

# Synthesis of Phosphonic Acid Ligands for Nanocrystal Surface **Functionalization and Solution Processed Memristors**

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Supporting Information

ABSTRACT: Here, we synthesized 2-ethylhexyl, 2-hexyldecyl, 2-[2-(2-methoxyethoxy]ethyl, oleyl, and *n*-octadecyl phosphonic acid and used them to functionalize CdSe and HfO<sub>2</sub> nanocrystals. In contrast to branched carboxylic acids, postsynthetic surface functionalization of CdSe and HfO2 nanocrystals was readily achieved with branched phosphonic acids. Phosphonic acid capped HfO<sub>2</sub> nanocrystals were subsequently evaluated as memristors using conductive atomic force microscopy. We found that 2-ethylhexyl phosphonic acid is a superior ligand, combining a high colloidal stability with a compact ligand shell that results in a record-low



operating voltage that is promising for application in flexible electronics.

## INTRODUCTION

Surface engineering of colloidal nanocrystals (NCs) is a prerequisite for advanced applications such as solar cells,<sup>1,2</sup> thermoelectrics,<sup>3</sup> field effect transistors,<sup>4</sup> smart windows,<sup>5</sup> superconductors,<sup>6,7</sup> catalysis,<sup>8</sup> and memristors.<sup>9</sup> In particular, threshold memristors garner intense research interest because they emulate synaptic responses in neuromorphic computing.<sup>10</sup> They also exhibit faster switching speeds, lower power consumption, higher scalability, and greater 3D stackability than standard complementary metal oxide semiconductor (CMOS) circuits, thus promoting further miniaturizing beyond Moore's law.<sup>11,12</sup> In such threshold switching, a bias is applied, resulting in current flow and a significant amount of internal Joule heating. Once above the metal-insulator transition,<sup>13</sup> the device is activated and maintains a low resistance state (LRS) until the voltage is removed and the device resets to an insulating high resistance state (HRS). A memristor device comprises an insulating oxide layer sandwiched between two metal electrodes, typically fabricated by a vacuum deposition processes. However, these conventional approaches are limited due to expensive fabrication equipment and small deposition areas.<sup>14</sup> A facile and costeffective alternative is the solution deposition of monodisperse, highly crystalline inorganic NCs (e.g., SrTiO<sub>3</sub>, HfO<sub>2</sub>) into ribbons of nanocrystals via evaporative assembly using flow coating.<sup>9,15,16</sup> In addition, conductive atomic force microscopy (c-AFM) has the ability to locally interrogate electrical

properties across length scales (a few nanometers to 100  $\mu$ m) relevant to both individual NCs and the nanoribbon assemblies. Therefore, we used c-AFM analysis to show that operating parameters such as set/reset voltage and LRS/HRS ratios of the nanoribbons inversely scale with the length of the ligand used to stabilize the NCs in solution.<sup>9</sup> Therefore, short ligands are desired, but ligands shorter than dodecanoic acid result in unstable dispersions, thereby restraining the minimum set voltage that could be used to switch the ribbons of NCs.

With respect to ligands, the oleyl fragment is ubiquitous in the nanocrystal field; many syntheses utilize either oleylamine or oleic acid as the surfactant.<sup>17-20</sup> The unsaturation provides a high dispersibility in organic solvents and offers a distinct signal in liquid <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy. The latter is especially appealing for surface chemistry studies because liquids NMR spectroscopy is the method of choice for monitoring ligand binding and exchange on colloidal NCs.<sup>21,22</sup> Peng and coworkers recently showed that NCs with short, branched ligands are more dispersible than NCs with long, straight chain ligands.<sup>23</sup> They used 2ethylhexanethiol as a champion ligand to obtain high conductance in solution processed thin films of CdSe NCs. Thiols bind well to CdSe and metal NCs but are poor ligands

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for metal oxides. Whereas carboxylic acids have a reasonably high affinity for metal oxides,<sup>24,25</sup> exchange of native oleate ligands for 2-hexyldecanoic acid proved to be unfavorable because of the steric encumbrance of the branched aliphatic chain.<sup>26</sup> Interestingly, phosphonic acid ligands are known to quantitatively displace carboxylate ligands on CdSe,<sup>27,28</sup> PbSe,<sup>29</sup> and ZrO<sub>2</sub><sup>30</sup> NCs and also bind well to flat surfaces.<sup>25,31</sup> Saturated phosphonic acids are also used in the synthesis of wurtzite CdSe NCs.<sup>32–34</sup> However, postsynthetic functionalization of NCs still mostly focuses on carboxylic acid or thiol ligands, even though the latter typically quench the photoluminescence quantum yield.<sup>35,36</sup>

Here, we explored the functionalization of NCs with phosphonic acid derivatives 1-5 (Scheme 1) and their

Scheme 1. Target Phosphonic Acid Ligands Tailored towards Nanocrystal Surfaces



fabrication into memristor devices. We selected novel, branched phosphonic acids (1 and 2), a versatile polyethylene glycol<sup>34,37-40</sup> derivative (3), as yet unreported oleylphosphonic acid (4), and a prototypical straight chain derivative (5). The convenient synthesis of these phosphonic acids is followed by surface functionalization methods that are facile, even for the branched substrates. Finally, using these ligands, we deposit HfO<sub>2</sub> NCs into ribbons of NCs by a simple flow coating process and measure their local memristive current–voltage response with c-AFM.

## RESULTS AND DISCUSSION

Phosphonic acids are usually synthesized via the Michaelis-Arbuzov reaction (Scheme 2).<sup>41,42</sup> High temperatures (160





°C) are often required, and generally, only primary, sterically unencumbered halides react (thus not suitable for target compounds 1 and 2).<sup>43</sup> The scope is also limited by side reactions with an ethyl bromide coproduct that leads to ethyl phosphonate ester byproducts. Alternative Michaelis–Arbuzov conditions have been developed that address some of these issues but remain ineffective for sterically congested substrates<sup>44</sup> or are only suitable for benzylic substrates.<sup>45</sup> Faster reactions and lower temperatures are accessible using the Michaelis–Becker approach, wherein a dialkyl phosphite anion is prepared from  $CsCO_3^{46}$  or sodium hydride in THF<sup>47</sup> or Na in hexane<sup>48</sup> in place of the tri*n*-alkylphosphite as the nucleophile. Following this precedent, we prepared diethyl phosphonate esters from sodium diethylphosphite and the appropriate alkyl bromide in dimethylformamide solution (Scheme 3).<sup>49</sup> Reactions reached completion within a few

Scheme 3. Appel Reaction Converts Alcohols in Bromides,<sup>50,51</sup> Michaelis–Becker Reaction Converts Bromides to Phosphonate Esters, and Finally, Phosphonate Esters Are Hydrolyzed to Phosphonic Acids



hours at room temperature for linear alkyl bromides and at 70 °C for branched substrates. Only compound 3 could not be synthesized in high purity using the Michaelis–Becker reaction (neither in DMF, nor in THF) due to slow conversion and the formation of various uncharacterized byproducts. In this case, the Michaelis–Arbuzov method was used, and the ethyl phosphonate ester byproduct was removed from 3 by distillation.

Pure phosphonate ester derivatives 1-4 are isolated in greater than 70% yield by distillation and provided pure samples of phosphonic acid upon treatment with bromotrimethylsilane and methanol (Scheme 3).<sup>52</sup> 5 was purified by recrystallization as the phosphonic acid. Via single crystal diffraction, it was found that 5 crystallizes in the monoclinic crystal structure and forms a stacked arrangement (Figure 1A). The acidic hydrogens form a hydrogen bond to the oxygen lone pairs of the P=O bond with the hydrogen bonds being inequivalent, measuring 1.84(4) and 1.79(5) Å, (Figure 1B). Compound 4 is a waxy solid and can in principle also be recrystallized from hexane, but the yield is low (20%), and this increases the relative amount of *trans*-2 compared to *cis*-2.

Next, we demonstrate the versatility of our compounds with respect to nanocrystal surfaces. As a model system, cadmium oleate capped CdSe NCs (d = 3.3 nm, Figure S1) were synthesized according to Cao et al.<sup>53</sup> and purified by precipitation with methyl acetate (see Supporting Information for experimental details). Figure 2A shows the characteristically broadened NMR resonances of bound oleate ligands in CDCl<sub>3</sub>. Although oleate ligands can be quantitatively replaced with linear phosphonic acids,<sup>27,28</sup> the question remains whether branched phosphonic acids react identically. To investigate this, we added 1.2 equiv of 1 to the CdSe NCs in CDCl<sub>3</sub>. Consequently, the alkene resonance narrows, and its multi-



**Figure 1.** Crystal structure of **5**. (A) View along the [010] direction; hydrogens are omitted for clarity. The aliphatic chains angle toward the reader at an angle of  $45^{\circ}$ . The chain packing density is  $3.3 \text{ nm}^{-2}$ . (B) View along the [001] direction; hydrogen bonds are displayed. Only the first carbon of the chain is depicted for clarity.



**Figure 2.** (A) <sup>1</sup>H NMR spectrum of oleate capped CdSe nanocrystals in CDCl<sub>3</sub> ([NC] = 261  $\mu$ M, [oleate] = 39 mM). The ligand density is 4.4 ± 0.5 nm<sup>-2</sup>. The inset shows the alkene resonance after addition of 1.2 equiv of 1. (B) <sup>1</sup>H NMR spectrum of CdSe nanocrystals in CDCl<sub>3</sub>, after ligand exchange for 1 and purification. ([NC] = 124  $\mu$ M, [phosphonate] = 20 mM). The ligand density is 4.7 ± 0.5 nm<sup>-2</sup>. The inset shows the <sup>31</sup>P NMR spectrum.

plicity, typical for free, unbound ligands, appears (Figure 2A, inset). After purification (see Supporting Information), the <sup>1</sup>H NMR spectrum features only the broadened resonances of 1, and no trace of oleate is detected (Figure 2B), indicating a successful exchange of oleate for 1. To further confirm the successful purification, we performed pulsed field gradient experiments. The resulting diffusion decay is fitted with a

single exponential (Figure  $S_2$ ), indicating that 1 is mostly bound to the nanocrystal, and the amount of free ligand, if any, is small (<5%). The diffusion coefficient of bound 1 is 133  $\mu$ m<sup>2</sup>/s, much smaller that the diffusion coefficient of free 1, 550  $\mu$ m<sup>2</sup>/s. The bound nature of **1** is further corroborated by a broad <sup>31</sup>P NMR resonance at 33 ppm (fwhm = 2000 Hz, Figure 2B, inset). This compares to a line width of only 65 Hz for free phosphonic acid. Following the exchange, the aerial density of surface ligands<sup>54</sup> was unchanged (4.4  $\pm$  0.5 oleates per nm<sup>2</sup> and 4.7  $\pm$  0.5 phosphonates per nm<sup>2</sup>). We conclude that a complete one-for-one exchange of oleate for the branched ligand 1 is achieved, and they exist as monohydrogenphosphonate ligands when bound to the surface, in line with earlier reports.<sup>27</sup> The complete exchange with 1 is interesting in light of the poor exchange reactivity of 2hexyldecanoic acid<sup>26</sup> and suggests that the higher binding affinity of the phosphonate headgroup for the surface overcomes any steric issue associated with the branched chain (note: the branch point is  $\beta$  to the phosphonate center, while it at the  $\alpha$ -position in 2-hexyldecanoate).

Using the same exchange strategy, CdSe nanocrystals are readily functionalized with ligands 2-5 in chloroform solution. Nanocrystals bound by 1, 2, 4, and 5 are dispersible in chloroform, toluene, and hexane. As expected, ligand 3 is more versatile and stabilizes NCs in a variety of solvents, including methanol, ethanol, acetone, chloroform, and toluene; however, hexane precipitates NCs functionalized with 3 from those solvents.

We utilize ligands 1-5 to prepare memristors based on hafnium oxide NCs. HfO<sub>2</sub> NCs (d = 3.75 nm) are synthesized in benzyl alcohol from hafnium(IV) *tert*-butoxide.<sup>55</sup> Assynthesized NCs are not stabilized by ligands and simply washed with diethyl ether to remove organics. Subsequently, the NCs are functionalized by the addition of ligands 1-5 and purified (see Supporting Information for experimental details). Transmission electron microscopy (TEM) images of these nanoparticles reveal an interparticle distance that varies from 1.6 nm for 1 to 2.4 nm for 5 (Figures 3A and B). The NCs with ligands 1, 2, 4, and 5 are well-purified by precipitation with methanol, as attested by solution  ${}^{1}H$  NMR (Figure 3C) and <sup>31</sup>P NMR (Figure 3D), so only a monolayer of ligands is attached to the NCs. HfO<sub>2</sub> NCs capped with 3 can only be precipitated using hexane; however, ligand 3 is also insoluble in hexane and is not readily separated from the HfO2 NCs (Figures 3C and D).

Thin films of hafnium oxide are typically used as a CMOScompatible high- $\kappa$  dielectric gate oxide<sup>56</sup> and in memristor applications.<sup>57</sup> HfO<sub>2</sub> NCs, when assembled into ribbons of nanoparticles, feature a low resistance state and a high resistance state, interesting for resistive random access memory (RRAM) applications.<sup>9,11,12</sup> Using a mixture of dodecanoic acid and 10-undecenoic acid as ligands adsorbed on the HfO<sub>2</sub> NCs, we previously achieved a minimal threshold switching set voltage of  $1.2 \pm 0.3 \text{ V.}^9$  In the same fashion, we assemble here the phosphonic acid capped HfO<sub>2</sub> NCs in ribbons of nanoparticles (Figures S3-S8, see Supporting Information for experimental details) and measured the switching properties in function of the ligands 1-5 (Figure 4). Use of a conductive scan probe as a top electrode enables measurements of nanoribbons in a geometry similar to the nanocrossbar memristor or atomic switch arrays used in thin filmbased devices,<sup>11,12</sup> where both the bias and current response occur across the nanostack dimension.



**Figure 3.** (A) TEM image of  $HfO_2$  NCs functionalized with 1. (B) TEM image of  $HfO_2$  NCs functionalized with 5. (C) Solution <sup>1</sup>H NMR and (D) solution <sup>31</sup>P NMR spectra of  $HfO_2$  NCs functionalized with 1–5 in CDCl<sub>3</sub>. The resonance with the asterisk is an unidentified impurity.

Conductive atomic force microscopy (c-AFM) was used in point spectroscopic mode to collect 40 I-V curves over four separate, individual nanoribbons for each ligand type. We observed the expected trend where operating voltage scales with ligand size. Here, the set voltage varies from extremely high  $(4.4 \pm 0.7 \text{ V})$  for ligands 4 and 5 to a record low  $(1.0 \pm$ 0.3 V) for ligand 1. Also, bipolar switching is observed for  $HfO_2$  nanocrystal assemblies with ligand 1 (Figure S9). Note that ligand 3 violates the trend and displays higher set voltages than expected for its ligand length. This may be caused by the presence of the free ligand (which proved difficult to remove from the nanocrystals as described above) or by the nature of the polyethylene glycol chain. Note that the triangular crosssection of the nanoribbons (Figures S3-S8) creates a thickness-dependence in the memristive response. The thickest portion of the nanoribbons is difficult to electroform using the  $\pm 10$  V bias supply of the microscope, and therefore, we performed all conductive probe measurements in thinner areas of equivalent thickness (~80 nm, circle marker Figure S10) for each nanoribbon tested. We anticipate that ribbons a few NCs in height will exhibit optimal switching character.

Because it is desirable to minimize the set voltage for future memory applications, the shortest possible ligand should be used, which is 1 in this case of  $3.75 \text{ nm HfO}_2 \text{ NCs}$ . However, larger HfO<sub>2</sub> NCs such as the 5 nm NCs synthesized from HfCl<sub>4</sub> and benzyl alcohol<sup>24</sup> cannot be stabilized by 1, and the NCs precipitate after functionalization and purification. This is rationalized by the van der Waals attraction between the cores (Figure S11). In this case, colloidal stability is provided by 2, which it is still considerably shorter than the standard ligands (such as oleic acid) that are typically used. Together, these results place the branched ligands 1 and 2 squarely in the focus of electronic applications where solution processing is combined with interparticle charge transfer after assembly.

## CONCLUSION

We developed a scalable synthesis of new phosphonic acid surfactant ligands. We subsequently showed their superiority in functionalizing nanocrystal surfaces. Whereas exchange for branched carboxylic acids is disfavored by the branching, the



**Figure 4.** (A-E) *I–V* curve of the threshold switching of HfO<sub>2</sub> nanoribbons using **1–5**, respectively, as ligand. (F) Switching voltage in function of the ligand chain length.

branched phosphonic acids readily undergo displacement of the parent carboxylate ligands. Finally, 2-ethylhexyl phosphonic acid leads to a record-low operating voltage in the resistive switching of  $HfO_2$  NC assemblies. Considering their high binding affinity, we expect the synthesized ligands to be heavily used to functionalize surfaces, even beyond the nanocrystal field.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.8b03768.

Crystallographic information for octadecylphosphonic acid (CIF)

UV-vis spectrum of CdSe nanocrystals, DOSY decay fittings, additional NMR spectra, AFM images of nanoribbons, and switching results and calculations of the interaction potential (PDF)

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#### Notes

The authors declare no competing financial interest.

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