

Photophysics of Doubly Reduced Quinacridone Dyes: Toward Redox Reactivity Activated by Red Light

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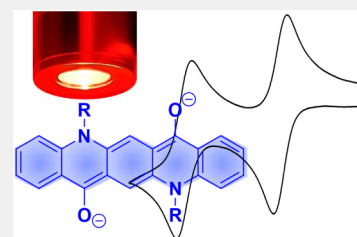
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ABSTRACT: Super-reductive photocatalysis is an emerging approach to broaden the conventional organic reactivity by exploiting reduced forms of a parent photocatalyst (PC) as the actual photoactive super-reductant. Recent reports have highlighted the advantages of using closed-shell, doubly reduced PC^{2-} with respect to open-shell, singly reduced $PC^{\bullet-}$, with the former having longer excited-state lifetime and enlarged reductive power. It is thus important to expand the families of super-reductants that fit these features. In this work, we investigate doubly reduced N,N -dialkylated derivatives of quinacridone (QA) industrial pigment as potential super-reductants, exploiting the use of low-energy red light. These give the possibility of electrochemically generating the radical anion and dianion forms, with the latter being characterized by an emissive excited state with nanosecond lifetimes (compared to ps lifetime of the radical anion excited state) and reductive power up to -3.5 V vs Saturated Calomel Electrode, ca. 0.9 V enhanced with respect to the radical anion excited state. The super-reductant activity of the bis-reduced species is demonstrated in the challenging reductive deamination of arylammonium derivatives. All-in-one, these findings will inspire the design of closed-shell super-redox photocatalysts based on industrial pigments, thus impacting sectors involving organic reactivity, photocatalysis, and sustainable chemistry.

KEYWORDS: super-reductant, photocatalysis, cyclic voltammetry, organic dyes, transient absorption spectroscopy



INTRODUCTION

Super-redox photocatalysis has emerged in the past decade as a novel route to access unprecedented reactivity toward the activation of inert organic substrates.¹ A general scheme is represented in Scheme 1A (for the sake of simplicity, only the super-reductive cycle is depicted, which is pertinent to this work): a photocatalyst PC is first reduced (or oxidized) via a chemical, electrochemical, or photochemical step, generating the active photocatalyst PC^{n-} (or PC^{n+} ; n indicates the number of redox steps involving the reduction/oxidation of PC, typically $n = 1$ or 2), that in its excited state, $^*PC^{n-}$ (or $^*PC^{n+}$) can promote the reduction (or oxidation) of the target organic substrate (Sub, Scheme 1).

The advantages of the super-redox photocatalysis approach are associated with a broader potential window accessible with the $^*PC^{n-}/^*PC^{n+}$ species with respect to classical photocatalysis involving *PC .² This has been estimated to span from -4.0 to $+4.0$ V vs Saturated Calomel Electrode (SCE),^{2,3} which enabled the expansion of photocatalytic processes to challenging redox transformations. The possibility of generating excited radicals was pioneered in the late 1970s and early 1980s of 20th century by Lund and Carlsson,⁴ Moutet and Reverdy,⁵ and Shukla and Rusling,⁶ while other contributions were given by Fox⁷ and Majima.⁸ A major breakthrough was reported in 2014 by Ghosh and coworkers, who exploited a perylene diimide (PDI) photocatalyst via a consecutive

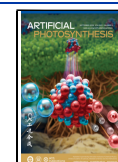
photoinduced electron transfer (conPET) for the reduction of aryl halides.⁹ The super-reductant $^*PDI^{\bullet-}$ was generated by a reductive quenching of *PDI with amine donors and consecutive excitation of $PDI^{\bullet-}$.⁹ Although the mechanism has been debated,^{10–12} this seminal work prompted the investigation of other families of photocatalysts, ranging from coordination compounds to organic PCs; selected examples are reported in Scheme 1B. In the reductive side, examples of PCs include iridium complexes,^{13,14} Rhodamine 6G,¹⁵ acridine radicals,¹⁶ dicyanoanthracene (DCA),^{17,18} naphthalene-based^{19,20} and benzo[ghi]perylene diimides (NDI and BPI),²¹ bis(borondifluoride)-8-imidazodipyrromethene (BOIMPY),²² benzocoronene diesters,²³ and thermally activated delayed fluorescence (TADF) dicyanobenzene derivatives, such as 2,4,5,6-tetrakis(diphenylamino)-isophthalonitrile (4-DPAIPN).^{24–28} For interested readers, examples of parent PCs employed in the oxidative route are

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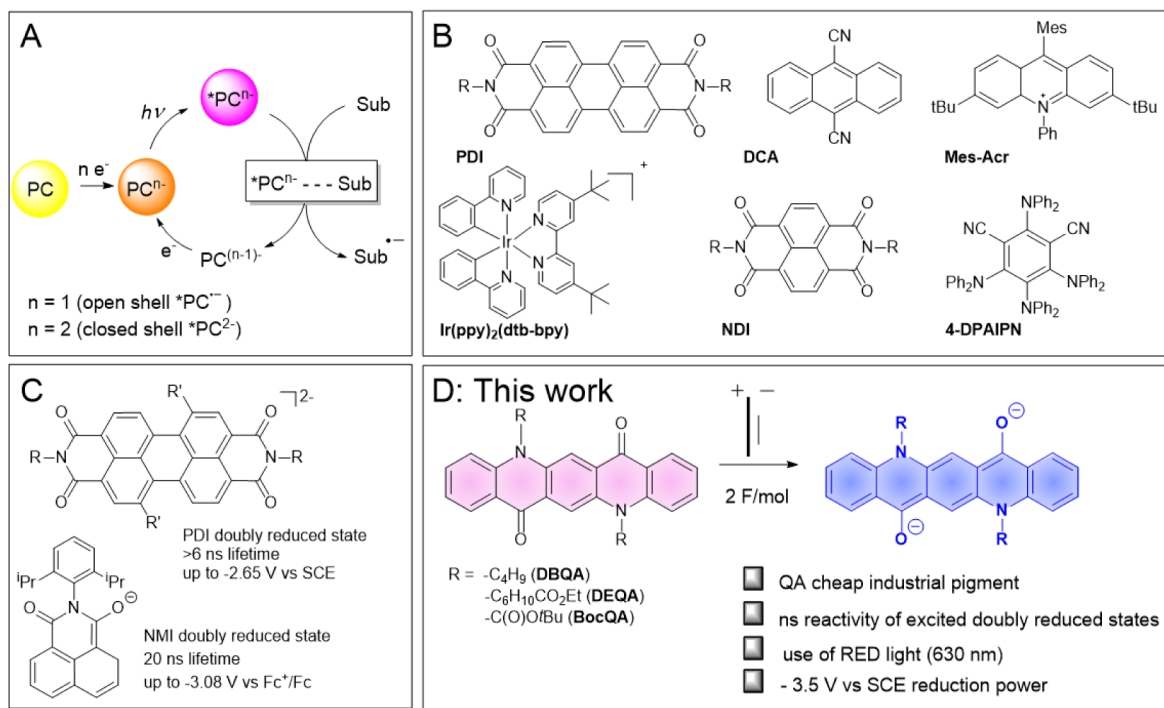
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Scheme 1. A: General Approach to Super-Redox Photocatalysis Compared to Classical Photocatalysis (only a Reductive Pathway is Shown); **B:** Examples of Photocatalysts Employed as Super-Reductants; **C:** Perylene Diimide (PDI)⁴¹ and Naphthalene Monoimide (NMI)²⁰ Doubly Reduced Singlet Species; In the Case of NMI the Bis-reduced form is also Protonated, Generating a Singly Charged Anion; **D:** Quinacridone Derivatives and the Doubly Reduced Forms Discussed in this Work



the trisaminocyclopropenium cation,^{29–32} *N*-phenylphenothiazine,³³ acridinium derivatives,³⁴ and triarylamines.³⁵

One major obstacle in developing super-redox photocatalysis is that most systems rely on the singly reduced or oxidized form of the photocatalyst ($n = 1$). The excited state of these radical species $PC^{\bullet-}$ (or $PC^{\bullet+}$) is typically in the picosecond time scale, making diffusion-controlled intermolecular electron transfer to a target substrate unfeasible.¹ In some cases, preassociation between the radical ion photocatalyst and the organic substrate has been proposed and spectroscopically demonstrated to facilitate picosecond electron transfer, consistent with the experimentally observed reactivity.^{36,37} In other systems, solvated electron formation from excited-state radical anions has been identified as an alternative pathway accounting for the observed reductive reactivity.^{26,38–40}

One strategy to mitigate the short lifetime issue is to employ a two-electron redox transformation of the parent PC; this approach has been verified in the super-reductant field with PDI⁴¹ and naphthalene monoimide (NMI)²⁰ generating doubly reduced, closed-shell singlet species with an excited-state lifetime of several nanoseconds (Scheme 1C). In addition, a further benefit of the excited state of a doubly reduced vs singly reduced photocatalyst PC^{2-} over its singly reduced analogue is its typically higher reductive power arising from its more electron-rich nature (in the case of PDI, the doubly reduced $^*PDI^{2-}$ excited species displays roughly 0.8 V enhanced reducing strength relative to the excited state of the singly reduced form, $^*PDI^{\bullet-}$, while simultaneously increasing the excited-state lifetime from the picosecond to the nanosecond regime).⁴¹

Therefore, the development of new PC families amenable to super-redox photocatalysis via doubly reduced (or oxidized)

species is a promising but underexplored approach in the field of electrophotocatalysis.

In this work, we introduce the use of doubly reduced *N*-alkylated quinacridone (QA)⁴² derivatives as potential super-reductants (Scheme 1D). Figures of merit of this study are (i) the use of derivatives of QA as a robust, cheap, and nontoxic industrial pigment,^{42–45} showing the possibility of undergoing reversible, two-electron redox chemistry; (ii) the transient absorption spectroscopy (TAS) characterization of the photo-excited reduced forms, providing an indication of ps and ns time-scale reactivity for the mono- and bis-reduced species, respectively; (iii) the super-reducing reactivity upon red light irradiation of the bis-reduced species (E up to -3.5 V vs SCE) toward the deamination of arylammonium substrates,²⁴ with electrochemical evidence of a photocatalyst/substrate preassociation. These results may inspire novel strategies for the development of super-redox photocatalysis, employing derivatives of cheap and available industrial pigments.

RESULTS AND DISCUSSION

Optical and Electrochemical Properties of Soluble QA Derivatives

The QA pigment is insoluble in most organic solvents and water, due to intermolecular hydrogen bonding. Solubility was achieved through *N*-alkylation⁴⁴ and *N*-functionalization with a *tert*-butoxycarbonyl (Boc) group, which effectively disrupts intermolecular hydrogen bonding and enables solution-phase studies.^{45,46} Following this strategy, *N,N'*-dibutyl-quinacridone (DBQA), *N,N'*-diethyl-hexanoate-quinacridone (DEQA), and *N,N'*-bis(*tert*-butoxycarbonyl)-quinacridone (BocQA) were considered (see Supporting Information for synthetic details).

In DMF, the absorption spectra of DBQA and DEQA show four vibronic components between 450 and 550 nm, with the most intense absorption at 520 nm for both dyes ($\epsilon = 1.1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) attributed to the transition from the ground state to the lowest excited state, associated with a $\pi \rightarrow \pi^*$ transition (Figure S1). The emission spectra are mirror-like to the absorption and are characterized by an excited-state lifetime of 18 ns for both dyes and a fluorescence quantum yield ϕ_F of 0.77 for DBQA and 0.74 for DEQA (Figure S1). By the interception of normalized absorption and emission spectra, an E_{0-0} of 2.36 eV is estimated for both species, suggesting that the nature of the alkyl chain impacts negligibly on the electronic properties of the pentacyclic aromatic scaffold. With respect to the *N*-alkylated derivatives, BocQA shows a blue-shifted and broader absorption band with comparable absorptivity, and emission characteristics with an excited-state lifetime of 17 ns, a ϕ_F of 0.94,⁴⁷ and an E_{0-0} of 2.50 eV (Figure S1).

The possibility of generating reduced forms of the dyes was confirmed by combining cyclic voltammetry and spectroelectrochemistry (see Figure 1 for DBQA and Supporting Information Figures S2–S3 for DEQA and BocQA). Under cathodic scan, DBQA shows two reversible waves with half-wave potentials ($E_{1/2}$) of -1.27 and -1.78 V vs SCE, corresponding to the stepwise reduction of DBQA to $\text{DBQA}^{\bullet-}$ and DBQA^{2-} , respectively (Figure 1A). Similarly, two cathodic waves are observed also for DEQA ($E_{1/2}$ of -1.20 and -1.74 V vs SCE) and for BocQA ($E_{1/2}$ of -0.94 and -1.28 V vs SCE).

Spectroelectrochemistry (SEC) allows characterization of the absorption and emission properties of reduced species. In the case of DBQA, both $\text{DBQA}^{\bullet-}$ and DBQA^{2-} show red-shifted absorption with respect to the parent dye. Specifically, reduction at -1.5 V vs SCE generated $\text{DBQA}^{\bullet-}$, which exhibits a broad absorption band at 850 nm (red trace in Figure 1B), whereas further reduction at -1.9 V vs SCE generated DBQA^{2-} , displaying an absorption band centered at 690 nm (blue trace in Figure 1B). TD-DFT calculations at the b3lyp/6-311g(d,p) level reproduce both spectral features (vertical bars in Figure 1B), indicating that the orbitals involved are π -type and delocalized over the pentacyclic scaffold, with no lower-lying electronic transitions predicted (Figure S4). Importantly, the spectra remain superimposable for over 1 h under SEC conditions, indicating a good electrochemical stability of both $\text{DBQA}^{\bullet-}$ and DBQA^{2-} reduced species.

Fluorescence spectroelectrochemical monitoring was performed during potentiostatic electrolysis at -1.9 V, corresponding to the second reduction process. As the electrolysis proceeded, the characteristic emission band of DBQA centered at 545 nm underwent a progressive decrease, eventually resulting in the complete disappearance of the signal (Figure S5). Concomitantly, two new bathochromically shifted emission bands emerged at 690 and 780 nm (Figure 1C), exhibiting a lifetime of about 0.8 ns (Figure S5). These spectral features are attributed to the emission of the electrogenerated DBQA^{2-} , being essentially a mirror image of the absorption (Figure S6). Notably, no emission signal ascribable to the $\text{DBQA}^{\bullet-}$ radical anion was detected throughout the experiment; this is likely due to the extremely short lifetime of its excited state, which precludes radiative decay under these conditions (*vide infra*). The combination of electrochemical and spectroscopic characterizations allows the estimation of

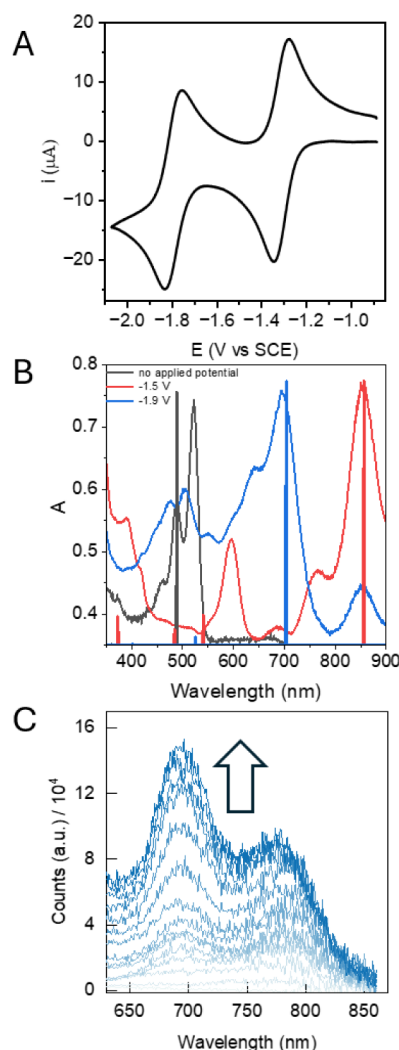


Figure 1. A: Cyclic voltammetry of DBQA under cathodic scan (1 mM in DMF, 0.1 M TBAPF₆ electrolyte); B: absorption spectroelectrochemistry analysis of DBQA (0.5 mM in DMF) at different potentials; the vertical bars indicate the TD-DFT calculated transitions for $\text{DBQA}^{\bullet-}$ and DBQA^{2-} , respectively (b3lyp/6-311g(d,p) level of theory). In the spectroelectrochemistry trace at -1.9 V, the weak absorption at 850 nm is likely ascribable to a residual trace of the radical anion $\text{DBQA}^{\bullet-}$. The absorption spectra start at ca. 0.35 A due to scattering of the Pt mesh electrode. C: Emission spectroelectrochemistry analysis of DBQA^{2-} , electrochemically generated at -1.9 V vs SCE (excitation at 600 nm).

the reduction potentials of the excited states of reduced DBQA through eqs 1 and 2:

$$E(\text{DBQA}/^*\text{DBQA}^{\bullet-}) \approx E(\text{DBQA}/\text{DBQA}^{\bullet-}) - E_{0-0}(^*\text{DBQA}^{\bullet-})/e \quad (1)$$

$$E(\text{DBQA}/^*\text{DBQA}^{2-}) \approx E(\text{DBQA}/\text{DBQA}^{2-}) - E_{0-0}(^*\text{DBQA}^{2-})/e \quad (2)$$

where $E(\text{DBQA}/^*\text{DBQA}^{\bullet-})$ and $E(\text{DBQA}^{\bullet-}/^*\text{DBQA}^{2-})$ are the excited state reduction potentials, $E(\text{DBQA}/\text{DBQA}^{\bullet-})$ and $E(\text{DBQA}^{\bullet-}/\text{DBQA}^{2-})$ are the ground-state reduction potentials, $E_{0-0}(\text{DBQA}^{\bullet-})$ and $E_{0-0}(\text{DBQA}^{2-})$ are the zero-point energies of the excited states (expressed in eV), and e is the elementary charge. We estimated E_{0-0} of 1.46 eV and 1.79

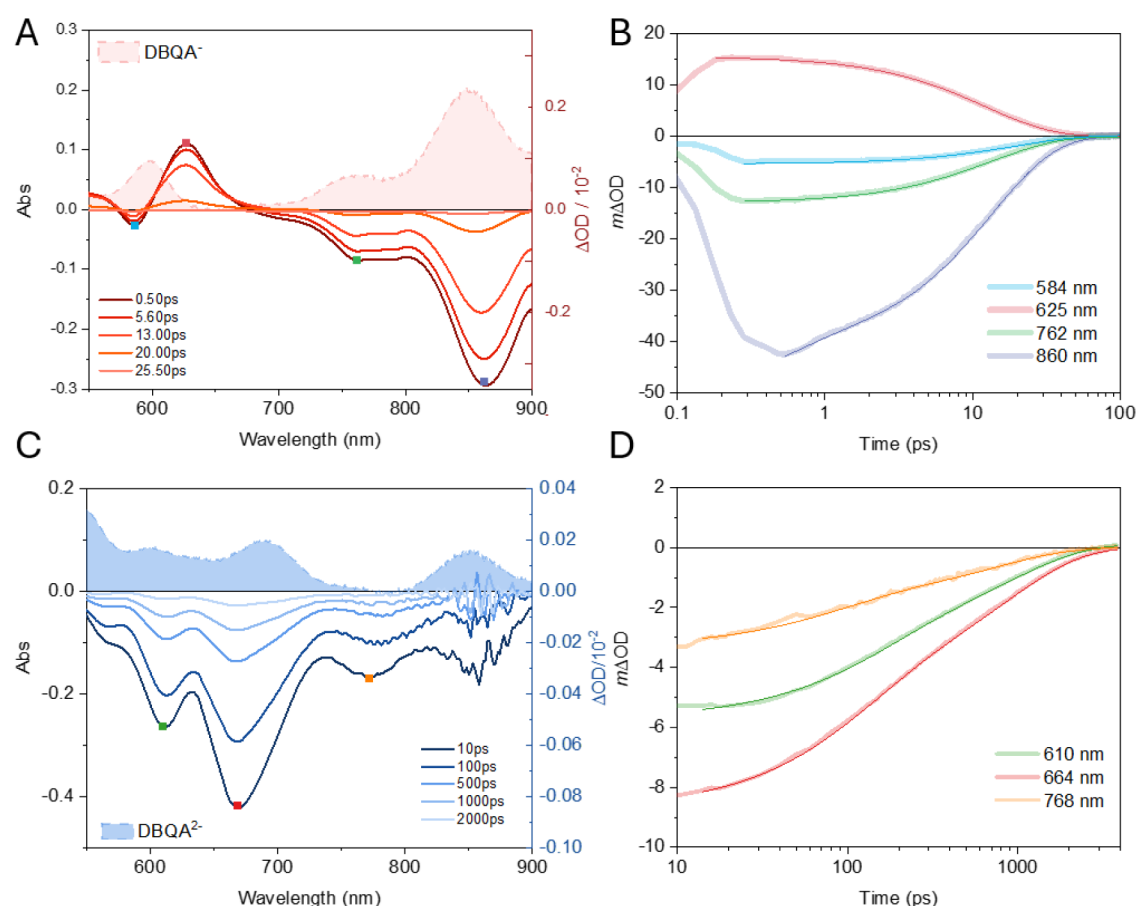


Figure 2. Differential transient absorption spectra and relative kinetic traces upon laser excitation of DBQA $\bullet^-$ ($\lambda_{\text{exc}} = 780$ nm, A–B panels) and DBQA $^{2\bullet-}$ ($\lambda_{\text{exc}} = 650$ nm, C–D panels). The absorption spectra of DBQA $\bullet^-$ and DBQA $^{2\bullet-}$ are reported in dashed traces and shaded area underneath (in DBQA $\bullet^-$, the absorption at 850 nm is attributed to a residual presence of DBQA $\bullet^-$ along the electrolysis). In the case of DBQA $^{2\bullet-}$, the dip in the GSB at 625 nm can be ascribed to excited-state absorption, while the negative signal at ca. 770 nm (where the parent DBQA $^{2\bullet-}$ does not absorb) is attributed to stimulated emission. The negative signal at 850, not observed in the SEC emission (Figure 1C), can be tentatively ascribed to excimer emission, since the TA experiments are performed at much higher concentrations than the SEC emission measurements.

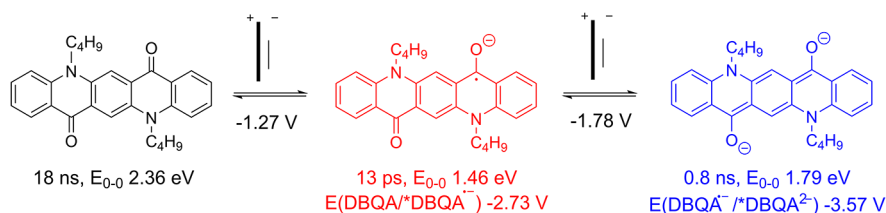
eV for *DBQA $\bullet^-$ and *DBQA $^{2\bullet-}$, respectively (in the case of DBQA $\bullet^-$, this corresponds to the energy of the most red-shifted absorption band maximum, while in the case of DBQA $^{2\bullet-}$, the maximum of the highest energy emission band was considered). Incidentally, DBQA $^{2\bullet-}$ shows a case of zero Stokes shift, with the highest energy emission band almost overlapping the lowest energy absorption band, at 690 nm (Figure S6); this effect may be ascribed to the rigidity of the conjugated scaffold, together with the interaction of DBQA $^{2\bullet-}$ with tetrabutylammonium cations from the electrolyte, reducing solvent reorganization effects.¹ Thus, $E(\text{DBQA}/\text{*DBQA}\bullet^-)$ and $E(\text{DBQA}\bullet^-/\text{*DBQA}^{2\bullet-})$ result in -2.73 and -3.57 V vs SCE, respectively.

Similar observations were obtained for DEQA (see Supporting Information, Figure S2). In the case of BocQA, SEC reduction at the first cathodic wave leads to the formation of a new broad absorption band centered at 570 nm, attributed to BocQA $\bullet^-$. At more negative potentials, absorption bands between 400 and 500 nm are observed, corresponding to the formation of BocQA $^{2\bullet-}$ (Figure S3). Under electrolysis conditions, however, BocQA proved unstable, with progressive precipitation of a pink solid attributable to the formation of the parent QA pigment upon Boc deprotection.^{45,46} The compound was therefore excluded for further spectroscopic measurements.

Transient Absorption Spectroscopy of Reduced QA Derivatives

The photophysical properties and the dynamics upon light irradiation of electrochemically reduced quinacridone derivatives were examined using UV–vis femtosecond transient absorption spectroscopy (fs-TAS).⁴⁸ The reduced species were generated through a controlled potential electrolysis (CPE) and then transferred into a 1 mm airtight cuvette suitable for fs-TAS experiments, with all operations performed in a glovebox. The electrochemical route provided efficient and controlled generation of the reduced species; these are extremely sensitive to air, precluding attempts to isolate them from the electrolyte solution. Attempts to generate them by chemical reduction were unsuccessful (Na, Mg, and NaH were used as reductants in degassed and anhydrous THF).

In the case of DBQA $\bullet^-$, the features and dynamics of the excited state were probed after direct laser excitation at 780 nm. The fs-TAS analysis of DBQA $\bullet^-$ revealed a ground-state bleaching (GSB) at 585, 762, and 860 nm (these features are indeed mirror-like to the absorption spectrum of DBQA $\bullet^-$ observed in SEC) and an excited-state absorption (ESA) at 625 nm, Figure 2. The relative kinetic traces revealed an excited state lifetime of 13 ps indicative of a fast nonradiative decay of the doublet excited state *DBQA $\bullet^-$, consistent with most organic radicals reported in the literature.^{1,49} DBQA $^{2\bullet-}$

Scheme 2. Photophysical Properties and Energetics of DBQA and Its Reduced Derivatives^a

^aPotentials are reported vs SCE.

was investigated upon laser excitation at 650 nm, where the absorption of the partially present radical anion is negligible. The TAS analysis revealed a GSB at 610 and 664 nm (mirror-like to the absorption spectra of DBQA^{2-} , see above discussion), while stimulated emission is responsible for the negative band at 770 nm. No net ESAs are observed, which can be justified by the high absorbance of the DBQA^{2-} ground state, Figure 2. The relative kinetic traces are characterized by two components: a short one of 112 ps (45.3%) and a long one of about 900 ps (54.7%), in fair agreement with the one observed under SEC. Although the origin of the biexponential decay is not clear, considering the rigidity of the quinacridone scaffold, this may be tentatively assigned to protonation events from the solvent or adventitious water. Scheme 2 summarizes the photophysical properties and energetics of DBQA and its reduced derivatives. Similar fs-TAS analyses were obtained for DEQA (Figure S7), while the electrochemical instability of BocQA hampered a proper investigation on this compound.

Photocatalysis Investigation by Cyclic Voltammetry

We tested the potential photocatalytic ability of reduced forms of DBQA by means of cyclic voltammetry under irradiation conditions,⁵⁰ according to a protocol that was recently reported by some of us.⁵¹ In short, along a cyclic voltammogram scan under irradiation, the possible reactivity of reduced species of a photocatalyst toward a target substrate is documented by the appearance of a photocatalytic current, from which kinetic parameters can be determined (while considering the contributions of local heating and enhanced mass transport).^{50,51} We selected *N,N,N*-trimethylanilinium hexafluorophosphate salt (1-PF_6) as the target substrate, since its reductive deamination was recently reported under electrophotocatalytic conditions.²⁴

The CV under cathodic scan reveals that the reduction of 1^+ occurs through an irreversible process characterized by a cathodic wave with a peak potential $E_{\text{pc}} = -2.4$ V vs SCE, which in the dark is unaffected by the presence of DBQA (black trace in Figure 3A and Figure S8). Performing the CV under irradiation of the electrode surface ($\lambda = 630$ nm with a red LED), the appearance of a photocatalytic current at the level of the second reduction wave of DBQA is observed (red trace in Figure 3A, see experiments including different substrate concentrations in Figure S9)^{50,51} supporting the photocatalytic activity of DBQA^{2-} toward 1^+ . An analysis of the CV traces combining digital simulation supports a diffusion-controlled reactivity (bimolecular $k \approx 10^{10} \text{ M}^{-1}\text{s}^{-1}$), as expected from the Marcus theory considering the redox potentials involved, with a partial contribution of preassociation between DBQA^{2-} and 1^+ (*vide infra* and see discussion in Supporting Information, Figures S10–S13). The almost unmodified shape and current intensity of the first wave ($\text{DBQA}/\text{DBQA}^{\bullet-}$) indicate instead a negligible reactivity of

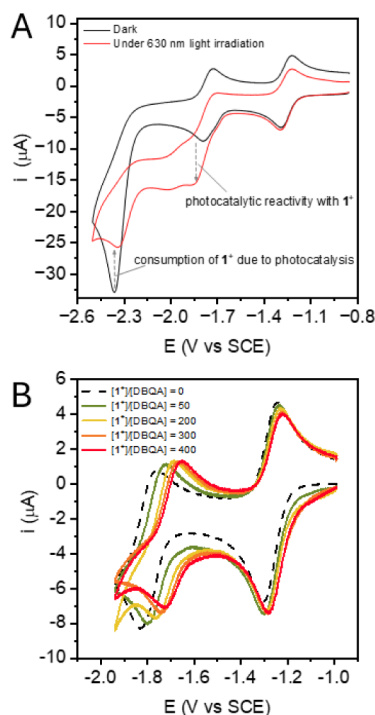


Figure 3. A: Cyclic voltammetry of 0.4 mM DBQA in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ in the presence of 0.8 mM 1-PF_6 . CVs were recorded in the dark (black line) and under 630 nm irradiation (red line). $T = 25$ °C. Scan rate $v = 0.1 \text{ V s}^{-1}$. CVs performed in DMF + 0.1 M $n\text{Bu}_4\text{NBF}_4$ with a glassy carbon working electrode (geometric area = 7.07 mm^2). It should be noted that under irradiation, local heating may lead to enhanced mass transport at the electrode and slight changes in the CV traces.⁵¹ Control CV experiments under irradiation of DBQA in the absence of substrate 1^+ are reported in Supporting Information, Figure S9. B: CVs of 0.5 mM DBQA recorded in the absence (dashed line) and in the presence of increasing amounts of 1-PF_6 (full lines). Scan rate $v = 0.15 \text{ V s}^{-1}$; $T = 25$ °C.

$\text{DBQA}^{\bullet-}$ with 1^+ (similar trends in CV traces were observed also upon irradiation at 730 nm, Figure S9). Finally, the wave peaking at -2.4 V due to the direct electrochemical reduction of 1^+ at the electrode decreases in intensity, consistent with the consumption of 1^+ in the photocatalytic process (red trace in Figure 3A).

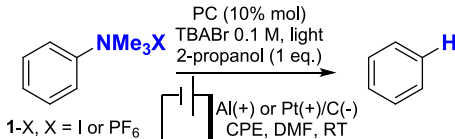
At high concentrations of 1^+ , the intensity of the photocurrent reaches a plateau, supporting indeed preassociation between DBQA^{2-} and 1^+ (Figure S9). Indeed, in the absence of light, a progressive anodic shift of the waves of DBQA was observed upon the addition of increasing amounts of 1-PF_6 ($[1^+]/[\text{DBQA}]$ up to 400, Figure 3B), suggesting an interaction between 1^+ and the reduced forms of DBQA. The analysis of the $E_{1/2}$ shift vs the concentration of 1 allows an estimation of the equilibrium constant K_1 of ca. 10 M^{-1} for the

association of 1^+ with $\text{DBQA}^{\bullet-}$ assuming a 1:1 ratio; this is close to the value of 5.9 predicted for a Coulombic interaction, while a similar equilibrium constant of 9.2 was observed for the association of naproxen radical anion and benzyltrimethylammonium in water.⁵² For DBQA^{2-} , a higher shift of the $E_{1/2}$ was observed, consistent with a K_2 of 150–200 M^{-1} for the association of 1^+ with DBQA^{2-} , still assuming a 1:1 $1^+:\text{DBQA}^{2-}$ ratio, see Supporting Information and Figures S10–S12.⁵³ The higher association constant observed for the doubly reduced form of the dye with respect to the singly reduced one is expected for the enhanced electrostatic interaction with **1**. Further weak association of **1** to DBQA^{2-} up to a 2:1 ratio is likely in the presence of excess **1**. Similar observations were noticed for the association of 1^+ with $\text{DEQA}^{\bullet-}$ and DEQA^{2-} , respectively (Figures S14–S15).

Electrophotoactivation of Reduced QA as Super-Reductants

Given the outcome from TAS and cyclic voltammetry analysis, we envisioned investigating the reduced DBQA forms as photocatalysts toward synthetic super-reducing applications, starting from the reductive deamination of 1^+ (Table 1).²⁴ We

Table 1. Electrophotochemical Approach for Deamination and Dehalogenation of Aryl Derivatives^{24a}



#	PC/Light	Potential vs SCE ^b	Yield ^c
1 ^d	4-DPAIPN (405 nm)	−1.6	70%
2 ^d	4-DPAIPN (white)	−1.6	45%
3 ^d	BocQA (white)	−0.9 or −1.4	n.d.
4 ^d	DBQA (white)	−1.75	2%
5 ^d	DEQA (white)	−1.80	7%
6 ^b	DBQA (red, 630 nm)	−1.75	14%
7 ^b	DEQA (red, 630 nm)	−1.80	17%
8 ^b	DBQA (red, 630 nm)	−1.4	Traces
9 ^b	DBQA (no light)	−1.75	–
10 ^b	DBQA (red, 630 nm)	No potential applied	–

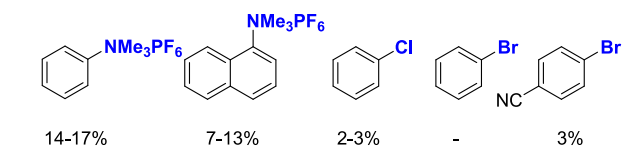
^aExperiments were conducted overnight in duplicate in a two-chamber cell, with separated cathodic and anionic compartments. ^b20 mM substrate as the hexafluorophosphate salt, 2 mM PC, irradiation at 635 nm, and Pt/TEA in the anodic chamber. ^cNMR yield, benzene was also quantified by GC and GC-MS. ^d80 mM substrate as the iodide salt, 8 mM PC, Al in the anodic chamber.

first validated our experimental electrophotochemical setup by conducting the reaction with the 4-DPAIPN photocatalyst: upon application of a potential of −1.6 V vs SCE for generating its radical anion $4\text{DPAIPN}^{\bullet-}$ and by irradiating either with blue LED or with white light (100 mW cm^{-2}), benzene was observed in good yields (entries 1–2 in Table 1, yield given both by ^1H NMR and by GC analysis), consistent with the reported photochemical activity of $4\text{DPAIPN}^{\bullet-}$.²⁴ Under these conditions and applying the suitable potential, we tested the activity of the title dyes. While BocQA was found to be completely inactive either applying a potential associated to the first or to the second reduction process (−0.9 or −1.4 V, entry 3 in Table 1), the alkylated DBQA and DEQA provided benzene in 2–7% NMR yield when operating at the second reduction process (electrochemical generation of the dianions,

entries 4–5 in Table 1). Since we noticed a major bleaching of the parent dye upon irradiation with white light (Figure S16), we used red light ($\lambda = 635$ nm) as the irradiation source to selectively excite the dianion and observed an increase of the benzene yield up to 14–17% (entries 6–7 in Table 1). The use of red light and irradiation at the lowest energetic absorption band suggests that the photochemical reactivity of the bis-reduced forms of DBQA and DEQA follows Kasha's rule.⁵⁴ Exploration of other reaction conditions including solvent and additives was not successful in improving the reaction yield, see Table S1 in Supporting Information).

Control experiments operating at the first reduction of DBQA, in the absence of light or applied potential, provided null reactivity (entries 8–10 in Table 1). Therefore, although the yields are not synthetically useful and are significantly lower than those obtained with the 4-DPAIPN benchmark catalyst, the results indicate a preferential activity of the bis-reduced forms of DBQA and DEQA toward the challenging deamination of 1^+ , with respect to their singly reduced states. The photochemical reactivity of the bis-reduced state of DBQA toward deamination or dehalogenation was investigated and confirmed with other substrates considered, although with limited and still not synthetically useful yields (Scheme 3).

Scheme 3. Substrates Considered for Deamination or Dehalogenation under Electrophotochemical Conditions with DBQA, and Corresponding Yield of Benzene, Naphthalene and Benzonitrile (Determined by Both ^1H -NMR and GC)



We attribute the unsatisfactory yields to the instability of the reduced forms of the title dyes in the reaction environment, as suggested by major spectroscopic changes of the spent reaction mixtures (Figure S17). Isolation of the spent state of the dyes was hampered by the complex reaction mixtures and multiple species observed in the TLC analysis. However, we speculate that the reduced forms of quinacridone should be powerful nucleophiles amenable to attack by polar or radical electrophiles. Considering the negative potentials of excited photocatalysts, the reduction of DMF to its distonic radical anion could also compete in generating reactive species.⁵⁵

CONCLUSIONS AND PERSPECTIVES

In this work, we describe the photophysics and photochemical reactivity of reduced states of soluble dyes (DBQA, DEQA, BocQA) derived from quinacridone (QA) industrial pigment. The enhanced lifetime (from tens of picoseconds to nanoseconds) and reductive power (ca. 0.9 V) of closed-shell, bis-reduced derivatives with respect to open-shell, singly reduced ones were demonstrated. Cyclic voltammetry enables the investigation of the photochemical reactivity of reduced species and the preassociation between the reduced dyes and the trimethylphenyl ammonium substrate. The electrochemically generated bis-reduced derivatives of DBQA and DEQA show indeed photochemical reactivity under electrolysis conditions exploiting low-energy red light toward the deamination of the aryl ammonium, although with limited and not synthetically

useful yields. Ongoing work in our laboratories targets a tuning of the title dyes to enhance robustness and solubility and to allow the investigation of reactivity in other solvents. A reasonable strategy to avoid parasitic reactions could consider the inhibition of nucleophilicity and basicity of reduced species; in this sense, protection of the C=O group of quinacridone will be taken into account.

We believe that these findings will contribute to (i) inspiring the development of novel super-redox photocatalysts, taking advantage of the vast arsenal of industrial organic pigments; (ii) considering the use of dyes showing multiple redox processes,⁵⁶ to access closed-shell photoactive species, for both reductive and oxidative transformations: to the best of our knowledge, the two-electron activation has not yet been considered in the field of superoxidants; (iii) encouraging the use of electrochemical and spectroscopic tools to map the photochemical reactivity of such systems, for a better mechanistic comprehension.

■ EXPERIMENTAL SECTION

Synthesis of DBQA, DEQA, BocQA Followed Literature procedures^{44,45}

Steady-state UV–vis absorption and emission spectra were recorded using a Cary 5000 spectrometer (Varian) and a Fluorolog-3–22 instrument from Horiba Jobin Yvon. The solutions used for luminescence spectroscopy were strongly diluted (optical density of <0.05 at the excitation wavelength) to avoid filter effects. All luminescence spectra were corrected for the wavelength-dependent detection sensitivity of the spectrometer. The luminescence lifetimes were determined on a LifeSpec II spectrometer from Edinburgh Instruments using the time-correlated single-photon counting (TCSPC) technique for the QA-DB dye. The excitation source was a 472 nm picosecond pulsed diode laser (ca. 60 ps pulse width).

Transient UV–vis absorption spectra with femtosecond time resolution were obtained using a HARPIA-TA spectrometer from Light Conversion in combination with a PHAROS laser (Light Conversion, Yb:KGW laser, source wavelength = 1030 nm, pulse duration = ~190 fs, repetition rate = 50 kHz, output power = 1.0 W, pulse energy = 0.2 mJ). The pump light was generated by an optical parametric amplifier ORPHEUS from Light Conversion, using 90% of the fundamental pulse energy. The probe light was generated by a sapphire white light crystal (5 mm thickness) with 10% energy of the fundamental pulse, resulting in a probe pulse covering the spectral range from 520 to 900 nm. Using a global fitting procedure, the obtained transient absorption UV–vis spectra were analyzed by CarpetView software from Light Conversion.

Cyclic voltammetry and spectroelectrochemistry: Cyclic voltammeteries were performed in a three-electrode cell with a glassy carbon working electrode (geometric area = 7.07 mm²), a Pt counter electrode and a SCE reference electrode, degassing the solution with N₂. Spectroelectrochemistry, both in absorbance and fluorescence, was performed with a quartz cuvette with a 0.5 mm path equipped with a Pt grid working electrode (being positioned in correspondence of spectrophotometer's light beam), a Pt counter electrode, and an SCE reference electrode. Corrected emission spectra were recorded with an Edinburgh photoluminescence spectrometer model FLS1000, with double monochromators, equipped with a 450 W Xe arc lamp as the excitation source. An extended red photomultiplier (Hamamatsu R13456, spectral response 185–980 nm) was used as the detector. For all emission spectra, the step size and dwell time were set to 2 nm and 0.01 s, respectively. Monochromator slit widths were optimized according to the spectral region analyzed: for DBQA emission (between 500 and 700 nm), the excitation slit was 1 nm and the emission slit was 0.7 nm. For DBQA²⁻ emission (between 600 and 850 nm, Figure 1C), these were increased to a 5 nm excitation slit and a 10 nm emission slit.

Time-Correlated Single Photon Counting (TCSPC) was used for time-resolved emission experiments; the same spectrometer was connected to a TCC2 acquisition electronic module, and an EPL picosecond pulsed diode laser at 635 nm combined with a high-speed photomultiplier (Hamamatsu, spectral response 185–850 nm) were used as the excitation source and detector, respectively, to measure the fluorescence lifetime decays at 700 nm (10 nm emission slit, time range 5 ns).

DFT and TD-DFT calculations were performed with Gaussian 16 and GaussView 6. For all molecules, geometry optimizations and frequency calculations were performed to obtain the free energies of the species using the b3lyp method and the 6-311g(d,p) basis set.

General Procedure and Setup for the Electrophotocatalysis Experiments: The electrochemical setup is an H-cell separated by a salt bridge. The cathodic compartment is composed of a glassy carbon rod as the working electrode and a silver wire as the pseudoreference electrode. Before the controlled potential experiment was started, cyclic voltammetry was recorded to determine the proper potential for the reduction of the dye. The anodic compartment is composed of a spiral platinum wire as the counter electrode. The cathodic compartment (2.5 mL final volume) is filled with 2 mM dye, 0.1 M TBABr as the supporting electrolyte, and where applicable, 20 mM 1-PF₆ and 20 mM 2-propanol. The anodic compartment (2.5 mL final volume) was filled with 0.1 M TBABr as the supporting electrolyte and 0.3 M TEA as a sacrificial electron donor. Both compartments are purged with argon, and all of the setup is moved to a glovebox. In the glovebox room, both compartments are filled with 2.5 mL of anhydrous DMF. The potentiostat is then connected, and the appropriate potential is applied. After this step, the procedure diversifies for femtosecond laser experiments or for preparative experiments. For fs-laser experiments, after the accumulation of the target reduced form of the dye, the solution was transferred into a 1 mm cuvette and analyzed. For preparative experiments, the solution is instead irradiated in the cell (Figures S18 and S19) concomitantly to the application of the potential.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/aps.6c00006>.

Synthesis of QA derivatives, electrochemical analysis of precomplexation and of photochemical reactivity, electrophotocatalytic experiments, and optimized geometries^{S7–S9} (PDF)

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Notes

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ABBREVIATIONS

Boc, *tert*-butoxycarbonyl group; BocQA, *N,N'*-bis(*tert*-butoxycarbonyl)-quinacridone; CPE, controlled potential electrolysis; DBQA, *N,N'*-dibutyl-quinacridone; DEQA, *N,N'*-diethylhexanoate-quinacridone; DMF, dimethylformamide; NMI, naphthalene monoimide; PC, photocatalyst; PDI, perylene diimide; QA, quinacridone; SCE, saturated calomel electrode; SEC, spectroelectrochemistry; TAS, transient absorption spectroscopy

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