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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 $B_{12}(OCH_2Ar)_{12}$ ($Ar = Ph$ or C_6F_5) can undergo photo-excitation with visible light, leading to a new class of metal-free photooxidants. Excitation in 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 bench-top 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 $B_{12}(OCH_2C_6F_5)_{12}$ 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.¹ 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.² 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.³ (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.⁴

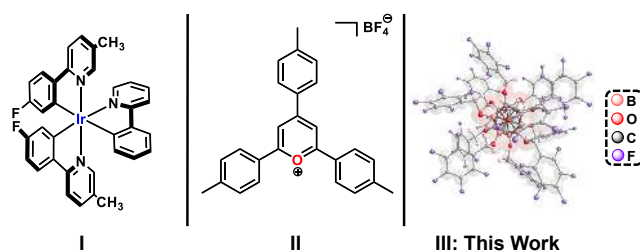


Figure 1. Molecular chromophores with photoredox activity include transition-metal complexes (e.g., **I**⁵) and organic dyes (e.g., pyrylium⁶ **II**). This work reports $B_{12}(OR)_{12}$ clusters as a new class of photoredox-active molecular chromophores (**III**).

A class of molecules that can contain characteristics of both metal-complexes and organic molecules are boron-rich clusters.⁷⁻¹⁰ Many polyhedral boron clusters are robust, kinetically stable, and can undergo facile functionalization chemistry.⁹⁻¹¹ In particular, dodecaborate clusters feature a unique, 3D aromatic bonding situation in which the skeletal electrons are delocalized in three dimensions.¹¹⁻¹² 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.^{13,14} However, researchers previously demonstrated that several classes of perfunctionalized polyhedral boron clusters are capable of undergoing reversible redox processes.^{11a-b,f 15-19} For example, colorless ether-functionalized $[B_{12}(OR)_{12}]^{2-}$ clusters can undergo two sequential quasi-reversible one-electron redox processes leading to $[B_{12}(OR)_{12}]^{1-}$ and neutral $B_{12}(OR)_{12}$, respectively, both of which exhibit strong visible light absorption bands (Figure 2A-C).¹⁶⁻¹⁹ We hypothesized that this light absorption can be used to generate reactive photo-excited spe-

cies, though up to this point no such behavior has been realized for this class of boron-rich clusters.^{20,21} Herein, we demonstrate the visible light photoredox behavior of $B_{12}(OR)_{12}$ 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).

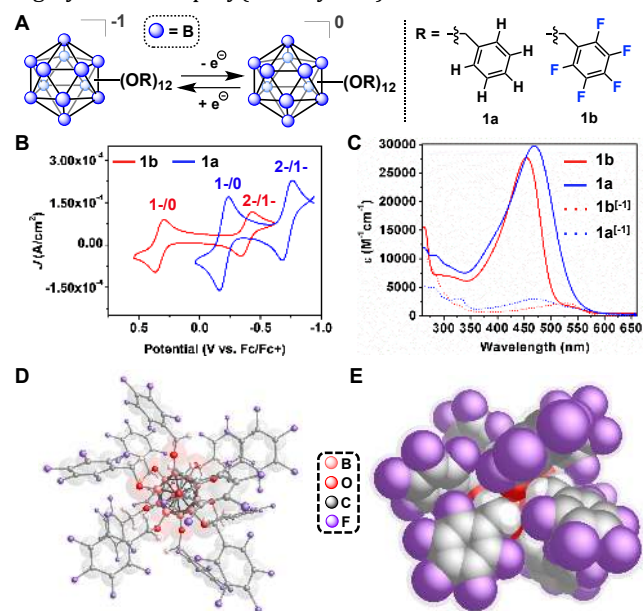


Figure 2. (A) Reversible oxidation/reduction of substituted boron-rich clusters (0/-1 is shown). (B) Cyclic voltammogram of **1a** and **1b**. (C) UV-Vis spectrum of photo-oxidants **1a** and **1b** in their fully oxidized states and mono-anionic states. (D-E) Ball-and-stick and space-filling representations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

We recently developed an improved synthetic method which affords perfunctionalized $B_{12}(OR)_{12}$ clusters with tunable electrochemical properties (Figure 2).^{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_2Cl_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_2Cl_2 at room temperature under an N_2 atmosphere with 0.5 mol% **1a** ($\lambda_{max,abs} = 470$ 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 pyrilium-catalyzed (**II**, Figure 1) photo-mediated polymerization protocol of **2a** and suggested that the mechanism of the polymerization likely occurs through a cationic route.²² We hypothesized that a similar process might be in operation with the $B_{12}(OBn)_{12}$ system and if so, a cluster functionalized with more electron-withdrawing substituents would increase the oxidation potential of the photo-initiator, thereby providing greater photo-oxidizing power

of these species. Therefore, $B_{12}(OCH_2C_6F_5)_{12}$ (**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 λ_{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_2Cl_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 0.05 mol% **1b** in a 0.2 M CH_2Cl_2 solution of **2a** with 450 nm light for 6 hours produced 198 kDa polymer in 97% yield (Table 1).

Oxidant (mol%)	Conc.	Φ	M_n (kDa)	Time	Yield
1a (0.5)	2 M	1.3	13.8	4 h	< 10%
1b (0.1)	2 M	15.2	255	< 1m	81%
1b (0.005)	2 M	1.7	198	< 1m	90%
1b (0.05)	0.2 M	1.7	198	6 h	97%

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

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).

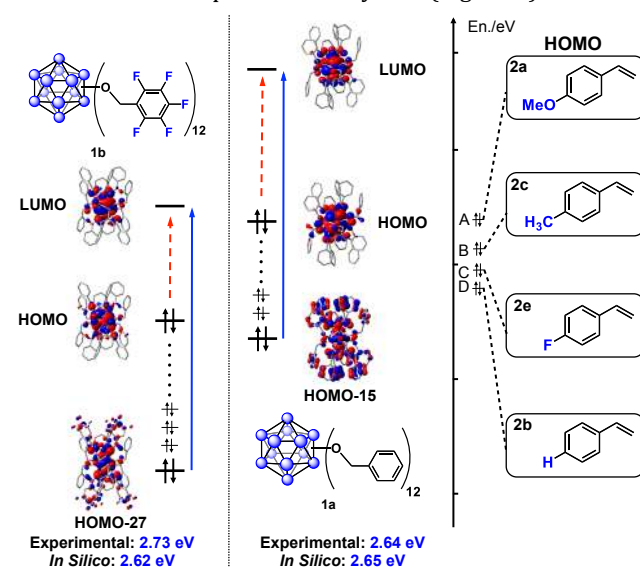
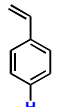
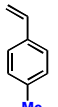
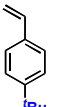
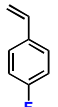
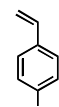
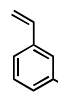
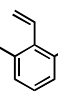
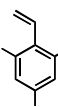


Figure 3. TD-DFT studies indicating charge transfer excitation pathway in **1a/1b**. Also shown are the relative energies of the HOMO levels of monomers **2a-c, e**.

This is consistent with the previous computational work of Schleid on $B_{12}(OH)_{12}^{1-}$ monoradical species.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^{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 ~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 ~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 as that 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 poly-**2b** (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**

			
4 hours, 96% M_n : 9.9 kDa; \bar{D} : 2.3	4 hours, 96% M_n : 21.2 kDa; \bar{D} : 5.8	4 hours, 85% M_n : 9.7 kDa; \bar{D} : 2.4	4 hours, 99% M_n : 170 kDa; \bar{D} : 2.4
			
4 hours, 94% M_n : 227 kDa; \bar{D} : 3.2	4 hours, 41% M_n : 6.2 kDa; \bar{D} : 2.2	4 hours, 28% M_n : 10.0 kDa; \bar{D} : 1.6	4 hours, 98% M_n : 76.9 kDa; \bar{D} : 2.6

^a**General reaction conditions:** Monomer (50 μ L, 0.2–2.0M CH₂Cl₂ solution), **1b** (0.1 mol%), 4–24 hours. Isolated yields after precipitation.

Notably, the pyrilium-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 π - π 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 CH₂Cl₂. 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 π - π type interactions are essential to polymerization. Therefore, this experiment suggests that if π -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 CH₂Cl₂ at pressures of isobutylene as low as 1 psi for 4 hours at room temperature produced polymeric material.

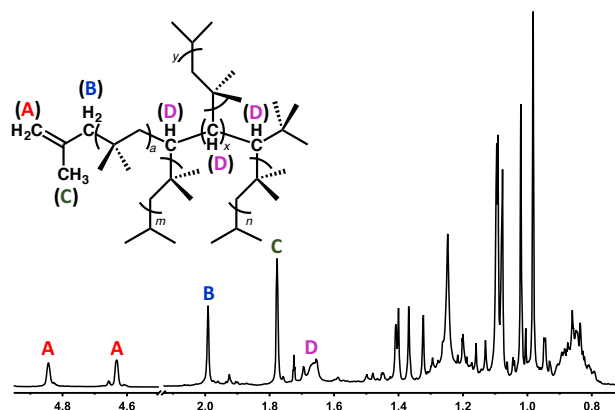


Figure 4. ¹H NMR spectrum of poly(isobutylene) produced from irradiation of **1b** with 450 nm light under 4 psi isobutylene. Label A indicates protons of the olefinic chain end; B/C, allylic protons of the chain end; D, methine protons.

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, ¹H and ¹³C 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 icosahedral dodecaborate clusters of the type B₁₂(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, aryl-based orbital on the cluster substituent to an unoccupied cage-based orbital by visible (~450 nm) light. Overall, our work indicates that B₁₂-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.^{11,27} Current efforts in our group are focused on underpinning the mechanism of the discovered photoexcitation and the further tuning of the disclosed system.²⁸

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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