank Benjamin Rudshteyn for his helpful advice. V. S. B. acknowledges supercomputing time from both NERSC and the Yale University Faculty of Arts and Sciences High Performance Computing Center, whose acquisition was partially funded by the National Science Foundation under grant number CNS08-21132. V. S. B. acknowledges support from the Argonne-Northwestern Solar Energy Research (ANSER) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award Number DE-SC0001059. The synthetic and structural work was funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through grant #DE-FG02-02ER15372 to PC and JBB.

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