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# Molecular surface functionalization of carbon materials via radicalinduced grafting of terminal alkenes

Yongqian Zhang<sup>†</sup>, Ali A. Tamijani<sup>‡</sup>, Megan E. Taylor<sup>†§</sup>, Bo Zhi<sup>⊥</sup>, Christy L. Haynes<sup>⊥</sup>, Sara E. Mason<sup>‡</sup>, Robert J. Hamers<sup>†</sup>

<sup>†</sup>Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, USA <sup>‡</sup>Department of Chemistry, University of Iowa, Iowa City, IA 52242, USA

 $^{\perp}$ Department of Chemistry, University of Minnesota Twin Cities, 207 Pleasant St SE, Minneapolis 55455, USA

Supporting Information Placeholder

**ABSTRACT** Formation of functional monolavers on surfaces of carbon materials is inherently difficult because of the high bond strength of carbon and because common pathways such as S<sub>N</sub>2 mechanisms cannot take place at surfaces of solid materials. Here we show that the radical initiators can selectively abstract H atoms from H-terminated carbon surfaces, initiating regioselective grafting of terminal alkenes to surfaces of diamond, glassy carbon, and polymeric carbon dots. Nuclear magnetic resonance (NMR) and X-ray photoelectron spectroscopy (XPS) demonstrate formation of self-terminating organic monolayers linked via the terminal C atom of 1-alkenes. Density functional theory (DFT) calculations suggest that this selectivity is at least partially thermodynamic in origin, as significantly less energy is needed to abstract H atoms from carbon surfaces compared with typical aliphatic compounds. The regioselectivity favoring binding to the terminal C atom of the reactant alkenes arises from steric hindrance encountered in bond formation at the adjacent carbon atom. Our results demonstrate that carbon surface radical chemistry yields a versatile, selective, and scalable approach to monolayer formation on H-terminated carbon surfaces and provide mechanistic insights into the surface selectivity and regioselectivity of molecular grafting.

#### INTRODUCTION

Carbon-based materials such as diamond, glassy carbon, and polymeric carbon materials are of great interest because the extraordinary chemical, thermal, and electrochemical stability of carbon enables a wide range of applications including as selective electrodes,<sup>1-3</sup> as platforms for biosensing,<sup>4-5</sup> and as robust optical probes,<sup>6-7</sup> Carbon dots made by pyrolysis of polymers have recently attracted attention as optical probes with tunable emission,<sup>4-5,8</sup> while diamond in both planar and nanoparticle form has enjoyed intense interest as a platform for quantum-based sensing and quantum computation.<sup>9-13</sup> In these and other application, functionalization of carbon surfaces with molecules species plays a key role by controlling chemical and physical properties such as catalytic activity, charge state, and biocompatibility.

While prior studies have shown that functionalization of carbon surfaces using "all-carbon" scaffolds (e.g., with direct C-C bond formation at the interface) yields functional monolayers with outstanding chemical stability,<sup>4,14-26</sup> few methods are available to produce such interfaces. All-carbon interface scaffolds can be achieved by stimulating reaction of H-terminated carbon surfaces with organic alkenes using ultraviolet (UV) light,<sup>4,14-15,19,27</sup> but ultraviolet light can also induce unwanted photochemistry and is not easily scalable to nanoparticles or powders. Selective reduction of aryldiazonium salts has been used to functionalize carbon surfaces,<sup>20-21,28-31</sup> but is restricted to a small number of diazonium precursors and is susceptible to multilayer formation.<sup>32-33</sup> A key challenge to forming all-carbon surface scaffolds is that many of the approaches to C-C bond formation used in organic chemistry<sup>34-37</sup> are not readily adapted to functionalization of solid surfaces due to steric effects that limit certain reaction mechanisms (e.g.,  $S_N 2$ reactions) or the use of bulky catalysts. Among methods that can be applied at surfaces, radical chemistry is particularly attractive because radical reactions frequently involve less complex intermediate structures<sup>38-39</sup> that are amenable to reaction at highly restricted geometries such as solid surfaces. The reaction of radicals with alkenes has been used in synthetic organic chemistry<sup>40</sup> but the

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controlled formation of radicals at carbon surfaces and the subsequent reaction of carbon surface radicals with akenes to achieve controlled surface functionalization have not been previously demonstrated.

Here, we present a combined experimental and computational study demonstrating that surface functionalization of model carbon materials can be achieved using radical initiators to abstract surface H atoms, with the resulting surface carbon radicals binding selectively to the terminal C atom of 1-alkenes in an anti-Markovnikov geometry.<sup>41</sup> We demonstrate breadth of applicability using H-terminated surfaces of diamond, glassy carbon, and polymeric carbon dots as model carbon materials and by demonstrating functionalization of H-terminated diamond with alkenes bearing anionic, neutral, and cationic functional groups. Nuclear Magnetic Resonance (NMR) and X-ray Photoelectron Spectroscopy (XPS) measurements show that abstraction of H atoms from H-terminated carbon surfaces leads to selective grafting of terminal alkenes with little or no polymerization of the reactant molecules. Density functional theoretical (DFT) calculations show that this selectivity arises because it is more energetically favorable to abstract H atoms from H-terminated carbon surfaces compared to abstraction from reactant molecules in the adjacent liquid phase. NMR and DFT calculations further show that the alkenes link to the diamond surface regioselectively at the anti-Markovnikov terminal С atom, in an configuration, due to severe hindrance that would result from lining at the second C atom. A similar trend has been noted in organic reactions of radicals with terminal alkenes, and similarly attributed primarily to steric effects.<sup>42</sup> Our results show that that surfaceselective H-atom abstraction offers a stable, scalable, selective, and flexible approach for functionalization of carbon-based materials with molecules via an allcarbon scaffold.

### EXPERIMENTAL SECTION

**Materials.** To demonstrate the versatility towards molecules with different functionalities, we used three representative molecules: 1H,1H,2H-perfluoro-1-octene (99%), allyl trimethylammonium bromide, and di(ethylene glycol) vinyl ether (98%). Allyl trimethylammonium bromide was synthesized and characterized following the procedure described in Supporting information (SI), S2. All reagents were purchased from Sigma-Aldrich, unless noted otherwise. Water purified using a Barnstead GenPure system (resistivity  $\geq$ 18 M $\Omega$  · cm) was used for all



Figure 1. Functionalization process of a) the alkene terminus molecules on 5 nm-core hydrogen-functionalized DNPs (H-DNPs) and b) 1H,1H,2H-perfluoro-1-octene on 5 nm-core DNPs (PFO-DNPs). Molecules and diamond nanoparticles are not drawn to scale.

experiments. Fig. 1 shows an overview of the process used for functionalization of carbon surfaces using detonation nanodiamond (DNPs) as an example.

H-termination of carbon surfaces. In this paper, we use four different carbon surfaces (detonation nanodiamond, boron-doped diamond electrode, vitreous carbon planchet, and citric acid-derived polymeric carbon dots) in combination with three different reactant molecules to demonstrate the generality of radical-facilitated coupling. We terminated the surface of each carbon material with H atoms using the best-known methods. While oxygenterminated diamond surfaces has been used as a starting point for surface functionalization,43-45 oxidation of diamond typically produces multiple types of oxidized species at the surface<sup>45</sup> and can increase the graphite content,<sup>43</sup> thus diminishing the diamond-specific properties for some applications. Therefore, we use hydrogenated surfaces as a foundation in our study to perform radical coupling. Detonation nanodiamond nanoparticles (DNPs, Nanostructured & Amorphous Material Inc.) were hydrogen-terminated by heating in a flow of pure H<sub>2</sub> gas (1 atm, 50 standard  $\text{cm}^3 \text{min}^{-1}$ ) at 600 °C for 6 h, following methods reported previously.<sup>46-47</sup> We chose low-temperature annealing because previous studies have shown that these conditions optimize removal of oxygenated surface groups without forming reactive sp<sup>2</sup> carbon.<sup>17,46</sup> The Supporting Information (SI) includes TEM micrographs of the DNPs with an

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average primary particle size of 5 nm; these show no evidence for graphitic shells (SI, S3). The hydrogenated DNPs (H-DNPs) were suspended in the desired anhydrous solvent under an argon atmosphere and disaggregated using a cup ultrasonicator (Cole Parmer Ultrasonic Processor) set at 40% amplitude power, using a repeated cycle of 50 sec on followed by 10 sec off, for 6 h with water cooling. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray photoelectron spectroscopy (XPS) were used to verify H-termination of DNPs (SI, S3).

Boron-doped polycrystalline diamond electrodes (Element Six.) and vitreous carbon planchets (Ted Pella Inc.) were first cleaned by soaking in aqueous piranha solution (A 3:1 v:v mixture of concentrated sulfuric acid and 30% hydrogen peroxide) overnight and then rinsed with water. SEM images of the diamond samples revealed large crystallites exposing large, flat (111) facets. The carbon surfaces were then hydrogen-terminated using a hydrogen plasma in a custom-built microwave plasma chamber. The conditions of the experiments were 600 W microwave power (450-500 °C, 48 torr) with 200 standard cubic centimeters per minute (sccm) H<sub>2</sub> flow for 1 h. Samples were stored in an argon glove box until use. 27

The citric acid-derived polymeric carbon dots (CAPCDs) were synthesized using a previously reported procedure in which citric acid is mixed with a polyamine and exposed to intense microwave excitation, leading to an extensive polymerization and the formation of small luminescent carbon nanoparticles.48-49 Full characterization data for our CAPCDS is contained in Ref. 42. The CAPCDs were used in their "as-synthesized condition due to the presence of accessible C-H bonds at their surfaces (vide infra).

Procedure for grafting alkene terminus molecules to carbon surfaces. Each H-terminated carbon material was functionalized by introducing the sample into a solution containing benzoyl peroxide (Luperox A98,  $\geq$  98%) as a radical initiator, the alkene-terminus molecule of interest, and an appropriate anhydrous solvent. The reactant solution and the sample were stirred and heated in an oil bath at 85 °C for 3.5 h under an argon atmosphere and then cooled to room temperature overnight. Different solvents were required for different reactant alkenes in order to fully solubilize the alkene. Details of the conditions used for the four different carbon materials and all the alkene terminus molecules are included in the Supporting Information, S5. After functionalization, all samples were purified to remove excess reactants. The diamond and vitreous carbon samples were purified with ultrasonic agitation in

reaction solvent for 15 mins (x2), and then repeated with water (x2). The samples were dried with nitrogen and stored in an Ar glove box. The powdered samples (DNPs and carbon dots) were purified using solvent with ultrasonic agitation (until resuspension) followed by centrifugation at 4480xg for 10-20 min. The supernatant (containing residual molecules and impurities) was discarded. The washing and centrifugation steps were then repeated with water (rinsing solvent may require modification, depending on the sample) a minimum of 3 times, and the resulting pellets of functionalized DNPs and CAPCDs were dried at room temperature in a vacuum oven and stored dry with desiccant.

XPS characterization of carbon surfaces. All functionalized samples were characterized by X-ray photoelectron spectroscopy using a Thermo Scientific K-alpha XPS system with a micro-focused monochromatic Al Ka X-ray source and 180° hemispherical electron energy analyzer with a 128channel detector. Analyzer pass energies were set at 50 eV for all samples. XPS data were analyzed using Casa XPS software<sup>50</sup> using a Shirley backgroundcorrection.<sup>51</sup>

For XPS measurements, samples of DNPs and CAPCDs were prepared by drop-casting 20  $\mu$ L of a dilute sample onto a B-doped, polished silicon wafer (resistivity:0.1-1 ohm·cm, Electro-Optic Materials). Surface coverage of atomic and/or molecular species was determined by measuring the XPS peak areas of surface species, and using the 284.8 eV C(1s) peak of bulk diamond as an internal standard. Using the bulk atomic density of diamond electron, electron mean free paths, and atomic sensitivity factors, this allows absolute coverages to be determined (see SI, S15 for quantification details).

NMR characterization diamond of nanoparticles. Diamond nanoparticles (DNPs) that were used as a model system were characterized using nuclear magnetic resonance (NMR). The concentrations of samples are at least 10 mg/mL. The sample core sizes were ~5-10 nm (SI, S3) for NMR measurement. Most NMR measurements were performed using a Bruker Avance-600 spectrometer with TCI-F cryoprobe. The recycling time (d1) was always 3-5 times longer than the longest  $T_1$  of each sample. Most spectra were obtained with at least 500 scans. Quantitative <sup>13</sup>C NMR spectra were obtained after 4000 scans using a Shigemi tube on a Bruker Avance-500 MHz spectrometer with DCH cryoprobe.

Thermogravimetric Analysis (TGA). Functionalized diamond nanoparticles were cleaned following the protocol described earlier. The pelleted nanodiamond was transferred to a titanium heating pan, which was placed into a TA Instruments Q500 thermogravimetric analysis instrument. The temperature was increased by 10 °C·min<sup>-1</sup> until it reached 600 °C.

Surface Area Measurements. The Brunauer-Emmett-Teller (BET) specific surface area of diamond nanoparticles functionalized was determined from  $N_2$ adsorption/desorption isotherms obtained using a Micromeritics Gemini VII surface area analyzer. 2390 The pelleted nanodiamond was outgassed at 180°C under vacuum for 1 h using a Micromeritics VacPrep 061 sample degas system. The sample was subsequently introduced into the surface area analyzer and measured over the relative pressure range  $(P/P_0)$  of 0.05-0.3, where  $P_0$  is the saturated pressure of N<sub>2</sub>.

**DFT calculations.** Density function theory (DFT) calculations were carried out using the open-source Quantum ESPRESSO package<sup>52-53</sup> along with GBRV pseudopotentials.<sup>54</sup> A plane-wave cutoff of 40 Ry was chosen for the wavefunctions as well a 320 Rv cutoff for the charge density. All atoms were allowed to relax during the calculations. As DFT falls short in fully predicting long-range interactions,<sup>55-60</sup> dispersion correction terms were added using the Grimme D2 scheme.<sup>61</sup> This correction algorithm has been previously tested and benchmarked for several systems and its performance is deemed satisfactory overall.<sup>62</sup> The structure of bulk diamond was optimized using a  $4 \times 4 \times 4$  grid of k-points, and the (100) and (111) surfaces of DNP were simulated using a 2×2 supercell. The (100) surface was modeled as the reconstructed (dimerized) (100)-(2x1)H surface with one H atom per surface C atom, referred to as the "monohydride" surface.<sup>63</sup> The (111) surface was modeled as the (111)-(1x1)H surface.<sup>64</sup> For each surface, a vacuum of proper thickness was added to ensure the absence of interactions between periodic images along the direction normal to the planes of interest. 2x2 surface calculations were performed using a 2×2×1 *k*-mesh. Spin-polarization effects were included to model radical species. An implicit solvation model was invoked to incorporate the effect of benzene as the solvent.<sup>65</sup> When modeling H abstraction from diamond surfaces, the calculations were performed in a manner that preserved the inversion symmetry of the slab. In studies of H abstraction, one H was removed from each side of the slab. However, we report the  $\Delta E$  as the energy change per H atom in order to maintain consistency.

Due to the flexibility of the PFO structure, a larger 4×2 supercell was created to accommodate the effective volume of PFO as the adsorbate. All geometry optimization calculations were initiated assuming an upright configuration for the PFO. In order to mimic steric constraints and exclude the volume effects at

the surface, we assume that one out of every eight surface C atoms could bind to a PFO molecule. The net energy changes upon binding of the alkene ( $E_{bind}$ ) were calculated using the equation:

$$E_{\text{bind}} = \frac{E_{\text{slab}+2*\text{alkene}} - (E_{\text{slab}}+2*E_{\text{alkene}})}{2} \tag{1}$$

The factor of 2 in the denominator of equation (1) arises because in our centrosymmetric model there are binding sites on both top and bottom of the 2-dimensional slab. Hence, dividing the total energy change by two yields the energy per site. The  $E_{\text{bind}}$  was calculated for diamond surfaces that were functionalized in two ways: 1) through the C atom at the terminal position (denoted as C1) and 2) through the adjacent C atom (denoted as C2).

#### RESULTS

Functionalization and structural analysis of the surface monolayer on the DNPs. Figure 1a depicts the overall scheme described here for covalent grafting of terminal alkenes to carbon surfaces. Prior studies have shown that benzoyl peroxide (BPO) dissociates into benzoate radicals at temperatures of 80-95°C.<sup>66</sup> This temperature range is for BPO decomposition in benzene solution and may change slightly when using other solvents. We hypothesize that the benzoate radicals selectively abstract hydrogen atoms from the H-terminated carbon surfaces, creating surface carbon radicals. The terminal alkene group then reacts with the radical sites on the carbon surfaces, forming a monomolecular layer via covalent bond between the alkene molecule and the surfaces. A key requirement for preference for surface functionalization over solutionphase polymerization is that the radical initiator must selectively abstract H atoms from the carbon materials without excessively initiating radical polymerization of the alkene within the reactant mixture. To demonstrate this approach, we investigated the grafting of 1H,1H,2H-perfluoro-1octene (PFO) onto the surface of detonation diamond nanoparticles (DNPs) as a model system (shown in Figure 1b); we then extended this approach to a wider range of terminal alkenes and carbon materials, as described later. We chose PFO for initial studies because fluorine shows a distinctive signature in XPS and NMR, facilitating mechanistic understanding of the surface bonding structures and detailed study of monolayer coverage.

Figure 2a and 2b show XPS data for the C(1s) and F(1s) regions of DNPs before and after functionalization. We calibrated the  $sp^3$  diamond peak to 284.8 eV and used it as a reference for the F(1s) XPS spectra. Before functionalization, the H-terminated

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DNPs (H-DNPs) show a single C(1s) peak at 284.8 eV from the NP core (Fig. 2a). Compared to an oxidized sample, the H-terminated sample shows a 98% reduction in the O(1s) intensity, (SI, S3), demonstrating that there are very few oxidized surface sites remaining. After the radical coupling reaction, the DNPs show several more peaks at higher binding energy that we attribute to  $CF_x$  groups, including C-CF<sub>2</sub> (285.4 eV), CF<sub>2</sub> (287.1 eV) and CF<sub>3</sub> (289.2 eV).<sup>67-69</sup> While C-O and C=O moieties have chemical shifts in the same range as CF<sub>2</sub> and CF<sub>3</sub> moieties, from the observed O(1s) intensity and the known sensitivity factors for C and O, it can be shown that C-O and C=O species contribute a negligibly small contribution to the overall C(1s) signal and can therefore be neglected. The F(1s) XPS spectra in Fig. 2b show that before functionalization the DNPs show no F(1s) emission (H-DNPs), while after grafting the F(1s) region shows a large peak at 689.4 eV from the covalently-bonded PFO molecules (PFO-DNPs w/BPO on H-DNPs). Quantitative analysis of the XPS data (SI, S15) yields a coverage of approximately 0.9 PFO molecule/nm<sup>2</sup>. Prior studies of fluorinated molecular

0.252 nm between adjacent surface sites of the diamond (111) and (100) surfaces. As a result, binding of one PFO molecule to either surface occludes the nearest set of surface sites. On the most common (111) surface, random packing of such occluded sites yields a maximum coverage of 0.096 monolayer, or 1.7 molecules/nm<sup>2</sup>.

To confirm that the PFO has linked to DNP surfaces through covalent bond, we compared our result with a control sample that is made by exposing the H-DNPs to PFO without any added radical initiator, shown in Fig. 2b (PFO-DNPs w/o BPO on H-DNPs). The result of the control shows a much smaller F(1s) emission intensity that corresponds to a coverage of <0.2 PFO molecule per nm<sup>2</sup> that is consistent with a small amount of physically adsorbed PFO reactant. To examine whether the small number of remaining oxidized surface react with the PFO, we performed a control experiment using oxidized DNPs as the starting material. Our result in Fig. 2b (PFO-DNPs w/BPO on ox-DNPs) shows that attempted grafting using oxidized diamond samples produce only a small F(1s) peak that is comparable to the physisorbed signal (0.08 PFO molecule per nm<sup>2</sup>). Thus, we conclude that PFO does not graft onto oxidized surface sites.

Figure 2c and 2d show thermogravimetric analysis (TGA) of the PFO-DNPs using  $N_2$  as the carrier gas. Figure 2c shows that for the PFO-DNPs grafted using BPO, there is little or no mass loss at temperatures <250°C. In contrast, TGA for a sample prepared identically without BPO present (Fig. 2d) shows substantial mass loss peaking at 144 °C, which we attribute primarily to desorption of physisorbed PFO. The boiling point of PFO is 102-105 °C at atmospheric pressure. Both samples show mass loss peaking at near 394 °C, which we attribute to thermal decomposition of the PFO. The TGA analysis and the XPS analysis above confirm that the introduction of a radical initiator leads to covalent grafting of the PFO molecule to the diamond surface. Thermogravimetric analysis (TGA) measurement and Brunauer-Emmett-Teller (BET) surface area measurements used as an independent estimate of the molecular density of PFO PFO-DNPs grafted content in using BPO. Thermogravimetric analysis shows that the mass loss from 200 °C to 450 °C is 0.4955 mg, while BET measurement shows a surface area of  $1.3 \cdot 10^{18}$ nm<sup>2</sup>·mg<sup>-1</sup>; these values yield a surface density of 0.7 molecule per nm<sup>2</sup> further supporting the XPS quantification. 70

More structural analysis of the PFO monolayer on the DNP surfaces using 1D and 2D  $^{19}\mathrm{F}$  NMR are

Figure 2. The XPS spectra comparison of a) the C(1s) regions and b) the F(1s) regions of the PFO-DNPs (with BPO), control for PFO-DNPs (without BPO) and H-DNPs. TGA analysis of c) DNPS grafted with PFO using BPO d) Control experiment showing DNPs exposed to PFO without BPO; the peak corresponds to removal of physisorbed PFO.

layers have reported a minimum molecular separation of 0.59 nm, corresponding to a molecular radius of 0.295 nm.<sup>70</sup> This value is larger than the



included in the Supporting Information; these NMR results are complementary to the analysis above. The 1D  $^{19}$ F NMR spectra (SI, S8) show an upfield shift of all six fluorine peaks upon attachment to DNP surfaces; these changes in the chemical shifts upon grafting to the DNP surfaces were consistent with the transformation of the alkene end from sp<sup>2</sup> to sp<sup>3</sup> hybridization.<sup>71</sup>

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The 2D spectrum (SI, S8) shows clear <sup>19</sup>F-<sup>19</sup>F chemical-bond correlations after grafting that are nearly identical to those of the parent molecule, implying the PFO remains intact as a monomer after the functionalization. Together, the 1D and 2D spectra establish that the PFO binds to DNPs via the alkene terminal end to form a monolayer. Further, these NMR data are consistent of the structure of a PFO monomer forming a molecular layer, with no signs of either polymerization or fragmentation.



Figure 3. (a) Comparison of <sup>1</sup>H spectra of free PFO ligand and (b) PFO-DNPs. (c) Expanded view of PFO-DNPs. (d-e) Schematic illustration depicting chemical structures of the two possible bonding configurations upon grafting on DNP surfaces.

Regioselective binding behavior at the DNP surfaces. Bonding configuration at the molecule-NP interface can be a critical factor controlling the molecular packing. To gain a detailed understanding of the bonding configuration at the nanoparticle interface, we need to first establish that grafting occurs at the unsaturated vinyl group. We compared the <sup>1</sup>H-NMR spectra of the free PFO in solution and the PFO attached to the DNPs (PFO-DNPs), as shown in Fig. 3. The free PFO molecule (Fig. 3a) exhibits two multiplets at 5.79 ppm and 5.96 ppm corresponding to methine proton (-CH-) and the -CH<sub>2</sub>- protons from the alkene terminal (labeled "H<sub>a</sub>" and "H<sub>b</sub>"), respectively. After grafting (Fig. 3b), these <sup>1</sup>H peaks at 5.96 ppm and 5.79 ppm are absent, and two new peaks appear at 1.41 and 1.11 ppm, the range characteristics of alkane C-H bonds. Notably, spectra of the starting nanodiamond (SI, S11) under similar conditions do not show NMR features near these values. The changes in NMR spectra demonstrate that the alkene moiety has reacted to graft the molecules to the DNP surface.

As depicted in Fig. 3d-3e, the terminal alkene can link to the DNP surface through the terminal CH<sub>2</sub> (C1, Fig. 3d) or the adjacent CH (C2, Fig. 3e). To establish which of these configurations occurs, we used multiplicity-edited <sup>13</sup>C NMR with Distortionless Enhancement of Polarization Transfer (DEPT).<sup>72</sup> Fig. 4a-b portrays the two possible bonding configurations involving bonding to the terminal C atom (labeled in pink) or the second C atom (labeled in blue). Figure 4 shows a standard <sup>13</sup>C spectrum (Fig. 4c) and a <sup>13</sup>C-DEPT spectrum of the PFO-DNPs (Fig. 4d).

The standard <sup>13</sup>C spectrum shows all carbon species from the PFO-DNP surfaces, revealing five peaks from 0 ppm to 65 ppm that correspond to four different aliphatic surface carbons from the PFO-DNP and one from TMS at 0 ppm. In the DEPT-135 spectrum, methyl (CH<sub>3</sub>) and methine (CH) protons are expected to give rise to positive signals, methylene (CH<sub>2</sub>) to negative signals, while quaternary carbons are not expected to produce detectable signals.<sup>72-73</sup> The DEPT-135 spectrum in Fig. 4d shows positive peaks at 0 ppm (CH<sub>3</sub> from TMS) and 31.2 ppm (CH and CH<sub>3</sub>) and negative peaks at 29.6 ppm ( $CH_2$ ) and 60.1 ppm  $(CH_2)$ . The peak at 31.2 ppm also appears in the spectrum of the H-DNPs (SI, S11) and comes from the surface carbons that are hydrogenated during the hydrogen treatment. The peak at 38.1 ppm (quaternary <sup>13</sup>C) corresponds to the carbons from the diamond core, consistent with prior studies showing a peak near 37 ppm that is characteristic of the core

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Figure 4. (a-b) Schematics illustration depicting the two possible surfaces with different bonding configurations that are analogous of Anti-Markovnikov and Markovnikov. (c) The standard <sup>13</sup>C and d) DEPT-135 spectra of the PFO-DNPs, revealing the number of attached protons

for <sup>13</sup>C peak. All spectra were acquired with 4000 scans using a TCI-F cryoprobe on a 600 MHz spectrometer.

diamond carbons.<sup>74-78</sup> The small peak at 29.6 ppm is 39 assigned to the CH<sub>2</sub> carbon adjacent to the CF<sub>2</sub> group 40 (shown in blue in Fig.4a) based on the chemical shift 41 of previously reported compounds with mixed CF<sub>2</sub> 42 and CH<sub>2</sub> motifs.<sup>79-81</sup> The fluorine atoms couple to this 43 hydrocarbon and split the <sup>13</sup>C peaks, leading to the 44 lower intensity and broadening of the peak at 29.6 45 46 ppm. Previous studies have shown that fluorine atoms 47 couple strongly with the adjacent carbon atom through 2-bond coupling,<sup>82</sup> reducing the peak 48 49 intensity due to the splitting into multiplets. We assign 50 the peak at 60.1 ppm to the CH<sub>2</sub> carbon that is directly 51 bonded to the diamond surface (labeled in pink in Fig. 52 4a). The <sup>13</sup>C chemical shifts of nanodiamond have 53 been studied extensively in the literature74-76,78,83-84 54 and similar observation on the downfield chemical 55 shifts ( $\sim 60$  ppm) of the surface carbons on DNPs has 56

been reported by several groups  $^{76,83\text{-}84}$  and have also been supported by *ab initio* calculations.  $^{85}$ 

multiplicity-edited  $^{13}C$ The NMR result demonstrates that both hydrocarbons from the PFO molecular at the diamond surface become CH<sub>2</sub> moieties upon chemical grafting, corresponding to bonding configuration 1 Figure 4a. The fact that we observe CH<sub>2</sub> carbon signals at 29.6 ppm and 60.1 ppm and no CH and CH<sub>3</sub> signals at these corresponding chemical shifts shows that the alkene terminus binds onto the DNP surfaces via the first carbon (C1), resulting in a bonding configuration at the surface that is analogous to Anti-Markovnikov binding.86-87 To confirm our assignments, we collected quantitative <sup>13</sup>C NMR spectra<sup>73,88</sup> of the PFO-DNPs and obtained the integrated peak areas associated with these carbons. Our results show that the integration ratios of CH<sub>2</sub> carbon at 60.1 ppm and the CH<sub>2</sub> carbon at 29.6 ppm are the same within experimental error: 1.0 to 0.8. This quantification result further supports our interpretation of the Anti-Markovnikov binding.

Selective binding mechanism at the DNP surfaces. The above results show that the introduction of a radical initiator into the liquid-phase reactant solution leads to selective functionalization of the diamond surface, reacting with the terminal C atom (C1) of the reactant alkene. Our results indicate that a radical initiator is able to selectively abstract H atoms from the carbon surfaces more favorably than from the liquid reactants. It is worth highlighting that the latter hypothetical case would lead to polymer formation in the liquid phase. To understand the preference of the alkene for binding to the DNP surface over self-polymerizing, we employed DFT calculations. We also computed the differences in energy penalty to extract a H atom from a liquid-phase reactant, and that of a diamond surface. The enthalpy change has been calculated for the process:

$$\text{RC-H} \to \text{RC} \bullet + \text{H} \bullet \tag{1}$$

where "R" represents the carbon material or organic molecule of interest. Surface radicals such as the ones in equation (1), are commonly referred to as "dangling bonds." We determined the energy required to form a radical as the difference between DFT total energies of the H-terminated carbon before and after the removal of the H atom. For the energy of the product H atom, we used a fixed value of -13.61 eV. For comparison, we calculated the energies associated with abstraction of an H atom from each of the three different locations of the terminal vinyl functionality of the alkene reactants ( $H_{b1}$ ,  $H_{b2}$  and  $H_{a}$ , as denoted in Fig. 3a), corresponding to formation of a molecular radical in the liquid PFO reactant.

Tab	le 1.	Energ	y requi	red ab	stract an	•
H a	atom	from	H-term	inated	diamond	
sur	faces	and	from	the	terminal	
alk	ene g	roup c	of the	PFO mol	Lecule. H	1
ata	me of		aro ind	hinsted	in Fia	

	C(100)- (2x1)H	C(111)- (1x1)H	PFO vinyl group		
			H <sub>b1</sub>	H <sub>b2</sub>	Ha
E(eV)	4.59	4.43	5.48	4.97	4.98

The data in Table 1 show that the overall energy change in abstracting an H atom from an organic alkene (thereby creating a radical in the liquid phase) is 0.3-0.5 greater than that involved in abstracting an H atom from the H-terminated diamond C(100)-(2x1)H or C(111)-(1x1)H surface (thereby creating a surface radical). This difference indicates that the lowest-energy reaction of thermally produced benzoate radicals is abstraction of an H atom from the diamond surface rather than abstraction of H from the PFO reactant, which would induce polymerization of the starting alkene. Using the same computational method, we find that benzoic acid has a predicted homolytic C-H bond dissociation energy of 5.68 eV; this value indicates that the resulting benzoate radical should be able to abstract H atoms from the vinyl group of the alkenes as well as from the H-terminated diamond surfaces. While Table 1 compares the enthalpies of reactions, prior studies have shown that rates of H atom abstraction are strongly anticorrelated with the strength of the C-H bond being broken.<sup>89</sup> Thus, H atom abstraction should occur fastest from H-diamond surfaces.

To identify the origins of the regioselective binding behavior, we also calculated the overall energy associated with binding to the diamond C(111) surface via each of the two different possible radical positions of the terminal alkene group (C1 and C2). The total enthalpy change was calculated as  $E_{\text{bind}}$  –  $E_{\text{alkene}}$ - $E_{\text{Hdiamond}}$ , where  $E_{\text{bind}}$  is the energy of the surface-grafted molecule,  $E_{\text{alkene}}$  is the energy of free alkene reactant, and  $E_{\rm H diamond}$  is the energy of the Hterminated diamond surface. Figure 5 is a pictorial representation of the optimized structures on the (111) surface. According to our calculations, the overall enthalpy change in binding the alkene (PFO) to the (111) surface through the terminal C1 is negative,  $(E_{\text{bind}} = -0.93 \text{ eV/PFO})$ , whereas binding through C2 is appreciably disfavored

 $(E_{\rm bind} = +0.48 \text{ eV/PFO}).$ 

Through additional calculations (not shown), we have demonstrated that the large difference between C1 and C2 binding energies arises from the steric repulsion associated with the close proximity of the terminal CH<sub>3</sub> group to the diamond surface when bonding via C2. We also performed similar calculations with the diamond (100) surface yielding energies of -0.80 eV (via C1) and -0.22 eV (via C2) (SI, S12). Thus, on both surfaces binding is strongly favored via the terminal carbon (C1).

In summary, <sup>13</sup>C NMR and density functional calculations both indicate that PFO binds regioselectively to diamond surfaces via the terminal carbon (C1) from the alkene. A similar behavior has been noted in the reaction of more typical organic reactions of radicals with alkenes. While in liquid-phase reactants branched products (formed by C-C bond formation at C2) are lower in energy than



Figure 5. Schematic illustration depicting the bonding configuration that bind through C1 (left) and C2 (right) per-PFO at the (111) face of diamond. Black, yellow, and light grey spheres are C, F, and H atoms, respectively.

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bonding at C1, prior studies of radical reactions with alkenes have found a strong preference for linking to the terminal C1 due to the smaller steric constraints there.<sup>40,42</sup> Similarly, we find that binding via the C2 position is strongly disfavored on both (111) and (100) diamond surfaces. Taken together from both experimental and computational results, our data demonstrate that radicals first form on the diamond surfaces and then regioselectively bind with the alkene terminus via covalent linkage to form a monolayer.

# Versatility using various alkene terminus molecules on DNP surfaces.

**PEG-modified DNPs.** Carbon materials have become a popular choice for many applications including biosensors and imaging.<sup>90-93</sup> These



Figure 6. (a-c) <sup>1</sup>H NMR spectra comparison of the di(ethylene glycol) vinyl ether (PEG-DNPs), trimethylammonium (amine-DNPs) and H-DNPs. Features marked with red asterisks correspond to peaks from residual solvent, black corresponds to impurities from DNPs and blue correspond to impurities from the reactants. (d) XPS spectra comparing the C(1s) regions of the amine-DNPs and H-DNPs. (e) XPS spectra comparing the N 1s regions of the PEG-DNPs and H-DNPs.

applications frequently require functionalization with molecules that are hydrophilic, either by virtue of having polar groups or charged functional groups. We investigated functionalization with two representative hydrophilic molecules, (1) di(ethylene glycol) vinyl ether and (2) allyl trimethylammonium bromide, to demonstrate the tunability of the head groups from the alkene terminus molecules on DNPs and other carbon materials. To show that these molecules can be successfully grafted to nanodiamond surfaces, we used <sup>1</sup>H NMR. Figure 6a-c shows <sup>1</sup>H NMR spectra of H-DNPs that were functionalized with di(ethylene glycol) vinyl ether (PEG-DNPs), and with trimethylammonium (amine-DNPs), along with a spectrum of the starting hydrogenated DNPs (H-DNPs). For the PEG-DNPs (Fig. 6a), the <sup>1</sup>H NMR spectrum shows three major peaks at 1.18 ppm, 3.65 ppm and 3.74 ppm. The peaks at 1.18 ppm and 3.65 ppm arise from residual ethanol (labeled with a red asterisk), and we attribute the peak at 3.74 ppm to the protons linked to the carbon atom adjacent to oxygen atoms that are labeled in blue. The appearance of the O-CH<sub>2</sub> moiety in the NMR spectrum after the reaction demonstrates successful grafting of di(ethylene glycol) vinyl ether onto the DNPs.

To estimate the molecular coverage, we collected high-resolution C (1s) XPS spectra before and after functionalization. Before functionalization, the H-DNP sample (Fig. 6d, bottom) shows a major peak at 284.8 eV with an asymmetric tail at lower binding energies and a small shoulder at 286 eV, which is related to C-O component due to hydroxyl or ether group.<sup>44,78,94</sup> After functionalization (Fig. 6d, top), the sample shows additional peak at higher binding energy at 286.5 eV that corresponds to the carbon atoms associated with the ether C-O-C linkages of the PEG group.<sup>95-98</sup> The broad widths at half-maxima result from the sample size inhomogeneous broadening.44 Based on the areas of the low-binding energy and high binding-energy regions., we estimated the molecular coverage to be  $1.0 \pm 0.1$  molecule per nm<sup>2</sup> (quantification detail see SI, S15)

**Quaternary amine-modified DNPs.** For Amine-DNPs, the <sup>1</sup>H NMR spectrum (Fig. 6b) shows that functionalization leads to three major new peaks at 1.18 ppm, 3.10 ppm and 3.66 ppm. The peak at 3.10 ppm corresponds to the nine protons from the -N(CH<sub>3</sub>)<sub>3</sub> head group (labeled as H<sub>b</sub>). The two protons from the carbon adjacent to the trimethyl amine head group (in Fig. 6b labeled as H<sub>a</sub>) overlap with the -CH<sub>2</sub> from the ethanol at 3.66 ppm. By subtracting 2/3 of the integral for the -CH<sub>3</sub> ethanol peak (at 1.3 ppm) from the overlap at 3.66ppm, we obtain the integral value for just the H<sub>a</sub> peak and get a ratio of H<sub>a</sub>: H<sub>b</sub> as 2:9 (SI, S16), which is consistent with the molecular structure shown in Fig. 6b. N(1s) XPS spectra (Fig. 6e) show that the starting DNPs contain some nitrogen that arises from their production via explosive decomposition of nitrogen-rich compounds.<sup>16,78,99-100</sup> After functionalization, the N(1s) spectrum show a prominent peak at 402 eV (assigned as C-N-C), which is consistent with a positively charged quaternary amine group.<sup>47,101-102</sup> Quantitatively analyzing the N(1s) and C(1s) integrated areas yields an surface coverage of  $1.2 \pm 0.3$  molecule per nm<sup>2</sup> (SI, S15). The combination of NMR and XPS demonstrate that the use of a radical initiator successfully grafts the PEG and quaternary amine monolayer to the DNP surfaces. The quantitative result of the monolayer coverage shows that the molecular densities for different surface species (with similar atomic size) on DNPs are nearly identical (within experimental error),  $\sim 1.0$ molecule per nm<sup>2</sup>, suggesting  $\sim$ 320 molecules per nanodiamond (with 14 ± 1 nm hydrodynamic diameter).

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Versatility using various alkene terminus molecules on different carbon materials. To



Figure 7. The XPS spectra comparison of before and after surface modification (a-c: PFO-surfaces, d-f: PEG-surfaces) for boron doped diamond (BDD, a and d), glassy carbon (b and e) and citric acid carbon dots (CAPCDs, c and f). The insert boxes highlight the C1s regions from the survey. The H-surfaces were used to represent the surfaces before the modification for BDD and glassy carbon, and the none-treated-surface was used for CAPCDs.

demonstrate that radical-initiated grafting is a general approach to functionalization of carbon-based materials, we extended our studies to planar samples of boron-doped diamond (BDD), vitreous carbon (glassy carbon) and CAPCDs.<sup>48-49</sup> Figure 7 shows six sets of XPS comparison spectra before and after surface modification of these materials with PFO (hydrophobic) and PEG (hydrophilic) molecules. Data are shown for boron-doped diamond electrode (Fig. 7 a,d), glassy carbon (Fig. 7 b,e) and CAPCDs (Fig. 7 c,f). We chose both molecules that have hydrophobic and hydrophilic moieties on these three materials to demonstrate that radical-induced grafting is generalizable to carbon materials and versatile towards a wide range of terminal alkene molecules. For BDD and glassy carbon, we used hydrogenated surfaces (labeled as "before") to compare with the functionalized surfaces; and for CAPCDs we used the as-synthesized material as the CAPCDs are expected to contain many C-H bonds at their surfaces. The first column in Fig. 7 shows a comparison of these three carbon materials before and after reaction using PFO. As shown in each spectrum in Fig 7 a-c, a significant F(1s) emission is only observed after functionalization. Using the same quantification approach (SI, S15), our data suggest that the molecular densities of PFO on all three carbon surfaces are approximately the same,  $\sim 1$  molecule per nm<sup>2</sup>. As control samples, we also performed experiments in which the radical initiator was eliminated (SI, S17), while all other steps remained identical. Our data show that the presence of a radical initiator increases the F(1s)/C(1s) ratio by more than 8-fold compared with control samples that were treated identically except for the absence of the radical initiator. The XPS and NMR data show that the introduction of a mild radical initiator (benzoyl peroxide) into the PFO reactant leads to successful grafting onto boron-doped diamond, H-terminated glassy carbon, and CAPCDs. While CAPCDs are synthesized from polymers, we conducted NMR studies (SI, S18) showing that nearly all the C atoms in polymeric carbon dots are quaternary or tertiary in character. Thus, the surfaces of CAPCDs are expected to expose surface C<sub>3</sub>C-H moieties similar to those of diamond and glassy carbon.

As an additional test, we explored radical-induced grafting of an alkene-terminated di(ethylene glycol)vinyl ether (PEG) reactant molecule, as an example of grafting hydrophilic functional groups to different types of carbon surfaces, with results shown in Fig. 7d-7f. XPS spectra in Fig. 7d and 7e show that radical-induced grafting of di(ethylene glycol)vinyl ether onto BDD and glassy carbon produces an obvious C(1s) peak associated with O-C-O linkages. Because the CAPCDs contains peptide bonds as part of

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the material, we observe both ether-like linkages at 286.6 eV<sup>95-98</sup> and carbonyl-like linkages at 288 eV<sup>4,103-</sup> 2 <sup>104</sup> from the non-functionalized materials in black traces from the insert box in Fig. 7f. However, a significant increase in the ether-like carbon peak at 5 286.6 eV is observed after functionalization, 6 suggesting the successful grafting of the PEG 7 molecule. The quantification of the PEG monolayer on 8 these carbon surfaces is about 1 molecule per nm<sup>2</sup>. 9 Because the approximate monolayer coverage shows 10 that the molecular densities with both PFO and PEG 11 on diamond, glassy carbon and CAPCDs are nearly the 12 same within error and are  $\sim 1$  molecule per nm<sup>2</sup>, 13 indicating that under the same reaction condition and 14 within similar size, the grafting efficiency depends 15 only on the alkene terminus but not on the functional 16 group head (as long as the head group sustains the 17 radical environment and does not degrade during 18 reaction). This further suggests that when the 19 reaction conditions are optimized, the grafting 20 efficiency should be the same for different type of 21 alkene terminus molecules. We have also extended 22 our studies using a charged molecule with an amine 23 moiety (allyl trimethylammonium bromide) on these 24 carbon surfaces, and the XPS analysis using allyl 25 trimethylammonium on BDD and glassy carbon 26 surfaces reveal monolayer coverage of  $\sim 1$  molecule 27 per nm<sup>2</sup> (SI, S15). Previous studies of organic 28 monolayers on planar diamond yielded a maximum 29 packing density of 4-7 molecules per nm<sup>2,4</sup> while 30 31 studies reported on nanodiamond vielded lower 32 packing density of 1 molecule per nm<sup>2,105</sup> Our results 33 vield an average of 1 molecule per nm<sup>2</sup>, which is 34 comparable to the reported value in the literature. 35

Origins of selectivity. The above results demonstrate that the radical-facilitated grafting of alkenes to H-terminated carbon surfaces is a versatile approach yielding highly stable C-C interfacial bonds and that can be applied to a range of H-terminated carbon materials reacting with organic alkenes bearing different functionalities.

Abstraction of H atoms from H-terminated silicon surfaces has been used previously to graft alkenes to the surface via direct Si-C bond formation.<sup>106-109</sup> On H-Si surfaces the observation of selective functionalization is not surprising, since the energy required to form Si surface radicals is very low,  $\sim 2$ eV.<sup>110</sup> In contrast, abstraction of H atoms from carbon surfaces requires much more energy, although still less than that of typical organic molecules.

Our data in Table 1 show trends in C-H bond energies that are similar to those observed in gasphase reactions. Gas-phase bond dissociation energies for C-H bonds of secondary carbon atoms of organic molecules are typically ~100 kcal/mole or 4.3

eV (e.g., 98.6 eV for propene<sup>111</sup>) while the C-H bond energy on the H-terminated diamond(111) surface was measured at 4.0 eV, a value 0.3 eV lower than that of typical aliphatic molecules.<sup>112</sup> Experimental<sup>113</sup> and computational<sup>114</sup> studies of H-terminated diamond(100) both report an even lower energy of 330 kJ/mole or 3.4 eV to remove an H atom to form a surface "dangling bond" in vacuum. These trends are in qualitative agreement with our calculations (Table 1) and show that it thermodynamically easier to form radicals at carbon surfaces compared with formation at typical aliphatic organic molecules.

The benzoyl peroxide radical initiator used here produces the benzoate radical  $(C_6H_5COO\bullet)$ .<sup>115</sup> While no experimental values have been reported, a prior computational study estimated a gas-phase O-H homolytic bond strength for benzoic acid (forming benzoate radical and H) of 4.8 eV.<sup>116</sup> This large value indicates that the benzoate radical is thermodynamically capable of abstracting H atoms from H-carbon surfaces and, in addition, from common organic reactants like those used here. Tsubota and co-workers showed previously that BPO was able to abstract H atoms from H-terminated diamond surfaces.<sup>117</sup> While in that earlier work there was no alkene added to produce the "all-carbon" surface functionalization scaffold, Tsubota's work confirms the ability of BPO to abstract H from diamond. Because BPO is also thermodynamically capable of abstracting H from the reactant alkene molecules, the ability to selectively functionalize the surfaces without excessive polymerization in the liquid phase cannot definitively be attributed solely to differences in thermodynamics of H-atom abstraction at surfaces vs. in liquid phases. There may also be kinetic factors affecting the reaction of the resulting radicals with the organic alkenes. In particular, we conjecture that rigid, tetrahedral geometry at carbon surfaces might also lead carbon surface radicals to be exposed in a manner that yields faster kinetics with reactant alkene molecules.

A unifying concept in this work is that diamond, glassy carbon, and CAPCDs all have surface bonding motifs that expose hydrogen-terminated tertiary carbon species C<sub>3</sub>C-H at their surfaces. H atoms can be abstracted more readily from these surface sites compared with abstraction from C-H bonds of reactant molecules, leading to selective formation of surface radicals that can in turn link to the terminal C1 site of reactant alkenes. While there may be some polymerization in the liquid phase, our XPS results demonstrate that the extent of surface functionalization is comparable to that expected from a self-terminating monolayer and cannot be attributed to polymers formed in the liquid phase. Potentially, the approach used here could also work on surfaces terminated with secondary carbon atoms. However, because the dissociation energy of C-H on secondary carbons can be higher than that for tertiary carbons,<sup>118</sup> it is likely that radical abstraction from surface atoms would be less selective compared with inducing polymerization in the bulk.

## CONCLUSIONS

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Radical-initiated grafting of alkenes to Hterminated carbon surfaces provides a versatile approach to molecular functionalization that can be applied to a wide range of carbon materials. The use of "all-carbon" interface scaffolds provides extraordinary chemical stability,<sup>4,19</sup> while the use of alkenes as reactants provides versatility due to the wide range of functionalized alkenes available commercially<sup>14</sup> or via simple synthetic methods.<sup>4,119</sup> Compared with grafting induced by ultraviolet light,<sup>14</sup> the use of radical initiators allows more facile functionalization of bulk nanoparticles and complex 3-dimensional structures while also potentially avoiding unwanted photochemical reactions. The combined use of XPS and multiple NMR methods provides important insights into the molecular origins of the observed surface selectivity and regioselectivity of C-C bond formation.

### ASSOCIATED CONTENT

#### SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website. Experimental conditions details, DFT calculations details, characterization data for trimethylammonium bromide and characterization data of functionalized carbon materials (TEM, IR, NMR and XPS quantification) (PDF).

### AUTHOR INFORMATION

### **Corresponding Author**

Email: rjhamers@wisc.edu

### Present Address

<sup>§</sup>University of Missouri- Columbia, Department of Chemistry, Columbia, USA

### ORCID

Yongqian Zhang: 0000-0001-9637-5314 Ali Abbaspour Tamijani: 0000-0003-4867-0487 Sara E. Mason: 0000-0003-1515-6780 Christy L. Haynes: 0000-0002-5420-5867

Robert J. Hamers: 0000-0003-3821-9625

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