Visible-Light-Induced Olefin Activation Using 3D Aromatic Boron-Rich Cluster Photooxidants

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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 138(22)

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2016-06-08

10.1021/jacs.6b03568

 Peer reviewed
Visible Light-Induced Olefin Activation using 3D Aromatic Boron-Rich Cluster Photooxidants


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Supporting Information Placeholder

ABSTRACT: We report a discovery that perfunctionalized icosahedral dodecaborate clusters of the type \( \text{B}_{12}(\text{OCHAr})_{12} \) (Ar = Ph or \( \text{C}_6\text{F}_5 \)) can undergo photoredox activation with visible light, leading to a new class of metal-free photooxidants. Excitation of these species occurs as a result of the charge transfer between low-lying orbitals located on the benzyl substituents and an unoccupied orbital delocalized throughout the boron cluster core. Here we show how these species, photo-excited with a benchtop blue LED source, can exhibit excited-state reduction potentials as high as 3 Volts and can participate in electron-transfer processes with a broad range of styrene monomers, initiating their polymerization. Initiation is observed in cases of both electron-rich and electron-deficient styrene monomers at cluster loadings as low as 0.005 mol%. Furthermore, photo-excitation of \( \text{B}_{12}(\text{OCHC}_6\text{F}_5)_{12} \) in the presence of a less activated olefin such as isobutylene results in the production of highly branched poly(isobutylene). This work introduces a new class of air-stable metal-free photoredox reagents capable of mediating chemical transformations.

Photoredox processes are ubiquitous in chemistry and require a chromophore to absorb a photon, triggering the formation of an excited state with a dramatically different redox potential than the parent ground state. Well-defined molecular chromophores typically possess functional groups that are capable of absorbing light, upon which an electron is promoted into a higher energy molecular orbital; in many of these cases, these photo-excited species can behave as photooxidants or photo-reductants. There exist two broad classes of molecular-based chromophores capable of undergoing photoredox processes: metal-based complexes and organic dyes. Metal-based chromophores possess excited states with highly tunable lifetimes, as they are able to reach triplet states and are also able to delocalize electrons over a number of molecular orbitals. On the other hand, the majority of organic chromophores possess relatively short-lived excited states featuring \( \pi \rightarrow \pi^* \) electronic excitations with radicals centered primarily within \( s \) or \( p \) orbitals. (Figure 1). Both classes have been utilized to harness energy from visible light enabling the formation of new chemical bonds in the context of building complex and diverse molecular architectures. A class of molecules that can contain characteristics of both metal-complexes and organic molecules are boron-rich clusters. Many polyhedral boron clusters are robust, kinetically stable, and can undergo facile functionalization chemistry. In particular, dodecaborate clusters feature a unique, 3D aromatic bonding situation in which the skeletal electrons are delocalized in three dimensions. Importantly, unfunctionalized boron-rich clusters containing B-H bonds do not absorb light in the visible region and also cannot undergo well-defined redox processes. However, researchers previously demonstrated that several classes of perfunctionalized polyhedral boron clusters are capable of undergoing reversible redox processes for example, colorless ether-functionalized \( \text{B}_{12}(\text{OR})_{12} \) clusters can undergo two sequential quasi-reversible one-electron redox processes leading to \( \text{B}_{12}(\text{OR})_{12}^+ \) and neutral \( \text{B}_{12}(\text{OR})_{12} \), respectively, both of which exhibit strong visible light absorption bands (Figure 2A–C). We hypothesized that this light absorption can be used to generate reactive photo-excited spe-

![Figure 1. Molecular chromophores with photoredox activity include transition-metal complexes (e.g., I) and organic dyes (e.g., pyrylium II). This work reports B_{12}(OR)_{12} clusters as a new class of photoredox-active molecular chromophores (III).](image-url)
cies, though up to this point no such behavior has been realized for this class of boron-rich clusters.\textsuperscript{20,21} Herein, we demonstrate the visible light photoredox behavior of B\textsubscript{12}(OR)\textsubscript{12} clusters which interact with olefinic species and subsequently initiate their polymerization. Specifically, we show that this process occurs across a wide array of both electron-rich and electron-deficient styrene monomers as well as isobutylene. The latter process represents the first visible light-induced metal-free polymerization leading to highly branched poly(isobutylene).

![Figure 2](image1)

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Figure 2. (A) Reversible oxidation/reduction of substituted boron-rich clusters (0/1 is shown). (B) Cyclic voltammogram of 1a and 1b. (C) UV-Vis spectrum of photo-oxidants 1a and 1b in their fully oxidized states and mono-anionic states. (D-E) Ball-and-stick and space-filling representations of the X-ray crystal structure of 1b.

We recently developed an improved synthetic method which affords functionalized B\textsubscript{12}(OR)\textsubscript{12} clusters with tunable electrochemical properties (Figure 2).\textsuperscript{18,19} During the course of our synthetic investigations, we discovered that upon leaving cluster species 1a in the presence of 4-methoxystyrene (2a) in a dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) solution, a viscous mixture resulted, indicating polymerization of 2a (see SI). Interestingly, the same reaction did not produce any polymer when left in the dark, suggesting that this process is likely photo-driven. We decided to investigate this interesting behavior more closely via controlled irradiation of a 2M solution of 2a in CH\textsubscript{2}Cl\textsubscript{2} at room temperature under an N\textsubscript{2} atmosphere with 0.5 mol\% 1a (\(\lambda_{\text{max abs}} = 470\) nm) illuminated under blue LED light (450 nm). After 4 hours of irradiation, the reaction produced polymer in less than 10% yield (Table 1). During the course of our investigations, Nicewicz reported an elegant pyrilli-catalyzed (II, Figure 1) photo-mediated polymerization protocol of 2a and suggested that the mechanism of the polymerization likely occurs through a cationic route.\textsuperscript{22} We hypothesized that a similar process might be in operation with the B\textsubscript{12}(OBn)\textsubscript{12} system and if so, a cluster functionalized with more electron-withdrawing substituents would increase the oxidation potential of the photoinitiator, thereby providing greater photo-oxidizing power of these species. Therefore, B\textsubscript{12}(OCH\textsubscript{2}F)\textsubscript{12} (1b) was synthesized in a manner analogous to that of 1a and was isolated as a yellow solid in 63% yield (Figure 2D). UV-Vis absorption shows that 1a and 1b exhibit similar \(\lambda_{\text{max}}\) wavelengths (470 and 454 nm, respectively; Figure 2C), and, notably, cyclic voltammetry (CV) experiments show a 500 mV increase in the -1/0 redox couple of 1b compared to 1a (Figure 2B).

Addition of 0.1 mol\% 1b to a 2M CH\textsubscript{2}Cl\textsubscript{2} solution of 2a under ambient lighting resulted in the instantaneous formation of a polymer gel with a high dispersity (see SI and Table 1). Surprisingly, reducing the loading of 1b to 0.005 mol \% still resulted in immediate gelation upon addition to 2a. Under optimized conditions, irradiation of 0.5 mol \% 1b in a 0.2 M CH\textsubscript{2}Cl\textsubscript{2} solution of 2a with 450 nm light for 6 hours produces 198 kDa polymer in 97% yield (Table 1).

![Figure 3](image2)

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In order to understand the observed photo-initiation we performed TD-DFT studies on 1a and 1b. This work reveals the existence of a favorable charge transfer (aryl to boron cluster) excitation pathway leading to an excited species with a redox potential roughly matching the one-electron oxidation potential of styrene (Figure 3).

Table 1. Polymerization of 2a. Number—average molecular weight (\(M_n\)) and molecular weight dispersity (D) determined by GPC. Reported data are the average over two runs.

<table>
<thead>
<tr>
<th>Oxidant (mol%)</th>
<th>Conc.</th>
<th>(M_n) (kDa)</th>
<th>Time</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a (0.5)</td>
<td>2 M</td>
<td>1.3</td>
<td>13.8</td>
<td>4 h</td>
</tr>
<tr>
<td>1b (0.005)</td>
<td>2 M</td>
<td>2.2</td>
<td>15.0</td>
<td>255 h</td>
</tr>
<tr>
<td>1a (0.05)</td>
<td>0.2 M</td>
<td>1.7</td>
<td>188</td>
<td>1 h</td>
</tr>
</tbody>
</table>

This is consistent with the previous computational work of Schleid on B\textsubscript{12}(OH)\textsubscript{12} monoradical species.\textsuperscript{23} Our proposed mechanism involves the generation of a potent photo-oxidant by visible light promotion of an electron from a low-lying occupied orbital on an aryl ring to the cluster-based LUMO. The resulting excited species initiates polymerization via a single electron oxidation of styrene (or styrene derivative), producing a cluster-based radical...
anion—the stabilities of which are documented\textsuperscript{12,19}—and a monomer-based radical cation. Fluorescence decay measurements were employed to benchmark the photoexcited properties of 1b. The excited-state lifetime of 1b, measured from the 600 nm emission maximum, was found to be $\sim$380 picoseconds (see SI, Figure S50). From this data and the known ground-state reduction potential (-1/0 couple), an excited-state reduction potential value of $\sim$2.98 V (vs. SCE) was estimated for 1b (see SI, Section VI). This value is consistent with the ability of 1b to initiate the polymerization of 2a. The photo-induced oxidative behavior of these persubstituted clusters is unprecedented and stands as a new contribution to the field of molecular photoredox chemistry. Furthermore, the kinetic stability of both the neutral and monoanionic clusters due to the 3D delocalization of valence electrons within the cluster core provides an opportunity for implementation in systems amenable to photochemistry involving a diversity of functional groups and reactive radical species. Notably, the polymerization of 2a initiated by 1b also proceeds under ambient conditions, affording a polymer of similar quality that was generated from a reaction set up under inert gas conditions. Given this successful polymerization, we were interested in further exploring the reactivity and electron transfer processes of 1b. We set out to expand our substrate scope by employing styrene monomers 2b-2i, which possess a range of electronic and steric profiles. Polymerization of styrene (2b) with 0.1 mol% 1b produced polystyrene in yields averaging 96% in 4 hours without incorporation of 1a in the polymer (See SI, Figures S22 and S23). Varying the cluster loading did not have an effect on the molecular weight or dispersity of polystyrene (See SI, Figure S15). Furthermore, propagation proceeds in the absence of light indicating that formation of the radical anion on 1b is irreversible (See SI, Figure S46).

Table 2. Substrate scope for polymerization using 1b.$^a$

![Chemical structures and polymerization conditions](image)

Table 2: Substrate scope for polymerization using 1b.$^a$

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Polymerization Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu</td>
<td>4 hours, 96%</td>
</tr>
<tr>
<td>CH</td>
<td>4 hours, 96%</td>
</tr>
<tr>
<td>BuF</td>
<td>4 hours, 85%</td>
</tr>
<tr>
<td>Cl</td>
<td>4 hours, 99%</td>
</tr>
</tbody>
</table>

$^a$General reaction conditions: Monomer (50 $\mu$L, 0.2–2.0 M CH$_2$Cl$_2$ solution), 1b (0.1 mol%), 4–24 hours. Isolated yields after precipitation.

Notably, the pyridinium-based catalyst utilized by Nicewicz does not produce polymer, which is consistent with the stronger photooxidizing power of 1b compared to II. Polymers of other electron-rich styrenes are generated in the presence of 1b within hours in good yield (Table 2: 2c-e, 2i); more electron-poor substrates can also be polymerized (Table 2: 2f-h) albeit with somewhat diminished efficiency, consistent with our mechanistic hypothesis. The perfluorinated nature of 1b led us to wonder whether the successful polymerization of such a wide range of styrene monomers in comparison to either 1a or II (Figure 1) may be due in part to specific interactions between the fluorinated rings of the initiator and the monomer. Such intermolecular $\pi$-$\pi$ type interactions are well-recognized.$^{24}$ We therefore subjected styrene (2b) to the optimized polymerization conditions in the presence of 1b employing benzene as solvent. Polymerization of 2b produced polystyrene in 96% yield in 4 hours, though $M_w$ values observed for polystyrene produced in benzene are slightly smaller than that of polymers produced in CH$_2$Cl$_2$. Given the likelihood of competitive association of solvent with the fluorinated aryl rings of 1b, one would expect a reduction in polymer yield using aromatic solvents if these $\pi$-$\pi$ type interactions are essential to polymerization. Therefore, this experiment suggests that if $\pi$-$\pi$ type interactions between the initiator and the monomer exist, they are not critical for the polymerization overall.

We were further interested to see if 1b, in light of its high excited-state reduction potential (vide supra), might coax reactivity out of more challenging substrates. Cationic polymerization of isobutylene, a less activated vinyl substrate than styrene, typically utilizes metal catalysts or harsh conditions.$^{25}$ Irradiation (450 nm) of a 2mM solution of 1b in CH$_2$Cl$_2$ at pressures of isobutylene as low as 1 psi for 4 hours at room temperature produced polymeric material.

Figure 4: $^1$H NMR spectrum of poly(isobutylene) produced from irradiation of 1b with 450 nm light under 4 psi isobutylene. Label A indicates protons of the olefinic chain end; B/C, allylic protons of the chain end; D, methine protons. Neither irradiation of isobutylene in the absence of 1b nor stirring 1b in the presence of isobutylene in the dark, under otherwise identical reaction conditions as described above, afforded polymer. Interestingly, $^1$H and $^{13}$C NMR spectra of the formed polymer material closely resembles the polymer obtained previously by Michl and is consistent with the formation of a highly branched poly(isobutylene) (see Figure 4 and SI).$^{26}$ This represents the first example of a visible light-activated polymerization of isobutylene under metal-free conditions. In conclusion, we have demonstrated—for first time—that icoshedral dodecabrate clusters of the type $\text{B}_{12}(\text{OR})_{12}$, where R is a benzyl derivative, can undergo photoexcitation with visible light and activate styrene derivatives towards polymerization. Increasing the electron-withdrawing power of the benzyl substituents results in increased activity, and that allowed...
us to develop the first example of a metal-free visible light photooxidant capable of polymerizing isobutylene. DFT calculations suggest that photoexcitation in these species occurs through the promotion of an electron from a low-lying, aryly-based orbital on the cluster substrate to an unoccupied cage-based orbital by visible (~450 nm) light. Overall, our work indicates that B2-based clusters can behave as powerful yet air-stable photoredox reagents. This work also expands on an exciting untapped potential of molecular main-group systems as unique photoactive components. Current efforts in our group are focused on underpinning the mechanism of the discovered photoexcitation and the further tuning of the disclosed system.  

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures and characterization, crystallographic and computational data, and fluorescence spectroscopy. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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ACKNOWLEDGMENT

A.M.S. thanks UCLA Department of Chemistry and Biochemistry for support start-ups and 3M for a Non-Tenured Faculty Award. M.S.M. thanks the NSF for the Bridge-to-Docotrate and the Predoctoral (GRFP) Fellowships. H.B.G. and O.S.S. acknowledge funding from the NIH (DK019037) and the Arnold and Mabel Beckman Foundation. A.N.A. thanks the NSF CAREER Award CHE-1351968. Y.W. thanks the CSST Scholarship. H.D.M. thanks the NSF (CHE-1507735) for funding. B.M.I. thanks UCLA for a Dissertation Year Fellowship. The authors thank Mr. Daniel Hatfield (UCLA) for assistance with computational studies and Prof. Andrea Kasko (UCLA) for generously allowing access to her GPC instrument.

REFERENCES

visible light

Air-Stable Boron Cluster Photooxidant