Phenylene-bridged bis(benzimidazolium) (BBIm\textsuperscript{2+}): a dicaticonic organic photoredox catalyst\textsuperscript{†}

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A dicaticonic photoredox catalyst composed of phenylene-bridged bis(benzimidazolium) (BBIm\textsuperscript{2+}) was designed, synthesised and demonstrated to promote the photochemical decarboxylative hydroxylation and dimerisation of carboxylic acids. The catalytic activity of BBIm\textsuperscript{2+} was higher than that for a monocation analogue, suggesting that the dicaticonic nature of BBIm\textsuperscript{2+} plays a key role in these decarboxylative reactions. The rate constant for the decay of the triplet–triplet absorption of the excited BBIm\textsuperscript{2+} increased with increasing concentration of the carboxylate anion with a saturated dependence, suggesting that photoinduced electron transfer occurs within the ion pair complex composed of the triplet excited state of BBIm\textsuperscript{2+} and a carboxylate anion.

Introduction

Given the widespread availability of carboxylic acids from nature and commercial sources, the decarboxylative transformation of carboxylic acid derivatives represents an attractive synthetic organic method.\textsuperscript{1} However, the direct decarboxylation of unactivated carboxylic acids remains a challenge, and the use of stoichiometric amounts of metal oxidants,\textsuperscript{2} or pre-activation to acid chlorides or activated esters, such as Barton esters\textsuperscript{3} and N-(acyloxy)phthalimides (NHPI esters),\textsuperscript{4} are still required. Although organic electron acceptors such as acidinium,\textsuperscript{5} iminium,\textsuperscript{6} phthalimide,\textsuperscript{7} and cyanoarene\textsuperscript{8} have been reported to promote the decarboxylation of carboxylic acids under photolysis conditions, a stoichiometric amount of these acceptors is needed for the reaction to reach completion. The use of transition metal catalysts and photoredox catalysts for the catalytic decarboxylative transformation of carboxylic acids has extensively been studied (Scheme 1). In transition metal catalysed reactions, the metal carboxylates are generated \textit{in situ} and then undergo decarboxylation to produce an aryl-metal species (Scheme 1a).\textsuperscript{1,9–11} However, the substrates are limited to the highly activated aromatic carboxylic acids bearing electron-withdrawing groups, such as nitro or fluorine group(s), at the ortho position, except for the Ni/PPh\textsubscript{3}-catalysed decarboxylative olefination of alkyl carboxylic acids.\textsuperscript{9} The other catalytic method involves the use of photoredox catalysis,\textsuperscript{1,9–11} in which the photoinduced single electron oxidation of an alkyl carboxylate anion with a photoexcited catalyst occurs, with the formation of an alkyl carboxyl radical (Scheme 1b). The alkyl carboxyl radical then spontaneously undergoes decarboxylation to produce an alkyl radical, which can participate in subsequent reactions. However, the application of this protocol to simple carboxylic acids is still difficult due to their highly positive oxidation potentials (e.g., CH\textsubscript{3}COO\textsuperscript{−}: E\textsubscript{1/2}(CH\textsubscript{3}COO\textsuperscript{−}/CH\textsubscript{3}COO) = +1.47 V vs. SCE).\textsuperscript{11} When commonly used ruthenium polypyridyl complexes are employed as a photoredox catalyst (e.g., Ru(bpy)\textsubscript{3}\textsuperscript{2+}; bpy = 2,2'-bipyridyl: E\textsubscript{1/2}(Ru\textsuperscript{3+}/Ru\textsuperscript{2+}) = +0.77 V vs. SCE),\textsuperscript{12} The use of iridium complexes containing pyridine-based ligands bearing electron-withdrawing groups has recently emerged as viable photocatalysts for promoting the oxidative decarboxylation of simple aliphatic carboxylic acids.\textsuperscript{13,14} However, these transition-metal complexes are expensive and potentially toxic.\textsuperscript{15} In the light of the above situation, the development of a simple and robust catalyst system that

![Scheme 1](image-url)

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enables oxidation of unactivated carboxylic acids without the use of harmful reagents would be highly desirable. Organic photoredox catalysts have the potential to address these issues.\textsuperscript{16–18} An organic acridinium dye could be used in photocatalytic decarboxylative reactions of alkyl carboxylic acids including hydrodecarboxylation and decarboxylative trifluoromethylthiolation.\textsuperscript{16,17} Yoshimi and co-workers reported on decarboxylative transformations of a wide variety of alkyl carboxylic acids using an arene/electron acceptor system by photoinduced electron transfer.\textsuperscript{16,19} Although these examples demonstrate the potential utility of organic photoredox catalysts for use in oxidative decarboxylative transformation of unactivated organic acids, new classes of organic catalysts\textsuperscript{20} continue to be developed to further expand the scope of these reactions.

We envisioned that dicationic organic salts could function as photoredox catalysts with high oxidation ability because their electron deficient nature allows the HOMO energy level to be lowered, thereby making the reduction potential in the excited state to be sufficiently high to allow carboxylates to be oxidised. To date, organic dicationic molecules have not been applied to photoredox reactions, except for 2,7-diazapyrenium,\textsuperscript{22} trisamino cyclopropenium\textsuperscript{23} and bisphosphonium.\textsuperscript{23} Herein, we report on the design, synthesis and properties of a new dicationic organic photocatalyst based on a bis(benzimidazolium) (BBIm\textsuperscript{2+}) framework, and its application to photocatalytic decarboxylative reactions is also demonstrated.

Results and discussion

As cationic moieties, we focused on imidazolium scaffolds, which have found various applications in modern synthetic and material chemistry, for example, as precursors of N-heterocyclic carbenes\textsuperscript{24} and components of ionic liquids.\textsuperscript{25} Thermal stability,\textsuperscript{26} redox properties,\textsuperscript{27} and ease of structural modification would be desirable properties of such a catalyst. We designed a new phenylene-bridged bis(benzimidazolium) (BBIm\textsuperscript{2+}), with the expectation that two cationic imidazolium moieties should result in sufficiently low HOMO energies that would permit unactivated carboxylic acids to be oxidised upon photoexcitation (Scheme 2a). Density functional theory calculations at the \textit{ω}B97XD/6-31G(d,p) level of theory were performed to investigate the structural and electronic properties of the BBIm\textsuperscript{2+}. Structural optimisation revealed that the benzimidazolium rings of BBIm\textsuperscript{2+} are twisted relative to the central phenyl ring by 47° with a \textit{C}\textsubscript{2h} symmetry. The electrostatic potential indicated that the majority of the positive charges in BBIm\textsuperscript{2+} are distributed over the imidazolium rings (Scheme 2c). BBIm\textsuperscript{2+} possesses a lower HOMO (\(\psi_{161} = -13.48\) eV) than that of monocation analogue 1\textsuperscript{+} (\(\psi_{1\text{+}} = -11.60\) eV, Scheme 2d, cf. Fig. S5 in the ESI\textsuperscript{†} for details), possibly because of the more positive nature of the molecule. These results indicate that BBIm\textsuperscript{2+} would be reduced more easily than 1\textsuperscript{+}, thereby serving as a stronger oxidant than 1\textsuperscript{+} as we initially envisioned. Indeed, the calculated HOMO energy of BBIm\textsuperscript{2+} was lower than that of 9-mesityl-10-methylacridinium (Acr-Mes\textsuperscript{+}, \(\psi_{83} = -11.24\) eV, cf. Fig. S5 in the ESI\textsuperscript{†}), which can oxidize alkyl carboxylic acids in the photo excited state.\textsuperscript{16,17} The HOMO of BBIm\textsuperscript{2+} is distributed across the benzimidazolium and central phenylene rings, whereas the LUMO is largely located at the N=–C=N moiety of the benzimidazolium ring and the phenylene moiety.

Having estimated theoretically that BBIm\textsuperscript{2+} has a sufficient oxidation ability to oxidise carboxylates by photoinduced electron transfer, we commenced our synthetic studies of BBIm\textsuperscript{2+}. BBIm\textsuperscript{2+} was synthesised by a commonly used condensation reaction between a diamine and an aldehyde (Scheme 3).\textsuperscript{28} Thus, the treatment of diamine 2 with terephthalaldehyde and a catalytic amount of \(p\)-toluenesulfonic acid afforded the double cyclised product 3 in 83% yield. Subsequent oxidation of 3 with N-bromoacetamide provided BBIm\textsuperscript{2+}·2[Br\textsuperscript{−}]. Because of the poor solubility of BBIm\textsuperscript{2+}·2[Br\textsuperscript{−}] in common organic solvents,
the counter anion was changed to PF_6^- by treatment with AgPF_6 in acetonitrile to give BBIm^{2+}\cdot[PF_6^-] in 89% yield (2 steps from 3), which is soluble in acetonitrile, DMF, and hexafluoroisopropanol.

Recrystallization from DMSO/methanol gave colorless crystals of BBIm^{2+}\cdot[PF_6^-], which were suitable for a single X-ray crystallographic analysis (Fig. 1a, see Fig. S1 in ESI†). The dihedral angle for the central phenyl ring and benzimidazolium moieties was found to be 59° (Fig. 1b), which was larger than the calculated value. This difference can be attributed to the existence of counter anions and/or a packing force. The counter anions were located close to the imidazolium moieties in the crystal, in good agreement with the sites predicted based on the calculated electrostatic potential (Scheme 1b).

Absorption and emission spectra of BBIm^{2+}\cdot[PF_6^-] (Fig. 2a) displayed an intense absorption band at around 290 nm with a weak broad tail in the longer wavelength region (~500 nm), while a single emission peak with \lambda_{\text{max}} at 428 nm was observed. A large Stokes shift (~140 nm) of BBIm^{2+}\cdot[PF_6^-] suggested that BBIm^{2+}\cdot[PF_6^-] undergoes a significant structural change in the excited state. According to the time-dependent (TD) ωB97XD/6-31G(d,p) calculation of BBIm^{2+}, the absorption band at around 290 nm of BBIm^{2+} is assigned to HOMO (j = 161)/LUMO (j = 162) transitions (λ = 288 nm and f = 0.99).

The cyclic voltammogram (CV) of BBIm^{2+}\cdot[PF_6^-] in acetonitrile exhibited a reversible redox wave (E_{1/2} = −1.02 V vs. SCE) (Fig. 2b). The corresponding monocation 1^+\cdot[Br^-] displayed an irreversible wave (E_{p/2} = −1.47 V vs. SCE, Fig. S6 in ESI†). Therefore, the advantage of using BBIm^{2+}\cdot[PF_6^-] over the corresponding monocation 1^+\cdot[Br^-] can be attributed not only its higher reduction potential as we initially envisioned, but also to the stability of the reduced species. Optical and electrochemical measurements led us to estimate the excited singlet state reduction potential of BBIm^{2+}\cdot[PF_6^-] to be 1 E_{\text{red}} = +2.56 V vs. SCE,38 the value of which is sufficiently high to permit a wide variety of organic compounds such as benzene44 or carboxylic acids to be oxidised.41 The triplet state reduction potential of BBIm^{2+}\cdot[PF_6^-] was also estimated to be 3 E_{\text{red}} = +0.89 V vs. SCE.40
We next examined the catalytic activity of BBIm$^{2+}$·2[PF$_6^-$] in the photocatalytic decarboxylative hydroxylation of carboxylic acids.$^{18}$ Irradiation of an acetonitrile solution of carboxylic acid 4a with a xenon lamp (~300 nm) in the presence of BBIm$^{2+}$·2[PF$_6^-$] (10 mol%) and NaOH (60 mol%) under an atmosphere of nitrogen for 5 h afforded the desired alcohol 5a in 68% yield, after reductive work up with NaBH$_4$ (Table 1, entry 1).$^{18}$ Control experiments revealed that both BBIm$^{2+}$·2[PF$_6^-$] and irradiation are essential for the reaction to efficiently proceed (entries 2 and 3). The reaction proceeded more efficiently under an atmosphere of oxygen compared with reactions performed under an atmosphere of nitrogen (entry 4). In the absence of NaOH, the yield was decreased to 32% (entry 5). The use of the corresponding monocation 1$^+$·[Br$^-$] (entry 6) or Acr-Mes$^+$·[ClO$_4^-$]$_{34,32}$ (entry 7) as a photocatalyst also gave 5a, but in lower yields of 40% and 46%, respectively. In addition, the quantum yield for the photocatalytic hydroxylation reaction using BBIm$^{2+}$·2[PF$_6^-$] was determined to be 0.60, which is significantly higher than that for 1$^+$·[Br$^-$] (0.004) or Acr-Mes$^+$·[ClO$_4^-$] (0.23) catalysed reactions.$^{33}$ The reaction also proceeded by using 365 nm or 405 nm LED lights instead of a xenon lamp (entries 8 and 9). It was possible to oxidise an array of carboxylic acids using BBIm$^{2+}$ under the optimised conditions (Table 2). Benzyl carboxylic acids bearing methyl (4a), phenyl (4b) and cyclohexyl (4c) groups at the benzylic position were successfully decarboxylated to give the corresponding benzylic alcohols (5a–5c) in good yields. Whereas primary benzylic (4d) and secondary non-benzylic (4e) carboxylic acids were not good substrates in this decarboxylative hydroxylation, tertiary alkyl carboxylic acids 4f and 4g underwent the reaction to give products in moderate to good yield.

During the course of our investigation of photocatalytic decarboxylative hydroxylation reactions using BBIm$^{2+}$·2[PF$_6^-$], we found that the tertiary benzylic carboxylic acid 6a underwent decarboxylative dimerisation to give 7a under identical conditions. Although this type of decarboxylative dimerisation reaction has already been reported, including Kolbe electrolysis$^{34a}$ and reactions using a stoichiometric amount of an oxidant, such as S$_2$O$_8^{2-}$,$^{14b}$ Hg(II)$^{34c}$ and a heterogeneous Pt–TiO$_2$ photocatalyst,$^{14b,c}$ this is the first example of the use of an organic photoredox catalyst, to the best of our knowledge. Further optimization for this dimerisation was performed using 6a as a substrate (Table 3). The yield of 7a was increased when the reaction was carried out under an atmosphere of air rather than oxygen (entries 1 and 2). Finally, shortening the reaction time to 3 h resulted in a better yield, because the undesired decomposition of 7a could be suppressed (57%, entry 3).$^{33}$

The use of the monocation 1$^+$·[Br$^-$] or Acr-Mes$^+$·[ClO$_4^-$]$_{34,32}$ as a catalyst resulted in lower yields of 4% and 33%, respectively (entries 4 and 5). These results again underscore the prominent activity of this dicaticon catalyst for the oxidation of unactivated organic acids.

A range of tertiary benzylic carboxylic acids (6a–6h) could be oxidatively dimerised by BBIm$^{2+}$·2[PF$_6^-$] under

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**Table 1** Photoinduced BBIm$^{2+}$-catalysed decarboxylative hydroxylation of 4a

| Entry | Variation from the standard conditions | GC yields (%) |
|-------|---------------------------------------|--------------|
| 1     | None                                  | 68           |
| 2     | Without BBIm$^{2+}$·2[PF$_6^-$]         | 0            |
| 3     | In the absence of light source         | 0            |
| 4     | Under N$_2$                            | 8            |
| 5     | Without base                          | 32           |
| 6     | 1$^+$·[Br$^-$] instead of BBIm$^{2+}$·2[PF$_6^-$] | 40           |
| 7     | Acr-Mes$^+$·[ClO$_4^-$] instead of BBIm$^{2+}$·2[PF$_6^-$] | 46           |
| 8     | 365 nm LED lamp (60 W) instead of Xe lamp | 67           |
| 9     | 405 nm LED lamp (60 W) instead of Xe lamp | 35           |

*a Reaction conditions: (a) 4a (0.15 mmol), BBIm$^{2+}$·2[PF$_6^-$] (0.015 mmol), NaOH (0.090 mmol), O$_2$, in acetonitrile (6.0 mL), xenon lamp (500 W) irradiation for 5 h, RT; (b) NaBH$_4$, MeOH.

**Table 2** Substrate scope for BBIm$^{2+}$-catalysed decarboxylative hydroxylation

| R$^+$·COOH | BBIm$^{2+}$·2[PF$_6^-$] (10 mol%) | NaOH (60 mol%) | R$^+$·OH |
|------------|----------------------------------|----------------|---------|
| 4a–4g      |                                 |                | 5a–5g   |

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*a Reaction conditions: carboxylic acid (0.15 mmol), BBIm$^{2+}$·2[PF$_6^-$] (0.015 mmol), NaOH (0.090 mmol) in acetonitrile (6.0 mL), xenon lamp (500 W) irradiation for 18 h, RT. b GC yield. c NMR yield.
The reaction was conducted in CH$_3$CN/H$_2$O (1 : 1).

To elucidate the mechanism for this photoinduced decarboxylation reaction, quenching measurements$^{37}$ were performed by fluorescence and triplet-triplet (T-T) absorption spectroscopies. Electron transfer from tBuCOO$^-$ to the singlet excited state of BBIm$_{2+}$ (1BBIm$_{2+}$*) is energetically favorable because the free energy change is significantly negative: $\Delta G_{et} = E_{ox} - E_{red} - E^* = 1.02 - (-0.50) - 3.58 = -2.06$ eV. However, no fluorescence quenching was observed when tBuCOO$^-$ was added to an acetonitrile solution containing BBIm$^{2+}$. The fluorescence lifetime of BBIm$_{2+}$ was determined to be 0.4 ns by time-resolved fluorescence measurements, which is too short to quench the low concentration of tBuCOO$^-$ (0–0.2 mM) under the present experimental conditions.$^{37}$ It therefore appears that the reactive species may be the triplet excited state of BBIm$_{2+}$ (3BBIm$_{2+}$*) rather than the short-lived singlet excited state. The free energy change for the electron transfer from tBuCOO$^-$ to 3BBIm$_{2+}$* was estimated to be $\Delta G_{et} = E_{ox} - E_{red} - 3E^* = 1.02 - (-0.50) - 1.91 = -0.39$ eV, where $3E^*$ was determined from the phosphorescence spectrum (861 nm) observed in an ethanol glass at 77 K. The negative $\Delta G_{et}$ value indicates that the electron transfer from tBuCOO$^-$ to 3BBIm$_{2+}$* is energetically feasible. To observe the electron transfer process between tBuCOO$^-$ and 3BBIm$_{2+}$*, the T-T absorption measurements were carried out by nanosecond laser flash spectroscopy (Fig. 3a). A typical T-T absorption at $\lambda_{max} = 580$ nm was detected taken at 0.8 ms after laser excitation at 355 nm due to the absorption of BBIm$_{2+}$. The T-T absorption decays obeying first-order kinetics with the rate constant ($k_1$) of $1.9 \times 10^2$ s$^{-1}$. tBuCOO$^-$ was added to an acetonitrile solution of BBIm$_{2+}$: 2[PF$_6$]$^-$ and the decay time profile was monitored at 580 nm. The observed decay rate constant ($k_{obs}$) increased with increasing concentration of tBuCOO$^-$, as shown in Fig. 3b. Interestingly, a saturated dependence was observed, rather than the typical linear relationship observed for a simple quenching...

### Table 3

| Entry | Cat. | Atmosphere | Time (h) | 7a (%) | 6a (%) |
|-------|------|------------|----------|--------|--------|
| 1$^a$ | BBIm$_{2+}$: 2[PF$_6$]$^-$. | O$_2$ | 18 | 23 | 0 |
| 2$^a$ | BBIm$_{2+}$: 2[PF$_6$]$^-$. | Air | 18 | 47 | 1 |
| 3 | BBIm$_{2+}$: 2[PF$_6$]$^-$. | Air | 3 | 57 | 9 |
| 4 | Ac-Mes$^+$ | Air | 3 | 4 | 0 |
| 5 | Ac-Mes$^+$ | Air | 3 | 33 | 0 |

$^a$ Reaction conditions: carboxylic acid (0.15 mmol), BBIm$_{2+}$ (0.015 mmol), NaOH (0.090 mmol) in acetonitrile/MeCN/H$_2$O (2 : 1 : 1), xenon lamp (500 W) irradiation, RT. $^b$ The reaction was conducted in CH$_3$CN/H$_2$O (1 : 1).

### Table 4

| Entry | Cat. | Atmosphere | Time (h) | 6a (%) | 6f (%) |
|-------|------|------------|----------|--------|--------|
| 6a | 52% | Air | 3 | 67% | 6c 64% |
| 6b | 52% | Air | 3 | 67% | 6d 36% |
| 6c | 52% | Air | 3 | 67% | 6e 65% |
| 6d | 52% | Air | 3 | 67% | 6f 33% |
| 6e | 52% | Air | 3 | 67% | 6g 41% |
| 6f | 52% | Air | 3 | 67% | 6h 41% |

$^a$ Reaction conditions: carboxylic acid (0.15 mmol), BBIm$_{2+}$: 2[PF$_6$]$^-$. (0.015 mmol), NaOH (0.090 mmol) in acetonitrile (4.0 mL)/MeCN (2.0 mL), xenon lamp (500 W) irradiation for 3 h, RT. $^b$ Run for 18 h.

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mechanism. The saturated behavior revealed that photoinduced electron transfer occurred with the formation of an ion pair complex composed of the $3^{\text{BBIm}^{2+}}$ and tBuCOO$, in competition with bimolecular electron transfer from tBuCOO$^-$ to $3^{\text{BBIm}^{2+}}$ and triplet decay of $3^{\text{BBIm}^{2+}}$ to the ground state without electron transfer (Scheme 4). The association constant ($K_{\text{assoc}}$) for the formation of an encounter complex $3^{\text{BBIm}^{2+}}$-$[\text{tBuCOO}$-$]^{\text{PF}_6^-}$ and the rate constant ($k_{\text{ET}}$) for intra-complex photoinduced electron transfer from tBuCOO$^-$ to $3^{\text{BBIm}^{2+}}$ were estimated to be $5.8 \times 10^4$ M$^{-1}$ and $3.4 \times 10^5$ s$^{-1}$, respectively, by curve fitting using eqn (1).

$$k_{\text{obs}} - k_T = k_{\text{ET}}K_{\text{assoc}}[\text{tBuCOO}^-][1 + K_{\text{assoc}}[\text{tBuCOO}^-]]$$

The electrochemical and optical properties of $3^{\text{BBIm}^{2+}}$ are summarised in Table 5 and an energy diagram of $3^{\text{BBIm}^{2+}}$ is shown in Scheme 4. The photoirradiation initially generates $3^{\text{BBIm}^{2+}}$, which is not quenched by tBuCOO$^-$ by electron transfer under the experimental conditions. Intersystem crossing, which is in competition with the fluorescence decay bound for the ground state, results in the formation of $3^{\text{BBIm}^{2+}}$. An intimate encounter complex between $3^{\text{BBIm}^{2+}}$ and the anionic tBuCOO$^-$ substrate is formed, and electron transfer in the complex then occurs to produce a radical pair (BBIm$^+$/tBuCOO$^-$). Based on the saturated behavior shown in Scheme 3b, an outer sphere electron transfer process from tBuCOO$^-$ to $3^{\text{BBIm}^{2+}}$ is presumably significantly slower than the intra-complex electron transfer. No back electron transfer from BBIm$^+$ to tBuCOO$^-$ occurs due to the rapid spontaneous decarboxylation of tBuCOO$^-$ leading to the products.

A plausible reaction mechanism for decarboxylative hydroxylation and dimerisation is shown in Scheme 5. Photoredox catalyst BBIm$^{2+}$ is initially excited by photoirradiation and subsequent intersystem crossing generates $3^{\text{BBIm}^{2+}}$, which oxidises the carboxylate A via single electron transfer (SET) to give the carboxyl radical B and the radical cation BBIm$^{2+}$. The carboxyl radical B rapidly releases CO$_2$ to produce the alkyl radical C. Under an O$_2$ atmosphere, the generated radical C is captured by oxygen$^{39}$ to generate peroxide radical D $[E_{\text{red}}$ (tBuO$_2$)/tBuO$_2$*] = +0.50 V vs. SCE$^{39,35}$ which is subsequently reduced by the radical cation BBIm$^{2+}$ ($E_{\text{red}}$ = −1.02 V vs. SCE) to form the peroxy anion E with the regeneration of BBIm$^{2+}$. Anion E is prone to undergo disproportionation to generate a mixture of an alcohol and a ketone, which was isolated as a single alcohol product by treatment with NaBH$_4$ in this study. When the reaction is performed under an atmosphere of air, in which the oxygen concentration is relatively low, two alkyl radicals C undergo radical–radical coupling to form dimer G before it is captured by oxygen.$^{40}$ In this case, SET from the radical cation BBIm$^{2+}$ to oxygen $[E_{\text{red}}$(O$_2$/O$_2^*$)] = −0.86 V vs. SCE$^{35}$ regenerates the catalyst BBIm$^{2+}$ with the concomitant formation of superoxide (O$_2^*$), which is eventually reduced to hydrogen peroxide.$^{33}$

The key to the successful application of BBIm$^{2+}$ in photocatalytic decarboxylative transformation of benzylic carboxylic acids is its dicaticonic nature, which serves to reduce the activation barrier of the SET from carboxylate by lowering the reorganization energy of the polar solvents.$^{35,36}$ When an electronically neutral photocatalyst (PC) oxidises a monoanionic substrate (S$^-$), a radical anion of PC (PC$^-$) and a neutral radical (S) are generated (Scheme 6a). In this process, the charges of the both components changes (PC: neutral $\rightarrow$ negative; S: negative $\rightarrow$ neutral), which requires the solvent molecules around PC and S.

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**Table 5** Summary of the electrochemical and optical properties of BBIm$^{2+}$-2[PF$_6$]$^-$

| $E_{\text{red}}$/V | $1E^*/eV$ | $1E^*/eV$ | $3E^*/eV$ | $3E^*/eV$ | $\lambda_{\text{max}}$/nm | $\lambda_{\text{em}}$/nm | $\tau_3$/ns |
|-----------------|-----------|-----------|-----------|-----------|-----------------|-----------------|----------|
| −1.02           | +3.58     | +2.56     | +1.91     | +0.86     | 290             | 428             | 0.4      |

$a$ All potentials in V vs. SCE. $E_{\text{red}}$ = ground state reduction potential, $1E^*$ = singlet excitation energy, $1E^*$ = excited singlet state reduction potential, $3E^*$ = triplet excitation energy, $3E^*$ = excited triplet state reduction potential. $\lambda_{\text{max}}$ = absorption peak, $\lambda_{\text{em}}$ = emission peak excited at 290 nm. $\tau_3$ = fluorescence lifetime.

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**Scheme 4** Energy diagram of BBIm$^{2+}$. $R$ = tBu, $\tau_3$ = fluorescence lifetime, $\tau_3$ = phosphorescence lifetime, $k_{\text{SC}}$ = rate constant for intersystem crossing, $k_{\text{ET}}$ = rate constant for electron transfer from tBuCOO$^-$ to $3^{\text{BBIm}^{2+}}$, $K_{\text{assoc}}$ = association constant for the formation of an encounter complex $3^{\text{BBIm}^{2+}}$-[tBuCOO$^-][\text{PF}_6^-]$. $k_{\text{ET}}$ = rate constant for intra-complex photoinduced electron transfer from tBuCOO$^-$ to $3^{\text{BBIm}^{2+}}$. Numbers in parentheses refer to energy levels of the species relative to BBIm$^{2+}$ in the ground state.

**Scheme 5** Proposed mechanism for the photocatalytic hydroxylation under O$_2$ (blue) and dimerisation of carboxylic acids under an atmosphere of air (red). SET: single electron transfer.
used, since the sign of the charge of PC remains unchanged. However, when a monocationic PC is used, the reorganization energy becomes lower when a dicationic PC is used (Scheme 6b, PC: neutral; S: negative). In contrast, the reorganization energy becomes lower when a dicationic PC is used (Scheme 6c, PC: positive → neutral; S: negative → neutral). In fact, BBIm$_2^+$ was demonstrated to be a viable photoredox catalyst BBIm$_2^+$, the photophysical and electrochemical properties of which indicate that it has a strong oxidation ability in the excited state. In fact, BBIm$_2^+$ was demonstrated to be a viable photoredox catalyst for promoting the decarboxylative hydroxylation and dimerisation of unactivated carboxylic acids. The striking feature of BBIm$_2^+$ is its dicationic nature, which allows it to form an intimate ion pair with an anionic substrate, resulting in an energetically favorable SET process. Further development of new cationic organic photocatalysts and their application to otherwise difficult oxidative transformations is now ongoing in our laboratory.

Conclusions

In conclusion, we report on the development of a novel dicationic photoredox catalyst BBIm$_2^+$, the photophysical and electrochemical properties of which indicate that it has a strong oxidation ability in the excited state. In fact, BBIm$_2^+$ was demonstrated to be a viable organic photocatalyst for promoting the decarboxylative hydroxylation and dimerisation of unactivated carboxylic acids. The striking feature of BBIm$_2^+$ is its dicationic nature, which allows it to form an intimate ion pair with an anionic substrate, resulting in an energetically favorable SET process. Further development of new cationic organic photocatalysts and their application to otherwise difficult oxidative transformations is now ongoing in our laboratory.

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\[ E_{\text{red}}^\ddagger = E^\ddagger + E_{\text{red}} = +1.91 + (-1.02) = +0.89 \text{ V vs. SCE, where } E^\ddagger \text{ was determined from the phosphorescence spectrum (} \lambda_{\text{max}} = 641 \text{ nm) observed in an ethanol glass at 77 K.} \]

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