A new Titanium Metal Organic Framework with visible-light responsive photocatalytic activity

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Abstract: we report the one step synthesis and characterization of a new and robust titanium-based Metal Organic Framework, ACM-1. In this new structure, based on infinite Ti-O chains and 4,4′,4″,4″′-(pyrene-1,3,6,8-tetrayl) tetrabenzoic acid as a photosensitizer ligand, the combination of highly mobile photogenerated electrons and a strong hole localization at the organic linker results in large charge separation lifetimes. The suitable energies for band gap and CBM offer great potential for a wide range of photocatalytic reactions, from hydrogen evolution to the selective oxidation of organic substrates.

Perhaps their most celebrated feature, Metal-Organic Frameworks (MOFs) offer an unmatched control over their physical properties, via the selection or modification of the organic and inorganic units that construct them. These properties include excitonics, which makes them alluring materials for photocatalysis. The typically preferred band gap of a MOF photocatalyst presents a gap constituted by occupied states from the organic ligand, and empty states by the metal. This prescribes ligand-to-metal charge transfer (LMCT) upon photoexcitation, which helps reducing rates of recombination, a primary bottleneck in photocatalysis. Clusters based on Ti4+ are particularly looked at, for they present an empty d-shell to make up the Conduction Band Minimum (CBM). In this context, there is a growing interest in the synthesis of new Ti-based MOFs. To date, there is only a handful one-step syntheses that yield (single-metal) Ti based MOFs. Pathways via preformed Ti clusters are more common, as well as other indirect routes such as postsynthetic metalation, or those via preformed heterometallic clusters.

In our search for new photocatalytically active Ti based MOFs, we selected 4,4′,4″,4″′-(pyrene-1,3,6,8-tetrayl) tetrabenzoic acid (H3TBPY) as a photosensitizer ligand. Previously used as organic building block for the synthesis of NU-901[8], NU-1000[9] and ROD-7,[10] among other structures. H3TBPY has been shown to display a broad visible light absorption spectrum derived from an extended n-electron system.[10-11] As we show in this work, the synergy between Ti and the H3TBPY ligand gives rise to a MOF with compelling photocatalytic properties.

The new Ti-carboxylate MOF, named ACM-1 (ACM for Advanced Catalytic Materials), was prepared by a one-step reaction between titanium isoproxyde, H3TBPY and propionic acid as modulator, in a solvent mixture of dry diethylformamide (DEF) and chlorobenzene. The resulting polycrystalline orange powder was repeatedly washed with DEF and recovered by filtration with ethanol (TiO3(TBPY)·2C6H5O). Images recorded by SEM show small platelets, mostly intergrown (Figure S3), with no visible contamination. It has to be noted that proper sonication and homogenization of the suspension was required to avoid the suspension stratification and formation of an amorphous Ti-rich byproduct. The peak indexation of ACM-1 reveals an orthorhombic unit cell with cell parameters: a = 30.491(2) Å, b = 6.8381(4) Å, c = 15.8644(9) Å.[12] The Le Bail profile refinement confirms a unit cell with space group Cmcm (Figure 1a). These cell parameters are identical to the single-crystal analysis of the previously reported ROD-7,[10] an in2+ based H3TBPY MOF. Indeed, ACM-1 is isostructural to ROD-7, with the only slight difference that the μ2-OH groups in ROD-7 are μ2-O in ACM-1 (to account for the +4 oxidation state of Ti) These oxygens construct infinite Ti-O chains in the c direction, with the ligand spanning the pores along the a and b directions (Figure 1b). Each Ti ion is octahedrally coordinated to six oxygen atoms: four deprotonated carboxylate oxygen atoms from four independent TBPY ligands and the two μ2-oxo anions. The octahedral TiO6(O)2 units are connected in a trans configuration to form infinite chains along the b axis. Each ligand is coordinated to four titanium cations from four independent chains. The 3D framework exhibits the sea topology.

As some MOFs decompose when brought into contact with water, the structural stability of ACM-1 was evaluated by immersing it in deionized water for 24 h. XRD patterns taken of the as-synthesized and water-exposed samples suggest that exposure to water and some common organic solvents does not...
affect the crystallinity and crystal structure of the material (Figure S4 and S5). Thermogravimetric analysis in air indicates that ACM-1 is thermally stable up to 375 °C, yielding bulk TiO$_2$ at higher temperatures (Figure S6). It is worth mentioning that the final amount of TiO$_2$, as determined from TGA, matches well with the expected framework stoichiometry, 18.2 vs. 19.1 wt. %, respectively.

We assessed the sorption properties of ACM-1 after solvent exchange with ethanol and subsequent evacuation at 200 °C under vacuum (4 mbar). A type I N$_2$ isotherm confirms the microporosity of ACM-1 with a Brunauer-Emmett-Teller specific surface area (S BET) of 1212 m$^2$ g$^{-1}$ and a pore volume (PV) of 0.55 cm$^3$ g$^{-1}$ ($P_{B_{max}}$ = 0.6 cm$^3$ g$^{-1}$, Figure S7a). These values are similar to those previously reported for the indium-based ROD-7. On top of that, CO$_2$ adsorption isotherms were measured at three different temperatures to derive the isosteric heat of adsorption (Q IS) at zero coverage (Figure S7b). The Q IS value of 28 kJ is lies close to that of ROD-7 (26 kJ mol$^{-1}$). [14]

Infrared spectra of ACM-1 confirm the absence of any residual ligand, as the shifted characteristic carboxylate peak is observed at 1409 cm$^{-1}$ (Figure S8). [15] Ti-O-R and Ti-O-Ti vibrations can be observed at 645 cm$^{-1}$ and 784 cm$^{-1}$, respectively. [58]

The optical properties of ACM-1 were investigated to evaluate the latter’s suitability as photocatalyst. The UV-Vis spectrum of ACM-1 shows an absorption band in the range of 200-550 nm (Figure 2a), suggesting the optical band gap value to be around 2.3 eV based on the linear extrapolation of the KM function.

![Figure 1](image1.png)

**Figure 1.** a) Le Bail profile fitting of ACM-1 that confirms its isostructure with ROD-7. Rwp = 12.9%, R$_{int}$ = 14.5%, R$_{f}$ = 2.75%, Chi$^2$=27.9. b) One step synthesis of ACM-1 from H$_2$TBAPy ligand, views of the simulated structure in the c direction, plan highlighting the microporous channels and b direction showing the view of the Ti-O-Ti chains along the b axis. Ti in blue, C in dark brown and O in red. H atoms are omitted for clarity.

The electron paramagnetic (EPR) spectroscopy was applied to study Ti-species behavior under UV and visible illumination. As shown in Figure 2b, in both cases the generation of a pronounced Ti$^{3+}$ signal with characteristic parameters g$_{||}$ = 1.944 and g$_{\perp}$ = 1.902 was readily observed, which evidences a LMCT (the reduction of Ti$_4^{4+}$ to Ti$_4^{3+}$). [56]

In order to characterize the redox properties of ACM-1, non-aqueous cyclic voltammograms (CVs) were measured. Reduction (Figure S9a) and oxidation (Figure S9b) regimes are shown separately. H$_2$TBAPy is a pyrene-based linker, [16] and the electrochemistry of pyrene and its derivatives are well known. [17] Pyrene, and the pyrene-based linker alike, undergo a multi-stage reduction through electrode and chemical steps beginning with a single-electron transfer radical anion formation (Figure S9). However, there is no evidence on the accessibility of the otherwise redox-active Ti in the secondary building unit as observed by EPR (vide supra). Pyrene derivatives form radical cations in an oxidative environment, [18] as was reported for MOFs with H$_2$TBAPy linker. [19] The two oxidation events found for the H$_2$TBAPy linker at +0.68 and +1.03 V (vs. Fc$^{+/−}$) were also seen in the CV of ACM-1 (Figure S9b), a clear sign of redox activity of the ligand embedded in the MOF.

As we wish to understand the excitonic properties, and their role in photocatalysis, we computed the electronic band structure of ACM-1. This calculation was done with the HSE06 functional, in order to reduce the electron self-interaction error, which leads to an underestimation of the band gap. [19] In addition, we expanded the wavefunctions through a Slater-type orbital (STO) basis set, allowing us to obtain accurately the atomic orbital contributions to the bands.

The band structure in Figure 3 reveals our preferred scenario; the Valence Band Maximum (VBM) resides on the ligand (dominant p character), and the CBM on the metal (dominant d character). The band gap is estimated at 2.15 eV, which is close to the experimentally observed value of 2.3 eV. Notably, the CBM is computed to lie at −4.10 eV, which predicts ACM-1 to be suitable as photocatalyst for the hydrogen evolution reaction (HER) (−4.44 eV), upon LMCT. These values are in good agreement with the flat band potentials obtained from a Mott-Schottky plot (CBM$_{gg}$ = −4.28 eV), and the ionization potential (CBM$_{sp}$ = −3.51 eV) from UV photoelectron yield measurements (Figure S12). Regarding the latter analysis, we note that the
absolute HOMO energy level of the bare linker lies close to that of ACM-1 (Figure S11).

The lowest-energy conduction band shows a good degree of dispersion along R-T-T and U-T-Z, directions in reciprocal space for which the wave vector describes periodicity along the infinite Ti-oxo chains. The highest-energy valence band is almost perfectly flat; a sign of strong electron localization. A more thorough look at the band character explains why; the VBM is located on the pyrene-like, four-ring component of the linker (Figures S13 and S14). In fact, the flat band is the highest occupied molecular orbital (HOMO) of the linker, a localized \( \pi \) state. And the equally flat \( \pi \)-band, 1 eV below, is the HOMO-1. As the orientation of the four-ring is found to be nearly perpendicular to that of the adjacent aromatic ring that connects to the metal with its carboxylate group, charge carriers are expected to remain strongly localized in these \( \pi \)-bands.

An inspection of the curvature eigenvalues at the VBM and CBM corroborates the analysis; we predict the effective mass of the excited electron to be lowest in the crystallographic direction corresponding to the Ti-O-Ti-O chains (\( \hbar m_{\text{e}} = 1.17 \)), while the hole on the linker is estimated to be an order of magnitude heavier.

Both steady-state and time-resolved photoluminescence (PL) were employed to study the lifetime of the excited states in ACM-1. As shown in Figure 4a, the steady-state PL intensity of ACM-1 markedly decreased compared to that of the bare H$_2$TBApy ligand. Additionally, ACM-1 showed faster decay in the time correlated single photon counting measurement (\( t_1 = 0.27 \) ns, 89% and \( t_2 = 1.55 \) ns, 11% for ACM-1 vs. \( t = 2.07 \) ns for H$_2$TBApy). This demonstrates the efficient electron transfer from the organic ligand to the Ti-O chains.

The charge recombination dynamics, obtained by femtosecond transient absorption (fs-TA) spectroscopy are compared between H$_2$TBApy and ACM-1 in Figure 4d. It can be seen that charge recombination is significantly slower for ACM-1 (\( t_1 = 375 \) ps, 72%; \( t_2 = 2.3 \) ns, 28%) than in H$_2$TBApy (\( t_1 = 1.2 \) ps, 68%; \( t_2 = 15 \) ps, 32%). This further indicates efficient charge separation, a prerequisite for enhanced photocatalytic performance.

As predicted by theory and spectroscopy, ACM-1 performs well in photocatalytic HER in which we used triethylamine as sacrificial agent. Bare ACM-1 produces hydrogen at rates of 5.9 \( \mu \)mol h$^{-1}$ (Figure 5a), but we sought to further exploit the electron mobility along the Ti-oxo chains, and deposited Pt nanoparticles on ACM-1 to serve as catalytic sites for the HER. Here, we anticipated ACM-1 to transfer electrons to Pt upon photocexcitation; Pt is a good catalyst for H-H bond formation.$^{[20]}$

In order to estimate the HER activity of ACM-1 unambiguously$^{[21]}$ we optimized the catalyst loading parameters (Figures S15 and S16). Results show that Pt/ACM-1 with a 3.38 wt.% Pt loading (default value hereafter, if not stated otherwise) exhibits the highest HER rates, around 11 times higher than bare ACM-1 (67 \( \mu \)mol h$^{-1}$). Over four catalytic runs, this catalyst remained crystalline and demonstrated no significant deactivation (Figures 5b and S17). Control experiments with H$_2$TBApy ligand (Figure S18) exhibited no activity. From these results it is clear that H$_2$TBApy alone cannot drive HER as efficiently as ACM-1 even when modified with Pt as the HER catalyst. In line with the discussed theory, LMCT and electron transport along Ti-oxo chains are thus necessary to drive the reaction over the designated catalytic centers.

The AQE of Pt/ACM-1, estimated at 440 nm, was 0.43% (Figure S1). This value is similar to other reported AQE for Ti based MOFs.$^{[22]}$ It worth to note that ACM-1 AQE was 3 times as efficient as well-studied NH$_2$-MIL-125 system tested in our reactor at the similar conditions (Figure S2).

A comparison between the catalytic performance of Pt/ACM-1 and its counterpart (ROD-7), post-synthetically modified with similar Pt loadings, demonstrates that Ti nodes with vacant $d$ orbitals are required for photocatalysis (Figure 5a). ROD-7 is based on In, which presents no low-lying $d$ orbitals, and correspondingly, cannot participate in efficient LMCT.$^{[10]}$

Figure 3. Band structure of ACM-1 along four paths in the Brillouin zone. The band colour indicates the atomic orbital type with the largest contribution to the wavefunction; \( p \) in blue and \( d \) in green. The Fermi level is indicated by a red line and the energies are referenced to the vacuum level. The \( \pi \) and \( \pi^* \) bands of the ligand's four-ring are designated.

Figure 4. a) PL emission spectra of ACM-1 and H$_2$TBApy. Inset in (a) normalized photoluminescence decay traces of ACM-1 and H$_2$TBApy following 372 nm laser excitation. Solid lines represent exponential fit to the data. b) Fs-TA spectra at different time delays of H$_2$TBApy. c) Fs-TA spectra at different time delays for ACM-1. d) Normalized GB kinetics in ACM-1 and H$_2$TBApy probed at 440 nm in response to 370 nm excitation in water. Solid lines represent exponential fit to the data.

Figure 5. a) Reaction kinetic for Pt/ACM-1 and Pt/TBA. b) Photocatalytic HER performance of Pt/ACM-1 and Pt/TBA under control conditions in MBF Membrane Reactor System. c) Reaction kinetic for Pt/ACM-1 and Pt/TBA probed at 440 nm in response to 370 nm excitation in water. Solid lines represent exponential fit to the data.

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comparison to ROD-7, where photoluminescence response is determined only by TBApy ligands and no LMCT takes place, the strong photoluminescence quenching of ACM-1 illustrates the lower rate of recombination of charge carriers owing to LMCT from ligands to Ti-oxo chains (Figure S19).

The band structure and CBM of ACM-1 forecast possibilities towards oxidation, too. A common photocatalytic oxidation pathway proceeds via the reduction of $\text{O}_2$ to $\text{O}_2^-$ (superoxide).[23] The absolute potential of this reduction is $-4.31 \text{ eV}$, which renders it thermodynamically feasible upon photoexcitation of ACM-1 (CBM: $-4.10 \text{ eV}$). We focused on the selective oxidation of benzyl alcohol and cyclohexanol under visible light irradiation.

In the oxidation of benzyl alcohol to benzaldehyde, we obtained a 6% conversion with 100% selectivity within the first three hours, after which we started to produce benzoic acid as side-product. After 12 h, we obtained a conversion of 42% with a product composition of 81% benzaldehyde and 19% benzoic acid (Figure 6a). The oxidation appears to involve molecular oxygen, as the conversion was negligibly low in the absence of $\text{O}_2$. In the oxidation of cyclohexanol, we obtained a conversion of 51% after 12 h, with a selectivity of 100% (Figure 6b, Table S2).

In summary, we reported the one step synthesis and characterization of a new and robust titanium-BOF. In ACM-1 the combination of highly mobile photogenerated electrons and strong hole localization at the organic linker results in long exciton lifetimes. The suitable energies for band gap and CBM offer plenty of potential for a wide range of photocatalytic reactions.

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References


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