

# meso-Antracenyl-BODIPY dyad as a new photocatalyst in ATRA reactions

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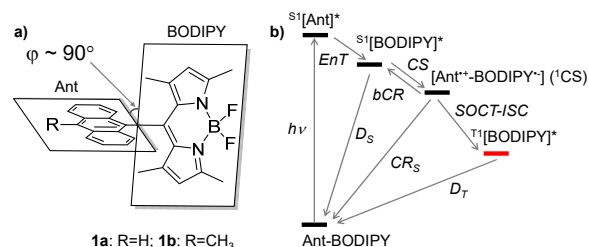
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**ABSTRACT:** We demonstrate that because of the efficient generation of triplet excited state under UV or visible-light irradiation, meso-antracenyl-BODIPY donor-acceptor dyad can catalyze ATRA reactions between bromomalonate and alkenes. This finding paves the way for the design and application of the new type of heavy atom-free organic chromophores for photocatalysis.

## INTRODUCTION

In the past few decades, the field of photocatalysis attracted much attention among synthetic chemists. Photocatalysis, as a method of activation of organic molecules, relies on the electron or energy transfer between photoexcited catalysts and substrates, and allows bond formation and breakage under mild conditions. Though the most used photocatalysts - ruthenium or iridium polypyridyl complexes - have already proved their efficiency in multiple reactions<sup>1-5</sup>, their high cost, laborious synthesis, and generation of heavy-atom wastes prompted chemists towards the search and development of new photocatalytic systems<sup>6-15</sup>. Among them, there are several examples of application of metal-free organic chromophores as photocatalysts in the reactions of oxidation<sup>16-20</sup>, reductive dehalogenation<sup>21</sup>, C-C bond formation<sup>22-26</sup> and others<sup>27-30</sup>. For the majority of catalysts, either organometallic complexes or metal-free chromophores, the ability to form long-lived excited states has been postulated as a prerequisite for the efficient photocatalytic activity<sup>31,32</sup>. Within this context, we turned our attention to the recently reported orthogonal electron donor-acceptor (D-A) boron dipyrromethene (BODIPY)-based dyads<sup>33</sup>. In these dyads the BODIPY chromophores are usually substituted at the meso-position with another  $\pi$ -conjugated "dye", e. g. anthracene (Ant), so that the planes of BODIPY and the "dye" form an angle close to 90° (Fig. 1a). The dyads possess long-lived triplet excited states of BODIPY, when selectively excited at either BODIPY or the "dye" unit of the dyad. Notably, in contrast to many other organic and organometallic compounds, the formation of the triplet excited states in "dye"-BODIPY dyads does not require the presence of heavy atoms in the structure of chromophores. In this case, the generation of the triplet excited state of BODIPY ( $T_1$ ) proceeds through the initial formation of the charge-separated state ( $^1CS$ ) within the dyad, where BODIPY unit usually serves as an electron acceptor, and the "dye" as a donor (Fig.



**Figure 1.** (a) Molecular structures and (b) Photophysical scheme of the catalysts. EnT = energy transfer; CS = charge separation; bCR = back charge recombination; CRs = singlet charge recombination; Ds = singlet decay; DT = triplet decay.

1b). Importantly, the spin-forbidden  $^1CS \rightarrow T_1$  transition, termed spin-orbit charge-transfer intersystem crossing (SOCT-ISC) is favored when the molecular orbitals of the donor ("dye") and acceptor (BODIPY) are orthogonal, creating a large enough orbital angular momentum for the spin flip.<sup>34-36</sup> The quantum yields of the triplet excited states formation can reach 90% and above in the dyads with the properly matching photophysical parameters of the BODIPY and the "dye" units (e. g., redox potentials, excitation energies, etc.). This trend of the "dye"-BODIPY dyads to the efficient formation of long-lived triplet excited states encouraged us to explore the possibility of their application as photocatalysts in chemical reactions.

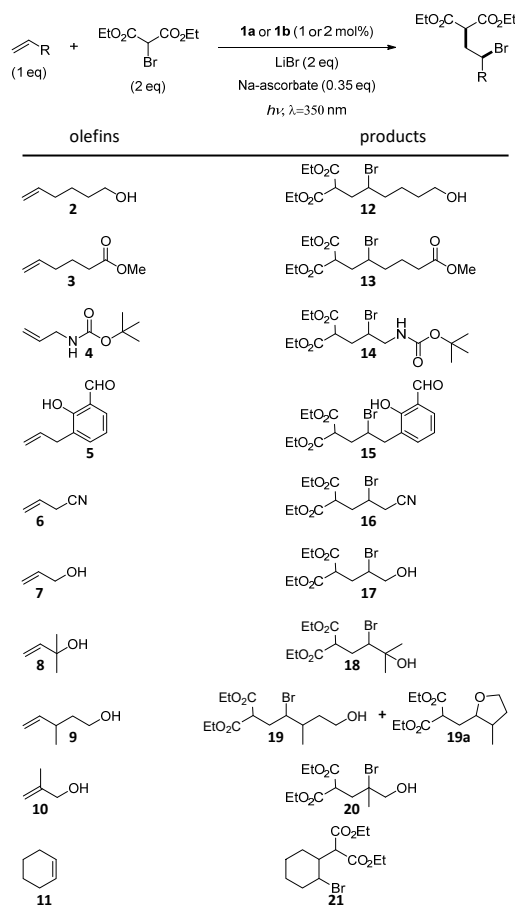
## RESULTS AND DISCUSSION

Among various types of chemical transformations, the C-C bond formation seemed to us the most attractive, as it constitutes the fundamental basis for the creation of new organic frameworks. When choosing the reaction, we also considered the fact that the catalytic cycles should include the oxidation or reduction of the photoexcited catalyst by

the substrate. While excited states of ruthenium or iridium complexes can be easily oxidized or reduced, the oxidation/reduction of the triplet excited state of BODIPY might be challenging due to the lower redox potentials. However, this issue can be overcome if a sacrificial reductant or oxidant is used to convert the excited state of the catalyst. Based on these considerations, we chose Atom Transfer Radical Addition (ATRA) as a model reaction to test the photocatalytic performance of “dye”-BODIPY dyad. Photoredox ATRA reactions between olefins and various halogen containing reagents have been thoroughly studied by Stephenson group<sup>37</sup>, using Ru(bpy)<sub>3</sub><sup>2+</sup> as photocatalyst and a wide range of sacrificial reductants from alkyl- and aryl-amino derivatives to sodium ascorbate. Moreover, recently it was shown, that diiodo-BODIPY in combination with sodium ascorbate can also catalyse ATRA reactions<sup>38</sup>. Though the last finding seemed reassuring, we anticipated that the “dye”-BODIPY dyads might perform differently in ATRA reactions due to the different mechanism of the triplet state formation. Indeed, it was shown, that the quantum yields of the triplet excited state formation in various “dye”-BODIPY dyads are largely determined by the energy of <sup>1</sup>CS, which in turn depends on the polarity of the solvent. Thereby, any factors, which make up the reaction microenvironment, e.g., substrates, solvent mixtures and additives can potentially affect the efficiency of photocatalysis.

We started the investigation with the reaction between 5-hexen-1-ol (**2**) and diethyl bromomalonate (Scheme 1), and have chosen anthracenyl-BODIPY (**1a**) and 9-methylantracenyl-BODIPY (**1b**) as the catalysts, due to the high quantum yields of the triplet excited state formation ( $\Phi_T = 0.93$  and  $0.90$  in acetonitrile, AcCN, respectively) and quite high reduction potentials ( $[\text{BODIPY}]/[\text{BODIPY}]^{\cdot-} = -1.01$  V vs SCE)<sup>33</sup>. All reactions were performed in deoxygenated solutions under Ar, using 350 nm excitation light source, which selectively excited anthracene unit in the dyads **1a** and **1b**. As the solvents, we have chosen *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and AcCN, since the triplet excited states in the dyads **1a** and **1b** form with the highest efficiency in polar solvents<sup>33</sup>. No product **12** formation was observed when the reaction was performed in DMF/H<sub>2</sub>O, 1:1 mixture, using triethylamine or 4-methoxy-*N,N*-diphenylaniline as sacrificial reductants, however the product was obtained with high yield of 87% when sodium ascorbate was used (Table 1, entry 1). Since we noticed a sufficient aggregation of the catalyst upon addition of water to the reaction mixture, the amount of water was reduced to solvent/water, 3:1 ratio. In DMF/H<sub>2</sub>O, 3:1 mixture the product was formed with 86% yield (Table 1, entry 3); quite good yield of 66% was obtained in DMSO/H<sub>2</sub>O, 3:1 (Table 1, entry 4); and almost quantitative yield of 96% was obtained in AcCN/H<sub>2</sub>O, 3:1 mixture (Table 1, entry 5). Our attempts to improve the yield in DMSO/H<sub>2</sub>O, 3:1 by varying the reaction time were unsuccessful (Table S1, SI). In fact, the highest yield of 66% was obtained, when the reaction proceeded for 24 h; and the yield decreased to 57% and 48% in the case of longer (30 h) or shorter (18 h) reaction time, respectively. In principle, these results were not surprising, since we anticipated that the yield of the product should depend on the solvent polarity. To get more insights on our observations, we measured the quantum yields of the triplet excited state formation for the dyad **1** in

**Scheme 1. ATRA reactions between diethyl bromomalonate and various olefins**



DMF/H<sub>2</sub>O, AcCN/H<sub>2</sub>O, and DMSO/H<sub>2</sub>O, 3:1, and for all solvent mixtures the obtained values were about the same and equal to  $\Phi_T > 0.90$  (SI). These results do not explain why in DMSO/H<sub>2</sub>O mixture the yield of the product is lower. Probably, other factors play a crucial role in this case, and more mechanistic studies are required to shed light onto this issue. We then performed the reaction in AcCN/H<sub>2</sub>O, 3:1 without the addition of LiBr to check whether it affects the reaction efficiency (Table S2, SI). The obtained yield of product **12** was c.a. 2 times lower, than for the case when LiBr was present in the reaction mixture. This observation is in the agreement with Stephenson’s hypothesis, that the addition of Lewis acids facilitates the carbon-halogen bond breakage and the formation of radicals in ATRA reactions<sup>39</sup>. Next, we studied the scope of the reaction in application to various functionalized alkenes (Scheme 1, Table 1). The reaction between bromomalonate and terminal alkenes proceeded well in the presence of hydroxy-, aldehyde, cyano-, alkoxy-carbonyl- and protected amino groups. As regards solvents, the best yields were obtained in AcCN/H<sub>2</sub>O, 3:1 mixture, as compared to DMF/H<sub>2</sub>O, 1:1 and DMSO/H<sub>2</sub>O, 3:1 (Table 1, entry 9 vs. 10 vs. 11; entry 12 vs. 13 vs. 14). In addition, in DMF/H<sub>2</sub>O we detected the formation of the oxidized byproducts in some cases (Table S1, SI), and in the case of DMSO/H<sub>2</sub>O - the formation of higher amount of debrominated malonic ester. This trend is similar to what

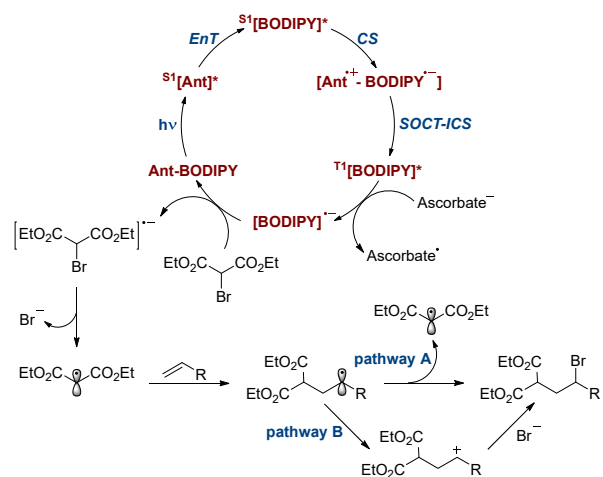
**Table 1. ATRA reactions of various olefins under different conditions**

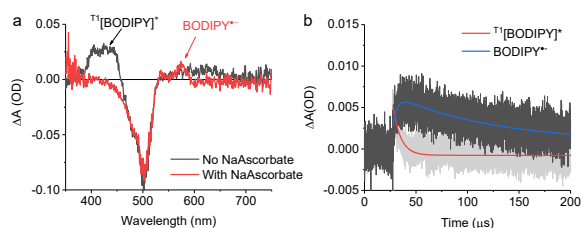
#	olefin	product	solvent	cat./load	time	yield
1	2	12	DMF/H <sub>2</sub> O, 1:1	1a, 1 mol%	24 h	87%
2	2	12	DMF/H <sub>2</sub> O, 1:1	1b, 1 mol%	24 h	88%
3	2	12	DMF/H <sub>2</sub> O, 3:1	1b, 1 mol%	24 h	86%
4	2	12	DMSO/H <sub>2</sub> O 3:1	1a, 1 mol%	24 h	66%
5	2	12	AcCN/H <sub>2</sub> O, 3:1	1a, 1 mol%	24 h	96%
6	3	13	AcCN/H <sub>2</sub> O, 3:1	1a, 1 mol%	24 h	99%
7	3	13	AcCN/H <sub>2</sub> O, 3:1	1b, 1 mol%	24 h	99%
8	4	14	AcCN/H <sub>2</sub> O, 3:1	1b, 2 mol%	48 h	94%
9	4	14	DMF/H <sub>2</sub> O, 1:1	1b, 2 mol%	48 h	90%
10	4	14	DMSO/H <sub>2</sub> O 3:1	1a, 1 mol%	24 h	15%
11	5	15	AcCN/H <sub>2</sub> O, 3:1	1a, 2 mol%	48 h	40%
12	5	15	DMF/H <sub>2</sub> O, 1:1	1b, 2 mol%	48 h	19%
13	5	15	DMSO/H <sub>2</sub> O 3:1	1a, 2 mol%	48 h	0%
14	6	16	AcCN/H <sub>2</sub> O, 3:1	1a, 1 mol%	48 h	15%
15	7	17	AcCN/H <sub>2</sub> O, 3:1	1a, 2 mol%	48 h	62%
16	8	18	AcCN/H <sub>2</sub> O, 3:1	1a, 2 mol%	72 h	56%
17	9	19+19a	AcCN/H <sub>2</sub> O, 3:1	1b, 2 mol%	48 h	46%
18	10	20	AcCN/H <sub>2</sub> O, 3:1	1a, 2 mol%	48 h	82%
19	11	21	AcCN/H <sub>2</sub> O, 3:1	1a, 2 mol%	48 h	10%

we observed initially for the reaction between 5-hexen-1-ol and diethyl bromomalonate. In respect of alkene substrates, the reaction proceeded well with terminal alkenes, but resulted in poor yields with secondary alkenes, e.g., only 10% yield was obtained for cyclohexene (Table 1, entry 19). For the terminal alkenes, almost quantitative yields were obtained when the functional groups were distant from the alkene fragment (Table 1, entries 5, 6). The presence of functional groups and/or alkyl substituents in the vicinity of the alkene resulted in lower, yet good yields. In addition, longer reaction time was required in the case of bulky substrates.

We assume, that in this case both, steric and electronic factors come to interplay. Thereby, the presence of highly electron withdrawing cyano- substituent at  $\alpha$ - position to alkene group led to a moderate 15 % yield of the product (Table 1, entry 14). For the substrate 7 with less electron withdrawing hydroxy group at  $\alpha$ - position, the yield was 62% (Table 1, entry 15), and for the substrate 5 with electron withdrawing aryl substituent at  $\alpha$ - position, 40 % yield was obtained (Table 1 entry 11). Methyl groups at  $\alpha$ - position to the alkene fragment in substrates 8 and 9 led to 56% and 46% yields respectively (Table 1, entries 16, 17). Interestingly, a high yield of 82% was obtained for the substrate 10, despite the presence of electron withdrawing OH group at  $\alpha$ - position to alkene, and a methyl substituent at the double bond. This result can be attributed to the intermediate formation of stable tertiary radical or tertiary carbocation during the reaction, and is in a good agreement with the proposed mechanism.

We hypothesised, that the mechanism of the ATRA reaction, catalysed by the dyads 1a and 1b should be similar to the one proposed for diiodo-BODIPY<sup>38</sup>, except that the triplet excited state of BODIPY in the dyads 1a and 1b forms from the <sup>1</sup>CS state (Scheme 2). The participation of the triplet excited state in the reaction is supported by the fact, that the reaction did not proceed in the presence of oxygen, which quenches the triplet states. Thereby, upon excitation of anthracene unit at  $\lambda_{ex}=350$  nm, ultrafast energy transfer from <sup>s1</sup>[Ant]\* to <sup>s1</sup>[BODIPY]\* occurs, which is followed by an electron transfer within the dyad 1a or 1b, resulting in the formation of <sup>1</sup>CS state [Ant]<sup>+</sup>-[BODIPY]<sup>-</sup>. Then, <sup>T1</sup>[BODIPY]\* forms as a result of SOCT-ISC process. In principle, <sup>T1</sup>[Ant]\* could also form. However, as it was shown earlier for the dyad 1a, the majority of the triplet excitation energy is on BODIPY, and the contribution of <sup>T1</sup>[Ant]\* is small.<sup>40</sup> Single electron transfer (SET) from the sacrificial reductant – sodium ascorbate – converts the triplet excited state <sup>T1</sup>[BODIPY]\* into radical-anion [BODIPY]<sup>-•</sup>, which has high enough reduction potential ([BODIPY]<sup>-•</sup>/[BODIPY]<sup>-</sup> = -1.01 V vs SCE)<sup>33</sup> to convert bromomalonate into malonic radical. Malonic radical further undergoes the addition to alkenes

**Scheme 2. Proposed mechanism for ATRA reaction catalysed by Ant-BODIPY dyad**



**Figure 2.** (a) Transient absorption spectra of **1a** at 10  $\mu$ s after the ns laser pulse ( $\lambda_{\text{ex}} = 355$  nm) in AcCN/H<sub>2</sub>O = 3:1 in the presence and absence of sodium ascorbate. (b) Decay kinetics of **1a** in AcCN/H<sub>2</sub>O = 3:1 in the presence of sodium ascorbate at the <sup>T1</sup>[BODIPY]\* absorption band (430 nm) and the [BODIPY]• absorption band (570 nm).

with the formation of the corresponding radical. The ATRA product could form through the abstraction of halogen from another equivalent of bromomalonate (radical propagation pathway, A), or through single-electron oxidation to carbocation with subsequent trapping by bromine-anion (radical-polar crossover pathway, B), as proposed by Stephenson<sup>37</sup>.

Hypothetically, the malonic radical could form through the SET from <sup>1</sup>CS state [Ant<sup>•+</sup>-BODIPY<sup>•-</sup>], followed by the reduction of [Ant]<sup>•+</sup> unit with sodium ascorbate. However, transient absorption spectroscopy studies eliminated this possibility by showing that the lifetime of the <sup>1</sup>CS state is too short to undergo intermolecular reactions (more details in SI), and further confirming that [BODIPY]• is produced by the reduction of <sup>T1</sup>[BODIPY]\* by sodium ascorbate (Fig. 2).

Finally, we confirmed that the ATRA reactions proceed with the same efficiency under visible light irradiation. Thereby, the reaction between diethyl bromomalonate and substrates **2** and **3** in AcCN/H<sub>2</sub>O, 3:1 mixture, and using catalyst **1b** and 470 nm excitation light source led to the products **12** and **13** with 98% and 99% yields respectively (Table S3, SI). In this case a BODIPY unit was selectively excited at  $\lambda_{\text{ex}}=470$  nm to produce <sup>S1</sup>[BODIPY]\*. The remaining steps of the mechanism are analogous to the described above for 350 nm excitation.

## CONCLUSIONS

In conclusion, we demonstrated that BODIPY-based donor-acceptor dyads can efficiently catalyse light-driven ATRA reactions. The dyads can be excited with UV and visible light. Given the ease of the synthesis, availability of the synthetic precursors and readily tunable photophysical and redox properties, these dyads can become a new inexpensive environmentally friendly alternative to the classical organometallic photocatalysts.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details and spectral characterizations of the catalysts and obtained compounds are available in the Supporting Information (SI).

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### Notes

The Authors declare no competing financial interest

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