Metal–Organic Frameworks

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A Flexible Photoactive Titanium Metal–Organic Framework Based on a $[\mathrm{Ti^{IV}_3(\mu_3\text{-}O)(O)_2(COO)_6}]$ Cluster

*Bart Bueken, Frederik Vermoortele, Danny E. P. Vanpoucke, Helge Reinsch, Chih-Chin Tsou, Pieterjan Valvekens, Trees De Baerdemaeker, Rob Ameloot, Christine E. A. Kirschhock, Veronique Van Speybroeck, James M. Mayer, and Dirk De Vos**

Abstract: *The synthesis of titanium–carboxylate metal–organic frameworks (MOFs) is hampered by the high reactivity of the commonly employed alkoxide precursors. Herein, we present an innovative approach to titanium-based MOFs by the use of titanocene dichloride to synthesize COK-69, the first breathing Ti MOF, which is built up from trans-1,4-cyclohexanedicarboxylate linkers and an unprecedented $[\mathrm{Ti^{IV}_3(\mu_3\text{-}O)(O)_2(COO)_6}]$ cluster. The photoactive properties of COK-69 were investigated in depth by proton-coupled electron-transfer experiments, which revealed that up to one $\mathrm{Ti^{IV}}$ center per cluster can be photoreduced to $\mathrm{Ti^{III}}$ while preserving the structural integrity of the framework. The electronic structure of COK-69 was determined by molecular modeling, and a band gap of 3.77 eV was found.*

Metal–organic frameworks (MOFs) have been intensely studied over the past decade, with a focus on creating more thermally and chemically robust materials, which are highly desirable for numerous applications, including catalysis, molecular separations, and gas storage.[1–5] In this context, various research groups have reported frameworks based on the Group IV elements, mainly $\mathrm{Zr^{IV}}$ and $\mathrm{Hf^{IV}}$. These oxophilic ions are known to yield clusters with a high connectivity, and the clusters are strongly coordinated by linker carboxylate groups to form robust MOFs.[6–13] However, for titanium, very few crystalline three-dimensional frameworks with guest-accessible porosity have been described. Despite the redox properties and photocatalytic potential associated with titanium, its low toxicity and the existence of numerous carboxylate-based Ti clusters,[14,15] the synthesis of titanium–carboxylate MOFs remains challenging. One notable exception is the titanium(IV) terephthalate MIL-125 and its variants,[16–18] which can be synthesized either directly from titanium(IV) butoxide or by the use of a preformed octameric cluster.[19–21]

The prime hurdle in the synthesis of Ti MOFs is the high reactivity of the commonly used Ti precursors, which are susceptible to fast olation and oxolation and thus readily form ill-defined oxyhydroxides.[15,22] To partly overcome this issue, mixed-metal MOFs containing titanium have been synthesized, either by introducing $\mathrm{Ti^{IV}}$ through postsynthetic metal exchange or by combining a Ti precursor and a divalent metal salt during synthesis.[23–30] Very recently, Zhou and co-workers used a hexanuclear Ti cluster as metal source to form the porphyrinic Ti MOF PCN-22.[31] Interestingly, this preformed cluster rearranged during synthesis to form the final heptameric node found in the framework.

Herein, we explore the use of a hydrolytically more robust organometallic Ti precursor for the formation of porous titanium carboxylates. More specifically, by using dicyclopentadienyl titanium(IV) dichloride ($[\mathrm{Cp_2Ti^{IV}Cl_2}]$), we were able to synthesize COK-69, a new, breathing titanium(IV) *trans*-1,4-cyclohexanedicarboxylate framework, which is among the few porous three-dimensional Ti MOFs reported to date. COK-69 contains a trinuclear $[\mathrm{Ti^{IV}_3(\mu_3\text{-}O)(O)_2(COO)_6}]$ cluster not previously reported in MOFs. This cluster closely resembles analogous motifs based on trivalent cations that are encountered in several well-known MOFs, such as MIL-88, MIL-96, MIL-100, and MIL-101.[32–36] With the introduction of an analogous Ti cluster in MOF chemistry, the road to the synthesis of a series of new structures with titanium is opened.

The treatment of $[\mathrm{Cp_2Ti^{IV}Cl_2}]$ with *trans*-1,4-cyclohexanedicarboxylic acid ($\mathrm{H_2cdc}$) in *N*,*N*-dimethylformamide (DMF), in the presence of acetic acid as a synthesis modulator (110 °C, 48 h, Ar atmosphere), led to the formation of a blue-gray microcrystalline solid, COK-69_R (R = reduced). Upon exposure to air, this solid was rapidly transformed into off-white COK-69 or $[\mathrm{Ti^{IV}_3(\mu_3\text{-}O)(O)_2(cdc)_3{\cdot}DMF}]_n$. By the use of microwave irradiation (220 °C), the synthesis could be scaled up and the synthesis time could be significantly reduced to about 10 min. Nevertheless, a higher quality material was obtained from the solvothermal reaction.

COK-69 contains trimeric $\mathrm{Ti^{IV}_3(\mu_3\text{-}O)}$ secondary building units, which are interconnected by six $\mathrm{cdc^{2-}}$ linkers to form a framework with underlying **acs** topology that features both trigonal-bipyramidal cages and one-dimensional hexagonal channels (Figure 1; see also Figures S1–S4 in the Supporting Information). This topology is the same as that of the well-known MIL-88 family of materials.[36] Although MIL-88 and COK-69 contain similar trimeric clusters, the cyclohexanedicarboxylate linkers impose a tilt on the constituent $\mathrm{TiO_6}$

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[*] B. Bueken, Dr. F. Vermoortele, Dr. H. Reinsch, Dr. P. Valvekens, Dr. T. De Baerdemaeker, Prof. Dr. R. Ameloot, Prof. Dr. C. E. A. Kirschhock, Prof. Dr. D. De Vos
Centre for Surface Chemistry and Catalysis, KU Leuven
Celestijnenlaan 200F, p.o. box 2461, 3001 Leuven (Belgium)
E-mail: dirk.devos@biw.kuleuven.be

Dr. D. E. P. Vanpoucke, Prof. Dr. V. Van Speybroeck
Center for Molecular Modeling, Ghent University
Technologiepark 903, 9052 Zwijnaarde (Belgium)

Dr. C.-C. Tsou, Prof. Dr. J. M. Mayer
Department of Chemistry, Yale University
225 Prospect Street, p.o. box 208107, New Haven, CT 06511 (USA)

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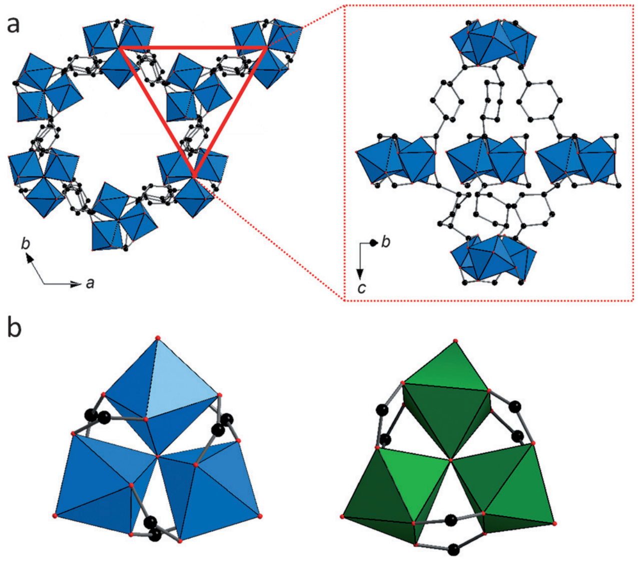

Figure 1. Structure of as-synthesized COK-69. a) 1D hexagonal channels are constructed by the stacking of trigonal-bipyramidal cages. b) The $[Ti^{IV}{}_3O(O)_2(H_2O)(COO)_6]$ cluster with tilted TiO_6 octahedra (blue) is shown on the left alongside the $[Cr^{III}{}_3O(Cl/F)(H_2O)_2(COO)_6]$ cluster from MIL-88 for comparison (O red, C black, Cr green).[36]

octahedra (Figure 1). By Rietveld refinement, the central μ_3-O atom was found to be located slightly above the plane defined by the Ti ions (see Figure S5).

Similar molecular Ti clusters were previously observed to result from the solvolysis of $[Cp_2Ti^{IV}Cl_2]$, for example, $[Ti_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}HCOO)_3(\eta^5\text{-}Cp)_3]^+$ $HCOO^-$.[37–40] Therefore, we assume that the synthesis of COK-69 involves the in situ preformation of cyclopentadienyl-capped $Ti_3(\mu_3\text{-}O)$ clusters through the solvolysis of labile Ti^{IV}–Cl bonds.[41,42] In the formation of these molecular species, the solvolytically more stable cyclopentadienyl ligands probably induce and direct cluster formation while shielding the titanium cations from fast and more extensive hydrolysis.[22,42] The absence of oxide/hydroxide impurities in COK-69 is supported by elemental analysis, which yielded 21.6 wt% Ti and 38 wt% C; these values agree well with the theoretical values of 20.5 and 41.0 wt%, respectively. Thermogravimetric analysis of COK-69 (see Figures S7 and S8) showed a first mass-loss step between 100 and 225 °C as a result of the loss of one DMF molecule per cage (8.8 wt%; theoretical value: 9.4 wt%), followed by slow framework decomposition between 240 and 530 °C. The residual mass of TiO_2, 30.7 wt%, corresponds well to the calculated value of 31 wt%. No cyclopentadienyl fragments were observed in COK-69 by solid-state ^{13}C CP MAS NMR or FTIR spectroscopy, thus indicating the complete removal of all of these ligands during solvothermal synthesis (see Figures S9 and S10). The amount of residual N and Cl in evacuated COK-69 (120 °C overnight in air) was found to be less than 1 wt%.

Although the presence of the central μ_3-O group is unambiguous from Rietveld refinement, the nature of the species occupying the apical position of each Ti octahedron (OH^-, O^{2-}, or H_2O) cannot be determined directly from the diffraction data. Therefore, ab initio level periodic calculations were performed on the COK-69 structure, starting from a cluster with three apical oxo groups (see Figure S26 a), as obtained from Rietveld refinement. The formation energies obtained after structure optimization show that charge neutrality can be achieved by removing one of the apical oxo groups from the cluster (ca. −2.8 eV/cluster; $[Ti^{IV}{}_3(\mu_3\text{-}O)(O)_2(COO)_6]$; see Figure S26 e). However, the structure is stabilized even more (ca. −6.1 eV/cluster) by the addition of two H atoms, either with the formation of two hydroxy groups ($[Ti^{IV}{}_3(\mu_3\text{-}O)O(OH)_2(COO)_6]$, COK-$69^{2OH}$) or by the introduction of a cluster-bound water molecule ($[Ti^{IV}{}_3(\mu_3\text{-}O)(O)_2(H_2O)(COO)_6]$, COK-$69^{H_2O}$; see Figure S26 b,c). The small energy difference between COK-69^{2OH} and COK-69^{H_2O} (see Table S4 in the Supporting Information) indicates that both structures are plausible. Under experimental conditions, however, H^+ might hop from a hydroxy group (see Figure S26 b) to another OH group to form a bound water molecule (see Figure S26 c), which could be lost upon thermal evacuation. Since no OH groups could be discerned in the FTIR spectrum of COK-69 (see Figure S10), we suggest $[Ti^{IV}{}_3(\mu_3\text{-}O)(O)_2(cdc)_3]_n$ and $[Ti^{IV}{}_3(\mu_3\text{-}O)(O)_2(H_2O)(cdc)_3]_n$ to be the likely formulae for the evacuated COK-69 material and that exposed to ambient conditions, respectively.

COK-69 showed an interesting and rare breathing behavior.[43–45] Upon washing the as-synthesized compound with DMF and methanol, followed by thermal evacuation, we observed a structural change due to the conformational flexibility of the cdc^{2-} linker. The cyclohexyl ring in the chair conformation allows the *trans* carboxylate groups at the 1- and 4-positions to adopt either the equatorial *e*,*e*′ or the axial *a*,*a*′ conformation. In the as-synthesized material, in which the pores were occupied by DMF, half of the cdc^{2-} linkers adopted the *a*,*a*′ conformation, whereas the other half assumed the elongated *e*,*e*′ conformation (Figure 2, right; see also Figure S11). Upon guest removal, all linkers were observed to adopt the kinked *a*,*a*′ conformation (Figure 2, left), as confirmed by ^{13}C NMR spectroscopy (see Figure S9), and the framework shrank drastically with a reduction of the unit-cell volume by 21% and a shift in peak positions and intensities in the powder X-ray diffractograms (Figure 2).

Immersion of the closed-pore solid (COK-69_{cp}) in solvents of low polarity, such as toluene or tetrahydrofuran, at 70 °C resulted in the complete recovery of the open-pore solid (COK-69_{op}), with a diffraction pattern identical to that of the as-synthesized material. On the other hand, polar solvents, such as acetonitrile or dimethyl sulfoxide, were incapable of reopening the evacuated material (see Figure S12). Furthermore, the presence of hydrogen-bond-donating groups seemed to be generally unfavorable in inducing the recovery of COK-69_{op}. For example, 2-butanol did not open COK-69_{cp}, whereas butanone did. Finally, the molecular shape and size of the solvent appear to be crucial. Whereas toluene induced pore opening, *ortho*-xylene did not. A similar guest-induced breathing mechanism was recently reported for the MIL-53 analogue [M(OH)(cdc)] or CAU-13 (M = Al, Ga).[46–48] On the other hand, the breathing behavior of COK-69 is distinctly different from that of its topological analogue MIL-88B, which contains rigid terephthalate linkers.[49] The flexibility of

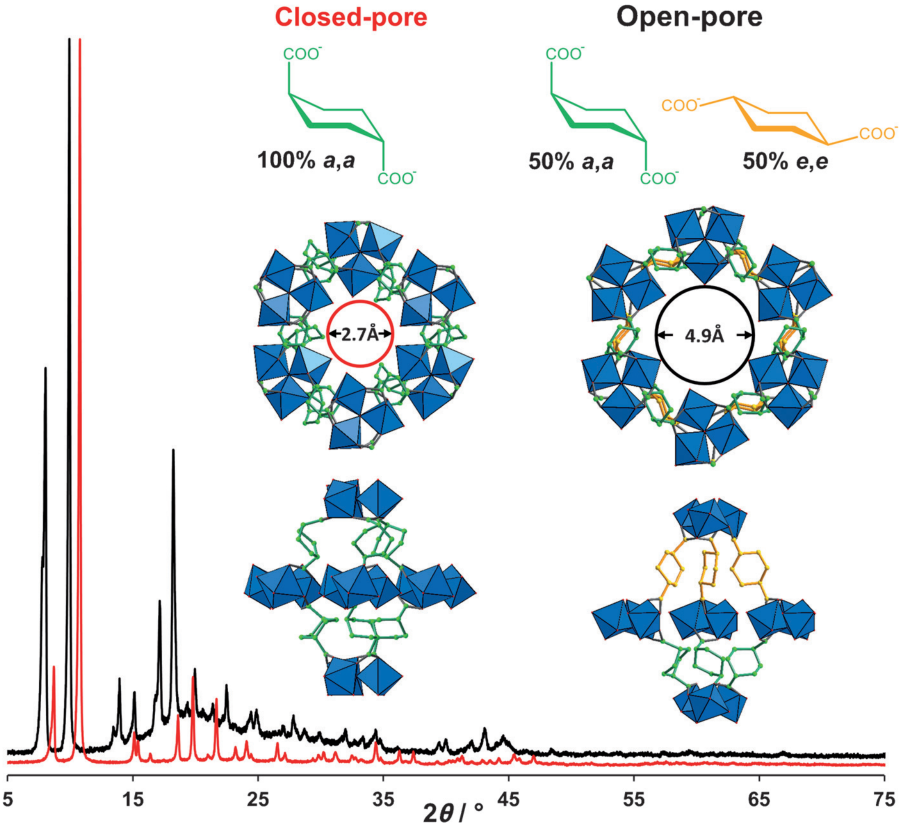

Figure 2. Powder X-ray diffraction patterns and structures of COK-69_{cp} (red; left) and COK-69_{op} (black; right). COK-69_{op} contains cdc^{2-} linkers in both the *e*,*e′* (yellow) and *a*,*a′* conformation (green) in a 1:1 ratio, whereas COK-69_{cp} contains solely *a*,*a′*-cdc^{2-}. Guests have been omitted for clarity.

MIL-88-type materials arises from rotation of the rigid linkers about the axis through the oxygen atoms of each carboxylate group (the so-called "knee-cap" mechanism; see Figure S13),[43] whereas for COK-69, breathing is a consequence of the inherent flexibility of the linker itself.

Owing to the contraction of the COK-69 framework upon evacuation, the diameter of the one-dimensional channels changes from 4.9 Å in the open form to 2.7 Å in the closed-pore system (Figure 2). As a result, the porosity of COK-69_{cp} for N_2 is rather limited, with a BET surface area of 29.1 $m^2\,g^{-1}$ (see Figure S14). Because it is impossible to determine the porosity of guest-loaded COK-69_{op} by gas adsorption, the void volume of the framework was estimated to be 37.3 % by the use of the Mercury software (N_2 probe radius: 1.82 Å; grid: 0.1 Å).[50] For COK-69_{cp}, a similar calculation found a void volume of 10.5 %; however, owing to the framework contraction, this void space is located in isolated pockets rather than in continuous one-dimensional channels (see Figures S15 and S16).

An important incentive for the development of titanium-based MOFs is their expected photoactivity and potential redox behavior. In the case of COK-69, the formation of a blue solid during synthesis already strongly hints at the presence of Ti^{III} species, possibly formed by the reduction of Ti^{IV} with DMF.[16,51] The diffuse reflectance UV/Vis spectrum of air-exposed COK-69 samples (see Figure S17) reveals a strong absorption in the 200–350 nm region, with a maximum around 314 nm. The electronic structures of some of the relevant models for COK-69 were determined by molecular modeling (Figure 3). For COK-69^{2OH} and COK-69^{H_2O}, a band gap of 3.42 and 3.77 eV, respectively, was determined, in fair agreement with the observed absorption spectrum (see Table S4 and Figure S17). The conduction band is made up of Ti states (cyan curves), as also seen in other MOFs.[52] The H atoms present on the Ti clusters only show contributions deep inside the valence bands (pink curves) and do not modify the electronic structure around the band gap.

Irradiation of COK-69 in ethanol with a UV-A ($\lambda = 315$–400 nm) light source readily afforded a blue solid, COK-69_R (Figure 4a). This reduced material displayed a broad absorption extending into the near infrared region (see Figure S18). The electron paramagnetic resonance (EPR) spectrum of COK-69_R shows a clear signal with fitted *g* parameters $g_{\parallel} \approx 1.914$, and $g_{\perp} \approx 1.954$ (Figure 4b); these values correspond to a Ti^{III} species in a dis-

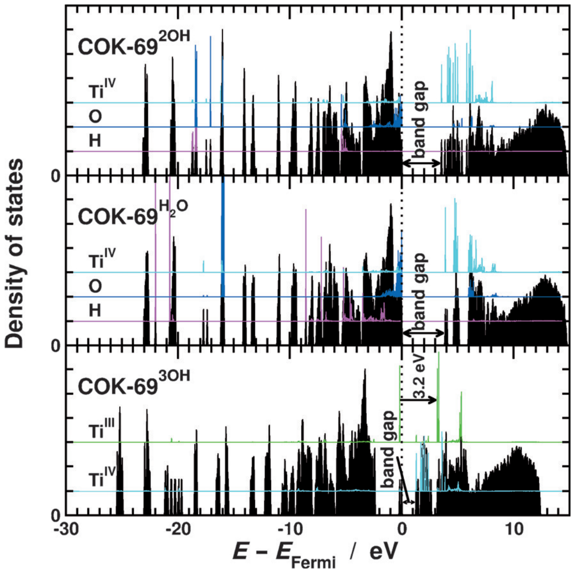

Figure 3. Total density of states (DOS; black curves) calculated by using the HSE06 functional[56] for COK-69^{2OH} (top), COK-69^{H_2O} (middle), and COK-69^{3OH} (bottom). The site-projected DOS of relevant atoms are indicated as offset curves: blue for μ_3-O and O, pink for H, cyan for Ti^{IV}, and green for Ti^{III}. The dashed line indicates the Fermi level, and the band gap is indicated with a double arrow. The excitation of Ti^{III} in COK-69^{3OH} is indicated with an arrow.

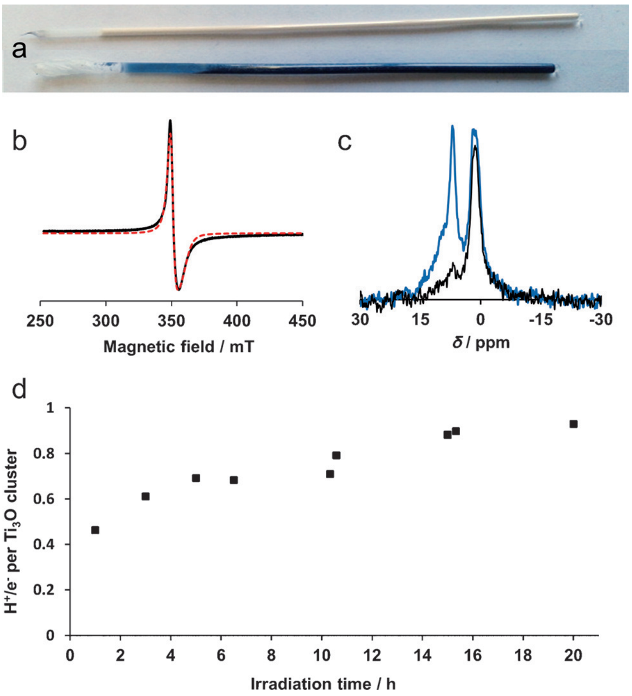

Figure 4. Photoreduction of COK-69. a) Photograph of COK-69 (white, top) and COK-69_R (blue, bottom). b) EPR spectrum (296 K) after photoreduction indicating the presence of a Ti^{III} species with parameters $g_{\parallel} \approx 1.914$ and $g_{\perp} \approx 1.954$ (the simulated spectrum is shown in red). c) ^{2}H MAS NMR spectra after photoreduction (blue) with C_2H_5OD as the reductant and subsequent reoxidation (black). The signal at 7.1 ppm is ascribed to a Ti–OD species. d) PCET from COK-69_R to tBu$_3$ArO$^{\bullet}$ (reaction time: 44 h) as a function of UV irradiation time for COK-69 in ethanol.

torted octahedral environment.[16,53] The photoreduced material did not show any loss in crystallinity (see Figure S19), which signifies that the $[Ti_3(\mu_3\text{-}O)(O)_2(COO)_6]$ cluster can accommodate changes in titanium valence without the framework collapsing or undergoing a phase change. From charge-balance considerations, however, the reduction of a Ti^{IV} atom to Ti^{III} should be accompanied by the introduction of an additional positive charge. The photoreduction mechanism thus most likely involves the transformation of an oxo group, for example, in a titanyl group, into a hydroxy group. To assess the plausibility of such a reduction, we modeled a hypothetical structure with three apical OH groups (COK-69^{3OH}; see Figure S26g), which was found to be even more stable than COK-69^{2OH} and COK-69^{H_2O}. Hirshfeld-I charges show the Ti atoms in a single cluster to be differentiated as two Ti^{IV} atoms and one Ti^{III} atom, with charges of 2.87 and 2.49 e, respectively,[54,55] in accordance with the EPR observation of a Ti^{III} species. The calculated electronic structure of COK-69^{3OH} (Figure 3) shows a semiconducting band gap upon reduction, comparable to that of Si in size, in agreement with the experimental absorption spectrum.

To further confirm the formation of hydroxy groups, an experiment was undertaken with C_2H_5OD as a reductant. ^{2}H MAS NMR spectroscopy showed the absence of deuterated hydroxy groups prior to photoreduction. After irradiation and the removal of residual C_2H_5OD, a distinct signal at 7.1 ppm, which can be attributed to the formation of Ti–OD groups, was observed in the ^{2}H NMR spectrum of COK-69_R (Figure 4c). Upon exposure to air, this signal disappeared again as a result of oxidation of the Ti^{III} cation and the concomitant reformation of an oxo group. The signal observed at 1.5 ppm is ascribed to naturally abundant deuterium on the cdc^{2-} linker.

These observations confirm that the photoreduction and reoxidation of COK-69 involve the simultaneous transfer of both an electron and a proton. Such proton-coupled electron transfer (PCET) has previously also been found for ZnO and TiO_2 nanoparticles upon UV irradiation and subsequent reoxidation with phenoxy or nitroxy radicals.[57] To quantify the maximum number of formed Ti^{III} centers in COK-69_R, we conducted PCET experiments at different UV-A irradiation times, whereby the amounts of e$^-$ and H$^+$ transferred from COK-69_R to the 2,4,6-tri-*tert*-butylphenoxy radical (tBu$_3$ArO$^{\bullet}$) in C_6D_6 were monitored by ^{1}H NMR spectroscopy (Figure 4d; see also Figures S20–S24). The results of these experiments indicate that up to one third of all Ti^{IV}, that is, one Ti^{IV} center per Ti$_3$ cluster, can be reduced, in accordance with the charges calculated for COK-69^{3OH}. Thus, even in the closed-pore form, essentially all clusters are able to participate in the photoreduction. On the basis of these PCET experiments, we propose the empirical formula $[Ti^{IV}_{3-x}Ti^{III}_{x}(\mu_3\text{-}O)(OH)_x(O)_{2-x}(cdc)_3]_n$ for COK-69_R ($x = 0$–1). The fraction of reduced Ti strongly depends on the applied irradiation time. The reaction between tBu$_3$ArO$^{\bullet}$ and COK-69_R is only complete after prolonged contact times. No significant difference in reduction rate was observed between COK-69$_{cp}$ and COK-69$_{op}$, as evidenced by EPR measurements (see Figure S25). This result indicates that there is efficient transport of both electrons and protons to and from the particle surface when the material is exposed to either reductants (e.g. ethanol) or oxidants (e.g. O_2).

In conclusion, we developed a new synthetic route to titanium metal–organic frameworks by employing titanocene dichloride as the metal source. This approach allows more precise control over the solvolysis of the metal precursor and led to the formation of COK-69, the first flexible Ti MOF, which features a photoactive trinuclear cluster. We expect that through this discovery, the road will be opened to the synthesis of a much more diverse library of photoactive Ti MOFs, including well-known topologies, such as MIL-100 and MIL-101. Furthermore, the use of other metallocenes (e.g. of Zr^{IV}, Hf^{IV}, V^{IV}, Mo^{IV}, Ta^{V}) in MOF synthesis holds great promise for the discovery of previously unattainable topologies.

Experimental Section

All chemicals used were obtained commercially and used without further purification. In a typical synthesis, $[Cp_2Ti^{IV}Cl_2]$ (0.5 mmol) and H_2cdc (1 mmol) were dissolved in DMF (5 mL) together with glacial acetic acid (1.73 mmol), and the mixture was transferred to a glass reactor and heated at 110 °C for 48 h. The resulting white precipitate (COK-69) was washed extensively with DMF and methanol and heated overnight at 120 °C in air. For the synthesis of COK-69_R, the reactor was flushed with Ar prior to the reaction. CCDC 1406339, 1406340 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Full experimental details, including characterization, structure solution, photoreduction, and PCET procedures can be found in the Supporting Information.

All theoretical calculations were performed by use of the density functional theory formalism within the projector augmented wave (PAW) method as implemented in the VASP program.[58,59] CCDC 1063991, 1063992, 1063993, and 1063994 contain the supplementary modeled crystallographic structures for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Full computational details can be found in the Supporting Information.

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