

Fast Dechlorination of Chlorinated Ethylenes by Green Rust in the Presence of Bone Char

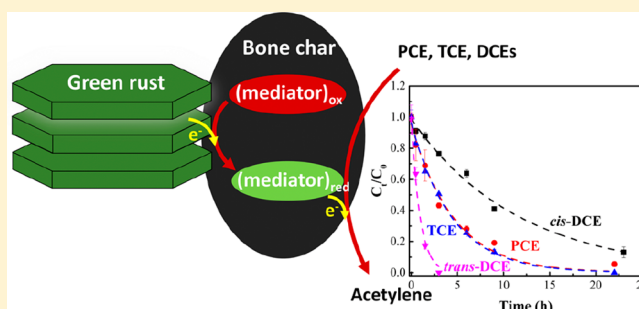
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S Supporting Information

ABSTRACT: Layered iron(II)–iron(III) hydroxides [green rusts (GRs)] constitute fast reductants for chlorinated methanes, but most studies of the reaction of GRs with chlorinated ethylenes (CEs) have reported little or no reduction. In this work, we demonstrate that bone char (BC) can eliminate the kinetic hindrance of dehalogenation of CEs by GR. Dechlorination of perchloroethylene (PCE), trichloroethylene (TCE), *cis*-dichloroethylene, and *trans*-dichloroethylene ($\sim 10 \mu\text{M}$ in aqueous phase) by GR/BC mixtures ($\sim 3.2 \text{ g/L}$ GR and 0.15 g/L BC) followed pseudo-first-order kinetics with half-lives of 3.15, 3.01, 7.97, and 0.63 h, respectively, with acetylene as the main product ($>85\%$), while no reaction took place in the absence of BC or GR. The rate of TCE removal was almost independent of GR concentration but increased linearly with BC concentration, indicating that the reactive sites for dechlorination are on the BC phase. GR could directly reduce BC in amounts of $\leq 0.21 \text{ mmol of } e^-/\text{g}$, suggesting that CEs were dechlorinated by reduced functional groups on BC that functions as an electron mediator with GR acting as the “bulk” reductant. The GR/BC mixture exhibited a similar rate of removal of PCE and TCE in contaminated groundwater and in the laboratory-spiked solutions. This opens new perspectives for both *in situ* remediation and natural attenuation of CEs in anoxic, neutral, and alkaline iron-rich contaminated sediments and aquifers.



INTRODUCTION

Polychlorinated alkane and alkene solvents such as carbon tetrachloride (CT), perchloroethylene (PCE), and trichloroethylene (TCE) are ubiquitous and worldwide contaminants in soils, sediments, and waters.^{1,2} They represent very troublesome pollutants due to their high density, mobility, volatility, toxicity, and persistence. Despite intensive research over the past several decades, major challenges to clean soils and water contaminated with these pollutants remain.^{3,4}

An efficient approach to the degradation of chlorinated solvents is reductive dehalogenation, either by anaerobic microbial degradation or by chemical processes such as the use of strong reductants. Zero-valent iron (ZVI) is well-known for its ability to reduce chlorinated ethylenes (CEs) to less chlorinated or nonchlorinated products,⁵ e.g., in the form of permeable iron walls/barriers (PRBs)⁶ or by injection of modified nanosized ZVI (nZVI) particles into contaminated plumes.^{7,8} Iron(II)-bearing minerals such as mackinawite (FeS), pyrite (FeS₂), and magnetite (Fe₃O₄) are also capable of reducing chlorinated compounds, contributing to the natural attenuation of chlorinated solvents, but usually at rates much lower than that of iron(0).^{9–12} Green rusts (GRs), another class of iron(II) minerals, belonging to the group of layered double metal hydroxides, have been considered as

reducing agents for a diversity of contaminants.^{13–18} Although reduction of CEs by GRs is thermodynamically favorable,¹⁹ reported reduction rates vary greatly with experimental conditions, and most studies have shown no or very slow reduction.^{20–24} Introducing transition and noble metal ions such as copper(II), platinum(IV), and silver(I) is one way to stimulate the reducing reactivity of GRs,^{24,25} but the use of these elements is both costly and unsustainable. Faster CT dehalogenation can be achieved by GRs intercalated with surfactants or in contact with graphene oxide as the hydrophobic carbon component enhances CT adsorption resulting in higher dechlorination rates.^{26,27}

Carbonaceous materials such as charcoal, activated carbon, and graphene are known to facilitate the reductive transformation of organic pollutants, such as nitroaromatic compounds^{26,28–30} and halogenated hydrocarbons,^{31–34} by a variety of reductants. The enhanced reactivity is typically attributed to the presence of electroactive polycondensed aromatic sheets and quinoid functional groups in the

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carbonaceous material.³³ As an example, bone char derived from animal bones has shown high adsorption capacity with respect to organic compounds^{35,36} and excellent electron conductivity due to a hierarchical pore and graphitic structure,^{35–38} suggesting the high potential of bone char as a redox mediator.

In this study, we have investigated how bone char affects the kinetics and pathways of dechlorination of CEs by GR. Further experiments are performed to identify the phase at which the dehalogenation reaction takes place to provide a first conceptual model of the reaction mechanism. The proof of concept is rounded off with a test of the GR/BC mixture applied to CE-contaminated groundwater.

MATERIALS AND METHODS

Chemicals. Bone char (BC) (Fluka AG, CH-9470) fabricated by pyrolysis at 1000 °C was pretreated by extraction with 1 M HCl to remove apatite before being used for reactivity experiments (Text S1). The specific surface area of the resulting BC measured by BET (Gemini VII 2390, Micromeritics) was 586 m²/g, and the average particle size was 1.21 μm measured using a Zetasizer Nano ZS (Malvern Instruments). The elemental composition of BC determined by ICP-OES and the particle size distribution provided by the supplier are listed in Tables S1 and S2, respectively.

Batch Experiments with CE-Spiked Waters. A stock suspension of the chloride interlayered form of GR (GR_{Cl}) with a concentration of ~6.3 g/L equivalent to that of iron(II) in GR {[iron(II)]_{GR}} of 44 mM was prepared according to the method described by Yin et al.³⁹ (Text S1). Portions (80 mL) of oxygen-free 5.0 g/L BC stock suspensions were prepared in 100 mL glass bottles by flushing the suspensions with argon at a rate of 30 mL/min for at least 1 h before they were transferred to an anoxic glovebox (Coy Laboratories, containing 95% N₂ and 5% H₂). The X-ray diffraction patterns for separate GR and BC and freshly prepared BC-mixed GR are shown in panels A and B of Figure S1.

Batch reactivity experiments were performed by transferring a 0.15 mL BC stock suspension to 10 mL headspace vials, followed by injection of 2.5 mL of a GR stock suspension and 2.35 mL of oxygen-free triply deionized water (TI water, resistivity of ≥20 MΩ cm⁻¹), resulting in initial GR and BC concentrations of ~3.2 and 0.15 g/L, respectively. No buffer was added because GR itself has the capacity to buffer the pH at ~8.^{40,41} Finally, 25 μL of a 4.0 mM CE [PCE, TCE, *cis*-dichloroethylene (*cis*-DCE), or *trans*-dichloroethylene (*trans*-DCE)] stock solution (in methanol) was spiked to obtain an initial mass of 0.1 μmol per vial, and the vials were sealed with Teflon-lined silicone septa (20 mm, ML33176, Mikrolab) and magnetic crimp caps (20 mm, blank 6 mm hole, Thermo Scientific). The prepared sample vials were placed on an orbital shaker at 300 rpm and ambient temperature (22 °C). All handling and mixing of suspensions until vials had been capped were performed in the glovebox. Specifications of the chemicals that were used are listed in Table S3. Kinetic data were fitted by pseudo-first-order kinetics using the equation $[C]_t = [C]_0 \times \exp(-k_{app}t)$ (no data weighting) in OriginPro 9.0, where $[C]_t$ and $[C]_0$ are the aqueous concentrations of CEs at time t and time zero, respectively, and k_{app} represents the observed pseudo-first-order rate constant.

Experiments with variable doses of BC or GR were performed to identify the rate-determining phase. For variable dosing of BC, 2.5 mL of the GR stock suspension described

above was injected into the vial followed by addition of 0.15, 0.20, 0.50, or 1.00 mL of an oxygen-free 5.0 g/L BC stock suspension, topping off with oxygen-free TI water to a final volume of 5.00 mL, and finally spiking with 25 μL of 4.0 mM TCE. For variable GR dosing experiments, 0.15 mL of the BC stock suspension described above was added to the vial followed by addition of 0.60, 1.00, 2.50, or 4.50 mL of ~6.3 g/L GR stock suspensions, topping off with water to a final volume of 5.00 mL, and spiking with 25 μL of a 4.0 mM TCE stock solution. Samples were shaken, and kinetic data fitted as described above.

Batch Experiments with Groundwater Contaminated with CEs. A groundwater contaminated with both PCE and TCE was sampled at Naverland, Glostrup, Denmark, and stored at 4 °C prior to use. The groundwater composition is listed in Table S4. For the reactivity experiment, 1 mL of a freshly prepared GR and BC stock slurry composed of ~13 g/L GR and 2.5 g/L BC was injected into 10 mL headspace vials, followed by addition of 4 mL of groundwater, resulting in initial aqueous concentrations of 2.3 ± 0.3 μM PCE, 6.6 ± 0.2 μM TCE, ~2.6 g/L GR, and 0.5 g/L BC in the vials. The initial pH in the vials was ~8, which was controlled by the buffering effect of GR. Samples were shaken, and kinetic data fitted as described above.

RESULTS AND DISCUSSION

Kinetics of Dechlorination in CE-Spiked Waters. The presence of BC in the GR suspension triggers fast reductive dechlorination of CEs, with at least 85% CE removal within 24 h (Figure 1, Figure S2, and Table S5) and 100% removal at 48

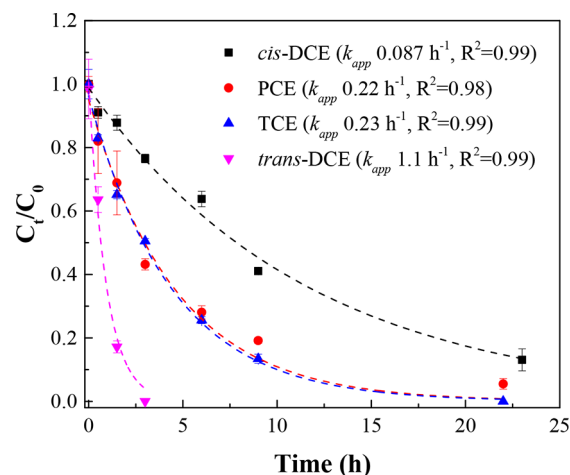


Figure 1. Kinetics of the removal of CEs in the presence of a GR/BC mixture in batch experiments at pH 8.0. Dashed curves represent pseudo-first-order kinetic fitting. Reaction conditions: 0.1 μmol of PCE, TCE, *cis*-DCE, or *trans*-DCE in a 5 mL solution in a nominal 10 mL headspace vial, ~3.2 g/L GR and 0.15 g/L BC, at room temperature (~22 °C). Error bars represent standard deviations calculated from triplicate experiments.

h. In contrast, control experiments with suspensions containing GR or BC separately showed that neither GR nor BC reacted with CEs over a period of at least 1 month (Figure S3A,B), confirming previous observations of no or very low reactivity of GR toward dechlorination of CEs.^{20–24,42} The highest pseudo-first-order rate constant (k_{app}) for CE removal was seen for *trans*-DCE (1.1 ± 0.1 h⁻¹) followed by those of TCE ($0.23 \pm$

0.01 h⁻¹), PCE (0.22 ± 0.02 h⁻¹), and *cis*-DCE (0.087 ± 0.006 h⁻¹). The *cis*-DCE reaction has been ranked as the slowest CE dehalogenation reaction in other studies of iron-bearing minerals and iron(0), which also found that the rate of dehalogenation follows the degree of chlorination (PCE > TCE > DCEs).^{43–45} However, the finding that *trans*-DCE is the fastest-reacting compound with PCE and TCE showing similar rates (Figure 1) is unusual and different from the findings of many other studies.^{9,10,44,46,47} The different trend in reactivity is attributed to the presence of BC shifting the reactive sites of dechlorination from the iron-containing phase (GR) to the carbonaceous phase (BC) and additionally introducing sorption sites for CEs.^{28,48} This is further supported by the product distribution where acetylene is seen as the only nonchlorinated product when BC is present, while ethylene and ethane are typically observed in CE dechlorination by GR alone and by other iron-containing reductants.^{9,10,21,43,45} The changes in reductive pathways due to the introduction of carbonaceous and electrical conductive materials have also been documented for both abiotic^{26–28,30} and microbial^{49,50} transformations in other studies.

For the reduction of *trans*-DCE by the GR/BC mixture, the absence of vinyl chloride (VC) suggests that the pathway is β -elimination to produce acetylene directly (Scheme S1). For *cis*-DCE, dechlorination is likely a parallel transformation comprising both β -elimination and hydrogenolysis, but because only traces of VC were detected, hydrogenolysis appears to play a less prominent role as in *cis*-DCE dechlorination by iron(0).⁴⁵ TCE dechlorination by the GR/BC mixture was dominated by β -elimination as acetylene made up 93% of the final products, while hydrogenolysis contributed to the formation of 7% of *cis*-DCE and traces of 1,1-DCE. Traces of VC (below LOD) may be attributed to hydrogenolysis of DCEs (Table S5 and Scheme S1), and the detection of traces of methylacetylene suggests that even a third pathway may be involved. Finally, for PCE dechlorination, the pathway was similar to that for TCE, with β -elimination dominating, resulting in acetylene making up 89% of the products. Hydrogenolysis of PCE led to the formation of a small amount of TCE ($\leq 1.3\%$) that reacted further by hydrogenolysis to form *cis*-DCE ($\leq 0.9\%$) and 1,1-DCE ($\leq 1.8\%$), with subsequent production of traces of VC. Traces of ethylene may derive from VC hydrogenolysis and/or α -elimination of 1,1-DCE.^{43,51–53} In the dechlorination of PCE, substantially larger amounts of the methylacetylene ($\leq 26\%$) intermediate were formed than in TCE reduction, but with the methylacetylene concentrations decreasing over time and disappearing at the end. Similar intermediates and products have been observed in dechlorination of PCE and TCE by iron sulfide except for the formation of methylacetylene.⁴⁶ Hence, we attribute the formation of methylacetylene in the GR/BC experiments to the BC phase.

Role of BC in Reductive Dehalogenation. At a constant initial GR concentration of ~ 3.2 g/L, the observed pseudo-first-order rate constant for TCE removal, k_{app} (h⁻¹), was observed to increase linearly with BC concentration (g/L) with a slope of 1.76 L g⁻¹ h⁻¹ (Figure 2A). However, the slope of linearity between GR concentration (g/L) and k_{app} (h⁻¹) was -0.030 L g⁻¹ h⁻¹ (Figure 2B), demonstrating that the GR concentration hardly affects the reaction rate of TCE dechlorination. Thus, the BC phase has a strong influence on dehalogenation rates pointing to BC as the rate-limiting phase providing the actual site for the dehalogenation reaction.

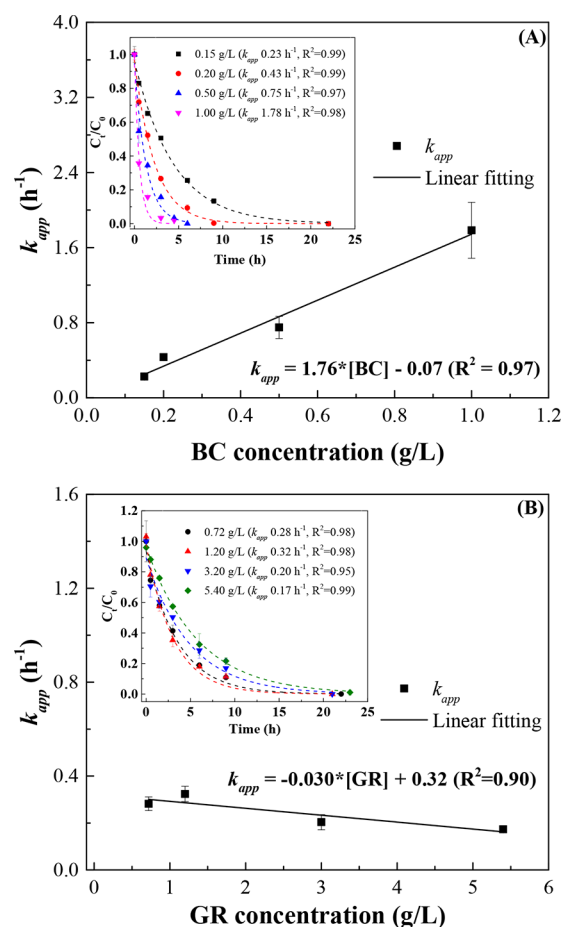


Figure 2. Pseudo-first-order rate constants (k_{app}) for TCE removal as a function of (A) BC concentration (0.15–1.00 g/L) at a constant concentration of GR of ~ 3.2 g/L and (B) GR concentration (0.72–5.40 g/L) at a constant concentration of BC of 0.15 g/L with linear fitting shown as black solid lines. Insets show the kinetic data and pseudo-first-order fits (dashed lines). Reaction conditions: 0.1 μ mol of TCE in a 5 mL solution in a nominal 10 mL headspace vial at pH 8.0 and room temperature (~ 22 °C). Error bars represent standard deviations calculated from triplicate experiments.

It is noteworthy that BC may sorb CEs because of its hydrophobic surface, implying that sorption may contribute to the overall rate of CE removal. A sorption isotherm of TCE is shown in Figure S4. From the Freundlich fit of the sorption isotherm, the fraction of TCE adsorbed at the BC concentration applied in the dehalogenation experiments (0.15 g/L) was estimated to be $\leq 7\%$ at start of the reaction, while it increased to 43% when the BC concentration increased to 1.00 g/L. It is obviously seen that both adsorption and transformation contribute to the overall rate of TCE removal, particularly at a high concentration of BC (1.00 g/L). However, the role of adsorption is very limited at low BC concentration.

The presence of reducible groups in BC was evidenced by the apparent oxidation of iron(II) in GR when GR and BC were mixed but in absence of CEs (Text S2 and Table S6). The electron-accepting capacity (EAC) of BC was calculated by normalizing the amount of oxidized iron(II) in GR to the mass of BC (Table S6), resulting in 0.21 mmol of e⁻/g of BC after averaging, which is close to the documented EAC of wood-derived biochar pyrolyzed at 700 °C of 0.22 mmol e⁻/g.⁵⁴

It is often reported that the electron-accepting moieties in biochars are dominated by quinone groups with an increasing contribution of non-quinoid structures, including polycondensed aromatic structures with increasing pyrolysis temperatures.^{54,55} Signals assigned to C=O groups (288.3 eV) and sp²-hybridized carbon (284.4 eV) were observed in the X-ray photoelectron spectroscopy (XPS) C 1s spectrum of BC (Figure S5A). Together with a G band at 1582 cm⁻¹ and four other deconvoluted bands in the Raman spectrum of BC (Figure S5B), this implies the quinoid-type groups and condensed polyaromatic structures are present in BC with a variety of defects from heteroatoms and disordered graphitic structures that were further confirmed by the XRD pattern (Figure S1A).⁵⁶

These observations indicate that graphitic components and/or quinone moieties in BC may contribute to the observed electron mediation activity of the BC. However, unlike plants biomass in which lignin and cellulose are the main substrates for biochar formation,^{55,57} bones consist of organic collagens together with 65–70% inorganic substances, mainly apatite.⁵⁸ With an ordered inorganic composite as a hard template, collagens undergo pyrolysis to form porous carbon with a high defect density, both structurally and due to heteroatom dopings, resulting in high electron conductivity.^{38,54,57,59} Although a systematic study of the unique role of bone chars as electron conductors and redox mediators is lacking, we cannot rule out the contribution of specific functional groups and structures to the electron mediation activity of BC.

Dehalogenation of PCE and TCE in Contaminated Groundwater by a GR/BC Mixture. Both PCE and TCE present at initial concentrations of 2.3 ± 0.3 and $6.6 \pm 0.2 \mu\text{M}$, respectively, in the contaminated groundwater were rapidly dechlorinated to acetylene (Figure 3). The pseudo-first-order rate constants for removal of PCE ($k_{\text{app,PCE}}$) and TCE ($k_{\text{app,TCE}}$) were 0.56 ± 0.13 and $0.24 \pm 0.09 \text{ h}^{-1}$, respectively.

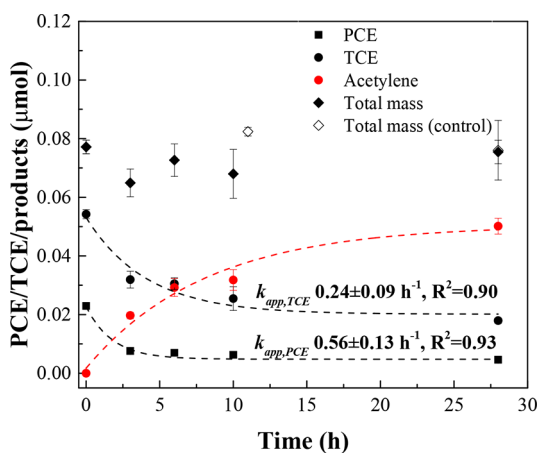


Figure 3. Pseudo-first-order kinetics of removal of PCE and TCE and acetylene formation by a GR/BC mixture in contaminated groundwater. Values on the y-axis refer to molar amounts of reactant/products per vial. Reaction conditions: initial masses of PCE of $0.023 \pm 0.001 \mu\text{mol}$ and TCE of $0.054 \pm 0.002 \mu\text{mol}$ in a 10 mL nominal headspace vial, corresponding to 2.3 ± 0.3 and $6.6 \pm 0.2 \mu\text{M}$ in aqueous solution, respectively, with $\sim 2.6 \text{ g/L}$ GR and 0.5 g/L BC, at room temperature ($\sim 22 \text{ }^\circ\text{C}$). Dashed curves for PCE, TCE, and acetylene mass vs. time are due to pseudo-first-order kinetic fitting. Error bars represent standard deviations calculated from triplicate experiments.

No remaining PCE and TCE could be detected after 140 h with a mass balance of 96%. Salt anions such as sulfate and bicarbonate present in groundwater may have the potential to affect the structure and reactivity of GRs by exchanging with interlayer anions and/or binding to the surface and blocking access to iron(II) in GR.^{18,60–63} Moreover, natural organic matter may adsorb on both GRs and BC, resulting in weakened affinity between GRs and BC.^{64,65} Though a variety of ions and dissolved organic matter were present in the tested groundwater (Table S4), it seemed that the addition of a higher concentration of BC compensated for the potential reactivity loss of the GR/BC mixture in the groundwater, exhibiting a slightly faster rate of removal of PCE and TCE than in laboratory-spiked waters. As seen to the experiments with laboratory-spiked waters, the GR was oxidized to a spinel-type phase (magnetite or maghemite) during dehalogenation (Figure S3), similar to what has been observed for GR reduction of nitrate and carbon tetrachloride by GR.^{13,15,43}

ENVIRONMENTAL SIGNIFICANCE

This study demonstrates that dechlorination of CEs by GR is facilitated by BC serving as an electron mediator and that this reaction takes place in both laboratory-spiked waters and contaminated groundwaters. In Table S7, the reaction rates for TCE dehalogenation by different iron-containing reductants are compared. The reactivity of GR/BC mixture is comparable with the reactivity of nZVI and sulfidized nZVI (S-nZVI) but much higher than that of pristine GRs or copper(II)-modified GR, magnetite (Fe_3O_4), pyrite (FeS_2), and mackinawite (FeS). Full dehalogenation but with a very low level of formation of VC or other undesired products represents a further quality of the GR/BC mixture system compared with other systems, where undesired intermediates at higher concentrations may be produced by copper(II)-modified GR,^{21,23} zinc(0),⁴⁴ iron(0),⁴⁵ and other iron minerals.¹⁰

Furthermore, both the GR and the BC (derived from waste materials) may be synthesized at low cost and easily modified in different ways to tune reactivity and polarity for application with different water types^{62,66–68} and even for DNAPL phases. Compared with iron(0), we did not observe any hydrogen formation from aqueous GR/BC suspensions as these were stable over longer time spans.

In summary, a GR/BC mixture has interesting potential as a new and fast-reacting reductant for *in situ* remediation of soils and aquifers contaminated with chlorinated solvents. Further work to elucidate the specific redox active moieties in the bone char and to investigate the reactivity in groundwaters and sediments is ongoing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.estlett.9b00053](https://doi.org/10.1021/acs.estlett.9b00053).

Texts S1 and S2, Scheme S1, Tables S1–S7, and Figures S1–S5 (PDF)

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Notes

The authors declare no competing financial interest.

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