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# Proton-Coupled Electron Transport in Anthraguinone-Based Zirconium Metal–Organic Frameworks

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Supporting Information

ABSTRACT: The ditopic ligands 2,6-dicarboxy-9,10-anthraquinone and 1,4dicarboxy-9,10-anthraquinone were used to synthesize two new UiO-type metalorganic frameworks (MOFs; namely, 2,6-Zr-AQ-MOF and 1,4-Zr-AQ-MOF, respectively). The Pourbaix diagrams (E vs pH) of the MOFs and their ligands were constructed using cyclic voltammetry in aqueous buffered media. The MOFs exhibit chemical stability and undergo diverse electrochemical processes, where the number of electrons and protons transferred was tailored in a Nernstian manner by the pH of the media. Both the 2,6-Zr-AQ-MOF and its ligand reveal a similar electrochemical  $pK_a$  value (7.56 and 7.35, respectively) for the transition between a two-electron, two-proton transfer (at  $pH < pK_a$ ) and a two-electron, one-proton transfer (at  $pH > pK_a$ ). In contrast, the position of the quinone moiety with respect to the zirconium node, the effect of hydrogen bonding, and the amount of defects in 1,4-Zr-AQ-MOF lead to the transition from a two-electron, three-proton transfer



to a two-electron, one-proton transfer. The pK<sub>a</sub> of this framework (5.18) is analogous to one of the three electrochemical  $pK_a$ values displayed by its ligand (3.91, 5.46, and 8.80), which also showed intramolecular hydrogen bonding. The ability of the MOFs to tailor discrete numbers of protons and electrons suggests their application as charge carriers in electronic devices.

## 1. INTRODUCTION

The application of metal-organic frameworks (MOFs) as active materials in electronic devices has been proposed as a suitable alternative to achieve efficient charge storage and energy conversion.<sup>1</sup> The characteristic synthetic tunability, high permanent porosity, and structural uniformity of MOFs position these materials as prospective candidates for assembling high surface electrodes containing well-organized redox moieties that are capable to store electricity.<sup>2</sup> In particular, the ability of MOFs to undergo electron transport has been achieved through three different synthetic approaches: (1) charge transfer through metal-ligand orbital overlap,<sup>3</sup> (2)  $\pi$ -stacking interactions between electroactive ligands within the framework,<sup>4</sup> and (3) redox hopping.<sup>5</sup> Nevertheless, the synthetic design of MOFs that exhibit proton-coupled electron transport (PCET) remains in its early stages. The two main necessities are the ability to facilitate high electron and proton conduction and a high water stability over a range of pH.

One way to address these requirements is to integrate ligands capable of undergoing PCET into isoreticular arrays of highly stable MOFs, such as the UiO series. These zirconium-based MOFs have demonstrated an exceptional stability in water and in acidic pH.<sup>6,7</sup> Similarly, quinone ligands are recognized as excellent PCET agents, since they play an important role in biochemical processes, including photosynthesis and oxidative phosphorylation.<sup>8</sup> The redox chemistry of quinones is strongly influenced by the pH of the media. Generally, at acidic pH, the quinone (Q) reduction is a single-step, two-electron, twoproton process that generates the respective hydroquinone  $(QH_2)$ .<sup>9</sup> At alkaline pH, the concentration of protons is too low to support PCET; therefore, the redox process is a two-electron transfer to form the dianion  $(Q^{2-})$ .<sup>9</sup> At neutral pH, the quinone can undergo either a two-electron, one-proton process resulting in the protonated dianion species (QH<sup>-</sup>), or alternatively it could lead to the formation of the dianion (Supporting Information, Scheme S2).<sup>9</sup> The electrochemical  $pK_a$  values of the different redox and protonation states of quinone species can be represented using a potential (E) versus pH plot (Pourbaix diagram).

Quinone-based ligands have served as an inspiration to the synthesis of covalent-organic frameworks (COFs)<sup>10,11</sup> and other MOFs that show potential applications in batteries and supercapacitors.<sup>12-14</sup> However, understanding the effect of local pH in the pore environment of these frameworks remains vague. A hitherto study of the reduction of MOF UMCM-1 containing a nanoconfined anthraquinone molecule (Alizarin red S) in its pores showed that a typical two-electron, twoproton process at acidic pH was experienced only in anthraquinone molecules located at the MOF surface.<sup>15,16</sup> In contrast, the deficiency of protons inside the MOF pores created a local alkaline environment during the two-electron reduction that led to the formation of the negatively charged

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dianion, which was ejected from the framework to stabilize internal charge.  $^{15,16}\,$ 

Furthermore, the protonation state of the zirconium nodes of UiO-MOFs is also directly influenced by the local pH.<sup>17</sup> As a result, assembling these frameworks with ligands that exhibit quinone moieties in the proximity of the zirconium cluster may result in the occurrence of other complex processes, such as hydrogen bonding or linker-to-node proton transfer. Additionally, the pore size and the amount of defects (missing ligands) in the framework may play an important role in the transport of protons within the MOF pores. To elucidate these factors, we sought to study the effect of applied potential and pH on the equilibrium between different quinone species in these materials, where the specific number of protons and electrons transferred can be accounted. Herein, we report the first example of Pourbaix diagrams for two different anthraquinonebased zirconium MOFs that exhibit diverse electrochemical response in aqueous electrolytes due to the positioning of the quinone moiety with respect to the zirconium node, the amount of defects, and the pore size. To the best of our knowledge, these types of studies have not been performed on redox-active frameworks to date. These results demonstrate the potential of MOFs to be employed as proton-electron carriers in energy transport systems.

#### 2. EXPERIMENTAL SECTION

Synthesis of 2,6-Dicarboxy-9,10-anthhraquinone (1). The synthesis of 1 was achieved in two steps by adapting previous procedures described in the literature (Scheme S1).<sup>18,19</sup> Benzoquinone (3.25 g, 30 mmol), isoprene (10.0 mL), and traces of hydroquinone (two spatula tips), were suspended in 20.0 mL of absolute ethanol. The mixture was placed in a 40.0 mL autoclave and heated at 130 °C for 6 h. Once the autoclave reached room temperature, the mixture was dissolved in a potassium hydroxide solution in ethanol (8.5 g of KOH in 200 mL of EtOH) in a round-bottom flask. The solution was stirred and heated for 8 h at 40 °C under air. Stirring was continued for 12 h at room temperature under air. The mixture was heated again at 50 °C for 2 h, allowed to reach room temperature, and filtered in vacuum to give a white cream solid. The solid was placed in a vial containing absolute ethanol and left in the fridge overnight. Subsequently, the solid was filtered again, washed with cold ethanol and water, and dried under air. <sup>1</sup>H NMR confirmed the identity of the product as 2,6-dimethyl-9,10-anthraquinone.<sup>18</sup> A solution of 2,6dimethyl-9,10-anthraquinone (1.0 g) in 12.0 mL of 25% nitric acid was placed in a 40.0 mL autoclave and heated at 220 °C for 3 h. After it cooled to room temperature, the yellow precipitate was filtered under vacuum and washed with water. The solid was dried overnight, affording pure 1 with 69% yield.<sup>19</sup> <sup>1</sup>H NMR (400 MHz, dimethyl sulfoxide (DMSO)): δ 13.77 (s, 2H), 8.69(dd, J = 1.8 Hz, 0.4 Hz, 2H), 8.44(dd, J = 8 Hz, 1.8 Hz, 2H), 8.36(d,d J = 8 Hz, 0.4 Hz, 2H). Highresolution mass spectrometry (HRMS): (M+H)<sup>+</sup>: 297.0375.

Synthesis of 1,4-Dicarboxy-9,10-anthhraquinone (2). The synthesis of 2 was achieved in two steps by adapting previous procedures described in the literature (Scheme S1).<sup>19,20</sup> First, a solution of 1,4-naphthoquinone (9.35 g, 0.059 mol) and 2,4-hexadiene (5.0 g, 0.605 mol) in toluene (35 mL) was heated at 65 °C for 4 d. Subsequently, the solvent was evaporated, and the remaining oily solid was used in the next step without further purification. The oily solid (15.0 g) was disolved in 250 mL of absolute ethanol and added to a solution of KOH (30 g) in ethanol (1.25 L), while cooled at 10 °C. Then a current of oxygen was bubbled through the solution for 1 h, while the temperature was maintained at 10 °C. After the solvent was evaporated, the semisolid residue was treated with water (600 mL) and extracted with benzene. Removal of the aromatic solvent afforded 1,4dimethyl-9,10-anthraquinone with 70% yield.<sup>20</sup> A solution of 1,4dimethyl-9,10-anthraquinone (1.0 g) in 12.0 mL of 25% nitric acid was placed in a 40.0 mL autoclave and heated at 220 °C for 3 h. After it cooled to room temperature, the yellow precipitate was filtered under vacuum and washed with water. The solid was dried overnight, affording pure **2** with 69% yield.<sup>19</sup> <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  13.37 (s, 2H), 8.19 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H), 7.99 (dd, *J* = 5.6 Hz, 3.2 Hz, 2H), 7.89 (s, 2H). HRMS: (M+H)<sup>+</sup>: 297.0376.

Synthesis of 2,6-Zr-AQ MOF  $[Zr_6O_4(OH)_4(C_{16}O_6H_6)_6-(C_3H_7NO)_{17}(H_2O)_{22}]$ . The synthesis was performed using a similar procedure previously reported in the literature.<sup>21</sup> ZrCl<sub>4</sub> (23.0 mg, 0.1 mmol) was disolved in 2.0 mL of dimethylformamide (DMF) and sonicated for 5 min. Then, the ligand 2,6-dicarboxy-9,10-anthraquinone 1 (29.6 mg, 0.1 mmol) was added to the solution, as well as 47 equiv (0.3 mL) of acetic acid as a modulator. The mixture was sonicated for 15 min before being set at 120 °C for 24 h. The 2,6-Zr-AQ-MOF was obtained as a pink powder and isolated by centrifugation. The pink solid was washed and centrifuged three times with fresh DMF and dried under vacuum at room temperature (yield 31.3 mg, 75%).

Synthesis of 1,4-Zr-AQ-MOF  $[Zr_6O_4(OH)_4(C_{16}O_6H_6)_4-(C_2O_2H_3)_{2.76}(CO_2H)_{1.24}(C_3H_7NO)_{11}(H_2O)_{40}]$ . A mixture of ZrCl<sub>4</sub> (23.0 mg, 0.1 mmol), the ligand 1,4-dicarboxy-9,10-anthraquinone 2 (29.6 mg, 0.1 mmol), acetic acid (1.2 mL, 200 equiv), and DMF (3.0 mL) was sonicated for 15 min. The mixture was heated at 120 °C for 48 h. After it cooled at a rate of 1 °C/min, the 1,4-Zr-AQ-MOF was obtained as a pink powder, which was isolated by centrifugation. The pink solid was washed and centrifuged three times with fresh DMF and dried under vacuum at room temperature (yield 30.0 mg, 72%).

#### 3. RESULTS AND DISCUSSION

The ligands 2,6-dicarboxy-9,10-anthraquinone (1) and 1,4dicarboxy-9,10-anthraquinone (2) were synthesized in two steps by means of a Diels–Alder reaction followed by oxidation, according to Scheme S1.<sup>18–20</sup> The powdered samples of  $Zr_6O_4(OH)_4(C_{16}O_6H_6)_6(C_3H_7NO)_{17}(H_2O)_{22}$ [2, 6 - Z r - A Q - M O F] a n d Z r <sub>6</sub> O <sub>4</sub> (O H) <sub>4</sub> - $(C_{16}O_6H_6)_4(C_2O_2H_3)_{2.76}(CO_2H)_{1.24}(C_3H_7NO)_{11}(H_2O)_{40}$ [1,4-Zr-AQ-MOF] were obtained by the solvothermal synthesis of ZrCl<sub>4</sub> and either 1 or 2 in DMF, using acetic acid as a modulator (Figure 1). Specifically, the addition of 1 and 47 equivalents of acetic acid to a solution of ZrCl<sub>4</sub> in DMF, followed by heating at 120 °C for 1 d, afforded 2,6-Zr-AQ-MOF as a pink powder.<sup>21</sup> Similarly, the treatment of 2 and ZrCl<sub>4</sub> in a mixture of acetic acid and DMF (1:2.5 by volume) at 120 °C for 2 d, gave 1,4-Zr-AQ-MOF as a pink powder.



Figure 1. Synthesis of 2,6-Zr-AQ-MOF and 1,4-Zr-AQ-MOF.

Powder X-ray diffraction (PXRD) patterns of 2,6-Zr-AQ-MOF and 1,4-Zr-AQ-MOF reveal that both MOFs are isostructural with the UiO series (Figure 2). Le Bail refinement



Figure 2. PXRD patterns of (A) 2,6-Zr-AQ-MOF and (B) 1,4-Zr-AQ-MOF. (insets) The corresponding  $N_2$  adsorption isotherms.

of the powder patterns using crystallographic data for UiO-67 and UiO-66 as starting models, respectively, revealed a lattice parameter of a = 27.0472 Å for 2,6-Zr-AQ-MOF and a =20.6825 Å for 1,4-Zr-AQ-MOF (Figures S9 and S10), which is consistent with the length of each ligand. On the one hand, scanning electron microscopy (SEM) images of 2,6-Zr-AQ-MOF show that it consists of octahedral-shaped crystallites, characteristic of UiO-type frameworks. The 1,4-Zr-AQ-MOF, on the other hand, exhibited a more inconsistent morphology (Figures S11 and S12), presumably due to incorporated defects (vide infra). The N<sub>2</sub> adsorption isotherms of both MOFs are shown in Figure 2. A Brunauer–Emmett–Teller (BET) surface area of 175.6 m<sup>2</sup> g<sup>-1</sup> was found for 2,6-Zr-AQ-MOF, while the 1,4-Zr-AQ-MOF exhibited a surface area of 554.16 m<sup>2</sup> g<sup>-1</sup>.

The redox behavior of the ligands in aqueous phosphate buffer was studied by cyclic voltammetry (CV), using a glassy carbon (GC) working electrode. Reduction potentials were recorded at different pH, to construct the Pourbaix diagrams. Both ligands show a single-step, reversible CV wave, which shifted to more negative reduction potentials with increasing pH (Figure 3A,B).



Figure 3. Cyclic voltammograms (10 mV s<sup>-1</sup>) of (A) ligand 1, 0.1 M phosphate buffer–DMF (9:1 volume) as supporting electrolyte, and (B) ligand 2, 0.1 M phosphate buffer as supporting electrolyte. Pourbaix diagrams of (C) ligand 1 and (D) ligand 2.

This linear dependence of the reduction potential with respect to pH is expected to follow the modified Nernst equation:

$$E = E^{\circ} - \frac{0.059\,16}{n} \log \frac{1}{[H^+]^m} \tag{1}$$

where m is the number of protons, and n is the number of electrons involved in the process. Therefore, the derivative of this relationship can be expressed as

$$\frac{\partial E}{\partial pH} = 0.059 \, 16 \frac{m}{n} \tag{2}$$

and represents the slope of the linear regression between *E* and pH in the different segments of the Pourbaix diagrams (Figure 3C,D). As a result, this expression allows the elucidation of the number of protons and electrons transferred during the reduction. For instance, two different electrochemical processes are apparent in the Pourbaix diagram of ligand 1 (Figure 3C). An experimentally determined relationship of dE/d(pH) of  $-53 \pm 6$  between pH 1.33 and 7.35 suggests a two-electron, two-proton transfer to the quinone moiety of the ligand to form

the respective hydroquinone. In addition, from pH 7.35 to 11.38, a slope (dE/d(pH)) of  $-26 \pm 6$  evidenced a twoelectron, one-proton transfer from the quinone to the correspondent protonated dianion. The appearance of these two processes in ligand 1 is typical of many anthraquinone systems in aqueous buffer and has been extensively discussed in the literature.<sup>8,9,22,23</sup>

The boundary between the two types of electrochemical processes defines the electrochemical  $pK_a$  of 1 (7.35). In addition, the two chemical  $pK_a$  values for the carboxylic acids of 1 were determined via the titration with NaOH (Figure S7). These  $pK_a$  values ( $pK_{a1} = 4.2$  and  $pK_{a2} = 6.1$ ) are also represented in the Pourbaix Diagram of 1 as vertical lines (Figure 3C). Similarly, the titration of 2 (Figure S8) allowed the determination of  $pK_{a1} = 3.7$  and  $pK_{a2} = 5.6$  for the two carboxylic acid in 2 (Figure 3D).

Interestingly, ligand 2 was found to undergo four different PCET processes (Figure 3D). Similar to ligand 1, a twoelectron, one-proton transfer from the quinone to the corresponding protonated dianion was observed from pH 5.46 to 8.80, as evidenced by a slope of  $-27 \pm 2$ . In addition, for pH between 3.91 and 5.46, the slope was found to be  $-66 \pm 16$ , suggesting a two-electron and two-proton transfer process of the quinone moiety of 2 to form the hydroquinone.

However, two other processes were evidenced at the highest and lowest pH ranges tested in this study: at high pH (from pH 8.80 to 12.22) a four-electron one-proton transfer, represented by a slope of  $-13 \pm 3$ , involved the reaction of two ligand molecules to produce both the dianion and protonated dianion.<sup>24–26</sup> The formation of equal amounts of these species of 2 at alkaline pH, which was not observed in 1, may be a result of the difficulty to protonate this moiety due to the proximity of the carboxylic acid.

Moreover, at pH below 3.91, a slope of  $-105 \pm 7$  involving a transfer of either two electrons and three protons or two electrons and four protons characterized the last process. Since the carboxylic acid groups of 2 are fully protonated at pH < 3.7, a maximum of two protons can be transferred to the quinone to form the hydroquinone. The apparition of a third or fourth proton during the reduction can be explained based on the proximity of the carboxylic acids to the quinone moiety in 2. First, it is expected that the  $pK_a$  of the carboxylic acids of 2 in the hydroquinone state is much lower (~2) compared to the quinone state.  $^{27,28}$  As a result, the observed transfer of two electrons and three/four protons could be attributed to a simultaneous protonation of the carboxylic acid of the reduced hydroquinone moiety that is stabilized through hydrogen bonding. Figure 3D shows the proposed seven-membered ring structure formed during the two-electron, three-proton transfer. Predominantly, hydroquinones have been found to form both intermolecular<sup>29,30</sup> and intramolecular hydrogen bonding with other -OH functionalities.<sup>31</sup> In fact, the existence of hydrogen bonding between hydroquinone moieties and carboxylic acids is well-documented.<sup>31,32</sup> Consequently, the proximity of the carboxylic acids to the hydroxyl group in the hydroquinone species could also lead to intramolecular stabilization due to hydrogen bonding. To test this claim, the Pourbaix diagram of a similar derivative, 1,4-dimethyl-9,10-anthraquinone, was obtained under identical conditions (Figure S18). In this analogue, the carboxylic acid groups are replaced with methyl groups. A slope of  $-52 \pm 2$  was determined for pH between 1.69 and 6.15 indicating that this analogue undergoes a twoelectron, two-proton transfer. This finding supports the earlier

explanation for the transfer of additional protons during the reduction of **2** at pH < 3.91 with the third/fourth proton originating from the protonation of the carboxylate in the hydroquinone form of **2** and stabilized through intramolecular hydrogen bonding. This stabilization is less likely in **1**, since carboxylic acid and hydroxyl functionalities are further apart.

CV of the anthraquinone frameworks was performed on the dried slurry of the MOF powder (10 mg), graphite (10 mg), poly(methyl methacrylate) (3.34 mg), and tetrahydrofuran (THF; 1 mL) deposited on a GC electrode. Subsequently, this working electrode was used in a three-electrode assembly, with a 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES)-buffered aqueous solution as supporting electrolyte (see Supporting Information for detailed procedure). UV-vis spectroscopy was used to monitor the stability of the frameworks, evidenced as the absence of ligand absorption in solution before and after the CV measurements over the range of pH (Figures S20-S22). The 2,6-Zr-AQ-MOF showed stability from pH 1.74 to 9.67, while the 1,4-Zr-AQ-MOF was stable from pH 1.66 to 6.75. Both MOFs showed a reversible redox process that shifted to more negative potential with increasing pH (Figure 4A,B).

The behavior of 2,6-Zr-AQ-MOF was very similar to that observed for its free ligand in solution. The Pourbaix diagram of this MOF showed two electrochemical processes, defined by an electrochemical p $K_a$  of 7.56 (Figure 4C). For pH < 7.56, a slope of  $-63 \pm 4$  was observed indicating the two-electron, twoproton transfer to the quinone resulting in the hydroquinone state of the ligand inside 2,6-Zr-AQ-MOF. Furthermore, for pH > 7.56 either a two-electron, one-proton transfer or a twoelectron, two-proton transfer took place, as evidenced by a slope of  $-39 \pm 3$ . For clarity, only the two-electron, one-proton transfer is shown in the corresponding segment of the Pourbaix Diagram in Figure 4C. The similarity in the electrochemical  $pK_a$ of 2,6-Zr-AQ-MOF (7.56) and its ligand in solution (7.35) reveals that the pore dimensions of this framework allow a sufficient transport of protons inside the MOF pores. Consequently, the pH in the pores is the same as in the bulk solution, and only the pH tailors the number of protons transferred to the quinone moiety during the reduction. This fact corroborates the benefits of introducing anthraquinone moieties as ligands instead of encapsulating them in the MOF pores as nanoconfined molecules.<sup>15,16</sup>

Unlike its ligand, 1,4-Zr-AQ-MOF revealed only two electrochemical processes (Figure 4D). For pH > 5.18, the formation of the protonated dianion through a two-electron, one-proton transfer was characterized by a slope of  $-29 \pm 8$ . This behavior is comparable to the one of its ligand in solution at pH between 5.46 and 8.80 (Figure 3D) and to the 2,6-Zr-AQ-MOF (Figure 4C). This observation suggests that 1,4-Zr-AQ-MOF also allows the efficient penetration of protons into the MOF structure and demonstrates the consistency between the pore environment with respect to the bulk.

The Pourbaix diagram of 1,4-Zr-AQ-MOF also showed a slope of  $-96 \pm 5$  for pH < 5.18, representing a two-electron, three-proton transfer, similar to the one observed for 2 at pH < 3.91 (Figure 3D). Since the ligand of 1,4-Zr-AQ-MOF can only accept maximum of two protons without breaking the metal-carboxylate bonds, this behavior could be explained based on the level of defects in the MOF. Particularly, the UiO frameworks exhibit two different types of defects. On one hand, "missing linker defects" refer to the absence of ligands coordinated to the Zr-oxide cluster, which is commonly



Figure 4. Cyclic voltammograms (100 mV s<sup>-1</sup>, 0.1 M HEPES buffer as supporting electrolyte) of (A) 2,6-Zr-AQ-MOF and (B) 1,4-Zr-AQ-MOF. Pourbaix diagrams of (C) 2,6-Zr-AQ-MOF and (D) 1,4-Zr-AQ-MOF.

compensated by modulator molecules connected to the node.<sup>33</sup> On the other hand, the recently discovered "missing cluster defects" correspond to the absence of  $Zr_6(\mu_3-O)_4(\mu_3-OH)_4$ node, as well as the 12 ligands connected to it, in correlated nanoregions of the **reo** topology.<sup>34,35</sup> We sought to calculate the defects in 1,4-Zr-AQ-MOF using quantitative NMR analysis (Figure S23), finding a total modulator-to-linker molar ratio of 0.96, suggesting an equivalent amount of linker and modulator in the framework, presumably due to the high concentration of acetic acid utilized during the synthesis (Figure 1). Elemental analysis on the framework (Table S1) also supported these findings. This framework is an analogue of the UiO-66 MOF, which has been typically recognized to have a high amount of defects, 33,35,36 and the shape of the anthraquinone ligand suggests steric hindrance during its formation (Figure 1). More importantly, the PXRD pattern of 1,4-Zr-AQ-MOF (Figure 2B) displays a broad peak at  $2\theta$  range of ca.  $3-6^\circ$ , which has been recently assigned as a fingerprint of missing node defects in UiO frameworks, where one-quarter of the MOF clusters are missing.<sup>34</sup> The high defectivity of 1,4-Zr-AQ-MOF can explain

the observed two-electron, three-proton transfer shown in Figure 4D, when considering two different possibilities.

The existence of ligands connected only to one node could lead to intramolecular hydrogen bonding between the free carboxylic acid and the reduced hydroquinone moiety, in a similar fashion to its ligand in solution (Figure 3D). Alternatively, the proximity of the quinone moiety to the zirconium node (2.6-2.8 Å) inside the framework could also lead to hydrogen bonding between the hydroquinone and the protons present on the inorganic cluster, as represented in Figure 4D for pH < 5.18. Two of the three types of protons present in the zirconium node are recognized as -OH and  $-OH_2$  groups that occupy the place of missing linkers.<sup>17</sup> The acidity of these protons in UiO-66 has been recently studied, finding  $pK_a$  values of 8.30 and 6.79, respectively.<sup>17</sup> This fact suggests that at pH < 5.18 the highly defected node of 1,4-Zr-AQ-MOF is most likely protonated, facilitating hydrogen bonding between the hydroquinone and the protons in the node (Figure 4D). A related cooperative behavior between linker and node was postulated for the electrocatalytic water oxidation in PCN-224, where the node acts as a proton acceptor.<sup>37</sup> These processes are not observed in the Pourbaix diagram of 2,6-Zr-AQ-MOF, because the quinone moiety is relatively distant (5.0-5.2 Å) from the zirconium node (Figure 1).

### 4. CONCLUSION

In summary, we have shown that PCET can be modulated in anthraquinone-based Zr MOFs as a function of the pH. The positioning of the quinone moiety with respect to the zirconium node, the amount of defects, and the pore size of these materials are directly influencing the amount of protons transported to the frameworks. These results demonstrate that MOFs have potential as proton—electron carriers for electronic applications and encourage further research in this area.

### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01656.

Detailed experimental procedures, NMR, HR-MS spectra, IR spectra, titration curves of ligands, SEM images, PXRD refinement, elemental analysis, TGA traces, and CV and UV-vis spectra for determination of MOF stability (PDF)

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#### Notes

The authors declare no competing financial interest.

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