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Singlets-Driven Photoredox Catalysts: Transforming Noncatalytic Red Fluorophores to Efficient Catalysts

Sara Abuhadba,§ Charlotte Fuqua,§ Anthony Maltese, Caroline Schwinn, Neo Lin, Angela Chen, Rilee Martzloff, Tatiana V. Esipova,* and Tomoyasu Mani*

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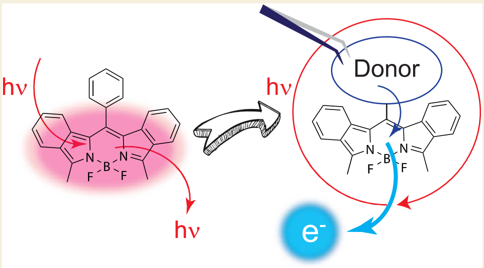

ABSTRACT: Red-light absorbing photoredox catalysts offer potential advantages for large-scale reactions, expanding the range of usable substrates and facilitating bio-orthogonal applications. While many red-light absorbing/emitting fluorophores have been developed recently, functional red-light absorbing photoredox catalysts are scarce. Many photoredox catalysts rely on long-lived triplet excited states (triplets), which can efficiently engage in single electron transfer (SET) reactions with substrates. However, triplets of π-conjugated molecules are often significantly lower in energy than photogenerated singlet excited states (singlets). Combined with the inherent low energy of red light, this could limit the reductive/oxidative powers. Here, we introduce a series of sustainable heavy atom−free photoredox catalysts based on red-light absorbing dibenzo-fused BODIPY. The catalysts consist of two covalently linked units: a dibenzo-fused BODIPY fluorophore and an electron donor, arranged orthogonally. Excitation of the dibenzoBODIPY unit induces charge separation (CS) from the donor to the dibenzoBODIPY unit, forming a radical pair (RP) state. Unlike the regular BODIPY counterparts, these catalysts do not form triplets. Instead, SET occurs from the high-energy singlet-born RP states, preventing energy loss and effectively utilizing the low-energy red light. The proximity of donor molecules allows efficient charge separation despite the CS being uphill in energy. The molecules demonstrate efficient catalysis of Atom Transfer Radical Addition (ATRA) reaction, yielding products with high yields ranging from 70 to 90%, while the molecule without a donor group does not exhibit catalytic activity. The mechanistic studies by transient absorption and electron paramagnetic resonance (EPR) spectroscopy methods support the proposed mechanism. The study presents a new molecular design strategy for converting noncatalytic fluorophores to efficient photoredox catalysts operating in the red spectral region.

KEYWORDS: *heavy atom-free photoredox catalysts, green chemistry, sustainable photoredox catalysts, benzoBODIPY, electron transfer, red light*

INTRODUCTION

Photoredox catalysis has garnered considerable attention in the chemical community and beyond, as it enables a wide range of chemical reactions,[1−5] which are usually unattainable with thermal activation. Photoredox catalysts work by absorbing light to reach an excited state that enables them to transfer electrons to or from stable substances. This process forms highly reactive intermediates, like radical cations and anions, allowing chemical reactions to occur gently and precisely.

Most photoredox catalysts developed to date require ultraviolet (UV) or visible light for excitation. However, UV and visible light have low penetration through the reaction media, impeding the efficiency of large-scale reactions. Moreover, in the case of modifications of biological molecules, such as proteins,[6] DNA,[7] etc., treatment with high-energy light is undesirable due to the potential damage. Red/Near-Infrared (NIR) light-absorbing photoredox catalysts could overcome these problems. The red/NIR photons have lower energy and higher penetration depth through various media, including in vivo, since most organic substrates and all biological molecules do not absorb light in the red to near infrared (NIR) region (600−1100 nm). In the future perspective, red/NIR-photoredox catalysts could complement the traditional UV/vis-photoredox catalysts in multistep one-pot synthesis, where one or another type of reaction will be initiated upon selective excitation with light of particular wavelengths. Yet, there are only a few examples of NIR photoredox catalysts identified: Os(II) polypyridyl complexes,[8] cyanine-based photoredox catalysts,[9] porphyrins,[10,11] Cu(I) bis(α-diimine) complex −9,10-dicyanoanthracene dual catalyst system,[12] and Sn(IV) complex of chlorine.[13]

Most current generation of photoredox catalysts,[5,14] including those NIR photoredox catalysts mentioned above

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use heavy atoms, such as iridium (Ir), ruthenium (Ru), and bromine (Br), to enhance the production of triplet excited states (triplets) via heavy-atom effects.[15] The long lifetime of triplets (>100 ns) is beneficial for efficient single electron transfer reactions, compared to singlet excited states (singlets), whose lifetime is usually <10 ns for π-conjugated molecules. However, the reliance on heavy atoms in the production of triplets could lead to unwanted side effects and constrain photocatalyst design. Recently, we reported a strategy to enhance triplets' formation through spin−orbit charge-transfer intersystem crossing (SOCT-ISC)[16−19] in a series of orthogonal Donor−Acceptor (D−A)-type boron dipyrromethene (BODIPY)-based dyads without relying on heavy atoms. In the SOCT-ISC mechanism, photogenerated singlet radical pairs (RP) recombine into the local triplets. Furthermore, we demonstrated that those molecules can efficiently catalyze UV- and visible-light-driven Atom Transfer Radical Addition (ATRA) reactions.[20]

In parallel, various red/NIR fluorophores have been developed for biomedical optical microscopy and spectroscopy applications.[21−35] They often have high extinction coefficients and high emission quantum yields, including π-extended BODIPYs, xanthene, constrained cyanine dyes, porphyrins, and other π-conjugated molecules. Yet, due to the large exchange couplings, the energy of triplets of π-conjugated molecules is often >0.6−0.8 eV lower in energy than photogenerated singlets,[36,37] resulting in a significant waste of the initial photon energy.

In this work, we converted one of such fluorophores into functional photoredox catalysts. We synthesized a new series of (D−A) dibenzoBODIPY-based dyads with excitation in the red spectral region where dibenzoBODIPY acts as a photon absorber and electron acceptor (Figure 1). (D−A) dibenzoBODIPY can efficiently catalyze ATRA reactions, whereas no catalytic activity was observed without a donor group. The catalytic activity comes from the high-energy singlet-born charge-separated states (or singlet RPs) that were not readily available from the triplets, preserving the low energy of red lights. Our work presents a new design strategy for photoredox catalysts using low-energy red/NIR lights.

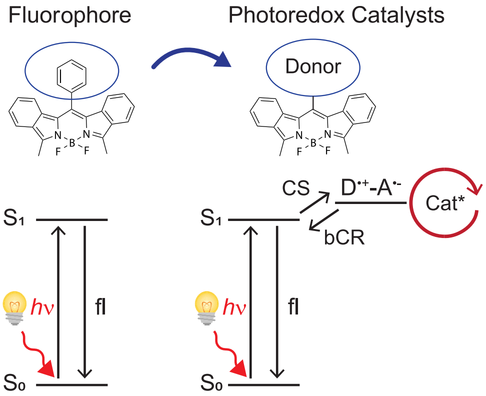


Figure 1. Inserting a donor group converts a red fluorophore to efficient photoredox catalysts.

■ RESULTS AND DISCUSSION

The photoredox catalyst is based on a highly emissive red-light absorbing *meso*-phenyl substituted dibenzoBODIPY (**4a**).[38] We substituted a phenyl group with an electron donor, covalently linked to the *meso*-position of dibenzoBODIPY such as 9-anthracenyl (**4b**), 3-perylenyl (**4c**), 1-pyrenyl (**4d**) and N-ethylcarbazol-4-yl (**4e**) (Figure 2a). In these dyads, dibenzoBODIPY units serve as an electron acceptor. The combination of benzene extensions of BODIPY and bulky donor keeps the two units physically close to each other and locks the two planes of these units orthogonal to each other. The (D−A)-dibenzoBODIPY-based dyads **4b**−**e** were synthesized using pyrrole **1**[38] and the respective carbaldehydes **2b**−**e** following the procedure developed by Ono for **4a**,[38] with slight modifications. In this context, dibenzoBODIPY dyads **4a**−**e** were obtained with 50−60% yield from intermediate bicyclo-fused BODIPY dyads **3a**−**e** through a thermal retro-Diels−Alder reaction. The preparation of bicyclo-fused BODIPY dyads **3a**−**e** is a sequential three steps, one-pot process, which involves condensation of bicyclo-fused pyrrole **1** with corresponding carbaldehydes under acidic conditions, oxidation of the formed dipyrromethanes into dipyrrins using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), and boron insertion under basic conditions through treatment with $BF_3 \cdot Et_2O$.

The catalysts' absorption spectra are composed of two bands: the absorption of the dibenzoBODIPY unit, with a maximum at λ_{max} = 600 nm ($\varepsilon_{max} \sim 10^5$ M^{-1} cm^{-1}), and the absorption of the corresponding donor in the UV region, 300−400 nm (Figure 2b and Table S1). Thus, the catalysts can be selectively excited either in the UV or red spectral region.

We assessed the performance of (D−A) dyads in light-driven photoredox reactions and examined how this performance correlates with the photophysical processes of the excited states. As our model reaction, we used the Atom Transfer Radical Addition reaction (ATRA). We tested compounds **4b**−**e** and a reference compound **4a** in the ATRA reaction between bromomalonate and methyl 5-hexenoate (Scheme 1, entries 1−5). The reaction was performed for 48 h by light irradiation (λ = 575 nm) of deoxygenated acetonitrile/water, 3:1 solutions in the presence of 1.5 mol % of the catalyst, and sodium ascorbate as a sacrificial donor. Lewis acid − LiBr was added to facilitate carbon−halogen bond dissociation in bromomalonate as previously described.[20,39] The reaction mixtures after reactions were purified by column chromatography on silica gel, and the yields of the isolated compounds are shown in Scheme 1. All catalysts **4b**−**e** showed quite good catalytic activity, and the product was isolated with ∼70% yield in all cases. In the case of catalyst **4d**, a yield of 91% was obtained (Scheme 1, Entries 2−5). However, when reference compound **4a** was used as the catalyst, only traces of the product were observed by thin-layer chromatography (TLC) (Scheme 1, Entry 1). Catalyst **4e** performed well in the ATRA reaction with other alkenes, such as 5-hexenol and *N*-Boc-protected allylamine, giving the products with 70 and 64% yields, respectively (Scheme 1, Entries 6−7). We also performed several control experiments, which showed that the reaction does not proceed without the catalyst or in the dark, confirming the photocatalytic activation. No product formed when the reaction was performed in an oxygenated solution, and the catalyst completely degraded within 2 h. In the absence of a sacrificial donor, sodium ascorbate, the product was isolated with a 15% yield, and complete degradation of the catalyst was observed within 2−4 h (Scheme S1 and Table S3). Additionally, using **4c** and **4e** as examples, we demonstrated that the catalysts can work under UV irradiation (λ = 350 nm, Scheme 1, Entries 8−9).

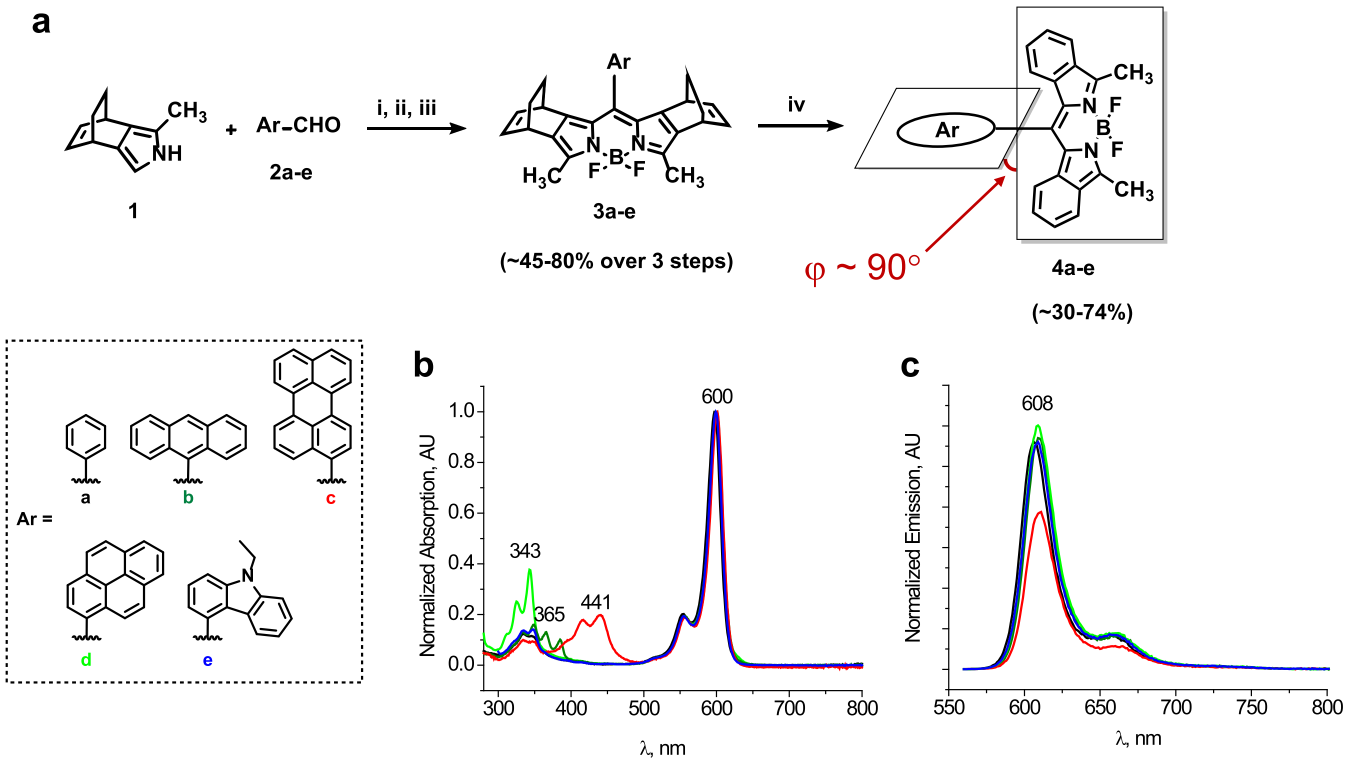


Figure 2. (D–A) dibenzoBODIPY-based dyads **4a–e** (a) Synthetic scheme: (i) TFA (cat.), CH_2Cl_2, r.t., 24 h; (ii) DDQ, CH_2Cl_2, r.t., 2 h; (iii) DIPEA, $BF_3{\cdot}Et_2O$, CH_2Cl_2, r.t., 2 h; (iv) 210–220 °C, 1 h; (b) Absorption and (c) Emission spectra, normalized by the fluorescence quantum yield (Φ_{fl}): **4a** (black), **4b** (dark-green), **4c** (red), **4d** (green) and **4e** (blue).

However, the yields of the isolated products are slightly lower than those obtained when the reaction was performed under excitation with red light, approximately 48–49%. This might be due to the lower penetration of UV light through the reaction media.

All molecules exhibit very high emission quantum yields (Φ_{fl} = 0.92–1.0) except for **4c**, which maintains a slightly lower, yet still notable, quantum yield of 0.65 (Figure 2c). The emission lifetimes (τ_{fl}) for all molecules are ~6 ns (Table S1). While the catalytic efficiencies of **4b–e** are high, the reactions take longer to complete compared to our previously reported regular BODIPY-based photoredox catalysts (12 to 24 h vs 48 h).[20] Previously, BODIPY-based laser dyes with high Φ_{fl}, PMT546, and PM597 showed promise in facilitating chemical reactions;[40] however, they required a stoichiometric ratio with the substrates, and therefore, these reactions cannot be considered truly catalytic.

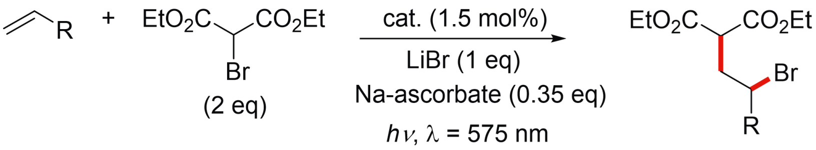
Given this earlier report, we hypothesize that the slightly prolonged reaction time observed in the case of **4b–e** is attributed to the fact that the reaction proceeds not through the formation of triplets but through a singlet-born charge-separated state. To test this hypothesis, we studied the photophysical processes of the excited states in the catalyst series using optical and electrochemical methods.

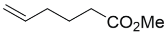
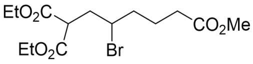
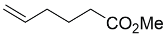
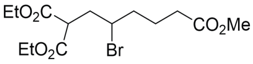
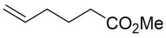
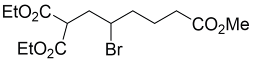
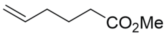
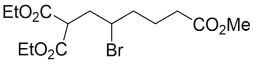
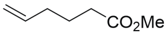
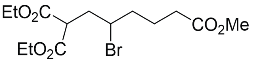
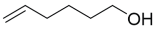
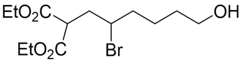
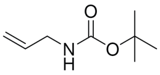
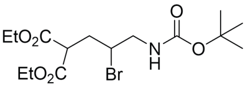
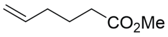
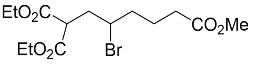
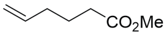
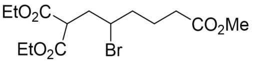
Electrochemical measurements showed that the reduction potential of the donor radical cation ($D^{\bullet+/0}$) is >0.5 V higher than that of the acceptor radical cation ($A^{\bullet+/0}$) (Figure S2). The estimated Gibbs energy changes associated with the charge separation (CS) (ΔG_{CS}) within the dyads are positive, indicating that the CS process is not energetically favorable (Table S2). This is consistent with the unchanged fluorescence τ_{fl} and Φ_{fl} of **4b–4d**, compared to **4a** (Table S1) and density functional theory (DFT) calculations (Supporting Information).

High Φ_{fl} is not a typical characteristic of high-performing photoredox catalysts. If the single electron transfer (SET) reaction occurs directly from the singlets of dibenzoBODIPY, we expect to see equally good catalytic activity from control **4a** (Scheme 1). This signifies the critical role played by the donor moiety in our dyads (**4b–e**). Even though the intramolecular CS step is energetically uphill, the proximity of the two units makes the RP state accessible, especially in a polar solvent: note that ΔG_{CS} becomes lower in solvents containing water than in pure acetonitrile. Transient absorption (TA) spectroscopy revealed the bleaching of the donor absorption bands, showing that a hole can still move from the dibenzoBODIPY to donors, producing RP states (Figure S3). We also found no other long-lived species (i.e., triplets) in the TA spectra. The high emissivity and production of the RP states appear counterintuitive, but this can be explained by faster back-charge recombination (bCR) than CS. A simple three-state kinetics modeling showed that Φ_{fl} and τ_{fl} are almost unchanged when k_{bCR}>k_{CS} and $1/\tau_{fl} > k_{CR}$, where k_{CR} is the rate of charge recombination of RP to the ground state (Supporting Information).

These data suggest the excitation energy stayed in the singlet spin manifold. To further confirm the lack of formation of triplets, we created the triplets of **4a** and **4e** by the triplet–triplet energy transfer (TTET) method,[41] thereby passing the direct photoexcitation of these molecules. We used diiodo-BODIPY (I_2BD)[42,43] as a donor; their triplet energy is higher than those of dibenzoBODIPYs: π-extension in dibenzoBODIPYs lowers the triplet excited states, supported by DFT calculations (Supporting Information). We could produce the triplets of **4a** and **4e**, which have significantly longer lifetimes,

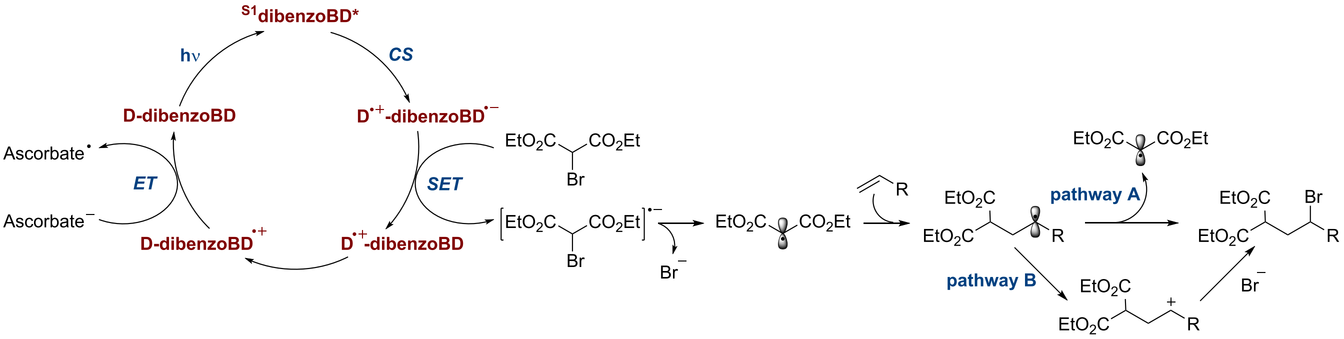
Scheme 1. ATRA Reaction, Catalyzed by 4a−e



#	Alkene	Product	Catalyst	Yield
1			**4a**	traces[a]
2			**4b**	68%
3			**4c**	70%
4			**4d**	91%
5			**4e**	71%
6			**4e**	70%
7			**4e**	64%
8			**4c**[b]	49%
9			**4e**[b]	48%

[a]The formation of the product was only observed by TLC; no isolated yield was obtained. [b]The reaction was performed under UV irradiation, λ = 350 nm.

Scheme 2. Proposed Mechanism for ATRA Reaction Catalyzed by (D−A) Dibenzo-BODIPY Dyads



expected for (π,π*) triplets, with spectra features distinct from those we observed upon photoexcitation of **4a** and **4e**. Please see Supporting Information for more details on the TTET method and data.

With these data, we propose the following reaction mechanism (Scheme 2). The photoexcitation of (D−A) dibenzoBODIPY-based dyads results in a rapid equilibrium between the singlets and RP state. This physical charge separation (dibenzoBD$^{\bullet-}$-D$^{\bullet+}$) makes an electron on dibenzoBD$^{\bullet-}$ accessible for the SET to diethyl bromomalonate (E_{red} ∼ −1.4 V vs Fc$^{+/0}$),[44] initiating the catalytic activity. SET is energetically favorable as ΔG_{SET} is negative from the RP state (Table S2). We further confirmed the production of malonate radicals by in situ EPR spectroscopy, where we used 5,5-dimethyl-1-pyrroline-*N*-Oxide (DMPO) as a spin trap of radicals. The experimental procedure was described in Supporting Information. Upon light irradiation of (D−A) dibenzoBODIPY-based dyads (**4e**) in the presence of diethylbromomalonate, we observed a significant increase in DMPO radical formation (Figure 3a).

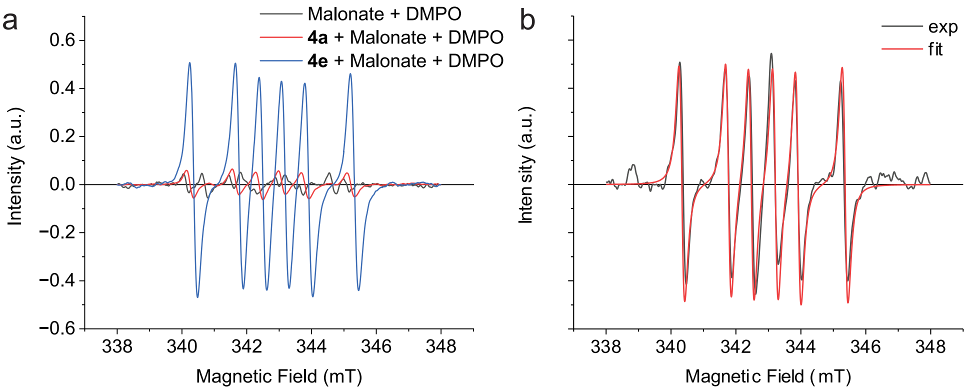


Figure 3. (a) EPR spectra of the deoxygenated samples containing bromomalonate + DMPO, **4a** + bromomalonate + DMPO, and **4e** + bromomalonate + DMPO upon light ($\lambda > 475$ nm) exposure for 15 min. The experiments were performed under the same conditions for all the samples. (b) The experimental and fitted spectra of the DMPO adduct formed upon photoexcitation of the **4e** + bromomalonate + DMPO solution.

The experimental spectrum of this DMPO adduct can be reasonably reproduced by simulation[45,46] and fitted with two isotropic hyperfine coupling constants (A_N and A_H = 1.45 and 2.15 mT, respectively). A relatively large A_H is characteristic of alkyl adducts of DMPO,[47] and indeed the observed EPR spectra agree well with them.[48] This observation showed the production of critical malonate radical as in Scheme 2. We observed much less production of these adducts with the control (**4a**), which agreed with the catalysis experiments, confirming the critical role of an electron donor and RPs in the catalytic activity. Here, the donor simply acts to donate an electron to dibenzoBODIPY, making high-energy radical anions. The orthogonal D/A planes keep an electron localized. After SET, a hole left in the donor will likely move to dibenzoBODIPY based on the reduction potentials difference (Table S2, Supporting Information), which will then be filled by ascorbate anions. This explains the observation of catalytic activity without ascorbate but the degradation of the catalysts. This is different from the triplet-driven catalysts such as the (D−A) BODIPY-based dyads[20] and I_2BD,[43] where sacrificial electron donors are necessary to make high-energy radical anions for catalytic activities. The ATRA products could form a radical propagation pathway (Pathway A) or a radical-polar crossover pathway (Pathway B), as proposed by Stephenson.[49] The current work shows that we can convert noncatalytic red/NIR-absorbing fluorophores to efficient photoredox catalysts by inserting a donor moiety whose reduction potentials are not even energetically favorable for charge separation. Using the singlets to initiate the catalytic activity prevents us from losing additional energy out of the already low-energy photons of red/NIR lights. This simple approach can complement the previous approach of accessing long-lived triplets by the SOCT-ISC mechanism.[16]

In conclusion, we present a new series of (D−A) dyads based on dibenzoBODIPY that possess remarkable efficiency as "red" catalysts in ATRA reactions. We have substantiated the pivotal role of singlet-born RPs in initiating redox reactions. Our work shows a new approach for developing heavy atom-free photoredox catalysts with customizable excitation properties. We envision that this simple approach can convert highly fluorescent organic fluorophores, previously overlooked in photoredox catalysis, into effective catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.4c00877.

Experimental details, more photophysical characterization, electrochemical characterization, transient absorption spectroscopy data, kinetic simulation, TTET method description, computational data, synthetic procedures, controls/optimization of photocatalytic ATRA reactions, and NMR data (PDF)

AUTHOR INFORMATION

Corresponding Authors

Tatiana V. Esipova − *Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, Illinois 60660, United States;* orcid.org/0009-0001-7528-9297; Email: tesipova@luc.edu

Tomoyasu Mani − *Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060, United States;* orcid.org/0000-0002-4125-5195; Email: tomoyasu.mani@uconn.edu

Authors

Sara Abuhadba − *Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, Illinois 60660, United States*

Charlotte Fuqua − *Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060, United States*

Anthony Maltese − *Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, Illinois 60660, United States*

Caroline Schwinn − *Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, Illinois 60660, United States*

Neo Lin − *Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060, United States;* orcid.org/0000-0002-0535-564X

Angela Chen − *Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060, United States*

Rilee Martzloff − *Department of Chemistry, University of Connecticut, Storrs, Connecticut 06269-3060, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/jacsau.4c00877

Author Contributions

[§]S.A. and C.F. contributed equally to this work. All authors have given approval to the final version of the manuscript. CRediT: **Sara Abuhadba** formal analysis, investigation, writing - original draft, writing - review & editing; **Charlotte Fuqua** formal analysis, investigation, writing - review & editing; **Anthony Maltese** investigation; **Caroline Schwinn** investigation; **Neo Lin** formal analysis, investigation, visualization, writing - original draft, writing - review & editing; **Angela Chen** investigation; **Rilee Martzloff** investigation; **Tatiana V. Esipova** conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, visualization, writing - original draft, writing - review & editing; **Tomoyasu Mani** conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, supervision, validation, visualization, writing - original draft, writing - review & editing.

Notes

The authors declare no competing financial interest.

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