

## Photocatalysis

## Photophysics of Perylene Diimide Dianions and Their Application in Photoredox Catalysis

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**Abstract:** The two-electron reduced forms of perylene diimides (PDI) are luminescent closed-shell species whose photochemical properties seem underexplored. Our proof-of-concept study demonstrates that straightforward (single) excitation of PDI dianions with green photons provides an excited state that is similarly or more reducing than the much shorter-lived excited states of PDI radical monoanions, which are typically accessible after biphotonic excitation with blue photons. Thermodynamically demanding photocatalytic reductive dehalogenations and reductive C–O bond cleavage reactions of lignin model compounds have been performed using sodium dithionite acts as a reductant, either in aqueous solution or in biphasic water–acetonitrile mixtures in the presence of a phase transfer reagent. Our work illustrates the concept of multi-electron reduction of a photocatalyst by a sacrificial reagent prior to irradiation with low-energy photons as a means of generating very reactive excited states.

## Introduction

Perylene diimides (PDIs) are an important class of organic dyes, which have been explored extensively in their native (charge-neutral) forms.<sup>[1]</sup> Recently, there has been significant interest in photochemical applications of the one-electron reduced (monoanion) forms of PDIs, whereas the two-fold reduced (dianion) PDI species have attracted less attention.<sup>[2]</sup>



Many fundamental studies of photoinduced electron transfer with donor-bridge-acceptor compounds incorporated PDI and related rylene diimides as electron acceptors,<sup>[3]</sup> for example to explore light-driven charge accumulation.<sup>[4]</sup> More recently, PDI monoanions attracted attention from the synthetic organic photochemistry community, triggered by work on reductive aryl dehalogenations that were interpreted to rely on photoexcited PDI<sup>•-</sup> as the key catalytic species (Figure 1a).<sup>[5]</sup> This (along with conceptually related studies with a rhodamine dye)<sup>[6]</sup> triggered interest by mechanistically

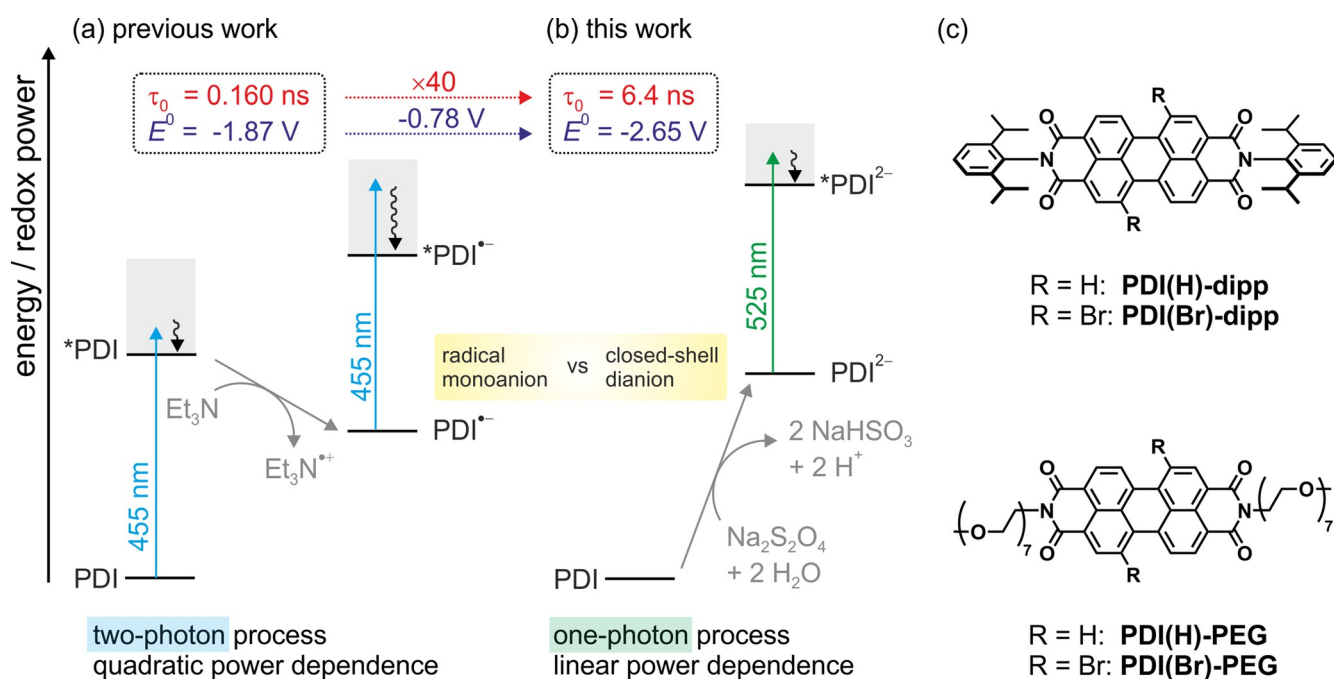
oriented investigators; in part, because the PDI radical monoanions have very short (sub-ns) excited state lifetimes.<sup>[7]</sup> Bimolecular diffusion competes poorly with such rapid excited-state deactivation at the relevant substrate concentrations,<sup>[8]</sup> and consequently the PDI<sup>•-</sup> photo-reactivity seems to depend crucially on the formation of pre-organized catalyst–substrate encounters.<sup>[9]</sup> In contrast to the PDI radical monoanions, PDI dianions are closed-shell species, and one can therefore anticipate substantially longer excited-state lifetimes (Figure 1b).<sup>[10]</sup> Moreover, since PDI<sup>2-</sup> is more electron-rich than PDI<sup>•-</sup>, one might expect even higher photo-reducing power. The combination of these two effects would lead to an enhanced kinetic and thermodynamic reactivity of electronically excited PDI<sup>2-</sup> with respect to photoexcited PDI<sup>•-</sup>.

The first ambient stable PDI dianion has been reported only relatively recently, and its exceptional stability relied on the presence of several strongly electron-withdrawing substituents at the PDI core and at the imide N-atom.<sup>[11]</sup> Unactivated PDIs (and related rylene diimides)<sup>[12]</sup> require strong reductants such as CoCp<sub>2</sub> for in situ formation of PDI<sup>2-</sup> in organic solvents, making their quantitative twofold reduction challenging, and the resulting samples are highly air-sensitive.<sup>[13]</sup> Thus, it is perhaps unsurprising that there seem to be no prior detailed studies of the photoredox properties of PDI dianions in organic solution. By contrast, a water-soluble PDI compound with polyethylene glycol (PEG) substituents at the imide N-atoms was found to be reducible by sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>), and its PDI<sup>2-</sup> form remained stable for months in deoxygenated aqueous solution.<sup>[10]</sup> The respective dianion showed photoluminescence,<sup>[10]</sup> and its structural properties were investigated computationally.<sup>[14]</sup> Studies of another water-soluble PDI<sup>2-</sup> compound (with phosphonate rather than PEG substituents) confirmed the ease of formation and the relative stability of the PDI dianion in water.<sup>[15]</sup> However, we are unaware of prior studies that reported on the use of PDI<sup>2-</sup> as a photocatalyst for the activation of organic substrates.<sup>[16]</sup> Very recent work on photocatalytic H<sub>2</sub> generation with TiO<sub>2</sub> nanoparticles implied a PDI<sup>2-</sup> intermediate formed photochemically from a charge-neutral PDI chromophore (using triethanolamine as sacrificial electron donor),<sup>[17]</sup> and this is an encouraging finding for photocatalysis of other reactions with PDI<sup>2-</sup>. Conceptually, the use of closed-shell dianions is substantially different from the use of open-shell radicals, as outlined above and illustrated in Figure 1.

Against this background including a very recent investigation of PDI dianions,<sup>[19]</sup> we report here an optical spectroscopic study of several PDI<sup>2-</sup> derivatives in both organic solvent and water. Furthermore, we disclose the usage

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**Figure 1.** Light-driven formation of PDI monoanion (a) and dianion (b) for photocatalysis. The lifetime ( $\tau_0$ ) of the D<sub>1</sub> excited state of \*PDI<sup>•-</sup> (160 ps)<sup>[7b,c]</sup> is too short for typical diffusion-controlled bimolecular reactions and likely requires pre-organized catalyst–substrate encounters for productive photochemistry.<sup>[7a,9a,13a]</sup> The S<sub>1</sub> lifetime of PDI<sup>2•-</sup> is 40 times longer and is anticipated to be more reducing than the D<sub>1</sub> state of \*PDI<sup>•-</sup>,<sup>[7c]</sup> and furthermore is accessible via excitation with a single green photon instead of requiring the consecutive absorption of two blue photons. This can be an advantage because biphotonic processes require typically much higher excitation densities to achieve comparable efficiencies than monophotonic processes.<sup>[18]</sup> c) Molecular structures of the PDI compounds investigated in this work (dipp = 2,6-diisopropylphenyl, PEG = polyethylene glycol chain comprised of an average of seven repeat units).

of a PDI<sup>2•-</sup> for the photocatalysis of organic reactions, both in neat water and in water-acetonitrile mixtures using a phase transfer reagent as co-catalyst. Specifically, we explored two different PDI cores, including unsubstituted as well as bromo-decorated versions (Figure 1 c). Lipophilic variants contained 2,6-diisopropylphenyl (dipp) groups at the imide N-atoms, whereas hydrophilic congeners contained PEG substituents at these positions. All four dianion compounds fluoresce with lifetimes of ca. 6 ns in solution at room temperature, and based on the Rehm–Weller equation<sup>[20]</sup> they are expected to exhibit excited-state oxidation potentials up to  $-2.7 \text{ V}$  vs. SCE, thus approaching the reducing power of some of the strongest photoreductants known to date,<sup>[21]</sup> although this is not a key point of the present study. The photocatalytic properties of PDI<sup>2•-</sup> in aqueous solution are illustrated by three examples of thermodynamically challenging reductive dehalogenations, whereas the photoreactivity in water–acetonitrile mixtures is demonstrated with four examples of C<sub>α</sub>–O bond cleavage in small molecules resembling lignin. In combination with photoluminescence, transient absorption, and electrochemical investigations, detailed insight into the photophysics and the photochemistry of perylene diimide dianions is obtained.

In recent photo(electro)chemical studies, pre-catalysts were activated by single electron transfer (SET) to afford the actual photo-catalytically active species, sometimes termed “electron-primed” photocatalysis.<sup>[22]</sup> Here, we introduce the concept of chemical multi-electron reduction of a PDI pre-catalyst to afford a very reactive PDI<sup>2•-</sup> photoreductant. This

concept is very simple, as it relies merely on a cheap chemical reductant and an ordinary monophotonic excitation process.

## Results and Discussion

The four compounds from Figure 1 c were synthesized and characterized as described in the Supporting Information (SI pages S4–S9). All cyclic voltammograms recorded from DMF solutions feature two separate waves, due to the consecutive reduction of the PDI cores to the mono- and dianion forms (Figure S2/S3),<sup>[7b]</sup> whereby bromo-substituents entail the expectable anodic shift (Table 1).<sup>[23]</sup> In aqueous solution, both reduction events of the PEGylated compounds appear jointly as a two-electron wave near  $-0.6 \text{ V}$  vs. SCE, as observed previously.<sup>[10]</sup> The UV/Vis absorption spectra of the charge-neutral, monoanion, and dianion forms of PDI(H)–PEG in Figure 2 a,d are representative of all four compounds considered herein (Figures S5–S7).<sup>[7b]</sup> The UV/Vis spectra of the PDI<sup>0</sup> (blue traces) and PDI<sup>•-</sup> forms (green traces) differ substantially between DMF and H<sub>2</sub>O. Vibrational fine structure and individual electronic transitions are clearly detectable in DMF, but this is no longer the case in H<sub>2</sub>O, indicative of aggregation phenomena.<sup>[9b,24]</sup> This effect is however much less pronounced for the PDI<sup>2•-</sup> forms, for which the UV/Vis spectra in DMF and H<sub>2</sub>O (black traces) are comparatively similar, in line with the prior notion that PDI dianions do not aggregate as strongly due to their charge.<sup>[3d,10,14,15]</sup> Consequently, the photoluminescence of

**Table 1:** Reduction potentials ( $E_{1/2}$  in V vs. SCE), excited-state lifetimes ( $\tau_0$ ), and emission band maxima ( $\lambda_{em}$ ) of the PDI dianions in DMF and H<sub>2</sub>O under argon at 20 °C.

Compound	DMF		H <sub>2</sub> O	Compound	DMF	H <sub>2</sub> O
	$E_{1/2}$ (PDI <sup>0/-</sup> )	$E_{1/2}$ (PDI <sup>-/2-</sup> )	$E_{1/2}$ (PDI <sup>0/2-</sup> ) <sup>[a]</sup>		$\tau_0$ [ns] ( $\lambda_{em}$ [nm])	$\tau_0$ [ns] ( $\lambda_{em}$ [nm])
PDI(H)-dipp	-0.51	-0.80		PDI(H)-dipp <sup>2-</sup>	6.2 (664)	
PDI(Br)-dipp	-0.38	-0.66		PDI(Br)-dipp <sup>2-</sup>	5.6 (731)	
PDI(H)-PEG	-0.56	-0.80	-0.66	PDI(H)-PEG <sup>2-</sup>	6.6 (644)	6.4 (623)
PDI(Br)-PEG	-0.42	-0.64	-0.57	PDI(Br)-PEG <sup>2-</sup>	6.5 (709)	6.1 (628)

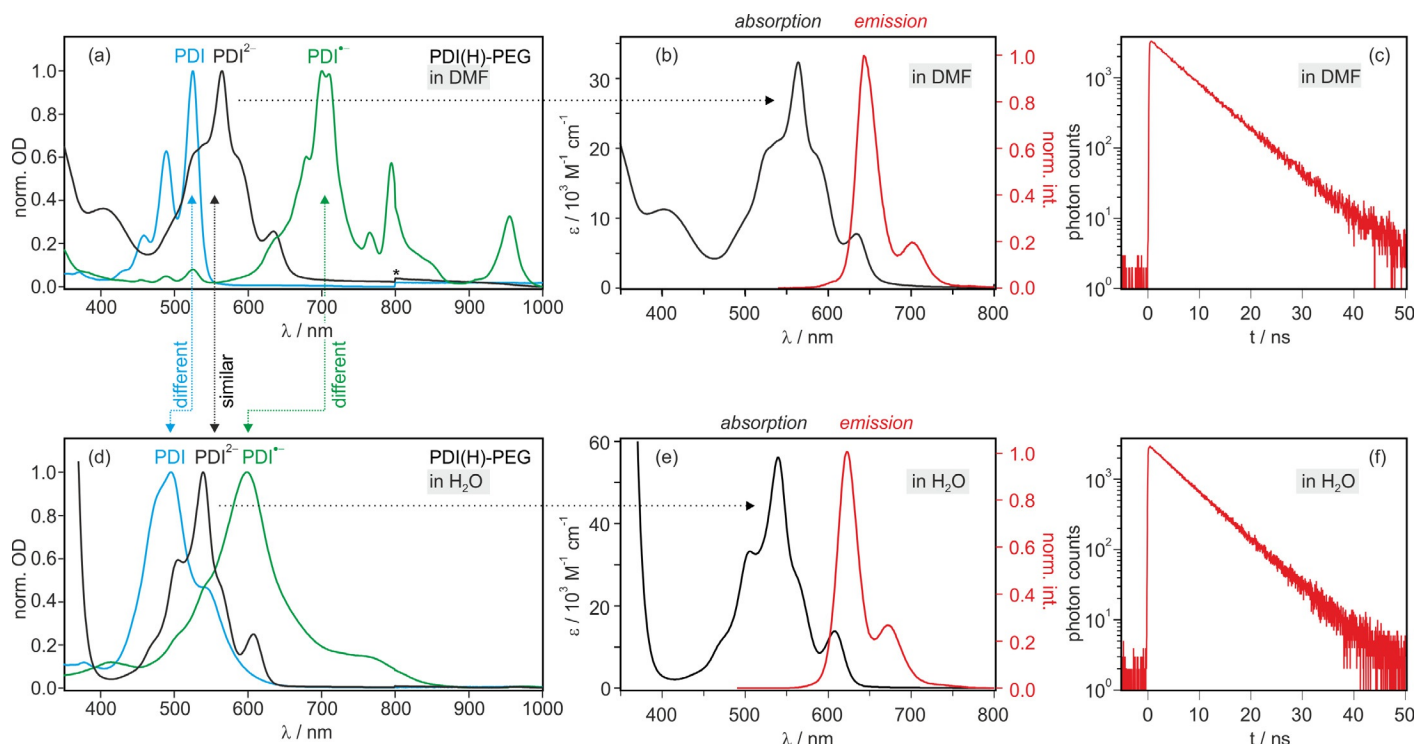
[a] The reduction of PDI<sup>0</sup> to PDI<sup>-</sup> and the reduction of PDI<sup>-</sup> to PDI<sup>2-</sup> appear together as a single (joint) two-electron wave in aqueous solution.<sup>[10]</sup>

PDI(H)-PEG<sup>2-</sup> is similar in DMF (Figure 2b) and H<sub>2</sub>O (Figure 2e). All dianion forms of the four compounds from Figure 1c emit in both DMF and H<sub>2</sub>O (Figures S8–S13, Table S3) with luminescence lifetimes of roughly 6 ns (Figure 2c,f, Table 1). Quantitative reduction to the dianion forms is readily possible by using an excess of an organic super-electron donor in neat DMF and by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in water (SI page S9).<sup>[10,25]</sup>

Twofold bromo-substitution at the PDI core in PDI(Br)-PEG and PDI(Br)-dipp causes a substantial red-shift of the lowest-energy absorption and the corresponding emission bands (Figures S8–S13) of the dianion compounds. The shortest-wavelength emission (band maximum at 623 nm) is observed for PDI(H)-PEG<sup>2-</sup> in water, whilst the longest

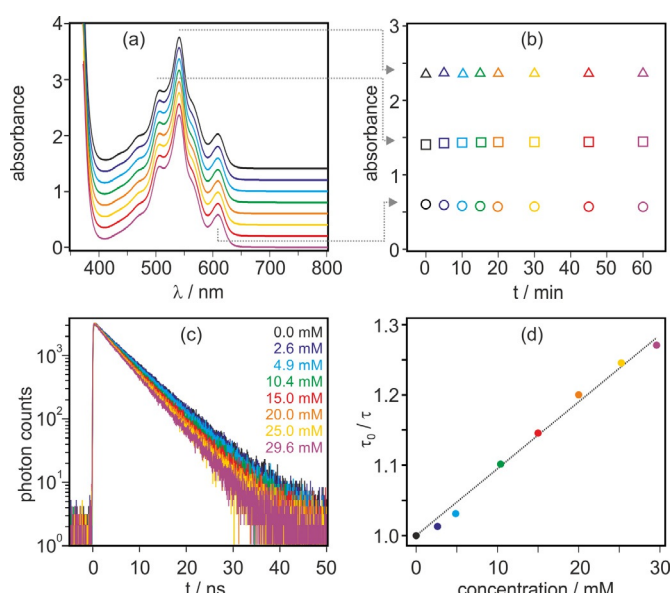
wavelength is observable for PDI(Br)-dipp<sup>2-</sup> in DMF (band maximum at 731 nm). Thus, PDI core substitution offers the possibility to tune the excited-state energies of the luminescent PDI dianions (Table S3). Using nanosecond transient absorption spectroscopy, we have been unable to detect any long-lived triplet excited states following singlet-excitation of PDI(Br)-PEG<sup>2-</sup> and PDI(Br)-dipp<sup>2-</sup>, from which we conclude that bromo-decoration of the PDI core is unable to facilitate substantial singlet-triplet intersystem crossing.<sup>[26]</sup>

Under continuous photoirradiation at 505 nm (using a 200 mW LED) in the presence of excess Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (here 1000 equivalents with respect to the PDI chromophore), the dianion form of PDI(H)-PEG remains stable on the hour timescale (Figure 3a,b), indicating that PDI(H)-PEG<sup>2-</sup> is a photorobust species in 50 mM aqueous NaOH solution. Following pulsed excitation at 532 nm (with a laser) in a transient UV/Vis absorption experiment, PDI(H)-PEG<sup>2-</sup> partially photo-oxidizes to PDI(H)-PEG<sup>-</sup>, but in the presence of excess Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in 50 mM aqueous NaOH the dianion form is regenerated on the millisecond timescale (Figure S14). This seems comparatively slow, and we tentatively



**Figure 2.** UV/Vis absorption spectra of the PDI(H)-PEG compound in three different oxidation states including the charge-neutral (PDI, blue), monoanion (PDI<sup>-</sup>, green) and dianion form (PDI<sup>2-</sup>, black) in de-aerated DMF (a) and water (d) at 20 °C. Optical densities were normalized to 1.0 at the respective absorption maxima in the visible range for better visualization and comparison. Chemical reduction occurred with an organic super-electron donor in DMF and with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in water (SI page S9).<sup>[25]</sup> b,e) Absorption and photoluminescence spectra (measured after excitation at 525 and 475 nm, respectively) of the dianion forms in de-aerated DMF and H<sub>2</sub>O at 20 °C. c,f) Luminescence decays of PDI(H)-PEG<sup>2-</sup> in DMF and H<sub>2</sub>O at 20 °C, following excitation at 473 nm, and detection at 644 and 623 nm, respectively. In aqueous solution, approximately 1000 equivalents of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> were used (e, f), whilst in DMF approximately 5 equivalents of the organic super-reductant were employed (b, c).





**Figure 3.** a) Photostability of 40 μM PDI(H)-PEG<sup>2-</sup> in de-aerated 50 mM aqueous NaOH solution in the presence of excess Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> at 20 °C. Absorption spectra were measured after different time intervals following irradiation at 505 nm with an LED (200 mW). The individual spectra were offset by 0.2 relative to each other for better visualization. b) Absorbance of the respective solution at selected wavelengths as marked by the dotted arrows (505, 540, 605 nm). c) Stern-Volmer luminescence quenching experiments with PDI(H)-PEG<sup>2-</sup> and 4-bromo-2-chloro-3-fluorobenzoate (substrate **1**) in aqueous solution at 20 °C. Excitation of PDI(H)-PEG<sup>2-</sup> occurred at 473 nm, and the luminescence decays were monitored at 623 nm in the presence of excess Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (here approximately 1000 equivalents with respect to the PDI chromophore) under argon. The concentrations of 4-bromo-2-chloro-3-fluorobenzoate were as indicated in the inset. d) Stern-Volmer plot resulting from the luminescence lifetime data in (c); the dotted black line is the result of a linear regression fit, yielding a Stern-Volmer constant ( $K_{SV}$ ) of 9.77 M<sup>-1</sup>.

attribute this to the fact that PDI(H)-PEG<sup>•-</sup> and S<sub>2</sub>O<sub>4</sub><sup>2-</sup> are both anionic, leading to inefficient formation of encounter complexes that can undergo electron transfer.

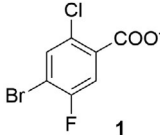
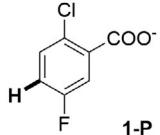
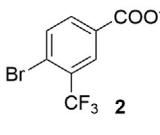
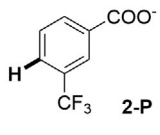
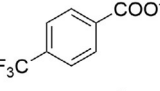
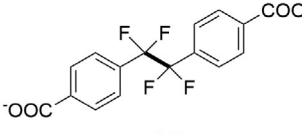
Based on the emission band maxima in Figure 2b,e (644 nm and 623 nm), we obtain energies of 1.93 eV and 1.99 eV for the photoactive excited state of PDI(H)-PEG<sup>2-</sup> in DMF and water, respectively. Using these energies and the reduction potentials in Table 1, we estimate a potential of ca. -2.7 V vs. SCE for one-electron oxidation of photoexcited PDI(H)-PEG<sup>2-</sup> in both solvents (SI page S16). Thus, PDI(H)-PEG<sup>2-</sup> should be a strong photoreductant, both in water and in organic solvent, and given the above-mentioned favorable photophysical properties, this seemed promising

for applications in photocatalysis. Since the formation of PDI(H)-PEG<sup>2-</sup> is particularly straightforward in water (because Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> can be used as a source of electrons), our initial studies focused on a few proof-of-principle reactions in aqueous solution.

Substrates **1-3** (Table 2) quench the excited state of PDI(H)-PEG<sup>2-</sup> with rate constants ( $k_Q$ ) between 1.55 × 10<sup>9</sup> and 2.42 × 10<sup>9</sup> M<sup>-1</sup>s<sup>-1</sup> according to Stern-Volmer luminescence quenching experiments (Figure 3c,d and Figures S17, S18), whereas the emission of charge-neutral PDI(H)-PEG remains unquenched (Figures S20-S22). Evidently, PDI(H)-PEG<sup>2-</sup> can easily induce a photoreaction with those substrates, whereas neutral PDI(H)-PEG is unable to do so. Photocatalysis experiments were performed in 50 mM aqueous NaOH solutions in the presence of approximately 280 equivalents of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with respect to the PDI chromophore (leading to essentially quantitative twofold reduction), where PDI(H)-PEG<sup>2-</sup> is photostable as noted above. Selective excitation of PDI(H)-PEG<sup>2-</sup> with an LED at 525 nm (40 W) in the presence of excess propan-2-ol (<sup>i</sup>PrOH) as H-atom source (SI page S37)<sup>[27]</sup> resulted in hydrodebromination of substrates **1** and **2** with 60% yield after 48 hours (Figures S27/S28 and S32/S33). Control experiments confirmed that PDI(H)-PEG, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> and photo-irradiation are all indispensable for successful reaction (Figures S25/S26 and S30/S31).

Reductive debromination typically occurs at less negative potentials than dechlorination or defluorination,<sup>[28]</sup> hence it is unsurprising that hydrodebromination is the dominant photochemical reaction observed here. The dechlorination of substrate **1** was previously shown to require hydrated electrons formed in a biphotonic excitation process based on the consecutive absorption of two blue photons.<sup>[29]</sup> Aryl debromination and dechlorination reactions performed previously with a PDI derivative in DMF solution relied on

**Table 2:** Photoreactions catalyzed by PDI(H)-PEG<sup>2-</sup> (5–10 mol%) in 50 mM aqueous NaOH solution under argon at room temperature using LEDs as excitation sources (see SI pages S37/S38 for details).

substrate	$\lambda_{exc}$	$k_Q$	additive <sup>a</sup>	product
	525 nm	1.55 · 10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup>	<sup>i</sup> PrOH	 <b>1-P</b> 60%
	525 nm	2.42 · 10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup>	<sup>i</sup> PrOH	 <b>2-P</b> 60%
	390 nm	1.79 · 10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup>		 <b>3-P</b> 36%

[a] No additive was present for the Stern-Volmer luminescence quenching experiments; see Figures S16-S18 and S20-S22 for details.

biphotonic blue excitation,<sup>[5]</sup> whereas here, monophotonic excitation with green photons seems sufficient to induce the reductive debromination.

A water-soluble variant of chlorobenzene, the 4-chlorobenzoate anion, quenches the luminescent excited state of PDI(H)–PEG<sup>2-</sup> with a rate constant ( $k_O$ ) of  $1.15 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Figure S19, Table S5), indicating that activating nitrile (or related electron-withdrawing) substituents are not needed to induce a photoreaction, unlike what was typically observed for the photoreactivity of PDI radical monoanions in organic solvents.<sup>[5]</sup> The observation of a rapid photoreaction with 4-chlorobenzoate suggests that the reducing power of excited PDI dianions is indeed higher than that of PDI monoanions, particularly in view of a recent mechanistic study, which found that substrates with reduction potentials more negative than  $-1.7 \text{ V}$  vs. SCE are unable to quench the very short-lived excited state of PDI radical monoanions in efficient manner.<sup>[7c]</sup> The reduction potential of 4-chlorobenzoate in DMF is estimated to  $-2.8 \text{ V}$  vs. SCE based on a cyclic voltammetry experiment (Figure S4). This is in line with the hypothesis that photoexcited PDI dianions are thermodynamically very reactive, in addition to being kinetically more reactive than PDI monoanions as a result of their substantially longer excited-state lifetimes (Figure 1).

A prior study found enhanced photocatalytic activity of an organic chromophore when shorter wavelength excitation was used,<sup>[30]</sup> and therefore we investigated the effect of exchanging the 525 nm light source by a 390 nm LED. Substrate **3** is largely unreactive under 525 nm excitation, but when using 390 nm as irradiation wavelength, the dimerization product **3-P** (Table 2) forms in 36% yield (84% conversion) after 24 hours (Figures S37/S38). This indicates that reductive C–F bond cleavage is induced under these conditions, which is a thermodynamically very challenging reaction that previously required solvated electrons and laser excitation when performed in water.<sup>[31]</sup> Though we have been unable to find direct spectroscopic evidence for hydrated electrons in our case, we speculate that 390 nm excitation promotes PDI(H)–PEG<sup>2-</sup> to an energetically highly excited state from which some photo-ionization can occur. This would imply the monophotonic generation of hydrated electrons (though inefficiently), complementing prior work on biphotonic photo-ionization processes with metal complexes.<sup>[29,31,32]</sup> The water-soluble compounds **1–3** seem to have more negative reduction potentials than their lipophilic congeners lacking the anionic carboxylate group (Figure S4). For instance, for substrate **3** we estimate a reduction potential of  $-2.8 \text{ V}$  vs. SCE in DMF, whilst a prior study reported a reduction potential of  $-2.5 \text{ V}$  vs. SCE for (trifluoromethyl)benzene in DMF.<sup>[33]</sup> For organic solution, several efficient photocatalytic methods for C–F bond activation in trifluoromethylarenes are known.<sup>[34]</sup>

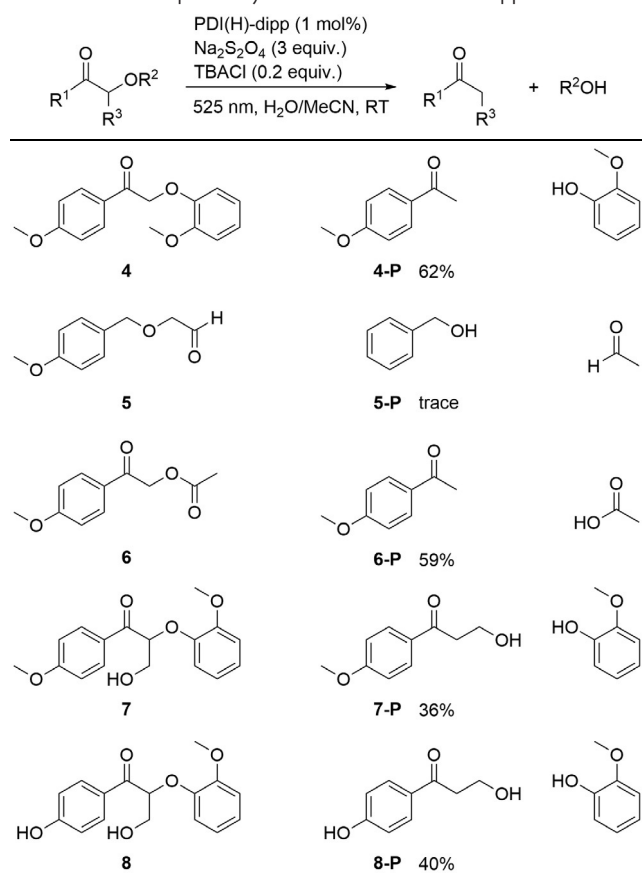
The photoreactions in Table 2 demonstrate that PDI(H)–PEG<sup>2-</sup> can be an effective photocatalyst in aqueous solution, able to induce dehalogenation reactions that are thermodynamically reasonably demanding. They provide the proof-of-concept for reductive aryl debromination with green light and C–F bond cleavage upon 390 nm irradiation. Photodegradation reactions of halogenated organic compounds are impor-

tant in environmental photochemistry, because these toxic and persistent substances tend to accumulate in water, soils, and sediments.<sup>[35]</sup> Since PDI(H)–PEG<sup>2-</sup> is evidently a strong photoreductant in aqueous solution, we explored its reactivity with chloroacetate, an often used model compound to explore photodegradation of recalcitrant chloro-organics. Irradiation of PDI(H)–PEG<sup>2-</sup> at 525 nm in 50 mM aqueous NaOH solution under N<sub>2</sub> for 17 hours indeed led to degradation of chloroacetate (Figure S39). This reaction is typically achievable either by using UV light,<sup>[35]</sup> or by using biphotonic visible excitation of suitable photocatalysts to form hydrated electrons.<sup>[31,32b,36]</sup> Under the experimental conditions applied here, it seems that monophotonic excitation of PDI(H)–PEG<sup>2-</sup> is sufficient to induce the degradation of chloroacetate. According to previous studies, chloroacetate has a reduction potential only slightly more positive than the standard potential of the hydrated electron ( $-2.9 \text{ V}$  vs. NHE).<sup>[36a,37]</sup>

Whilst aqueous photochemistry seems fundamentally interesting and important from an environmental perspective, photoreactions in organic solvents remain essential, because many substrates are not water-soluble. The formation of PDI dianions in neat DMF (and other organic solvents) requires however very strong reductants such as CoCp<sub>2</sub> or organic super-electron donors (Table 1, Figure S1),<sup>[38]</sup> the use of which seems unsustainable for our purposes. Therefore, we explored the possibility to reduce the lipophilic PDI(H)–dipp to PDI(H)–dipp<sup>2-</sup> in biphasic water–acetonitrile mixtures in which the photocatalyst and the substrate are mostly dissolved in the organic phase whilst Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is dissolved in water. We hypothesized that a phase-transfer co-catalyst could then facilitate the chemical reduction of PDI(H)–dipp by dithionite, thereby allowing us to use this reductant also in organic solvent.<sup>[39]</sup> To test this concept, we investigated the visible-light-mediated C<sub>α</sub>–O bond cleavage in small molecules resembling the lignin biopolymer (Table 3). This reaction requires fairly negative reduction potentials,<sup>[40]</sup> and it is of interest from an application-oriented perspective in which the controlled depolymerization of lignin would lead to useful commodity products.<sup>[40b,41]</sup>

Substrates **4–8** (Table 3) were dissolved along with 1 mol% of PDI(H)–dipp in acetonitrile, and then a mixture of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (3 equivalents) and tetra-*n*-butylammonium chloride (TBACl, 0.2 equivalents) in water was added under oxygen-free conditions (SI page S38). Irradiation of the resulting biphasic mixtures by a 525 nm LED (40 W) under argon at room temperature led to the desired C<sub>α</sub>–O bond cleavage reactions for all substrates except compound **5** (SI pages S55–S63). The isolated product yields for the four other examples ranged from 36% to 62% after a reaction time of 24 hours. Control experiments demonstrated that PDI(H)–dipp, Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, TBACl, and photo-irradiation are all essential for successful photoreaction. The few examples in Table 3 provide the proof-of-concept for the photoreactivity of the lipophilic PDI dianion variant in biphasic water/organic solvent mixtures, and no attempts for further reaction optimization were undertaken. Interestingly, 1 mol% PDI(H)–dipp in the water–acetonitrile mixtures was sufficient to achieve similar yields for the C<sub>α</sub>–O bond cleavage reactions as for the reductive dehalogenations in neat water with 5–

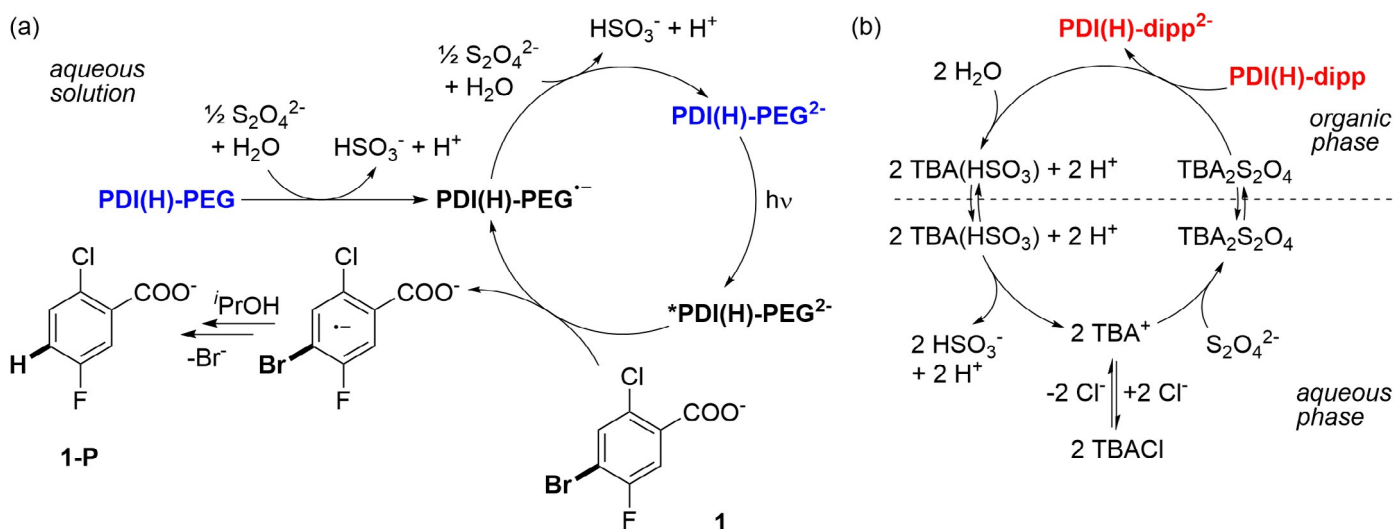
**Table 3:** C<sub>α</sub>-O bond cleavage reactions performed in water-acetonitrile mixtures with 1 mol% PDI(H)-dipp, 3 equivalents of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, and 0.2 equivalents of TBACl under irradiation at 525 nm (40 W) for 24 hours. Isolated product yields are indicated where applicable.



10 mol% PDI(H)-PEG over comparable reaction times. We speculate that the presence of PEG chains in the hydrophilic PDI(H)-PEG<sup>2-</sup> compound hinders the formation of photocatalyst-substrate encounter complexes to some extent, thereby decelerating the overall reaction compared to the lipophilic PDI(H)-dipp<sup>2-</sup> congener in which the dipp substituents cannot wrap around the redox-active PDI core. Since the photophysical studies presented above were performed in DMF, initial photoredox investigations focused on DMF-water mixtures, but no successful reactions could be observed in this case, and therefore we resorted to the acetonitrile-water mixtures.

A plausible mechanism for the observable aqueous photoreactions is given in Figure 4a, using the hydrodebromination of substrate **1** as a specific example. In water, PDI(H)-PEG<sup>2-</sup> forms spontaneously from PDI(H)-PEG in a known redox reaction with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, yielding two equivalents of HSO<sub>3</sub><sup>-</sup> as oxidation products. Photoexcitation of PDI(H)-PEG<sup>2-</sup> with green light populates an excited state (\*PDI(H)-PEG<sup>2-</sup>) that is thermodynamically competent for reductive debrominations in neat water. The primary photoproduct in the reductive dehalogenation reactions is a short-lived aryl radical that can undergo hydrogen atom transfer with *i*PrOH to form the final hydrodehalogenation product.<sup>[27]</sup>

In the biphasic mixtures, the organic phase is deep purple whilst the aqueous phase is comparatively weakly colored, signaling that the dianion form of PDI(H)-dipp remains hydrophobic despite its twofold negative charge (Figure 4b). TBACl is essential to shuttle S<sub>2</sub>O<sub>4</sub><sup>2-</sup> from the aqueous to the organic phase, and the role of the aqueous phase seems to be primarily that of a reservoir for dithionite.<sup>[39]</sup> Except for this key difference, it seems plausible that the photochemical mechanism in Figure 4a also prevails for the lignin model compound photo-degradations. The photocleavage of sub-



**Figure 4.** a) Proposed mechanism for the hydrodebromination reaction of substrate **1** to product **1-P**, catalyzed by PDI(H)-PEG<sup>2-</sup> in aqueous solution in the presence of excess Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (see SI page S38 for details) under photo-irradiation (*hν*) at 525 nm. b) Phase transfer of the chemical reductant in the biphasic acetonitrile-water systems, where the lipophilic PDI(H)-dipp compound remains largely in the organic phase both in its neutral and dianionic forms. For simplicity, the two-electron reduction of PDI(H)-dipp in (b) is shown as a single step, whereas in (a) the reduction of PDI(H)-PEG to PDI(H)-PEG<sup>2-</sup> is shown as two SET steps. Following formation of PDI(H)-dipp<sup>2-</sup> in (b), the same photochemical reaction cycle as in (a) is presumed to be operative.



strates 4–8 was previously explored with different photocatalysts,<sup>[40]</sup> among them a type of heteroleptic cyclometalated iridium(III) complex for which subsequent mechanistic studies demonstrated that in the presence of large excess of tertiary amine as sacrificial electron donor, the initial iridium(III) complex is first converted to another iridium(III) compound,<sup>[40b]</sup> which is then the actual catalytically active species.<sup>[8,42]</sup> Here, in the case of the PDI dianions, the lignin model substrate photocleavage seems to occur via a more straightforward mechanism. The key point with the substrates of Table 3 was to demonstrate that PDI dianions are amenable to photoreactions in organic (not just aqueous) solution using the principle demonstrated in Figure 4b.

The photocatalysis experiments reported herein were performed under conditions in which at least 100 equivalents of  $\text{Na}_2\text{S}_2\text{O}_4$  were present with respect to the PDI chromophore (SI pages S37/S38). This leads to essentially quantitative reduction of the PDI core to  $\text{PDI}^{2-}$  (Figure S24) and negligible concentrations of charge-neutral PDI and monoanionic PDI. Though  $\text{PDI}^{2-}$  appears in the catalytic cycles of Figure 4 as an oxidation product, we expect that the large excess of  $\text{Na}_2\text{S}_2\text{O}_4$  ensures that the  $\text{PDI}^{2-}$  concentration remains very small compared to the  $\text{PDI}^{2-}$  concentration throughout the entire photo-irradiation experiments, and the UV/Vis transient absorption data (Figure S14) are in line with that analysis. Photoexcitation of  $\text{PDI}^{2-}$  is therefore unlikely to interfere.<sup>[43]</sup>

## Conclusion

PDI dianions have remained a surprisingly little explored compound class until now.<sup>[19]</sup> A handful of prior studies demonstrated that when equipped with PEG chains or phosphonate groups, PDI dianions can be formed efficiently using dithionite as reductant in water.<sup>[10,14,15]</sup> One of these studies furthermore demonstrated that PEGylated  $\text{PDI}^{2-}$  can luminesce from a singlet-excited state in aqueous solution at room temperature.<sup>[10]</sup> Our work provides the following insights:

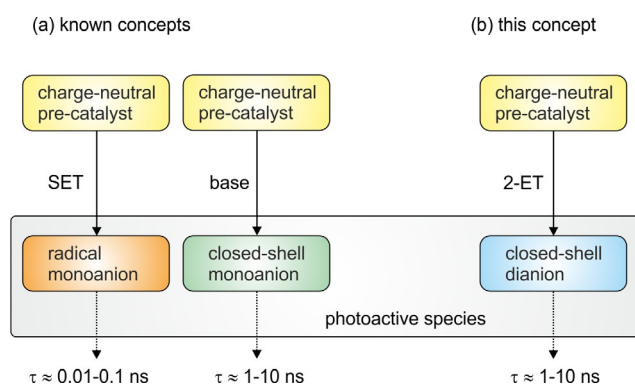
- 1) Luminescent PDI dianions with nanosecond excited-state lifetimes are also accessible in organic solution.
- 2) The emission color and the relevant excited-state energy of PDI dianions in both water and organic solvent are tunable over a range of ca. 0.3 eV by bromo-substitution of the PDI core, but the bromo-substituents do not mediate efficient intersystem crossing.
- 3) Water-soluble PEGylated PDI dianions are fairly strong photoreductants, capable of catalytic reductive dehalogenations in water in the presence of excess  $\text{Na}_2\text{S}_2\text{O}_4$ .
- 4) Similarly challenging catalytic photoreductions are possible in organic solvent, using a lipophilic dipp-substituted variant of PDI and a biphasic solvent system with a phase-transfer co-catalyst for  $\text{S}_2\text{O}_4^{2-}$ . Thus, a simple sacrificial reductant becomes useable in organic solution.
- 5) Owing to the spontaneous two-electron reduction of PDI by dithionite, green monophotonic excitation (525 nm) is sufficient to reach an excited state that seems to be more reducing than the much shorter-lived excited-state of PDI

monoanions, which has typically been formed via biphotonic blue excitation.<sup>[5]</sup> The use of long-wavelength light and low-intensity irradiation is often desirable in photocatalysis,<sup>[44]</sup> and longer excited-state lifetimes furthermore result in enhanced kinetic reactivity.

- 6) Photoionization of PDI dianions to form solvated electrons seems within reach and could potentially be exploited for photochemical Birch reductions, or for the photo-degradation of recalcitrant pollutants in wastewater treatment.<sup>[31,45]</sup>

On a conceptual level, the approach of our study is illustrated by Figure 5. As noted in the introduction, radical monoanions of perylene diimides and related compounds can be generated photochemically or electrochemically by single electron transfer (SET), leading to highly reducing species with very short excited-state lifetimes (Figure 5a, left).<sup>[5–7,22,43,46]</sup> Alternatively, closed-shell monoanions with longer-lived excited states that are also very reducing have been produced by deprotonation of suitable pre-catalysts with bases (Figure 5a, right).<sup>[16b]</sup> Our work adds the concept of two-electron transfer (“2-ET” in Figure 5b) to convert a pre-catalyst into a closed-shell dianion with high reducing power and comparatively long excited-state lifetime.

Our fundamental insights and our proof-of-principle photoreactions illustrate the suitability of PDI dianions for reductive photocatalysis, whilst our photophysical and electrochemical studies provide a basis for further rational development of PDI dianion luminophores and photoredox catalysts with tunable properties. Thus, our study informs the design of new metal-free catalysts for photoredox chemistry.<sup>[47]</sup> The concept of spontaneous multi-electron reduction of a pre-catalyst prior to its photoexcitation (Figure 5b) could become a generally applicable strategy to obtain strong photoreductants, complementing current research on photo-(electro)catalysis with a focus on the pre-reduction of photocatalysts by single electron transfer (Figure 5a). Recent organic-synthetically oriented work illustrated the value of mechanism-based screening methods,<sup>[48]</sup> and we hope that our study can make a useful contribution in that spirit.



**Figure 5.** Different concepts in photocatalysis with anions.  $\tau$  represents the typically relevant excited-state lifetimes. Two-electron pre-reduction (2-ET) provides a kinetically and thermodynamically very reactive compound that becomes catalytically competent under monophotonic excitation with light of comparatively long wavelength.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** electron transfer · luminescence · photocatalysis · photochemistry · photophysics

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