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

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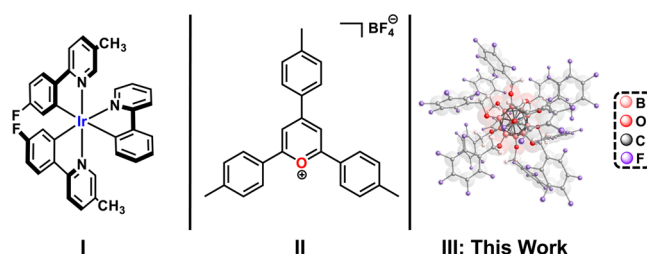
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Ⓢ *Supporting Information*

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 photoexcitation 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 benchtop blue LED source, can exhibit excited-state reduction potentials as high as 3 V 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 photo-redox reagents capable of mediating chemical transformations.

Figure 1. Molecular chromophores with photoredox activity include transition-metal complexes (e.g., **I**[5]) and organic dyes (e.g., pyrylium[6] **II**). This work reports $B_{12}(OR)_{12}$ clusters as a new class of photoredox-active molecular chromophores (**III**).

P hotoredox processes are ubiquitous in chemistry and require a chromophore to absorb a photon, triggering the formation of an excited state with a redox potential dramatically different than that of 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 photoexcited species can behave as photooxidants or photoreductants. 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 delocali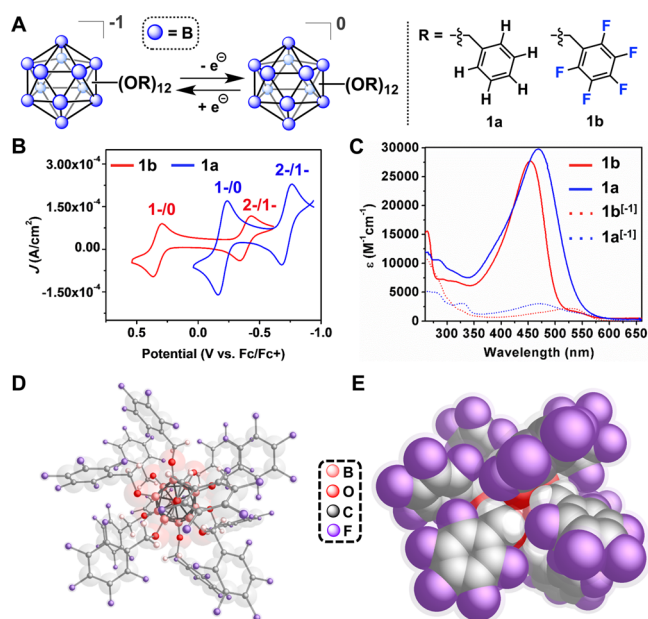ze electrons over a number of molecular orbitals.[2] On the other hand, the majority of organic chromophores possess relatively short-lived excited states featuring $\pi \rightarrow \pi^*$ electronic excitations with radicals centered primarily within s or p orbitals.[3] (Figure 1). Both classes have 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]

Boron-rich clusters are a class of molecules that can contain characteristics of both metal complexes and organic molecules.[7−10] Many polyhedral boron clusters are robust and 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] However, researchers previously demonstrated that several classes of perfunctionalized polyhedral boron clusters are capable of undergoing reversible redox processes.[11a,b,f,14−17] For example, colorless ether-functionalized $[B_{12}(OR)_{12}]^{2-}$ clusters can undergo two sequential quasi-

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 photooxidants **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**.

reversible one-electron redox processes, leading to $[B_{12}(OR)_{12}]^-$ and neutral $B_{12}(OR)_{12}$, respectively, both of which exhibit strong visible light absorption bands (Figure 2A−C).[15−17] We hypothesized that this light absorption can be used to generate reactive photoexcited species, though up to this point no such behavior has been realized for this class of boron-rich clusters.[18] Here 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(iso-butylene).

We recently developed an improved synthetic method which affords perfunctionalized $B_{12}(OR)_{12}$ clusters with tunable electrochemical properties (Figure 2).[17] 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 Supporting Information (SI)). Interestingly, the same reaction did not produce any polymer when left in the dark, suggesting that this process is likely photodriven. We decided to investigate this interesting behavior more closely via controlled irradiation of a 2 M 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 h of irradiation, the reaction produced polymer in <10% yield (Table 1). During the course of our investigations, Nicewicz reported an elegant pyrilium-catalyzed (**II**, Figure 1), photomediated polymerization protocol of **2a** and suggested that the mechanism of the polymerization likely occurs through a cationic route.[19] 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

Table 1. Polymerization of 2a: Number-Average Molecular Weight (M_n) and Molecular Weight Dispersity ($Đ$) Determined by GPC[a]

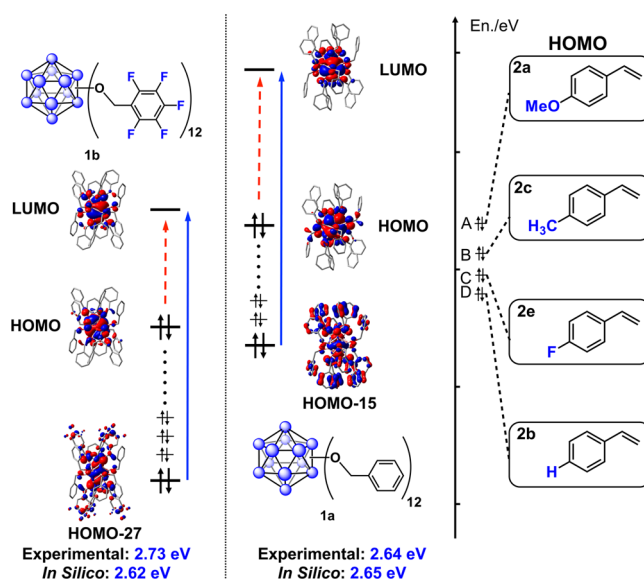| Oxidant (mol%)	Conc.	$Đ$	M_n (kDa)	Time	Yield
1a (0.5)	2 M	1.3	13.8	4 h	< 10%
1b (0.1)	2 M	15.2	255	< 1m	81%
1b (0.005)	2 M	1.7	198	< 1m	90%
1b (0.05)	0.2 M	1.7	198	6 h	97%

[a]Reported data are the average over two runs.

photoinitiator, thereby providing greater photooxidizing 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 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 2 M 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 h produced 198 kDa polymer in 97% yield (Table 1).

To understand the observed photoinitiation, 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).

This is consistent with the previous computational work of Schleid on $B_{12}(OH)_{12}^-$ monoradical species.[20] Our proposed mechanism involves the generation of a potent photooxidant by visible light promotion of an electron from a low-lying occupied orbital on aryl rings to the cluster-based LUMO. The resulting excited species initiates polymerization via a single-electron
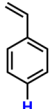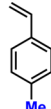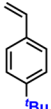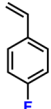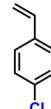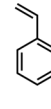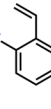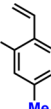

Figure 3. TD-DFT studies indicating charge-transfer excitation pathway in **1a/1b**. Also shown are the relative energies of the HOMO levels of monomers **2a−c,e**.

oxidation of styrene (or styrene derivative), producing a cluster-based radical anion—the stabilities of which are documented[12,17c]—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 ps (SI, Figure S50). From these 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** (SI, section VI). This value is consistent with the ability of **1b** to initiate the polymerization of **2a**. The photoinduced 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 mono-anionic 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 h without incorporation of **1a** in the polymer (SI, Figures S22 and S23). Varying the cluster loading did not have an effect on the molecular weight or dispersity of poly-**2b** (SI, Figure S15). Furthermore, propagation proceeds in the absence of light, indicating that formation of the radical anion on **1b** is irreversible (SI, Figure S46).

Notably, the pyrilium-based catalyst utilized by Nicewicz does not produce polymer, which is consistent with the stronger photooxiding 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,i**); more electron-poor

Table 2. Substrate Scope for Polymerization Using 1b[a]

2b	2c	2d	2e
H	Me	tBu	F
4 hours, 96%	4 hours, 96%	4 hours, 85%	4 hours, 99%
M_n: 8.4 kDa; Đ: 2.3	M_n: 21.2 kDa; Đ: 5.8	M_n: 9.7 kDa; Đ: 2.4	M_n: 170 kDa; Đ: 2.4

2f	2g	2h	2i
Cl	Cl	F, F	Me, Me, Me
4 hours, 94%	4 hours, 41%	4 hours, 28%	4 hours, 98%
M_n: 227 kDa; Đ: 3.2	M_n: 6.2 kDa; Đ: 2.2	M_n: 10.0 kDa; Đ: 1.6	M_n: 76.9 kDa; Đ: 2.6

[a]General reaction conditions: monomer (50 μL, 0.2−2.0 M CH$_2$Cl$_2$ solution), **1b** (0.1 mol%), 4−24 h. Isolated yields after precipitation.

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.[21] 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 h, though M_w values observed for polystyrene produced in benzene are slightly smaller than those 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 when 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.[22] Irradiation (450 nm) of a 2 mM solution of **1b** in CH$_2$Cl$_2$ at isobutylene pressures as low as 1 psi for 4 h at room temperature produced polymeric material. Neither irradiation of isobutylene in the absence of **1b** nor stirring **1b** in the presence of isobutylene in the dark, under reaction conditions otherwise identical to those described above, afforded polymer. Interestingly, ^{1}H and ^{13}C NMR spectra of the formed polymer material closely resembles those of the polymer obtained previously by Michl and are consistent with the formation of a highly branched poly(isobutylene) (see Figure 4 and SI).[23] This represents the first example of a visible light-activated polymerization of isobutylene under metal-free conditions.
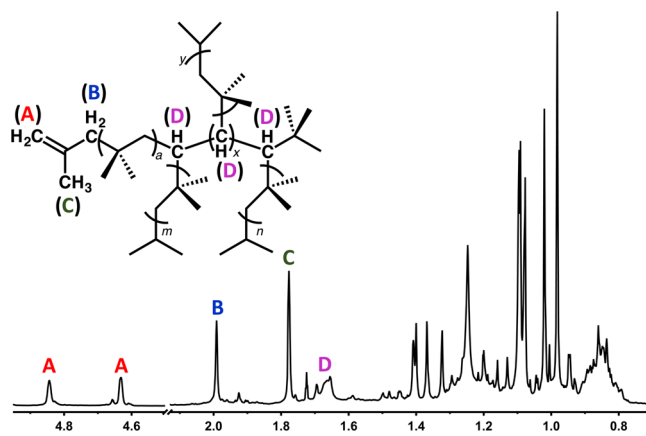

Figure 4. ^{1}H NMR spectrum of poly(isobutylene) produced from irradiation of **1b** with 450 nm light under 4 psi isobutylene. Label A indicates protons of the olefinic chain end; B/C, allylic protons of the chain end; D, methine protons.

In conclusion, we have demonstrated—for the first time—that icosahedral dodecaborate clusters of the type B$_{12}$(OR)$_{12}$, where R is a benzyl derivative, can undergo photoexcitation with visible light and activate styrene derivatives toward 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 B_{12}-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.[11,24] Current efforts in our group are focused on underpinning the mechanism of the discovered photoexcitation and the further tuning of the disclosed system.[25]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03568.

> Synthetic procedures and characterization, crystallographic and computational data, and fluorescence spectroscopy (PDF)
>
> X-ray crystallographic data for **1b** (CIF)
>
> Video showing the action of the catalyst (MOV)

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Author Contributions

‖M.S.M. and J.C.A. contributed equally to the project.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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