Interfacial Electron Transfer into Functionalized Crystalline Polyoxotitanate Nanoclusters


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Supporting Information

ABSTRACT: Interfacial electron transfer (IET) between a chromophore and a semiconductor nanoparticle is one of the key processes in a dye-sensitized solar cell. Theoretical simulations of the electron transfer in polyoxotitanate nanoclusters $\text{Ti}_{17}\text{O}_{24}\text{(OPr)}_{20}$ ($\text{Ti}_{17}$) functionalized with four $p$-nitrophenyl acetylacetone (NPA-H) adsorbates, of which the atomic structure has been fully established by X-ray diffraction measurements, are presented. Complementary experimental information showing IET has been obtained by EPR spectroscopy. Evolution of the time-dependent photoexcited electron during the initial 5 fs after instantaneous excitation to the NPA LUMO + 1 has been evaluated. Evidence for delocalization of the excitation over multiple chromophores after excitation to the NPA LUMO + 2 state on a 15 fs time scale is also obtained. While chromophores are generally considered electronically isolated with respect to neighboring sensitizers, our calculations show that this is not necessarily the case. The present work is the most comprehensive study to date of a sensitized semiconductor nanoparticle in which the structure of the surface and the mode of molecular adsorption are precisely defined.

INTRODUCTION

Dye-sensitized solar cells (DSSC) promise the environmentally friendly and cost-effective conversion of solar light into fuels and/or electricity.1-4 DSSCs are driven by photoinduced interfacial electron transfer (IET), which injects photoexcited electrons from the dye sensitizer into the conduction band of the semiconductor substrate. Naturally, the interfaces are critical to performance and much attention has been directed to them via experiment, theory, and computational modeling.5-8 However, due to the complexity of the surfaces, including the presence of multiple exposed facets and binding sites as well as surface defects and impurities, the correlation between experiment and simulations based on pristine surfaces remains uncertain. Here, we bridge the gap between theoretical modeling, crystallography, and spectroscopy by studying IET in functionalized polyoxotitanate (POT) nanocrystals $\text{Ti}_{17}\text{O}_{24}\text{(OPr)}_{20}$ ($\text{Ti}_{17}$) of which the structure has been precisely determined by X-ray diffraction. The precise structural information enables time-dependent electronic structure calculations that predict photoinduced IET in this model system. The sensitization of the nanoparticle by the acetylacetonate-anchored chromophore is confirmed spectroscopically by an increase in the onset of the photoinduced titanium and oxygen EPR signals from approximately 300 nm and lower for the unfunctionalized cluster to over 400 nm in the case of the functionalized nanoparticle. The comprehensive analysis described should contribute to a more detailed understanding of the chemistry and photophysics of sensitized semiconductor interfaces.

The structure of the interface can greatly influence the rate and efficiency of IET.5-7 In the case of the dye/semiconductor interface, strong electronic coupling between the dye excited state and the conduction band is desirable for ultrafast electron transfer. Fast injection into the semiconductor minimizes losses due to radiative and nonradiative relaxation of the dye excited state. We have recently shown that a new class of derivatized acetylacetone (acac) linkers can functionalize pure phase TiO$_2$ nanoparticles and be used to anchor photocatalytically active manganese complexes to the surface.9,10 These acac linkers provide robust coupling to the semiconductor substrate under aqueous and oxidative conditions. The characterization of the acac anchor binding mode to the TiO$_2$ surface has been only indirect, based on computational modeling and UV/vis and IR spectroscopy as in previous studies.8,10-16 Here, we structurally resolve TiO$_2$ surfaces functionalized by acac linkers by using X-ray diffraction methods.

POT clusters functionalized with catechol and isonicotinic acid have been proposed as models for the sensitizer/semiconductor interfaces in DSSCs.17 POT clusters are attractive analogues for pure phase TiO$_2$ nanoparticles since they possess structural features of bulk crystals, including similar coordination and connectivity, as well as features associated with nanoparticles, such as reactive four- and five-coordinate Ti$^{IV}$ centers and size-dependent band gaps.19 The clusters are also attractive building blocks due to their

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propensity to assemble into single crystals suitable for X-ray structure determination at atomic resolution. Here, we focus on the functionalization of the POT cluster Ti$_{17}$O$_{32}$(OPri)$_{20}$ (Ti$_{17}$) with the model sensitizer p-nitrophenyl acetylacetone (NPA-H) and the subsequent crystallization of the product to gain atomic resolution structural information about the sensitizer/semiconductor interface in these particles. The light-induced charge-separated states in functionalized and unfunctionalized POT clusters are compared by EPR spectroscopy and analyzed by quantum dynamics simulations of IET, providing a detailed description of charge injection for a structurally resolved sensitizer/semiconductor interface.

### Experimental and Computational Procedures

**Chemicals.** All reagents and solvents were purchased from commercial sources. Benzene (anhydrous, 99.9%, Alfa Aesar) was degassed prior to transfer and storage in a glovebox. All compounds containing titanium were stored and handled in a glovebox under an argon atmosphere. Ti$_{17}$ was prepared according to previously reported methods.

3-(4-Nitrophenyl)pentane-2,4-dione (NPA-H). The synthesis of NPA-H was carried out in an analogous manner to the preparation used by Jiang et al. to synthesize 3-(nitrrophenyl)pentane-2,4-dione. A mixture of 1-iodo-4-nitrobenzene (2.0 mmol), 2,4-pentanedione (6.0 mmol), cesium carbonate (8.0 mmol), freshly recrystallized copper(I) iodide (0.20 mmol), and t-proline (0.40 mmol) in dry DMSO (10 mL) was wrapped in aluminum foil to protect from light and heated at 70 °C under nitrogen atmosphere for 24 h. The cooled solution was poured into 1 M HCl and extracted with ethyl acetate. The organic layer was washed with water and brine for 24 h. The cooled solution was poured into 1 M HCl and extracted with ethyl acetate. The organic layer was washed with water and brine and dried over Na$_2$SO$_4$, and the solvent was removed in vacuo. The product to gain atomic resolution structural information

**Data Collection.**

Crystal data for Ti$_{17}$NPA$_4$ as a yellow solid. The product was then fractionated using a mixture of hexanes:ethyl acetate (7:3) as eluent to a yield of 66%.

**PROCEDURES**

Four equivalents of NPA-H were added to 20 mL vial containing Ti$_{17}$ (26.9 mg, 11.3 mmol) dissolved in 5.0 mL of benzene was added a solution of NPA-H (10.0 mg, 45.2 mmol) dissolved in 5.0 mL of benzene. The vial was loosely capped and allowed to slowly evaporate over a period of 2–3 days. After this time, pale yellow (nealy colorless) crystals suitable for single crystal X-ray diffraction were obtained.

Crystals obtained from a benzene solution are only stable in oil for 20–40 s. After numerous attempts, a single crystal 0.4 × 0.2 × 0.2 mm$^3$ was rapidly mounted on a glass fiber in oil and cooled to 90 K. The rapid decomposition of the crystals is likely due to the presence of seven benzene molecules per Ti$_{17}$NPA$_4$ in the lattice.

**Electron Transfer Dynamics.** To characterize the IET time scale, the survival probability was defined as the probability that the photexcited electron remains in the adsorbate molecule, NPA, at time $t$ after excitation of the system was computed. $P_{\text{NPA}}(t)$ was obtained as the projection of the time-evolved electronic wave function onto the atomic orbitals of the molecular adsorbate. The survival probability was computed as $P_{\text{NPA}}(t) = \sum_{\text{MOL}} B^\dagger(t)B(t)$, where $S$ is the overlap matrix and $B$ is a time-dependent expansion coefficient. Computing the time-dependent wave function $\Psi(t) = \sum_{\text{MOL}} B(t)\chi(t)$ expanded in the basis set of AO's $\chi(t)$ required the propagation of the expansion coefficients $B(t) = \sum_{\text{MOL}} Q_C \exp(-i/E_C t)$, where $C$ are the expansion coefficients of the initial state. The eigenvectors and eigenvalues $Q$ and $E$ were obtained from the ground state electronic density using the electronic structure package Gaussian 09, Revision A03, with the electronic structure described by DFT at the B3LYP/LANL2DZ level of theory. Initial states, $Q$ were defined in terms of the unoccupied orbitals of an isolated NPA-H molecule. Electron transfer dynamics simulations were performed on the previously relaxed Ti$_{17}$NPA$_4$ system. It should be noted that theoretical models do not include losses due to radiative and nonradiative relaxation of the dye excited-state, which typically occur on the nanosecond time scale. Likewise, the simulations have been performed in the low temperature (0 K) limit where nuclear motion is much slower than electronic relaxation; thus, coupling between the electronic wave function and the molecular vibrations has not been included.

**Electronic Optical Transitions.** To characterize the photoexcited electrons generated by optical transitions, excited states were computed by using time-dependent density functional theory (TDDFT) at the B3LYP/LANL2DZ level, as implemented in Gaussian 09. Optical transitions were computed for both the isolated NPA-H molecule and the Ti$_{17}$NPA$_4$ model. The minimum energy configuration of the isolated NPA-H molecule was obtained at the B3LYP/6-31G* level of theory.

**RESULTS**

The reaction between Ti$_{17}$ and NPA-H follows the same general scheme as reported for catechol and isonicotinic acid. Four equivalents of NPA-H, one for each reactive five-coordinate atom in Ti$_{17}$, are treated with 1 equiv of the POT cluster to give a Ti$_{17}$ cluster which contains four NPA ligands, Ti$_{17}$NPA$_4$. 

\[ \text{Ti}_{17} + 4 \text{NPA-H} \rightarrow \text{Ti}_{17}\text{NPA}_4 \]
Binding Mode. An examination of the crystal structure of Ti$_{17}$NPA$_4$ reveals that all four of the isopropoxide groups bound to the five-coordinate titaniuim of the initial Ti$_{17}$ cluster have each been replaced by NPA ligands. The NPA exhibits bidentate attachment to the titanium atom, increasing its coordination number from five to six. The nearly equivalent lengths of the four Ti–O bonds between the cluster and the two crystallographically independent NPA ligands (2.030, 2.020, 2.050, and 2.015 Å) and the lack of any residual electron density near the anchor oxygen atoms indicate that the acetylacetone (acac–H) anchor group has been deprotonated to the acetylacetone anion (acac). Additionally, deprotonation of the NPA–H ligand to NPA conserves the charge neutrality of the cluster. It is reasonable to assume that the proton from the ligand is transferred to the displaced isopropoxide (OPr$^-$) group to give 2-propanol (HOPr$^-$), thus the reaction becomes

$$\text{Ti}_{17}O_{24}(\text{OPr}^-)_{20} + 4\text{NPA–H} \rightarrow \text{Ti}_{17}O_{25}(\text{OPr}^-)_{16}(\text{NPA})_4 + 4\text{HOPr}^-$$

Two modes of bidentate attachment of the acac linker to the (101) surface of anatase were investigated previously.$^{10}$ Bidentate attachment of the acetylacetone anchor group at an oxygen vacancy on the surface of anatase was predicted to be the most energetically stable mode of attachment. The second bidentate mode resulted in the displacement of the titanium from the surface and the breaking of a subsurface Ti–O bond, a rearrangement that was energetically disfavored. Given the energetic analysis and the displacement of OPr$^-$ by the NPA ligand during functionalization, it is natural to expect that the NPA binding motif in Ti$_{17}$NPA$_4$ closely resembles the bidentate mode in the oxygen vacancy model of anatase.

Figure 1 shows the geometry of a fragment of Ti$_{17}$NPA$_4$ and the two models of bidentate attachment to the anatase (101). In the case of the four Ti–O bonds that attach the Ti/O/acac fragments to the larger nanoclusters, the bond lengths of the experimental geometry (from 1.897 to 1.933 Å) are closer to the values for the oxygen vacancy model (from 1.951 to 1.980 Å) than the surface chelation model (from 2.100 to 2.157 Å). In fact, the Ti–O bond lengths of both the experimental geometry and the oxygen vacancy model are quite similar to that of bulk anatase (1.934 and 1.980 Å). The distance between the two oxygens of the acac anchor are 2.594 and 2.544 Å for the experimental geometry and the surface chelation model, respectively. The larger value of 2.787 Å observed in the oxygen vacancy model is a consequence of the fact that the oxygen atom of the anchor that fills the vacancy also interacts with a neighboring titanium atom (not shown).

While nearly 100 crystal structures containing the acac group bound to titanium have been deposited in the CSD,$^{32}$ the vast majority contain only one or two titanium atoms. Prior to this report, the largest polyoxotitanate possessing a dione ligand had only five titanium atoms in its core (WIYCOW). In every one of these Ti-acac crystal structures, bidentate chelation of the acac group to a single titanium atom was observed. In several additional crystal structures of larger Ti/O clusters containing acac groups (to be reported), the observed binding is invariably bidentate.

Charge Separation. The light-induced charge-separated state was characterized using EPR spectroscopy. Under illumination, electrons in the conduction band are localized on titanium centers, generating $d^1$ Ti$^{3+}$ species, while holes are localized on oxygen atoms, producing oxygen-centered radicals. At low temperature with continuous illumination, both paramagnetic species are long-lived and easily observed by EPR. The spectra shown for Ti$_{17}$ and Ti$_{17}$NPA$_4$ in Figure 2 indicate contributions from both titanium- and oxygen-centered unpaired electrons. The signals at $g > 2$ are assigned to oxygen anion holes, and those at $g < 2$ are assigned to titanium electrons, consistent with previous reports of charge separations in TiO$_2$. $^{33-37}$ Preliminary spectral simulations suggest that both regions of the spectrum are composed of three overlapping signals resulting from contributions of oxygen and titanium centers in different coordination environments. Of the three contributing titanium signals, two axial components are present in both the Ti$_{17}$ and Ti$_{17}$NPA$_4$ spectra. A third axial component changes upon coordination of the NPA ligand, suggesting that it derives from the five-coordinate titanium center in Ti$_{17}$, which becomes six-coordinate upon NPA ligation. Complete analysis of the EPR results will be reported in a future publication.

The wavelength of light used to illuminate the sample may be varied with long-pass filters, used in order from longest to shortest wavelength. Comparison of the wavelength-dependent spectra of Ti$_{17}$ and Ti$_{17}$NPA$_4$ demonstrates that coordination
of NPA shifts the onset wavelength for charge separation. For unfunctionalized Ti$_{17}$, no oxygen or titanium radicals are seen for wavelengths greater than 345 nm. However, radical formation is observed when a >295 nm filter is used, suggesting that the excitation wavelength for the onset of charge separation lies between 345 and 295 nm. By contrast, some of the charge-separated state for Ti$_{17}$-NPA$_4$ clusters is observed with irradiation above 400 nm, and the EPR signal intensity increases with illumination at shorter wavelengths. The transition responsible for the generation of the EPR signal is significantly shifted by the addition of the NPA chromophore, suggesting that Ti$_{17}$ clusters are sensitized in a manner analogous to TiO$_2$ nanoparticles.

**Interfacial Electron Transfer.** Before reporting the results from the IET simulations, it is useful to look at the density of states (DOS) and projected density of states (pDOS) of the functionalized nanoparticle. The DOS for an unbound NPA-H molecule is included to examine the effect of ligation on the electronic structure of the sensitizer. Figure 3 shows the DOS of the [Ti$_{17}$O$_{24}$(OH)$_{16}$(NPA)$_4$] model system along with the pDOS of all four NPA adsorbates. The DOS shows that the HOMO−LUMO gap in the model system is ∼3.5 eV, with the HOMO and LUMO (both are quasi-4-fold degenerate states) populations localized mainly on the NPA adsorbates, as indicated by the pDOS. The pDOS also indicates that the majority of the NPA orbitals are energetically unperturbed upon complexation to the Ti$_{17}$ cluster with the exception of the NPA-H LUMO + 1. The ligand LUMO + 1 orbitals mix with the first unoccupied levels of the Ti$_{17}$ cluster to form new ligand−metal hybrid orbitals located at ∼4.2 eV above the HOMO.

Figure 4 shows the electron density of the four initial excited states used in the IET simulations. The initial states correspond to instantaneous photoexcitations to the LUMO, LUMO + 1, LUMO + 2, and LUMO + 3 of a single NPA with energies of 3.72, 4.83, 5.69, and 6.19 eV, respectively. The pDOS indicates that the first excited state (i.e., the NPA LUMO) is located below the unoccupied Ti/O orbitals of the cluster, indicating that IET from that state is unlikely to be observed. The remaining states are aligned with a large density of unoccupied
Ti$_{17}$ cluster levels, especially the LUMO + 1, indicating that IET could occur from these states. Figure 5 shows the survival probability $P(t)$ for an electron starting from one of the three initial states that overlap energetically with Ti/O orbitals: the LUMO + 1, LUMO + 2, and LUMO + 3 of the NPA adsorbate. The simulation using the NPA LUMO initial state resulted in a survival probability that shows minimal population transfer, <1%, of the photoexcited electron during the first 1 ps of dynamics and was not included in the figure. Thus, no injection can occur from photoexcited electrons populating the NPA LUMO. Charge injection from the NPA LUMO + 1 to the Ti/O cluster occurs extremely rapidly as $P(t)$ falls to nearly zero within 1−2 fs (Figures 5 and 6). Following electronic excitation, strongly coupled nondegenerate quantum mechanical systems generally exhibit Rabi oscillations, which are readily observed for IET from the LUMO + 1 and LUMO + 2 states. The larger oscillations and nonexponential behavior of the IET from the LUMO + 1 are a consequence of the finite number of empty Ti$_{17}$ orbitals available at this energy.38

The simulation of IET, using the NPA LUMO + 2 as the initial state, shows ultrafast IET with an injection time scale of approximately 12 fs. The NPA LUMO + 3 initial state shows fast initial IET, transferring about 20% of the electron population in the first 10 fs, followed by a much slower rate of IET. It is interesting that a large difference in the survival probability is obtained for the third and fourth initial states, since the density of unoccupied Ti$_{17}$ cluster states is similar at the energy of the initial states. Figure 6 shows snapshots of the time-evolved electron density after instantaneous photoexcitation to the NPA LUMO + 1. Each panel shows a snapshot of the electronic density at 1 fs intervals, progressing from left to right and then from top to bottom. Titanium atoms are green; oxygen, red; carbon, cyan; nitrogen, blue; and hydrogen, white.
Electronic Transitions. The simulations of IET indicate that ultrafast injection will occur from the NPA LUMO + 1 and LUMO + 2 but not from the NPA LUMO. It is important to see if an allowed optical transition will promote an electron into the LUMO + 1 or LUMO + 2 of NPA (Table S8, Supporting Information). The lowest energy transition of the isolated NPA, as computed using TDDFT, is a HOMO–LUMO transition at 349 nm with an oscillator strength of 0.0267 au. Unfortunately, as seen from the IET simulations, the NPA LUMO is below the energy level of the unoccupied Ti_{17} states and this excited state is predicted not to undergo ultrafast IET. While the NPA HOMO to LUMO + 1 does contribute to the fourth excited state, which is a weak transition at 300 nm, it is the predominant component of the much stronger seventh transition occurring at 258 nm with an oscillator strength of 0.1275 au, which also has considerable HOMO–LUMO + 2 character. The ninth electronic transition is also a relatively strong transition with an oscillator strength of 0.0938 au and is primarily HOMO to LUMO + 2 with considerable HOMO–LUMO + 1 character. Even though there are no electronic transitions in the visible region for this model sensitizer, the HOMO–LUMO + 1 and LUMO + 2 transitions are optically strong and, thus, suitable candidates for charge injection. Furthermore, it is possible that a direct transition from the NPA to unoccupied levels of the Ti_{17} cluster is allowed with a corresponding excitation wavelength in the visible region, according to the usual type II injection mechanism—i.e., electron injection directly from the ground state of the dye into the semiconductor conduction band without the involvement of excited dye molecular states. In contrast, the so-called type I injection involves electron transfer from an excited state of the dye (e.g., the LUMO or LUMO + 1 orbitals localized on the dye close to the interface) populated upon photoexcitation.

To investigate the possibility of direct transitions, a TDDFT calculation was performed on the [Ti_{17}O_{24}(OH)_{16}(NPA)_4] model (Table S7, Supporting Information). Due to the large size of the system, only the first 10 excited states were obtained. The third and seventh excited states possess relatively large oscillator strengths of 0.1391 and 0.1059 au, respectively. The photoexcited electron population for both states is occupied in the LUMO + 2 and LUMO + 3 of the [Ti_{17}O_{24}(OH)_{16}(NPA)_4] model. These virtual orbitals as well as the LUMO and LUMO + 1 are quasi-4-fold degenerate with an energy of 3.76 eV and correspond to the LUMO of the free NPA. Thus, nine of the 10 lowest energy transitions are effectively excitations into NPA orbitals that do not overlap with titanium. Only the ninth excited state, corresponding to an excitation wavelength of 357 nm and possessing a relatively small oscillator strength, shows population of the photoexcited electron on the Ti_{17} cluster, a direct consequence of populating the mixed Ti/NPA orbitals. Given the optical strength of the HOMO–LUMO + 1 transition in NPA-H, other strong direct sensitizer-to-Ti transitions undoubtedly occur beyond the first 10 excited states calculated here.

To the best of our knowledge, this is the first example of an IET simulation involving multiple independent sensitizers in close proximity, attached to a semiconductor surface that is fully structurally characterized by X-ray diffraction. Given the high loading densities, typically observed in DSSCs, it is highly probable that surfaces with chromophores in close proximity exist in these devices. While chromophores are generally considered electronically isolated with respect to neighboring sensitizers, our calculations show that this is not necessarily the case. For the LUMO + 2 transition, the excited electron diffuses through the Ti/O core and relocates on an NPA molecule on the opposite side of the cluster; density from a single excitation is observed on two sensitizer molecules simultaneously. Delocalization of electron density from an excited sensitizer onto neighboring sensitizer molecules could reduce the ability of the neighboring molecules to absorb light effectively, thereby reducing the efficiency of the device. Furthermore, delocalization of an excitation over multiple chromophores may lead to increased rates of charge transfer to redox shuttles that would also detrimentally impact device performance.

The strong mixing of the LUMO + 1 state with the cluster orbitals also has important implications for light-harvesting systems. An increase in the broadening of a sensitizer injecting state, upon coupling to the substrate, is associated with increased rates of electron transfer.39 Similar behavior is observed in the calculated IET rates for [Ti_{17}O_{24}(OH)_{16}(NPA)_4]. While the NPA LUMO + 2 and LUMO + 3 states do not split or shift upon complexation to the POT cluster (no broadening), the LUMO + 1 state does contribute to several new states and is effectively broadened over an energy range of approximately 1 eV. Initial rates of IET from the LUMO + 2 and LUMO + 3 states are similar at 0.02 and 0.03 fs^{-1}, respectively, and are considerably less rapid than the rate of injection from the LUMO + 1 state, which is nearly an order of magnitude faster at 0.19 fs^{-1}.

Given the fast injection and the low energy of the transition relative to the LUMO + 2 and LUMO + 3 states, injection from the NPA LUMO + 1 appears to be ideal. In addition, direct injection through a type II mechanism should be possible. However, the formation of new energetically isolated orbitals below the quasi-conduction band could mean that direct excitation into these orbitals might not lead to injection into the semiconductor substrate. Instead, the excitation may remain localized on these orbitals and such states may even act as low energy sinks for higher-energy excitations.

CONCLUSIONS

As part of our project on single-crystal analyses of functionalized Ti/O nanoclusters,17,19 the structure of the polyoxotitanate nanocluster Ti_{17}O_{24}(OPr)_{20} functionalized with four p-nitrophenyl acetylenecetone (NPA-H) adsorbates has been resolved by single crystal X-ray diffraction methods, revealing the exact way in which the acac anchor group attaches to the semiconductor surface via bidentate chelation, as previously predicted by computational modeling.10 The crystalline nature of the nanoclusters has allowed us, for the first time, to perform both spectroscopy and simulations for the same model structures at the DFT level. Theoretical calculations based on the functionalized cluster are used to predict the electronic properties relevant to light-harvesting devices. The density of states plot reveals that many of the unoccupied states of the free NPA-H are unaffected upon binding to the Ti_{17} cluster; however, the NPA-H LUMO + 1 states mix with cluster orbitals near the quasiconduction band edge, resulting in new states that are lower in energy by approximately 0.5 eV and have both NPA and Ti character. This mixing is expected to facilitate direct IET and a significant increase in the rate of IET.
Delocalization of the excitation over multiple chromophores is also identified.

**ASSOCIATED CONTENT**

**Supporting Information**

Additional figures of Ti$_2$NPA$_4$ complex and IET simulations, tables of crystallographic information, CSD recodes for titanium acetylacetone structures, TD-DFT results, the full ref 31, and .cif file for Ti$_2$NPA$_4$?C$_6$H$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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