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# Benzimidazolium naphthoxide betaine is a visible light promoted organic photo-redox catalyst

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**ABSTRACT:** Benzimidazolium naphthoxide (<sup>-</sup>ONap-BI<sup>+</sup>) was first synthesized and utilized as an unprecedented betaine photo-redox catalyst. Photoexcited state of <sup>-</sup>ONap-BI<sup>+</sup> generated by visible light irradiation catalyzes the reductive deiodination as well as desulfonylation reactions in which 1,3-dimethyl-2-phenylbenzimidazoline (Ph-BIH) cooperates with as an electron and hydrogen atom donor. Significant solvent effects on the reaction progress were discovered and specific solvation toward imidazolium and naphthoxide moieties of <sup>-</sup>ONap-BI<sup>+</sup> was proposed.



#### **INTRODUCTION**

Photoinduced electron transfer (PET) is a fundamental photochemical process in which radical ions are formed via single electron transfer (SET) between a photoexcited material and a ground state substrate. Because of the effective generation of radical ions from neutral organic molecules and the production of free radical species after the release of electro- or nucleofugal groups from such intermediates under the mild reaction conditions, PET reactions have been frequently applied to organic synthesis.<sup>1</sup> Thus, extensive investigations of PET reactions of organic compounds conducted during the past several decades have led to the development of a variety of synthetically useful organic transformations. In addition, these studies have uncovered a plethora of preparatively useful photo-redox catalyzed reactions using visible light.<sup>2</sup> Complexes of transition metals, such as ruthenium and iridium, are commonly utilized to promote these transformations. However, more economical as well as sustainable photocatalysts, which do not rely on the use of expensive

precious metals, are in great demand. Among the strategies employed to overcome this limitation are those that utilize organic photo-redox catalysts.<sup>3</sup> Although a variety of organic electron-acceptor photocatalysts, such as cyano arenes, aromatic ketones, quinones, cationic salts such as pyrylium, thiapyrylium, quinolinium, acridinium, have been developed in previous investigations,<sup>1,3</sup> their electron-donor counterparts have been less well developed.<sup>4</sup> Moreover, the fact that they are potentially useful for promoting atom transfer radical polymerizations heightens the need for further development of visible light absorbing organic electron donors.<sup>5</sup>

In a previous effort in the area of organic PET reactions, we discovered that 2-aryl-1,3-dimethylbenzimidazolines (Ar-BIHs) act as both an effective electron as well as hydrogen atom donors to promote reductive transformations of various organic substances.<sup>1c,4f,g,6</sup> Our findings have stimulated other studies exploring applications of PET reactions of BIHs.<sup>7</sup> Recently, we developed a new protocol in which hydroxynaphthyl substituted BIH (HONap-BIH) participates as a visible light absorbing strong electron donor that acts as an effective photo-reductant.<sup>6b</sup> In this effort, we found that addition of bases significantly enhances the efficiencies of the reduction reactions of various organic substances due to the generation of naphthoxide structure (Figure 1).<sup>6c,d</sup> Moreover, HONap-BIH is used in stoichiometrically larger amounts compared to the substrate and it is transformed to the oxidized product, 1,3-dimethyl-2-(2-naphthox-1-yl)benzimidazolium (CONap-BI<sup>+</sup>, 1). Because 1 contains a

naphthoxide chromophore, which absorbs visible light, we expected that it would also act as a visible light absorbing strong electron donor.



Figure 1. Evolution of benzimidazolium naphthoxide photocatalyst from benzimidazoline electron donor reagent

In this article, we describe the results of an investigation probing the ability of betaine 1 to serve as a visible light absorbing electron-donor photocatalyst (Figure 1). In the designed reaction sequence, photo-excited 1 initiates reaction and 1,3-dimethyl-2-phenylbenzimidazoline (2) serves as a reductant by donating an electron and a hydrogen atom.<sup>6</sup> Two types of substances, including o-allyloxyiodobenzene (3) and sulfonamides 5, 7 and 9 which undergo respective reductive deiodination and desulfonylation reactions,<sup>6d</sup> were selected as substrates to probe the viability of the

photocatalytic system of 1 with 2 (Figure 2).



Figure 2. PET promoted reduction reactions of *o*-allyloxyiodobenzene (3) and sulfonamides 5, 7 and 9.

#### **RESULTS AND DISCUSSION**

Betaine **1** was prepared via the sequential steps presented in Scheme 1 (see details in Experimental Section). HONap-BIH was first treated with phenacyl bromide to give the imidazolium bromide, HONap-BI<sup>+</sup>Br<sup>-</sup>. Then, deprotonation of this salt by KOH produced **1**.

Scheme 1. Preparation of betaine 1



Because the absorption spectrum of **1** (Figure 3) contains a maximum at 415 nm ( $\varepsilon = 8268 \text{ M}^{-1} \text{ cm}^{-1}$ ) that arises from the presence of a naphthoxide moiety (see Figure S1), **1** should absorb visible

light. Thus, the photocatalytic reduction reaction of **3** (0.1 M) promoted by **1** in the presence of **2** was first examined by using a 500 W Xe light source, a cut-off glass filter ( $\lambda > 390$  nm), and a 6 h irradiation time. As seen in Table 1, a catalytic quantity of **1** did promote the deiodination reaction of **3** to produce the expected cyclization product **4** in good yields in DMSO as well as DMF (entries 1, 2, 4, 5, 9, 10). While only 1 mol% of **1** could lead to the completion of the reaction (entry 10), no reaction proceeded in the absence of **1** (entry 11). Irradiation time did not significantly influence the yield of **4** (compare entries 2 and 5 to 3 and 7, respectively), which suggests that prolonged irradiation does not cause the decomposition and further reaction of **4**. On the other hand, no reaction proceeded in the absence of **2** (entry 6) or without irradiation (entry 8).



**Figure 3.** Absorption spectra of **1** and **2** in DMSO ( $4.0 \times 10^{-5}$  M), and the transmittance spectrum of the glass filter used for photoreaction.

Table 1. Photo-reductive cyclization of 3 promoted by the catalytic quantity of 1 with 2 <sup>a</sup>					
Entry	1 (mol%)	Solvent	Irrad tme (h)	Conv of $3 (\%)^{\mathrm{b}}$	Yield of $4 (\%)^{b,c}$
1	20	DMSO	6	100	71
			6		

2	10	DMSO	6	100	67
3	10	DMSO	1	71	47 (66)
4	20	DMF	6	100	65
5	10	DMF	6	100	82
6 <sup>d</sup>	10	DMF	6	0	0
7	10	DMF	1	51	44 (86)
8 <sup>e</sup>	10	DMF	1	0	0
9	5	DMF	6	100	66
10	1	DMF	6	100	69
11	-	DMF	6	0	0

<sup>a</sup>**3** (0.10 mmol), **1** (1~20 mol% vs **3**), **2** (1.2 equiv vs **3**), solvent (1.0 mL); 500 W Xe-lamp ( $\lambda > 390$  nm). <sup>b</sup>Determined by <sup>1</sup>H NMR, <sup>c</sup>The yield in the parenthesis is based on the conversion of **3**. <sup>d</sup>In the absence of **2**. <sup>e</sup>Stirred in the dark.

Owing to the characteristic betaine structure of **1**, we were interested in studying solvent effects on the reaction. We anticipated that the Lewis base and acid character of solvents, estimated by using respective donor numbers (DN) and acceptor numbers (AN),<sup>8</sup> would influence the nature of the imidazolium and naphthoxide moieties in **1** and have possible effects on the reaction progress. To evaluate this issue, reaction of **3** was conducted for shorter irradiation time (1 h) in various solvents including N,N-dimethylpyrimidineurea (DMPU). As can be seen by viewing the data in Table 2, the progress of the reaction of **3** does not simply correlate with solvent polarities as estimated by using  $E_{T}(30)$  values.<sup>9</sup> In fact, the reaction takes place in nonpolar solvents such as toluene (entry 11). Although the absorption spectra of **1** in MeCN and CH<sub>2</sub>Cl<sub>2</sub> are not significantly different from those in DMSO and DMF (See Figure S2 and Table S1), the reaction does not occur in the former solvents (compare entries 9 and 10 with entries 3 and 4). On the other hand, addition

of only 5 molar excesses (vs 3) of DMSO, DMPU and NEt <sub>3</sub> $(DN = 31.7)^{8b}$ was found to promote
reactions of <b>3</b> in CH <sub>2</sub> Cl <sub>2</sub> ( $DN = 1$ ) producing <b>4</b> in respective 24%, 41% and 53% yields and 26%,
51% and 57% conversion, and however this yield enhancement was not observed for the reaction in
the modest donor solvent MeCN ( $DN = 14.1$ ) (see Table S4). Protic solvents such as MeOH, which
has a significantly high AN, are expected to hydrogen bond with the naphthoxide moiety of 1 and
cause a decrease in its electron donating ability. <sup>10</sup> This effect and the fact that a significant blue shift
of the absorption spectrum of 1 takes place in MeOH are likely reasons for the lack of
photocatalytic reactivity when MeOH was used as solvent (entry 6, also see Figure S2 and Table
S1).

entry	solvent	$E_{\mathrm{T}}{}^{\mathrm{b}}$	DN <sup>c</sup>	$AN^{c}$	conv of $3 (\%)^{c}$	yield of $4 (\%)^{d,e}$
1	DMPU	42.1	33	-	50	41 (82)
2	Pyridine	40.2	33.1	14.2	48	29 (60)
$3^{\mathrm{f}}$	DMSO	45.1	29.8	19.3	71	47 (66)
4 <sup>g</sup>	DMF	43.2	26.6	16.0	51	44 (86)
5	THF	37.4	20.0	8.0	33	22 (67)
6	MeOH	55.4	19	41.5	0	0
7	AcOEt	38.1	17.1	9.3	44	12 (27)
8	Acetone	42.2	17	12.5	41	31 (76)
9	MeCN	45.6	14.1	18.9	> 0	trace
10	$CH_2Cl_2$	40.7	1	20	> 5	5
11	PhCH <sub>3</sub>	33.9	0.1	3.3	37	21 (57)

Table 2. Photo-reductive cyclization of 3 promoted by 1 and 2 in various solvents<sup>a</sup>

<sup>a</sup>**3** (0.10 mmol), **1** (10 mol% vs **3**), **2** (1.2 equiv vs **3**), solvent (1.0 mL); 500 W Xe-lamp ( $\lambda > 390$ 

nm), 1 h. <sup>b</sup>Empirical parameter of solvent polarity ( $E_T(30)$ , kcal/mol).<sup>9</sup> <sup>c</sup>Donor number (DN,

kcal/mol) and acceptor number (AN) of solvents.<sup>8</sup> <sup>d</sup>Determined by <sup>1</sup>H NMR. <sup>e</sup>The yield in the parenthesis is based on the conversion of **3**. <sup>f</sup>Same as entry 3 of Table 1. <sup>g</sup>Same as entry 7 of Table 1.

Next, DFT calculations and electrochemical measurements were performed to gain more insight into the structure and redox properties of **1** (Figure 4).<sup>11</sup> The results reveal that the imidazolium and naphthoxide rings in the energy minimized structure of 1 are not in parallel planes, thus preventing  $\pi$ -conjugation of these moieties (Figure 4a). Moreover, the oxy anion of the naphthoxide moiety is located close to the imidazolium nitrogen. In addition, although frontier orbitals are distributed over the entire molecule, the HOMO coefficients are greater in the naphthoxide moiety and the LUMO coefficients are relatively larger in the imidazolium moiety (Figure 4b). Thus, an electrostatic interaction exists between the negatively charged naphthoxide and the positively charged imidazolium groups. This interaction causes stabilization of 1, as reflected by the observation that the oxidation potential of 1 ( $E^{ox}_{1/2}$  = +0.64 V vs SCE in MeCN) is much greater than expected for a simple naphthoxide derivative ( $E^{ox}_{1/2} = +0.1$  V for 2-naphthoxy anion<sup>12</sup> and +0.03 V for 1-methy-2-naphthoxy anion in MeCN) (see Figures S3, S4 and Table S2). The electron donating ability of 1 should be enhanced in solvents that have high DN (entries 1~4 in Table 2) or low ANvalues (entries 5, 7, 8 and 11 in Table 2) because they should strongly coordinate to the imidazolium moiety and not tightly interact with naphthoxy anion.<sup>10</sup> Moreover, stronger coordination of DMSO

to **1** than MeCN, which should more enhance the imidazolium as well as naphthoxide character of **1** in former solvent, is confirmed by the comparison of <sup>1</sup>H NMR of **1** in these solvents (Figure 5). A peak of  $H_A$  appears in upper field and that of  $H_B$  appears in more downfield in DMSO- $d_6$  compared to CD<sub>3</sub>CN (see details in Experimental Section and SI).



**Figure 4.** The results from DFT calculations of **1** (B3LYP/6-311+G(d,p)). a) Optimized structure depicted by a ball-and-bond type model from different angles. b) Frontier orbital distributions.



**Figure 5.** Comparison of <sup>1</sup>H NMR chemical shifts of representative protons of 1 ( $H_A$  and  $H_B$ ) in DMSO-*d*<sub>6</sub> (above) and CD<sub>3</sub>CN (below).

In order to gain information about excited species derived from 1, laser flash photolysis

experiments using 1 were performed in the absence and presence of **3** in DMSO (Figure 6). Figure 6a contains transient absorption spectra of **1** at 510 nm and 700 nm. The long lifetime of 17  $\mu$ s and significant quenching by molecular oxygen indicate that the observed transient absorption is due to the excited triplet state of **1** (see Figure S8). In Figure 6b are shown transient absorption spectra of **1** with **3**. In addition to the triplet peaks, a new peak around 400 nm is observed, which is assigned to a reaction product of excited **1** and ground state of **3**. However, the intensity and lifetime of the triplet signal for **1** observed at 510 nm are unaffected by addition of **3** (see Figure S9), which indicates that the triplet state does not react with **3**. Therefore, a short-lived species derived from **1** upon irradiation that could not be detected by nanosecond laser experiment is tentatively considered to undergo SET to **3**.



**Figure 6.** a) Transient absorption spectra of Ar-saturated DMSO solution of **1** (0.15 mM). b) Transient absorption spectra of Ar-saturated DMSO solution of **1** (0.15 mM) and **3** (1.5 mM).

On the basis of the results described above, it is reasonable to propose the reaction pathways

shown in Scheme 2 for the reaction of **3** photocatalyzed by **1** and **2**. In the process, visible light irradiation generates the photo-excited state of 1, which should have short lifetime (see above) and a high oxidizing ability as reflected in an oxidation potential  $(E^{ox^*})$  of -2.08 V, estimated by using the end-absorption wavelength (456 nm with  $\varepsilon = 500 \text{ M}^{-1} \text{ cm}^{-1}$ ) to determine excited state energy  $(E_{ex} = 2.72 \text{ eV})$  and oxidation potential  $(E_{1/2}^{ox} = +0.64 \text{ V})$  of 1. Consequently, SET from the excited state of 1 to 3 ( $E^{\text{red}}_{1/2} = -1.51$  V, see Figure S5 and Table S3) should be energetically favorable.<sup>13</sup> Subsequent SET to the formed radical cation of 1 (imidazolium naphthoxyl radical 11) from 2  $(E^{\text{ox}}_{1/2} = +0.34 \text{ V})^{6b}$  regenerates 1 and forms the radical cation of 2 (2<sup>++</sup>). Deiodination of the formed radical anion of **3** produces aryl radical **12**, which subsequently undergoes rapid 5-exo cyclization to give the alkyl radical 13. Hydrogen atom transfer between  $2^{++}$  and 13 produces the observed product 4 and imidazolium ion 14. When 2 was replaced by Hantzsch ester  $(E_{1/2}^{ox} = +0.93 \text{ V})^{4g}$  and the mixture of NEt<sub>3</sub>  $(E_{1/2}^{ox} = +0.93 \text{ V})^{4g}$  and HCOOH in DMF, no formation of 4 was observed because SET processes between 11 and these amines would be endoergonic (see Table S4).

Scheme 2. Plausible reaction pathways of the reductive deiodination of 3 catalyzed by the photoexcited 1 and 2



Next, in order to further evaluate the PET catalyst system of 1 with 2, desulforylation reactions of sulfonamides 5, 7 and 9 (0.1 M) were chosen as another probe reactions (Table 3). The nitrogen-sulfur bond cleavage of their radical anions, in which either homolytic or heterolytic cleavages may occur depending on the substituents, are expected (Scheme 3).<sup>4a,4g,14</sup> Desulfonvlation reactions of N-sulfonylindols 5 (-1.67 V, -1.74 V, and -1.92 V for 5a, 5b, and 5c respectively) proceed smoothly to give the corresponding free indoles 6 in excellent yields (entries 1, 8 and 9). The weak electron accepting substrate 5c requires longer irradiation times for completion. Interestingly, irradiation of the solution not containing 2 resulted in some consumption of 5a with the formation of 6a, which may be a consequence of the stoichiometric reaction with 1 present (entry 2). As expected, these processes do not occur in the absence of 1 or without irradiation (entries 3 and 4). The observations suggest that the desulfonylation reactions follow a catalytic pathway that is similar to that presented in Scheme 2. Notably, the reactions proceed not only in toluene but also in CH<sub>2</sub>Cl<sub>2</sub>, although again not in MeCN (entries 5-7). In addition, while

photoreaction of N-sulfonyl benzamide 7 (-1.58 V) in the presence of 2 but in the absence of 1
forms 8 in 16% at 17% conversion of 7 (not shown in Table 3), the photocatalytic reaction using
both 1 and 2 leads to complete consumption of 7 and generation of 8 in an excellent 96% yield
(entry 10). <sup>15</sup> In contrast, diphenyl tosylamine 9 (-2.07 V), which is the weakest electron acceptor, is
less reactive than 7 (entry 11). Moreover, DMSO was found to be superior to DMF as a solvent for
reaction of 9 that produces 10, even though 9 was not completely consumed using a long irradiation
time (entry 12). DMSO is also a suitable solvent for the desulfonylation of 5a promoted by the
commercially available household white LED (7.3 W) irradiation for 24 h giving 6a in 97% yield
while same reaction did not lead to the completion in DMF (see Table S5).

entry	substrate	solvent	Irrad time (h)	conv (%) <sup>b</sup>	product	yield (%) <sup>b,c</sup>
1	5a	DMF	1	100	6a	98
$2^d$	5a	DMF	1	6	6a	4 (67)
3 <sup>e</sup>	5a	DMF	1	0	6a	0
$4^{\mathrm{f}}$	5a	DMF	1	0	6a	0
5	5a	MeCN	1	6	6a	4 (67)
6	5a	$CH_2Cl_2$	1	100	6a	97
7	5a	PhCH <sub>3</sub>	1	100	6a	98
8	5b	DMF	1	100	6a	93
9	5c	DMF	2	100	6b	89
10	7	DMF	0.5	100	8	96
11	9	DMF	6	9	10	trace
12	9	DMSO	6	42	10	33 (79)

Table 3. Photo-desulfonylation of *N*-sulfonamide 5, 7, 9 catalyzed by 1 and 2<sup>a</sup>

<sup>a</sup>Substrate (0.10 mmol), **1** (10 mol% vs substrate), **2** (1.2 equiv vs substrate), solvent (1.0 mL); 500 W Xe-lamp ( $\lambda > 390$  nm). <sup>b</sup>Determined by using <sup>1</sup>H NMR. <sup>c</sup>Yields in the parenthesis are based on

the conversion of **5**. <sup>d</sup>In the absence of **2**. <sup>e</sup>In the absence of **1**. <sup>f</sup>Stirred in the dark.

Scheme 3. Desulfonylation of sulfoneamide radical anions

While photo-redox reactions of  $\beta$ -ketosulfones were previously performed by using a ruthenium complex as a photocatalyst, an organic donor photocatalyst such as Eosin Y was recently reported to be ineffective for alkylcarbonyl substrate.<sup>16</sup> Thus, our photocatalyzed reaction condition was briefly applied for desulfonylation reactions ( $\lambda > 390$  nm) of  $\beta$ -ketosulfones **15a** ( $E^{\text{red}}_{1/2} = -1.48$  V) and **15b** ( $E^{\text{red}}_{1/2} = -1.89$  V) (Scheme 4). Reactions of **15** (0.1 mmol) using **1** (10 mol%) and **2** (1.2 equiv) in DMSO (1 mL) produced the respective ketones **16a** and **16b** in good to excellent yields .

#### Scheme 4. Photo-desulfonylation of β-ketosulfones 15



#### CONCLUSION

As demonstrated in the investigation described above, betaine 1 serves as an effective electron donating, organic photocatalyst for PET reactions. In the effort, solvent effects on the efficiencies of

the reactions were observed and attributed to specific solvation, such as donor and acceptor interactions with the benzimidazolium and naphthoxide moieties of **1**. Therefore, the findings show that a proper choice of solvent is crucial for the success of these photocatalytic reductions. While various betaines have been developed and their properties have been characterized,<sup>17</sup> these zwitterionic substances to the best of our knowledge have not been previously used as photo-redox catalysts.<sup>18</sup> Determination of the substrate scope as well as the detailed mechanism of these photo-catalytic reactions are under current investigation.

#### **EXPERIMENTAL SECTION**

**General methods.** NMR spectra were recorded on CDCl<sub>3</sub> with tetramethylsilane (Me<sub>4</sub>Si) as an internal standard, DMSO- $d_6$ , and CD<sub>3</sub>CN solutions at 400 MHz for <sup>1</sup>H NMR and 100 MHz for <sup>13</sup>C NMR. Proton-decoupled carbon data of <sup>13</sup>C NMR are reported. High resolution mass spectra (HRMS) were recorded on a doublefocusing mass spectrometer by using Atmospheric Pressure Chemical Ionization (APCI). Oxidation and reduction potentials in MeCN were measured using cyclic voltammetry and a previously described procedure.<sup>4f</sup> Calibration of the potential values were performed using the formal potentials of ferrocene/ferrocenium couple, which are 0.067 V and 0.442 V versus Ag/AgNO<sub>3</sub> and SCE, respectively. Half-wave potentials ( $E_{1/2}$ ) reported in the manuscript were obtained from the peak potentials by subtracting or adding 0.029 V.<sup>19</sup> Light

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sources for photoreactions were a 500 W Xe lamp with glass filter L-42 ( $\lambda > 390$  nm) and a 7.3 W white LED. Column chromatography was performed with silica gel. Anhydrous solvents for photoreactions were obtained as follows. THF was distilled over sodium-benzophenone under N<sub>2</sub>. CH<sub>2</sub>Cl<sub>2</sub> and PhCH<sub>3</sub> were purified in a same manner by the treatment with H<sub>2</sub>SO<sub>4</sub>, water, 5% NaOH, water, and CaCl<sub>2</sub> and then distilled over CaH<sub>2</sub>. MeCN was distilled over  $P_2O_5$  and subsequently distilled with K<sub>2</sub>CO<sub>3</sub>. EtOAc was washed with 5% Na<sub>2</sub>CO<sub>3</sub>, water, NaCl and K<sub>2</sub>CO<sub>3</sub> and subsequently distilled. Pyridine was washed with KOH, water and subsequently distilled with CaH<sub>2</sub>. Acetone was purified only by distillation. Anhydrous DMF, DMSO, and MeOH were purchased and used without distillation. Other reagents and solvents were used without further purification. Benzimidazoline  $2^{20}$  is known compound and HONap-BIH<sup>6b</sup> was prepared according to the previously reported procedure. Substrates  $3_{2}^{21}$   $5a_{2}^{22}$   $5b_{3}^{23}$   $5c_{3}^{24}$   $7_{4}^{15}$   $9_{5}^{25}$   $15a_{2}^{26}$  and  $15b^{16a}$  which are known compounds, were prepared by using reported procedures. Preparation procedure and spectroscopic data of the betaine 1 are described below.

# Preparation of 1,3-dimethyl-2-(2-naphthox-1-yl)benzimidazolium (1).

Synthesis of 1,3-dimethyl-2-(2-hydroxy-1-naphthyl)benzimidazolium bromide. A mixture of 1,3-dimethyl-2-(2-hydroxy-1-naphthyl)benzimidazoline (HONap-BIH, 901 mg, 3.10 mmol) and 2-bromoacetophenone (926 mg, 4.65 mmol) in THF (30 mL) was stirred at room temperature for 3

h. Precipitates formed by the addition of Et<sub>2</sub>O (ca 20 mL) were collected by filtration. The solid was

crystallized from MeOH-Et <sub>2</sub> O to give 1,3-dimethyl-2-(2-hydroxy-1-naphthyl)benzimidazolium
bromide (1.062 g, 2.87 mmol, 93%). Colorless solid; mp 283.0-284.0 °C; <sup>1</sup> H NMR (400 MHz,
DMSO- $d_6$ ) $\delta$ 11.47 (bs, 1H), 8.28 (d, $J = 8.8$ Hz, 1H), 8.18–8.12 (m, 2H), 8.06 (d, $J = 8.0$ , 1H),
7.82–7.77 (m, 2H), 7.57–7.44 (m, 3H), 7.32 (d, $J = 8.0, 1H$ ), 3.82 (s, 6H); <sup>13</sup> C NMR (100 MHz,
DMSO-d <sub>6</sub> ) δ 156.9, 148.1, 135.7, 132.1, 131.8, 129.1, 129.0, 127.6, 126.7, 124.4, 122.5, 118.2,
113.7, 99.0, 32.5; HRMS (ESI) m/z calcd for $C_{19}H_{17}N_2O[M-Br]^+$ 289.1335, found 289.1336.

Synthesis of 1,3-dimethyl-2-(2-naphthox-1-yl)benzimidazolium (1). To

1,3-dimethyl-2-(2-hydroxy-1-naphthyl)benzimidazolium bromide (793 mg, 2.00 mmol) was added a MeOH (25 mL) containing KOH (259 mg, 4.62 mmol). The resulting mixture was stirred at room temperature for 1 h and then extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL x8) after addition of water (30 mL). The extract was washed with brine and dried over anhydrous MgSO<sub>4</sub>. The residue obtained by concentration was subjected to column chromatography using MeCN (to remove impurity) and subsequently MeOH. The obtained solid was crystallized from CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O to give 1,3-dimethyl-2-(2-naphthox-1-yl)benzimidazolium (1) (477 mg, 1.66 mmol, 83%). Yellow solid; mp 218.0–220.0 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.00–7.95 (m, 2H), 7.67–7.62 (m, 2H), 7.59 (d, *J* = 9.2 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.18–7.13 (m, 1H), 6.91–6.87 (m, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 9.2 Hz, 1H), 3.75 (s, 6H); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN); 7.82-7.76 (m, 2H), 7.65-7.56 (m, 4H), 7.21-7.16 (m, 1H), 6.96-6.91 (m, 1H), 6.76-6.71 (m, 2H), 3.76 (s, 6H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 171.7, 155.0, 135.2, 133.5, 131.9, 128.4, 128.0, 127.0, 125.3, 122.9, 119.1, 118.0, 112.6, 94.4, 32.3; HRMS (ESI) m/z calcd for C<sub>19</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 289.1335, found 289.1339.

**Photoreaction procedure.** Solutions containing substrates **3**, **5**, **7**, **9**, or **15**, and **1** and **2** in Pyrex test tubes (1.4 cm diameter), immersed in a water bath at room temperature, were irradiated using a Xe lamp or with a white LED without using a water bath. A typical procedure is described below. An appropriate solvent (1.0 mL) containing **1** (2.9 mg, 10 mol%), **2** (26.9 mg, 0.12 mmol) and **3** (26.0 mg, 0.10 mmol) was purged with N<sub>2</sub> for 10 min and then irradiated with a Xe lamp through L-42 glass filter. The photolysate was diluted with water (30 mL) and extracted with Et<sub>2</sub>O (20 mL×3). The combined extracts were washed with water (30 mL×2), brine (30 mL), dried over anhydrous MgSO<sub>4</sub> and concentrated in vacuo to give a residue. The conversion of **3** and the yield of **4** were determined by using <sup>1</sup>H NMR analysis of the residue with 1,4-dimethoxybenzene or triphenylmethane as an internal reference in CDCl<sub>3</sub>. Photo-products **4**,<sup>21</sup> **6a**<sup>27</sup> and **8**<sup>15</sup> are known compounds, and **6b**, **10**, **16a** and **16b** are commercial materials.

**Density functional theory (DFT) calculations.** Calculations were carried out using the Gaussian 09 program package.<sup>11</sup> Geometry optimization was performed on a ground state structure at the restricted B3LYP/6-311+G(d,p) level. In addition, frequency calculations were performed on the optimized structure of **1** to confirm that no imaginary frequencies are obtained. The optimized

structure and molecular orbitals (MOs) were visualized with GaussView 5.0.9 software.

Laser flash photolysis. Transient absorption experiments with 1 in the presence and absence of 3 were carried out with an updated version of homemade laser flash photolysis setup described elsewhere.<sup>6b</sup> The third harmonics of a nanosecond Nd:YAG Laser (wavelength of 355 nm, pulse length of 6 ns, intensity of 2 mJ/0.20 cm<sup>2</sup>/pulse) and a 75 W Xe arc lamp equipped in an ellipsoidal mirror lamp house were used as pump and probe light sources, respectively. The probe light transmitted through the sample solution was dispersed by using a monochromator and detected with a photomultiplier tube. The output current from the photomultiplier was amplified with a fast current amplifier and recorded with a digital oscilloscope. The time resolution and dead time for this setup were 20 ns and 80 ns, respectively. Wavelength resolution was 6.8 nm. The samples were dissolved in dehydrated DMSO and placed in a 1 cm path-length quartz cuvette. The solutions were deoxygenated by Ar bubbling before the measurement unless otherwise stated.

#### ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: Data of absorption spectra, cyclic voltammograms, and <sup>1</sup>H NMR of some compounds. Additional photoreactions, DFT calculations, and laser photolysis (PDF), <sup>1</sup>H NMR and <sup>13</sup>C NMR charts of **1**.

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#### Notes

The authors declare no competing financial interest.

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