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Triplet state dissolved organic matter in aquatic photochemistry: reaction mechanisms, substrate scope, and photophysical properties

Kristopher McNeill*[a] and Silvio Canonica[b]

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Excited triplet states of chromophoric dissolved organic matter (^{3}CDOM*) play a major role among the reactive intermediates produced upon absorption of sunlight by surface waters. After more than two decades of research on the aquatic photochemistry of ^{3}CDOM*, the need for improving the knowledge about the photophysical and photochemical properties of these elusive reactive species remains considerable. This critical review examines the efforts to date to characterize ^{3}CDOM*. Information on ^{3}CDOM* relies mainly on the use of probe compounds because of the difficulties associated with directly observing ^{3}CDOM* using transient spectroscopic methods. Singlet molecular oxygen ($^1O_2$), which is a product of the reaction between ^{3}CDOM* and dissolved oxygen, is probably the simplest indicator that can be used to estimate steady-state concentrations of ^{3}CDOM*. There are two major modes of reaction of ^{3}CDOM* with substrates, namely triplet energy transfer or oxidation (*via* electron transfer, proton-coupled electron transfer or related mechanisms). Organic molecules, including several environmental contaminants, that are susceptible to degradation by these two different reaction modes are reviewed. It is proposed that through the use of appropriate sets of probe compounds and model photosensitizers an improved estimation of the distribution of triplet energies and one-electron reduction potentials of ^{3}CDOM* can be achieved.

Environmental impact

Photochemical processes are critically important in driving biogeochemical element cycling and in the breakdown of contaminants in surface waters. One of the most important and least understood sets of photochemical pathways involves triplet chromophoric dissolved organic matter (^{3}CDOM*), a form of electronically excited DOM. There has been a recent surge in the study of the properties and reactivity of ^{3}CDOM* and this review article is an attempt to organize and synthesize what has been discovered about ^{3}CDOM* over the past few decades.

Introduction

Sunlight-driven processes are central to both the buildup of complex molecules through photosynthesis and their breakdown through photodegradation reactions. These photodegradation processes may be initiated not only directly by the absorption of light, but also indirectly through reactions involving a menagerie of exotic chemical species such as free radicals and electronically excited molecules, referred to here collectively as photochemically produced reactive intermediates (PPRI).[1–4] Triplet excited states of chromophoric dissolved organic matter (^{3}CDOM*) are an important subset of the larger pool of PPRI formed in sunlit waters that also include singlet oxygen ($^1O_2$, $^1\Delta_g$), superoxide ($O_2^{-\bullet}$), hydrogen peroxide, hydroxyl radical ($OH^\bullet$), and others.[1–4] ^{3}CDOM* has been implicated in the degradation of contaminants, such as pesticides[5] and pharmaceuticals,[6,7] and holds a special position among the PPRI for at least two reasons. First, ^{3}CDOM* is known or suspected to be a precursor of other PPRI.[1–4] For example, ^{3}CDOM* is the primary source for $^1O_2$ in sunlit natural waters.[8,9] Second, unlike other PPRI, ^{3}CDOM* is not a well-defined species; rather, it is an infamously ill-defined mixture of triplet states, which vary in their excited state energies and excited state redox potentials.

The goal of this review article is to outline the reactivity modes of ^{3}CDOM* and to summarize what is known or can be reasonably inferred about both the triplet energy and redox potential of ^{3}CDOM*. In addition, some back-of-the-envelope calculations are presented that give rough answers to questions that often arise when discussing ^{3}CDOM*: why are triplet states more important than singlet states in CDOM-sensitized processes? And, what is the steady-state concentration of ^{3}CDOM*?

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[a] *Institute for Biogeochemistry and Pollutant Dynamics, ETH Zurich, Universitaetstrasse 16, 8092 Zurich, Switzerland. E-mail: kris.mcneill@env.ethz.ch*
[b] *Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland*

Steady-state concentration of ^{3}CDOM* in natural waters

Attempting to quantify the steady-state concentration of ^{3}CDOM* in an aquatic system would seem to be more challenging than other PPRI, due to the abovementioned problem that ^{3}CDOM* is a mixture of triplet states of diverse molecules. Therefore, it may seem surprising that we can actually estimate the steady-state concentration of ^{3}CDOM* within about a factor of two with a high degree of confidence. This is thanks to the inextricable link between $^1O_2$ and ^{3}CDOM*.

To understand this, it is helpful to consider the simplified kinetic scheme that connects ^{3}CDOM* and $^1O_2$ (Fig. 1). CDOM is excited by the absorption of a photon (symbolized by $h\nu$) to form the excited singlet state of CDOM, ^{1}CDOM*. Under optically thin conditions, the rate of light absorbance (R_{abs}), in units of M s^{-1}, is given by the product of the irradiance (mmol photons cm^{-2} s^{-1}), the Naperian absorption coefficient of CDOM (natural log-based absorption coefficient in units of cm^{-1}), and a conversion factor (mol L^{-1} (mmol cm^{-3})$^{-1}$ = 1). The efficiency of the conversion of ^{1}CDOM* to ^{3}CDOM* (*i.e.*, the intersystem crossing efficiency) is given by Φ_{ISC}. The rate constants for the O_2-independent and O_2-dependent deactivation pathways of ^{3}CDOM* are given by k_d^T and $k_{O_2}[O_2]$, respectively. Under normal air-saturated surface–water conditions, O_2-dependent relaxation almost certainly dominates over O_2-independent relaxation. Sharpless has estimated the O_2-independent lifetime of triplets through O_2-dependent formation kinetics of $^1O_2$ using Suwannee River and Pony Lake isolates, and determined a lifetime around 20 µs ($k_d^T \approx 5 \times 10^4$ s^{-1}).[10] Zepp has made a reasonable estimate of $k_{O_2} = 2 \times 10^9$ M^{-1} s^{-1}, based on O_2 quenching rate constants of well-defined sensitizers.[9] While there is certainly some variation in the individual k_{O_2} values among the numerous sensitizers that comprise ^{3}CDOM*, they are all expected to be quite high and near the diffusion-controlled limit. For air-saturated freshwater at 25 °C (258 µM O_2), $k_{O_2}[O_2]$ is thus approximately 5×10^5 s^{-1} (τ = 2 µs), which suggests that the O_2-dependent relaxation pathway is an order of magnitude more important than the O_2-independent pathway.

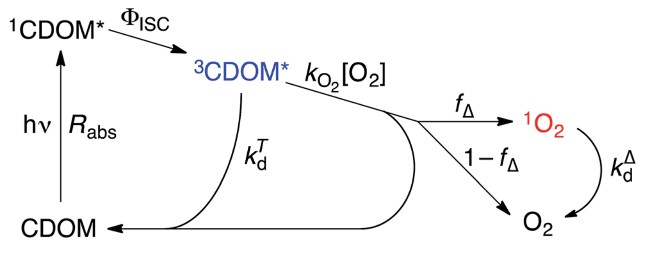

Fig. 1 Kinetic scheme illustrating the connection between ^{3}CDOM* and $^1O_2$. Definition of variables and symbols: CDOM, chromophoric dissolved organic matter; ^{1}CDOM*, singlet state dissolved organic matter; ^{3}CDOM*, triplet state dissolved organic matter; $^1O_2$, singlet oxygen ($^1\Delta_g$); $h\nu$, photon; R_{abs}, rate of light absorbance; Φ_{ISC}, intersystem crossing quantum yield; k_{O_2}, bimolecular rate constant for the quenching of ^{3}CDOM* by O_2; f_Δ, fraction of O_2-dependent quenching that produces $^1O_2$; k_d^T, rate constant for O_2-independent relaxation of ^{3}CDOM*; k_d^Δ, rate constant for relaxation of $^1O_2$ to O_2.

The quenching of triplet states by O_2 produces $^1O_2$, but the yield for this process (f_Δ) is different for each sensitizer. It has often been assumed that f_Δ is close to unity,[9] but studies with a range of well-defined triplet sensitizers have shown that this value can vary from near 0 (*e.g.*, coumarin[11]) to near 1 (*e.g.*, perinaphthenone[12]), depending on the sensitizer.[11] Indeed, the value of f_Δ varies with the sensitizer's triplet energy and sensitizer's excited state oxidation potential (*i.e.*, how strong a reductant the sensitizer is in the excited state), with high energy and strongly reducing triplet species generally being poorer $^1O_2$ sensitizers.[13,14] Once formed, $^1O_2$ mainly undergoes unimolecular deactivation, k_d^Δ.[15]

Expressions for the steady-state concentrations of ^{3}CDOM* and $^1O_2$ based on the scheme depicted in Fig. 1 are given by eqn (1) and (2).

$$\left[{}^3\mathrm{CDOM}^*\right]_{ss} = \frac{R_{abs}\Phi_{ISC}}{k_{O_2}[O_2] + k_d^T} \tag{1}$$

$$\left[{}^1O_2\right]_{ss} = \frac{\left[{}^3\mathrm{CDOM}^*\right]_{ss} k_{O_2}[O_2] f_\Delta}{k_d^\Delta} \tag{2}$$

One can rearrange eqn (2) to arrive at an expression for the ratio of the steady-state concentrations of $^1O_2$ and ^{3}CDOM* (eqn (3)).

$$\frac{\left[{}^1O_2\right]_{ss}}{\left[{}^3\mathrm{CDOM}^*\right]_{ss}} = \frac{k_{O_2}[O_2] f_\Delta}{k_d^\Delta} \tag{3}$$

Substituting values for k_d^Δ (2.5×10^5 s^{-1} for H_2O),[15] k_{O_2} (2×10^9 M^{-1} s^{-1}),[9] and $[O_2]$ (258 µM at 298 K), one arrives at eqn (4).

$$\frac{\left[{}^1O_2\right]_{ss}}{\left[{}^3\mathrm{CDOM}^*\right]_{ss}} \approx 2f_\Delta;\ \ 25\ {}^\circ\mathrm{C},\ \text{air-saturated water} \tag{4}$$

This result indicates that for 25 °C, air-saturated water, the ratio of $^1O_2$ to ^{3}CDOM* is linearly dependent on the yield of $^1O_2$ from the O_2-dependent quenching of ^{3}CDOM* (f_Δ) with a maximum $[^1O_2]_{ss}$ value of two times $[^3\mathrm{CDOM}^*]_{ss}$. While we do not know the value of f_Δ for ^{3}CDOM*, eqn (4) nevertheless suggests a useful rule-of-thumb of $[^3\mathrm{CDOM}^*]_{ss} \approx [^1O_2]_{ss}$. To reiterate, this will hold when the value for k_{O_2} is close to the estimate of 2×10^9 M^{-1} s^{-1} and the average f_Δ value is near 0.5. Under noon-time clear summer sky conditions, $[^1O_2]_{ss}$, has been found to be between 10^{-14} and 10^{-12} M in natural waters, depending on the concentration of DOM (1–100 mg$_C$ L^{-1}; see for example Peterson *et al.*[16]). Based on the above argumentation, we can therefore adopt this same concentration range for $[^3\mathrm{CDOM}^*]_{ss}$.

Why triplet states and not singlet states?

Could singlet excited state CDOM moieties (^{1}CDOM*) act as reactive intermediates in a similar manner to ^{3}CDOM*? After all, the lowest lying singlet excited state of a given sensitizer is higher in energy than its lowest lying triplet state and would therefore be expected to be more reactive than the triplet. While this is true, it is counteracted by the fact that the steady-state concentration of ^{1}CDOM* is much lower than that of ^{3}CDOM*.

To determine exactly how much lower [^{1}CDOM*]$_{ss}$ is than [^{3}CDOM*]$_{ss}$, we need estimates of the relative formation and decay rate constants for both species. Formation quantum yields for ^{3}CDOM* have been estimated to be in the range of 1–2%,[9,17] but could be as high as 6% or higher for some DOM samples, based on $^1O_2$ quantum yield measurements.[16,18] This indicates that ^{1}CDOM* formation rates are 15–100 times faster than those for ^{3}CDOM*. On the decay side, the ^{1}CDOM* lifetime is much shorter than that of ^{3}CDOM*, which has a lifetime of about 2 μs (*i.e.*, the inverse of $k_{O_2}[O_2]$; see previous section). Fluorescence lifetime studies give a direct measurement of the decay of ^{1}CDOM*, and, as expected, the mixture of fluorophores do not display a single lifetime. Rather, the data suggest a dominant pool of short lifetime ^{1}CDOM* species ($\tau < 150$ ps), with contributions from two other pools of ^{1}CDOM* ($\tau \approx 1$ and 3 ns).[19] For simplicity, we consider 100 ps to be the typical lifetime of ^{1}CDOM*.

Taken together, we see that while ^{1}CDOM* is formed 15–100 times faster than ^{3}CDOM*, it decays approximately 20 000 times faster, giving 200- to 1300-fold lower steady-state concentrations than ^{3}CDOM*. This corresponds to [^{1}CDOM*]$_{ss}$ of 10^{-17} to 10^{-14} M in sunlit surface waters, compared to [^{3}CDOM*]$_{ss}$ of 10^{-14} to 10^{-12} M. To put this into context of another PPRI, [^{1}CDOM*]$_{ss}$ is expected to be similar to $[OH^{\bullet}]_{ss}$. Thus, ^{3}CDOM* is expected generally to be the more important species, but ^{1}CDOM* could also play a role under the right circumstances. For example, we speculate that this could occur with CDOM samples that have low intersystem crossing quantum yields (*i.e.*, low rates of ^{3}CDOM* production) or when the rate constant for reaction with ^{1}CDOM* is orders of magnitude faster than with ^{3}CDOM*. Another case where ^{1}CDOM* could conceivably participate in bimolecular reactions despite being so short-lived is when its reaction partner is already associated with CDOM. Such intra-humic photosensitization reactions have been proposed for the photoreduction of mirex,[20,21] reactions involving $^1O_2$ with a highly hydrophobic probe molecule,[22,23] and the ^{3}CDOM*-sensitized degradation of amoxicillin.[24]

Energy transfer reactions

Triplet excited states of CDOM have been shown to undergo energy transfer reactions with selected substrates (Fig. 2). The best studied of these energy transfer processes is the formation of $^1O_2$ from the interaction of triplet ground state O_2 with ^{3}CDOM*, which was first reported by Zepp in 1977.[8]

$$\underset{\text{excited state}}{^3\text{CDOM}^*} + \underset{\text{ground state}}{O_2\,(^3\Sigma_g^-)} \longrightarrow \underset{\text{ground state}}{\text{CDOM}} + \underset{\text{excited state}}{^1O_2\,(^1\Delta_g)}$$

The energy required to promote ground state O_2 to $^1O_2$ is 94 kJ mol^{-1} (980 meV).[11] Since most triplet excited states of organic chromophores are much higher (typically 180–320 kJ mol^{-1}), O_2 has been proposed to be a universal energy acceptor, capable of accepting energy from all ^{3}CDOM* moieties.[9] This is an oversimplification as discussed above in the section on the concentration of ^{3}CDOM* in natural waters, but to a first approximation, it is a reasonable statement.

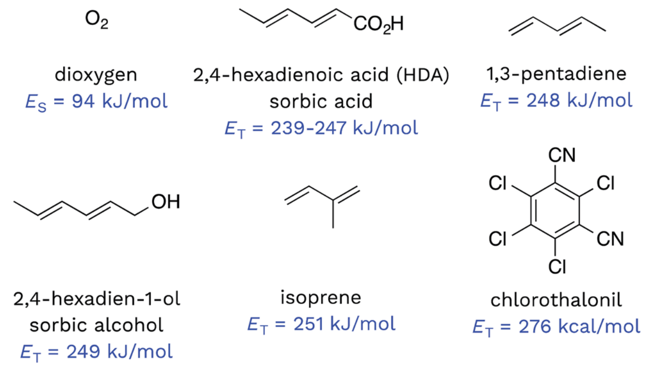

Fig. 2 Compounds that have been shown to act as energy acceptors with ^{3}CDOM*. Triplet energies (E_T) are given for each compound, except in the case of O_2, where the lowest singlet energy (E_S) is given.

Dienes have also been reported to participate in energy transfer reactions with ^{3}CDOM*. Zepp first demonstrated this with pentadiene (E_T = 248 kJ mol^{-1})[25] and 2,4-hexadien-1-ol (sorbic alcohol, E_T = 249 kJ mol^{-1}),[25] showing that various natural organic matter isolates could sensitize the reversible photoisomerization of the *cis*- and *trans*-forms.[9] Zepp[26] extended this reaction type to include 2,4-hexadienoate (HDA, also known as sorbic acid, E_T = 239–247 kJ mol^{-1}).[27] More recently, Grebel *et al.*[17] made an in depth study of the reaction of HDA with ^{3}CDOM*, and this work has sparked the use of HDA as both a quencher of ^{3}CDOM* and a molecular probe to quantify its concentration.[28–42] In a similar way, isoprene (E_T = 251 kJ mol^{-1})[25,43] has been effectively used as a triplet quencher, providing evidence for the involvement of ^{3}CDOM* in the oxidation of mefenamic acid,[44] some sulfa drugs,[45,46] and the amino acids tryptophan, methionine, and tyrosine.[47] Dienes have not only been used as probe molecules. Domoic acid, a naturally occurring diene and potent marine toxin, has been shown to undergo ^{3}CDOM*-sensitized isomerization, among other indirect photoprocesses.[48]

There are very few well-characterized energy transfer reactions between ^{3}CDOM* and non-diene organic substrates. A notable exception is chlorothalonil, which is promoted to its triplet state through a CDOM-sensitized process.[49,50] Porras *et al.* tested for the involvement of energy transfer between ^{3}CDOM* and chlorothalonil through quenching experiments.[49] In addition, they determined the triplet energy of chlorothalonil by low temperature phosphorescence measurements to be 276 kJ mol^{-1} and verified that excitation of CDOM with wavelengths longer than 450 nm (<266 kJ mol^{-1}) gave very little sensitized photoreaction.[49]

Triplet energy of ^{3}CDOM*

Given the heterogeneous nature of the components of ^{3}CDOM*, there is no one triplet energy, E_T, that can be used to describe it.

Rather, there is a distribution of triplet energies. Using the energy transfer reactions between ^{3}CDOM* and either O_2 ($E_S = 94$ kJ mol^{-1})[11] or dienes 1,3-pentadiene ($E_T = 248$ kJ mol^{-1})[25] and 2,4-hexadien-1-ol ($E_T = 249$ kJ mol^{-1}),[25] Zepp concluded that ^{3}CDOM* comprised both high-energy triplets ($E_T \geq 250$ kJ mol^{-1}) and low-energy triplets ($94 \leq E_T \leq 250$ kJ mol^{-1}).[9] The high-energy triplets were able to sensitize the isomerization of the 1,3-pentadiene and produce $^1O_2$, while the low energy triplets could only produce $^1O_2$. One conclusion of this study was that the high-energy triplets accounted for about 15–53% (mean = 37%) of the total triplet pool, depending on the DOM sample.[9] To visualize this result, a hypothetical normal (Gaussian) distribution of triplet energies with 37% of the triplet energies being greater than or equal to 250 kJ mol^{-1} is shown in Fig. 3. Also plotted in Fig. 3 are ranges of triplet energies found for representative compounds (Table 1) that contain chromophoric functional groups believed to be present in DOM. The data in Fig. 3 suggest that PAH-like moieties and quinones are most likely not major contributors to the high-energy triplet pool, whereas aromatic ketones and other carbonyl-containing compounds (*e.g.*, coumarins and chromones) are better candidates for high-energy triplets. However, it is not only the triplet energy that is important, but also the triplet yield (*i.e.*, intersystem crossing quantum yield). For example, aromatic ketones have triplet yields near unity,[51,52] while coumarins typically have poor triplet yields.[53]

Another piece of information that could be obtained by Zepp and coworkers in the CDOM-sensitized isomerization of 1,3-pentadiene was the apparent E_T of CDOM from the final *cis*–*trans* ratio, or the photostationary state, of 1,3-pentadiene.[9] This photostationary state was shown to reflect the sensitizer's E_T, and the values obtained for CDOM solutions were consistent with an apparent E_T of 250 kJ mol^{-1}.[9] Similar experiments conducted with functionalized carbon nanotubes[41] and petroleum[54] found the apparent E_T values to be lower and higher than CDOM, respectively. The petroleum value was estimated to be 288–303 kJ mol^{-1}, suggesting that the triplet photochemistry relevant to oil spills may differ substantially from CDOM-based photochemistry.[54] The high average E_T value found in petroleum stands in contrast to the low average triplet energies of PAH molecules in Table 1 and Fig. 3. This may mean that the small selection of PAHs (triphenylene, phenanthrene, naphthalene, pyrene, and anthracene) is not representative of the PAH mixture in petroleum or that other higher E_T species present in petroleum (*e.g.*, ketones formed from oxidation)[55,56] are dominating the sensitization of the diene probes.

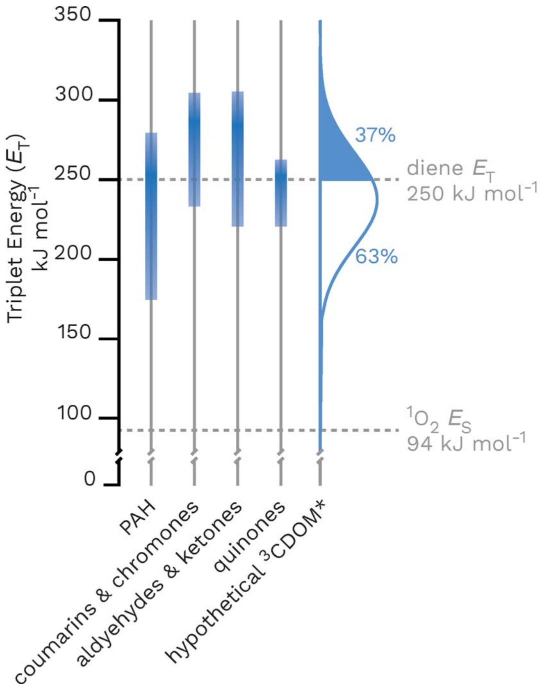

Fig. 3 Distributions of triplet energies found for different classes of organic molecules containing functional groups that are thought to be present in CDOM and a hypothetical normal distribution of ^{3}CDOM* triplet energies that fit the observation of 37% having $E_T \geq 250$ kJ mol^{-1}.[9] The data used for this figure is compiled in Table 1.

At least two spectroscopic estimates of the E_T value of ^{3}CDOM* have been made. Bruccoleri *et al.* applied magnetic circular dichroism (MCD) spectroscopy to an organic matter isolate and assigned an absorbance transition as $S_0 \rightarrow T_1$, and the wavelength for this transition (714 nm; 14 000 cm^{-1}) corresponded to an energy of 170 kJ mol^{-1}.[57,58] Mazhul *et al.* used room temperature phosphorescence spectroscopy to identify the opposite transition ($T_1 \rightarrow S_0$), with an onset near 405 nm, corresponding to the highest energy (phosphorescing) triplets having an E_T value of 300 kJ mol^{-1}.[59] In both of these studies, the estimates of E_T must be viewed with caution, as both techniques are almost certainly confounded by the complex mixture of DOM. Indeed, Mazhul *et al.* explicitly point out that they believe they are only observing phosphorescence from a minority of the ^{3}CDOM* components in their mixture.[59] Additionally, these spectroscopic values do not seem reasonable as average or representative values, since one is at the extreme low end and one is at the far high end of the range of triplet energies normally found for organic sensitizers.

^{3}CDOM* oxidation reactions

Redox reactions are the dominant reaction type between organic substrates and ^{3}CDOM*, with ^{3}CDOM* primarily acting as the oxidant. The oxidation reactions have been reviewed elsewhere[60] and the discussion here will be mostly confined to the substrate scope and the reduction potential of ^{3}CDOM*.

Some patterns are revealed by examining the structures of compounds for which triplet states have been established as playing a role in their organic matter-sensitized degradation. In Fig. 4, selected structures of compounds are presented that have been shown to react with ^{3}CDOM*. Excluded from this group are compounds that are suspected to be reactive toward ^{3}CDOM*, based on their reactivity toward model sensitizers (*e.g.*, anthraquinone-2-sulfonate; AQ2S), but that have not yet been investigated with CDOM.[61–65]

Examining the structures in Fig. 4, one can see that anilines and phenols are well represented. Anilines and compounds containing aniline substructures are especially susceptible to oxidation by ^{3}CDOM*. This includes simple aniline structures, such as *N*,*N*-dimethylaniline,[66] *p*-aminobenzoic acid,[67] and

Table 1 Ground-state reduction potentials (E°), triplet energies (E_T), triplet state reduction potentials ($E^{\circ*}$), and singlet oxygen quantum yields (Φ_Δ) for selected DOM model sensitizers and other widely used sensitizers

Entry	Sensitizer (S)	$E^\circ(S/S^-)$ V (SHE)	Solvent[a,b]	E_T (kJ mol^{-1})	Matrix[b]	$E^{\circ*}(^3S^*/S^-)$ V (SHE)	Φ_Δ	Solvent[b]
Quinones								
1	Benzoquinone	0.099 (ref. 139)	H_2O	224 (ref. 140)	Ne solid	2.42	0.13 (ref. 141)	H_2O (pH 7)
2	Naphthoquinone	−0.12 (ref. 142)	H_2O	241 (ref. 143)	MCIP	2.38	0.27 (ref. 141)	H_2O (pH 7)
3	Anthraquinone	−0.52 (ref. 144)	H_2O	265 (ref. 145 and 146)	EPA	2.23	0.62 (ref. 147)	CH_3CN
4	Duroquinone	−0.24 (ref. 139)	H_2O	235 (ref. 148)	PMMA	2.19	0.89 (ref. 147)	CH_3CN
Aldehydes and ketones								
5	Benzil	−0.47 (ref. 149)	50% EtOH	230 (ref. 150)	EtOAc	1.92	0.58 (ref. 151)	C_6H_6
6	CBBP[b]	−1.13 (ref. 152)	H_2O (pH 11)	286 (ref. 152)	EA	1.84	[d]	—
7	Acetophenone	−1.42 (ref. 149)	50% EtOH	308 (ref. 153)	MTHF	1.77	0.33 (ref. 151)	C_6H_6
8	Biacetyl	−0.79 (ref. 149)	50% EtOH	239 (ref. 146)	EPA	1.69	0.29 (ref. 151)	C_6H_6
9	Benzophenone	−1.31 (ref. 149)	50% EtOH	288 (ref. 150)	EtOAc	1.67	0.37 (ref. 11)	CH_3CN
10	3MAP	−1.50 (ref. 149)	50% EtOH	303 (ref. 149)	[c]	1.64	0.27 (ref. 154)	C_6H_6
11	2-Naphthaldehyde	−1.10 (ref. 149)	50% EtOH	249 (ref. 146)	MCIP	1.48	[d]	—
12	9-Fluorenone	−0.97 (ref. 149)	50% EtOH	223 (ref. 146)	MCIP	1.34	0.82 (ref. 11)	C_6H_6
13	2-Acetylnaphthone (2AN)	−1.48 (ref. 149)	50% EtOH	249 (ref. 146)	EPA	1.10	0.71 (ref. 11)	C_6H_6
Coumarins, chromones, and related								
14	Xanthone	−1.21 (ref. 155)	25% EtOH	306 (ref. 150)	EtOAc	1.96	0.27 (ref. 11)	C_6H_6
15	Coumarin	−1.16 (ref. 156)	75% MeOH	267 (ref. 157)	H_2O	1.61	0.01 (ref. 11)	D_2O
16	Flavone	−1.18 (ref. 158)	50% iPrOH	260 (ref. 146)	IPMC	1.51	0.16 (ref. 159)	MeCf
17	Umbelliferone	−1.23 (ref. 156)	75% MeOH	255 (ref. 157)	EtOH	1.42	[d]	—
18	Cinnamic acid	−1.14 (ref. 156)	75% MeOH	235 (ref. 160)	[c]	1.29	[d]	—
Polycyclic aromatic hydrocarbons								
19	Triphenylene	−2.22 (ref. 161)	DMF	281 (ref. 146 and 162)	EPA	0.69	0.40 (ref. 163)	C_6H_6
20	Phenanthrene	−2.22 (ref. 164)	75% dioxane	259 (ref. 146 and 162)	EPA	0.46	0.33 (ref. 163)	C_6H_6
21	Naphthalene	−2.25 (ref. 164)	75% dioxane	253 (ref. 150)	CFC–EA	0.37	0.50 (ref. 163)	C_6H_6
22	Pyrene	−1.86 (ref. 164)	75% dioxane	204 (ref. 146)	MCIP	0.25	0.38 (ref. 163)	C_6H_6
23	Anthracene	−1.70 (ref. 164)	75% dioxane	178 (ref. 165)	EPA	0.15	0.61 (ref. 163)	C_6H_6
Other sensitizers								
AQ2S	Anthraquinone-2-sulfonate	−0.39 (ref. 166)	H_2O	258 (ref. 167)	CH_3CN	2.28	~0 (ref. 125 and 147)	H_2O
LC	Lumichrome	−0.50 (ref. 168)	H_2O	232 (ref. 169)	EM	1.91	0.63 (ref. 170)	H_2O (pH 7.4)
RF	Riboflavin	−0.29 (ref. 171)	H_2O	209 (ref. 169)	EM	1.88	0.49 (ref. 11)	H_2O (pH 7.4)
MB	Methylene blue	0.024 (ref. 172)	H_2O	142 (ref. 133)	[c]	1.50	0.37–0.56 (ref. 173)	H_2O
RB	Rose bengal	−0.54 (ref. 93)	H_2O	171 (ref. 93)	EPA	1.23	0.75 (ref. 11)	D_2O (pD 8.2)
PN	Perinaphthenone	−0.67 (ref. 174 and 175)	50% EtOH	164 (ref. 176)	CH_3CN	1.03	0.98 (ref. 12)	H_2O

[a] Balance is H_2O when a percentage co-solvent is specified. [b] Abbreviations: CBBP = 4-carboxybenzophenone; 3MAP = 3-methoxyacetophenone; EtOH = ethanol; MeOH = methanol; iPrOH = isopropanol; DMF = *N*,*N*-dimethylformamide; MCIP = 5 : 1 methylcyclohexane : isopentane; EPA = 5 : 5 : 2 diethyl ether : isopentane : ethanol; PMMA = polymethylmethacrylate; EtOAc = ethyl acetate; EA = 3 : 1 diethyl ether : ethanol; MTHF = 2-methyltetrahydrofuran; IPMC = 5 : 1 isopentane : methylcyclohexane; CFC–EA = mixture of CFC-113 (1,1,2-trichlorotrifluoroethane) and EtOAc; EM = 9 : 1 ethanol : methanol; MeCf = 3 : 1 methanol : $CHCl_3$. [c] Matrix not specified. [d] No reported value found.

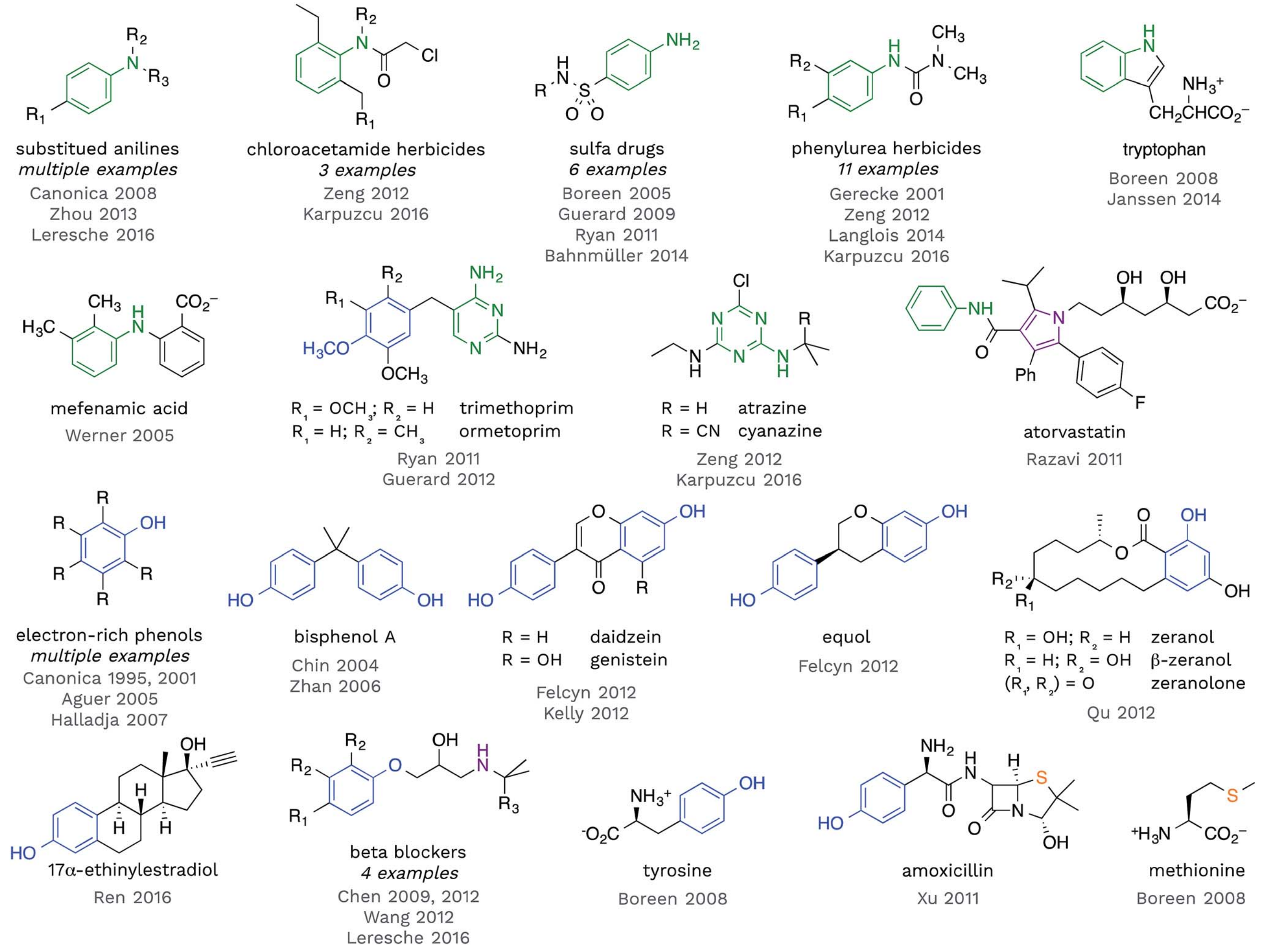

Fig. 4 Selected compounds that have been shown to react with ^{3}CDOM*. Aniline (and other aminoarene), phenol (and aryl ether), sulfide and related substructures are highlighted.

p-cyano-*N*,*N*-dimethylaniline,[68] but also more complex structures, such as found in phenylurea herbicides,[28,69–72] sulfa drugs,[45,46,73–75] chloroacetamide herbicides,[28,72] diarylamines (*e.g.*, mefenamic acid[44]), and arguably within the structure of tryptophan[47,76] and indole[77] (Fig. 4). There is also some evidence that this reactivity extends to aniline analogues that are amino-substituted aromatic heterocycles. For example, triazine herbicides atrazine and cyanazine have been shown to react with ^{3}CDOM*, and both of these compounds contain a diaminotriazine functional group.[28,72] The structurally similar diaminopyrimidine group in trimethoprim[45] and ormetoprim[78] may be responsible for the reactivity of these compounds toward ^{3}CDOM*, but these compounds also contain electron-rich methoxy-substituted benzene rings that could instead be the locus of reactivity. ^{3}CDOM* is capable of oxidizing both electron-rich and electron-poor anilines, although the rates of aniline oxidation are clearly modulated by their electron-richness.[60,69] By contrast, only electron-rich phenols appear to be susceptible to oxidation by ^{3}CDOM*.

Relatively simple alkyl- and methoxy-substituted phenols, such as *p*-cresol, 3,4-dimethoxyphenol, tyrosine, and 2,4,6-trimethylphenol, have been shown to be oxidized by ^{3}CDOM* (Fig. 4).[47,79–81] This reactivity has been found in more complicated phenol-containing compounds, including the polycarbonate constituent bisphenol A,[82,83] the oral contraceptive 17α-ethinylestradiol,[42] agricultural hormones zeranol, β-zeranol, and zeranolone,[84] and phytoestrogens daidzein, genistein, and equol[32,85] (Fig. 4). Presumably, the phenol functionality is the site of reactivity toward ^{3}CDOM* in these compounds.

The mechanism of oxidation of phenols to phenoxy radicals can be either electron transfer followed by proton transfer (2 steps) or proton-coupled electron transfer (PCET; 1 step), and one critical piece of evidence supporting PCET is the presence of a kinetic isotope effect when O–H is changed to O–D.[86] Canonica found weak isotope effects for oxidation of phenols by ^{3}CDOM*, favoring a two-step electron transfer-proton transfer mechanism being operative.[79]

For some of the polyfunctional compounds shown in Fig. 4, the primary target of ^{3}CDOM* oxidation is not clear. Atorvastatin contains an anilide functional group (aniline amide), but also contains a pentasubstituted pyrrole that could be the preferred site of oxidation. Indeed, the pyrrole has been proposed as the site of electrochemical oxidation of atorvastatin.[87] Amoxicillin reacts with ^{3}CDOM* and contains both phenol and sulfide functional groups.[24] While the reaction could be occurring at the phenol, S-containing compounds, such as methionine,[47] are also believed to be oxidized by ^{3}CDOM*. Beta blockers, atenolol, metoprolol, nadolol, and propranolol, have all been shown to react with ^{3}CDOM*.[29,68,88] While the initial site of reactivity is likely the electron-rich alkoxy-substituted benzene, analogous to phenol oxidation, Chen *et al.* have shown evidence for oxidation at the alkyl amine as the ultimate product.[88,89]

We have focused on the oxidation of organic molecules, but there is also evidence that ^{3}CDOM* can also oxidize inorganic species. Canonica demonstrated that triplet ketone sensitizers with similar reactivity to ^{3}CDOM* were capable of oxidizing carbonate, $\mathrm{CO_3}^{2-}$, to carbonate radical, $\mathrm{CO_3}^{-\bullet}$.[90] Recent work by Parker and Mitch has implicated ^{3}CDOM* in the oxidation of halides to dihalogen radical anions, $\mathrm{X_2}^-$ (X = Cl, Br).[48] The production of these reactive halogen species (RHS) could have major implications for the photochemical fate of organic contaminants in seawater. Brigante, Vione and coworkers previously showed the possibility of sensitized photochemical production of dihalogen radical anions $\mathrm{X_2}^-$ from Br^- and Cl^-, using AQ2S as a sensitizer.[91,92] AQ2S is a powerful oxidant (see below), and while it can be used to establish the viability of triplet-sensitized oxidation reactions, it may not be an ideal surrogate for quantitative predictions of CDOM-sensitized oxidation rates. For example, using authentic CDOM, Parker and Mitch estimate steady-state concentrations of RHS in surface seawater orders of magnitude lower than the estimates gained from AQ2S halide oxidation kinetics.[48,91,92]

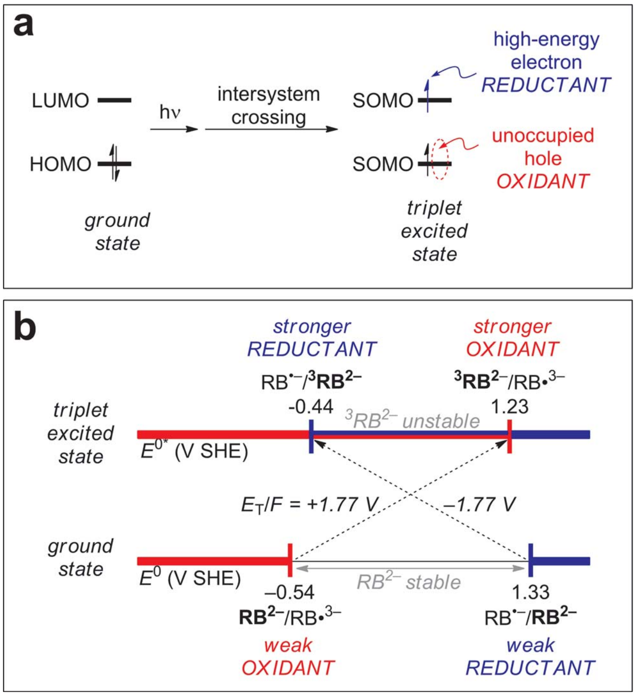

Fig. 5 (a) Frontier orbital occupancy diagram showing the difference between the ground state and its lowest triplet excited state, illustrating that the triplet state is both a stronger reductant and oxidant. HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital; SOMO = singly occupied molecular orbital. (b) Example of rose bengal (RB^{2-}), showing that the potential for reduction of RB^{2-} (*i.e.*, RB^{2-} as oxidant) moves from −0.54 to +1.23 V upon excitation to its triplet state, $^3\mathrm{RB}^{2-}$. Similarly, the potential for oxidation of RB (*i.e.*, RB^{2-} as reductant) moves from +1.33 to −0.44 V upon excitation to $^3\mathrm{RB}^{2-}$. RB^{2-} is thus a better oxidant and better reductant in its triplet state than in its ground state, and the difference in potential comes from the triplet energy, $E_\mathrm{T}/F = 1.77$ V.

^{3}CDOM* reduction reactions

Excited triplet states are both better oxidants and better reductants than their ground states. The reason for this can be seen visually in Fig. 5a, which shows the ground state and lowest triplet state electronic configurations of the frontier orbitals of a generic molecule. One can see that for the molecule to act as an oxidant (receive an electron), it requires less energy in the excited state than the ground state. Instead of the incoming electron having to occupy the high-energy lowest unoccupied molecular orbital (LUMO) in the ground state, it can occupy the lower energy singly occupied molecular orbital (SOMO) (formerly the highest unoccupied molecular orbital [HOMO]) in the excited state. Similarly, to act as a reductant (release an electron), it requires less energy for this process in the excited state than the ground state as one electron has already been promoted to the higher SOMO (former LUMO).

A concrete example is shown in Fig. 5b for the case of rose bengal dianion (RB^{2-}). RB^{2-} in its triplet state has been shown to act as both a reductant and an oxidant.[93] The potential associated with RB^{2-} as a reductant, $E^\circ(\mathrm{RB}^{\bullet-}/\mathrm{RB}^{2-})$, decreases by 1.77 V (from 1.33 to −0.44 V SHE) upon excitation to its triplet state, $^3\mathrm{RB}^{2-}$.[93] The potential associated with RB^{2-} as an oxidant, $E^\circ(\mathrm{RB}^{2-}/\mathrm{RB}^{\bullet 3-})$, increases by 1.77 V (from −0.54 to 1.23 V SHE).[93] The value 1.77 V is the triplet energy converted to potential, $E_\mathrm{T}(\mathrm{RB}^{2-})/F = 1.77$ V, and the reason this is combined with the ground state potential is discussed further in the next section. Note that RB^{2-} in its ground state exhibits a window of redox stability between −0.54 and 1.33 V SHE, but has no such window in its triplet state. Triplet state RB^{2-} is thermodynamically unstable with respect to oxidation above −0.44 V SHE and to reduction below 1.23 V SHE. Between these values, ^{3}RB is thermodynamically unstable with respect to both processes, and can thus act as both an oxidant and a reductant.

The most important photoreduction reaction involving ^{3}CDOM* is almost certainly reduction of $\mathrm{O_2}$ ($E^\circ(\mathrm{O}_{2,1\,\mathrm{M}}/\mathrm{O_2}^{\bullet-}) = -0.18$ V)[94] to superoxide ($\mathrm{O_2}^{-\bullet}$). Superoxide production has not been definitively linked to ^{3}CDOM*, but it is logical that a subset of these ^{3}CDOM* species would reduce dissolved $\mathrm{O_2}$, given the foregoing discussion and the fact that $\mathrm{O_2}$ is the dominant oxidant present in surface waters. A sense of the maximum quantum yield for such a process comes from $\mathrm{H_2O_2}$ production quantum yields, since the primary formation pathway involves dismutation of $\mathrm{O_2}^{\bullet-}$. $\mathrm{H_2O_2}$ production quantum yields are strongly wavelength dependent,[95–97] but are in the range of 0.5×10^{-4} to 10^{-3}, with typical quantum yields being about 10^{-4}.[95–99] Considering that two equivalents of $\mathrm{O_2}^{\bullet-}$ are needed to produce $\mathrm{H_2O_2}$ and that only a fraction of $\mathrm{O_2}^{\bullet-}$

goes down the dismutation pathway,[100–102] the quantum yield for superoxide production is higher, perhaps by a factor of four[98] or six,[100] giving 10^{-3} as a rough upper limit on the quantum yield of $O_2^{\bullet-}$ production. Of the superoxide-producing photoreductants, the fraction that is ^{3}CDOM* is unknown and, in fact, ^{3}CDOM* may not be involved at all. For example, Blough and others have argued that charge-transfer states of CDOM are more important photoreductants than ^{3}CDOM*.[98,100,103]

How strong are these ^{3}CDOM* reductants? Some information potentially comes from Krogh who examined the photoreduction of a suite of halogenated compounds sensitized by CDOM.[104] CCl_4 ($E^\circ(CCl_4/CCl_3^{\bullet},Cl^-) \approx -0.1$ V)[105] underwent facile photoreduction sensitized by Christina River water (18 $mg_C\ L^{-1}$) exposed to 310 nm radiation. This makes sense given that CCl_4 is thermodynamically easier to reduce than O_2 (-0.18 V).[94] Importantly, however, tetrachloroethylene (PCE) ($E^\circ(PCE/C_2Cl_3^{\bullet},Cl^-) \approx -0.60$ V)[105] was not reduced under the same conditions. This gives an effective oxidation potential of the photoreductants produced by 310 nm radiation between the reduction potentials of O_2 (-0.18) and PCE (-0.60 V SHE).

Reduction potential of ^{3}CDOM*

Returning to the topic of ^{3}CDOM* as an oxidant, the excited state reduction potential of ^{3}CDOM* ($E^\circ*(^3S*/S^{-\bullet})$) is a critical value that determines not only the thermodynamics, but also the kinetics of its electron transfer reactions.[105] The connection between the thermodynamics and kinetics of electron transfer are discussed in the following section. As with all other parameters involving DOM, there is no single value for $E^\circ*(^3S*/S^{-\bullet})$, but rather a distribution. It is important to realize that the excited state potential is a sum of the ground state potential and the excited state energy, divided by the Faraday constant ($F = 96.485$ kJ V^{-1}) to convert from energy to potential (eqn (5)).

$$E^\circ*(^3S*/S^{-\bullet}) = E^\circ(S/S^{-\bullet}) + E_T/F \tag{5}$$

This is shown visually in Fig. 6 for the half-wave reduction of an example aromatic ketone, 3-methoxyacetophenone (3MAP). While the ground-state reduction reaction is unfavorable in this example ($E^\circ(S/S^{-\bullet}) = -1.50$ V), the excited-state reaction is favorable ($E^\circ*(^3S*/S^{-\bullet}) = +1.64$ V), and the difference between the two is the triplet energy of the ketone ($E_T = 303$ kJ mol^{-1}; $E_T/F = 3.14$ V) (see Table 1). This means that compounds that are good oxidizers in the ground state (*e.g.*, quinones) and compounds that have high triplet energies (*e.g.*, ketones) are often powerful oxidants in their triplet state. We will return to this point below.

There have been some experimental attempts to put a value on the reduction potential of ^{3}CDOM*.[79,106] Using a set of phenols that vary in their electron richness, Canonica compared their relative rates of oxidation by both well-defined sensitizers (2-acetonaphthone, 2AN; 3MAP; and, benzophenone, BP) and by DOM (filtered Greifensee water, GSW; Suwannee River fulvic acid; Fluka humic acid; and, Contech humic acid).[79] The DOM solutions showed very similar kinetic selectivity for the various phenols, meaning that the ranges of relative rate constants k_{rel} (normalized to the reference compound TMP) observed for the set of phenols were almost equal. To compare selectivities, the slopes of log k_{rel} (DOM isolate or sensitizer) *vs.* log k_{rel} (GSW) plots were used. For all of the isolates as well as 3MAP ($E^\circ*(^3S*/S^{-\bullet}) = 1.64$ V SHE) compared to GSW, the slope was approximately 1, indicating equal selectivity. However, with BP ($E^\circ*(^3S*/S^{-\bullet}) = 1.69$ V SHE), the slope was lower than 1, indicating lower selectivity than ^{3}CDOM*, and with 2AN ($E^\circ*(^3S*/S^{-\bullet}) = 1.10$ V SHE), the slope was higher than 1, indicating higher selectivity than ^{3}CDOM*. Insofar as the kinetics of the phenol oxidation reaction are controlled by the $E^\circ*(^3S*/S^{-\bullet})$ value of the oxidant (see following section), this argues that the reduction potentials for the ^{3}CDOM* systems are centered near 1.64 V.[79] In a second study, in which the kinetics of phenol photooxidation by 2AN, 3MAP, and BP were followed using transient absorbance spectroscopy, $E^\circ*(^3CDOM*/CDOM^{-\bullet})$ was estimated to be between 1.36 and 1.90 V.[106] Parker and Mitch came to a similar conclusion using the sensitized photoproduction of halide radicals from bromide and chloride ions.[48] They found Suwannee River DOM to have halide radical production rates consistent with model ketone sensitizers in the $E^\circ*(^3S*/S^{-\bullet})$ range of 1.6 to 1.8 V.[48]

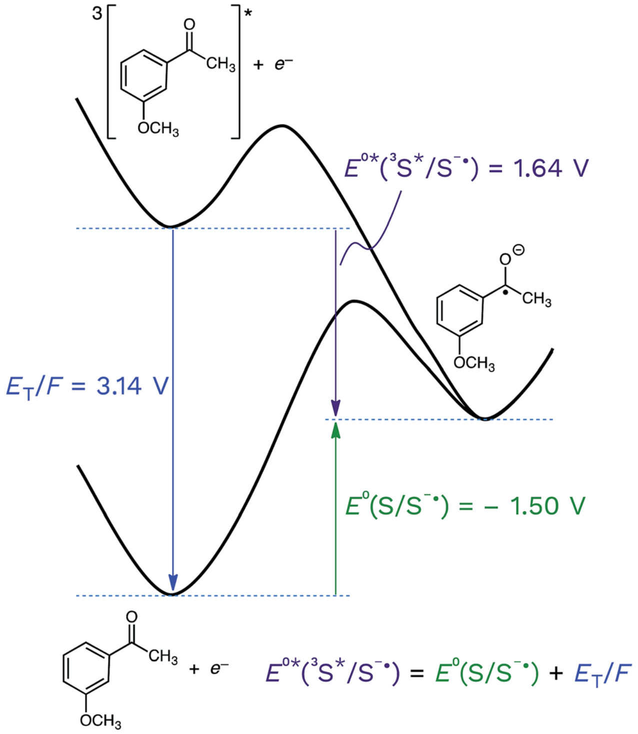

Fig. 6 Schematic representation of the half-wave reduction reactions of 3-methoxyacetophenone (3MAP) in its ground state and its triplet excited state, showing the relationship between the ground-state reduction potential ($E^\circ(S/S^{-\bullet}) = -1.50$ V *vs.* the standard hydrogen electrode, SHE), the excited-state reduction potential ($E^\circ*(^3S*/S^{-\bullet}) = +1.64$ V) and the triplet energy ($E_T/F = 3.14$ V).

Connecting excited state reduction potential to electron transfer kinetics

To assess whether or not ^{3}CDOM* will oxidize a substrate molecule at an appreciable rate, the standard molar Gibbs free energy change for the electron transfer reaction ($\Delta_r G^0_{et}$) can be taken as a proxy. As a rough estimate, the reaction will be relevant when $\Delta_r G^0_{et} \leq 0$. However, a detailed quantitative assessment of reaction rates requires kinetic considerations. Although kinetics and thermodynamics are not *a priori* connected, there are established approaches to correlate the rate of a reaction with the Gibbs free energy change of the reaction. For reactions involving the transfer of an electron from a donor (*e.g.*, a contaminant) to an acceptor (specifically ^{3}CDOM*) second-order rate constants, k_{et}, depend on $\Delta_r G^0_{et}$ following characteristic relationships that were developed in the frame of theoretical models. Electron transfer theories, originally developed for unimolecular reactions, are applied to bimolecular reactions by assuming the formation of an encounter complex of the electron donor and acceptor, called a precursor complex, which is in equilibrium with the reactants and for which a steady-state assumption can be made.[105] We consider here the Rehm–Weller relationship (eqn (6)),[105–107] which was found to be successful in explaining fluorescence quenching data:

$$k_{et} = \frac{k_d}{1 + \frac{k_d}{K_d Z}\left\{\exp(x) + \exp\left(\frac{\Delta_r G^0_{et}}{RT}\right)\right\}}$$
$$x = \frac{\sqrt{\left(\frac{\Delta_r G^0_{et}}{2}\right)^2 + \left(\frac{\lambda}{4}\right)^2} + \left(\frac{\Delta_r G^0_{et}}{2}\right)}{RT} \tag{6}$$

where k_d is the diffusion-controlled second-order rate constant for the formation of the precursor complex, K_d is the corresponding equilibrium constant, Z is the universal collision frequency factor according to transition-state theory (often taken to be 6×10^{11} s^{-1} for solution reactions[105]), and λ is the reorganization energy. The latter may be interpreted as the Gibbs free energy, related to bond and solvent reorganization, needed by the precursor complex to reach the equilibrium configuration of the successor complex. For organic redox reactions λ can vary over a broad range (20 to several hundreds of kJ mol^{-1}).[105] The reader should be aware that analogous relationships derived from Marcus' theory of electron transfer,[105] or Sandros–Boltzmann type relationships[108,109] could also be used.

Both $\Delta_r G^0_{et}$ and λ determine the activation energy of the electron transfer process. A basic qualitative feature of eqn (6) (see the thin lines in Fig. 7) is that for highly exergonic electron transfer reactions, k_{et} approaches the diffusion-controlled rate constant k_d. For highly endergonic reactions, the denominator of eqn (6) simplifies and $\log k_{et}$ decreases linearly with increasing $\Delta_r G^0_{et}$, with a slope of $-(2.3 \times RT)^{-1}$ (corresponding to $-(5.7 \text{ kJ mol}^{-1})^{-1}$ or $-(0.059 \text{ eV})^{-1}$ at 25 °C). The Rehm–Weller, Marcus or Sandros–Boltzmann equations were found to adequately fit sets of second-order rate constants obtained in aqueous solution for the quenching of the excited triplet state of individual acceptor photosensitizers using series of electron donor quenchers.[106,110] Moreover, in the case of electron-rich phenols as the electron donor quenchers, such triplet quenching rate constants[106] were almost equal to the second-order rate constants measured for phototransformation.[79] Thus, provided that each quenching event leads to transformation of the quencher, Rehm–Weller relationships of the type of eqn (6) could be used to predict the photooxidation rate constants of any organic contaminant in the aquatic environment.

The estimates for $E^\circ{*}(^3\text{S*}/\text{S}^{-\bullet})$ of ^{3}CDOM* that have been made so far[79,106] suffer from the simplification that ^{3}CDOM* is assigned a single "average" value of $E^\circ{*}(^3\text{S*}/\text{S}^{-\bullet})$, that is determined by comparison with the $E^\circ{*}(^3\text{S*}/\text{S}^{-\bullet})$ values of the model photosensitizers. Actually, a whole distribution of reduction potentials should be considered to account for the great variety of chromophores present in the CDOM. Let us assume that an ensemble of triplet excited chromophoric units of the CDOM, defined here as $^3\text{CDOM*}_i$ ($i = 1 \ldots N$), contributes to the photosensitized oxidation of a target compound (TC). The pseudo-first-order rate constant for this reaction, $k^{\text{sens}}_{\text{TC}}$, can then be expressed as:

$$k^{\text{sens}}_{\text{TC}} = \sum_{i=1}^{N} k_{et}\left(\text{TC} \rightarrow {}^3\text{CDOM}^*{}_i\right) \times \left[{}^3\text{CDOM}^*{}_i\right]_{ss} \tag{7}$$

where $[^3\text{CDOM*}]_{ss}$ is the steady-state concentration of each individual chromophoric unit of the CDOM. For the target compound, k_{et} varies with $\Delta_r G^0_{et}$, according to eqn (6), which is related to the difference between $E^\circ{*}(^3\text{CDOM*}_i/\text{CDOM}^{-\bullet}{}_i)$ (variable) and $E^\circ(\text{TC}^{+\bullet}/\text{TC})$ (fixed). To highlight this dependence, eqn (7) may be rewritten as eqn (8):

$$k^{\text{sens}}_{\text{TC}} = \sum_{i=1}^{N} k_{et}\left(E^\circ\left({}^3\text{CDOM}^*{}_i/\text{CDOM}^{-\bullet}{}_i\right) - E^\circ\left(\text{TC}^{+\bullet}/\text{TC}\right)\right) \times \left[{}^3\text{CDOM}^*{}_i\right]_{ss} \tag{8}$$

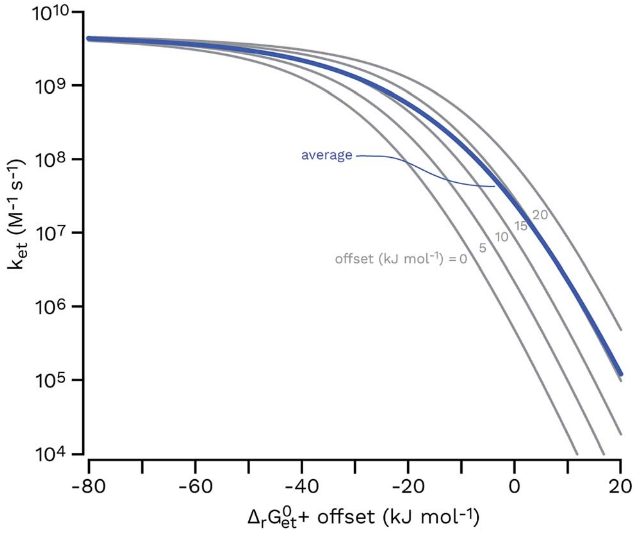

Fig. 7 Rehm–Weller plots (gray thin curves) for a set of five functions having the same parameters (eqn (6); $k_d = 6.2 \times 10^9$ M^{-1} s^{-1}; $k_d/(K_d Z) = 0.1$; $\lambda = 65$ kJ mol^{-1}; values from a typical fit in ref. 106 were used) and an offset of 0, 5, 10, 15 and 20 kJ mol^{-1} (from left to right) for $\Delta_r G^0_{et}$. The arithmetic average of these curves is shown as a thick blue line, showing that a hypothetical equimolar mixture of five sensitizers would be expected to show a smoother transition from the diffusion-controlled plateau to the log-linear kinetic regime.

Unfortunately the distributions of one-electron reduction potentials in excited triplet CDOM are not known, and one has to rely on model calculations to predict the impact of such distributions on $k_{\mathrm{TC}}^{\mathrm{sens}}$. Let us assume that k_{et} for the electron transfer reaction between TC and $^3\mathrm{CDOM}^*_i$ can be expressed by eqn (6) using constant values for k_{d} and λ. In Fig. 7, Rehm–Weller plots are shown for five hypothetical $^3\mathrm{CDOM}^*_i$ having $F \times E^{\circ}{}^*(^3\mathrm{CDOM}^*_i/\mathrm{CDOM}^{-\bullet}{}_i)$ that differ by 5 kJ mol^{-1} ($\Delta E^{\circ}{}^* = 52$ mV). Assuming equal $[^3\mathrm{CDOM}^*_i]_{\mathrm{ss}}$ for all chromophoric units, one can use the average of these five curves to represent k_{et} for this group of five chromophores. The resulting curve (in the logarithmic representation, see thick line in Fig. 7) has a similar shape but a smoother transition between the diffusion-controlled plateau and the steep linear decrease compared to the single Rehm–Weller curves. We therefore refer to this as a pseudo-Rehm–Weller curve. With these considerations in mind, one can conclude that the determination of $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet})$ for CDOM will remain fuzzy.

A possible approach to empirically determine the shape of the pseudo-Rehm–Weller curve for $^3\mathrm{CDOM}^*$ consists of using a suite of probe compounds (PCs) with different (and exactly known) oxidation potentials and unit product yield for excited triplet state quenching, as recently proposed elsewhere.[111] Thereby, it is suitable to define an "effective" concentration of $^3\mathrm{CDOM}^*$ capable of oxidizing a given PC by dividing an experimentally determined $k_{\mathrm{PC}}^{\mathrm{sens}}$ through the best guess for the maximum second-order rate constant for the electron-transfer reaction from the PC to $^3\mathrm{CDOM}^*$ (*e.g.*, $\approx 3 \times 10^9$ M^{-1} s^{-1}, but an optimized value might be obtained from a consistent set of quenching data for model photosensitizers in aqueous solution). The "effective" concentration of $^3\mathrm{CDOM}^*$ obviously decreases with increasing PC oxidation potential. In such a way, a function of $[^3\mathrm{CDOM}^*]$ *vs.* oxidation potential of PC can be constructed and used for the prediction of the "effective" concentration of $^3\mathrm{CDOM}^*$, and consequently of a pseudo-first-order transformation rate constant, for the transformation of any TC by $^3\mathrm{CDOM}^*$ (provided that the one-electron oxidation potential of the TC is known).

After the kinetic considerations made in this section, one might ask why a corresponding analysis is not available for triplet energy transfer rate constants. Indeed, energy transfer kinetics can be treated in the frame of analogous models, which lead to equations of the same or similar form as those derived for electron transfer processes.[112,113] Thereby, the difference in triplet energy between donor and acceptor assumes the same role as $\Delta_{\mathrm{r}}G_{\mathrm{et}}^0$ in electron transfer processes. To our knowledge, there has been no application of these concepts to the photochemistry of CDOM to date, but this approach appears to be promising.

Comparison to well-defined triplet oxidants

Another way to look at the question of the triplet state one-electron reduction potential of CDOM is to consider known values from well-defined compounds. Table 1 gives $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet})$ values for a series of compounds that have structures that could plausibly be similar to constituents of CDOM. These $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet})$ values come from the compounds triplet energies (E_{T}) and ground state reduction potentials ($E^{\circ}(\mathrm{S}/\mathrm{S}^{-\bullet})$) (eqn (5)), which are also listed in Table 1. These data are visualized in Fig. 8, with a plot of E_{T} *vs.* $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet})$.

A word of caution about excited state redox potentials is in order. There are several difficulties associated with obtaining accurate (ground state) aqueous one-electron reduction potentials for the various compounds listed, which lead directly to difficulties in calculating accurate excited state reduction potentials.[105] First, most of the compounds (excluding the quinones) are poorly behaved electrochemically, displaying irreversible redox couples, which necessitates some estimation of the true reduction potential. Second, the observed couples are also often not associated with pure one-electron transfers, but rather have an associated protonation process. For predicting the kinetics of electron transfer, the potential associated with just the one-electron process is needed. Third, the compounds are often poorly soluble, leading to the use of co-solvents or non-aqueous conditions, which can drastically alter the potentials. In compiling the data for Table 1, every effort was made to find values in water or water–alcohol mixtures. In the case of the polycyclic aromatic hydrocarbons, one value was only found in DMF and the others were from experiments in 75 : 25 dioxane : water mixtures. Additionally, for reduction potentials of the ketones and other carbonyl-containing compounds, values from the highest pH conditions were taken to get as close to the pure one-electron potential as possible. The values collected here differ somewhat from other compilations, for example the excellent compilation of Loeff, *et al.*[114] All of this is to say that, while we believe the values in Table 1 are the best available, they should be used with some caution.

Caveats aside, it can be seen that this relatively small selection of compounds covers a wide range of $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet})$, from 0.15 V for anthracene to 2.42 V for benzoquinone, suggesting that triplet CDOM oxidants will be found across the entire range of possible potentials in aqueous solution.

There are some other notable observations that can be made by examining this collection of representative triplets. One is that the $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet})$ values of different functional group classes are somewhat distinct, with polycyclic aromatic hydrocarbons having the lowest reduction potentials (*i.e.*, relatively weak oxidants, $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet}) \leq 0.69$ V) of this set and quinones having the highest (*i.e.*, strong oxidants, $E^{\circ}{}^*(^3\mathrm{S}^*/\mathrm{S}^{-\bullet}) \geq 2.19$ V). Indeed, excited state triplet quinones are such strong oxidants that they are above the one-electron reduction potential for water at pH 7 ($E^{\circ\prime}(\mathrm{OH}^{\bullet}/\mathrm{OH}^-) = 2.18$ V), which is actually the oxidation of hydroxide ion ($E^{\circ}(\mathrm{OH}^{\bullet}/\mathrm{OH}^-) = 1.77$ V) corrected for its activity at pH 7.[115,116] Incidentally, the one-electron oxidation of water itself requires a much higher potential of $E^{\circ}(\mathrm{H_2O}^{+\bullet}/\mathrm{H_2O}) = 2.65$ V.[117] This makes quinones one of the prime suspects in the CDOM-sensitized formation of hydroxyl radical or lower-energy hydroxyl radical-like species.[118–120] Whether or not quinones actually oxidize hydroxide ion (or water) to produce hydroxyl radical has been a controversial topic.[118,121–124] To give just two concrete examples, both methylbenzoquinone and

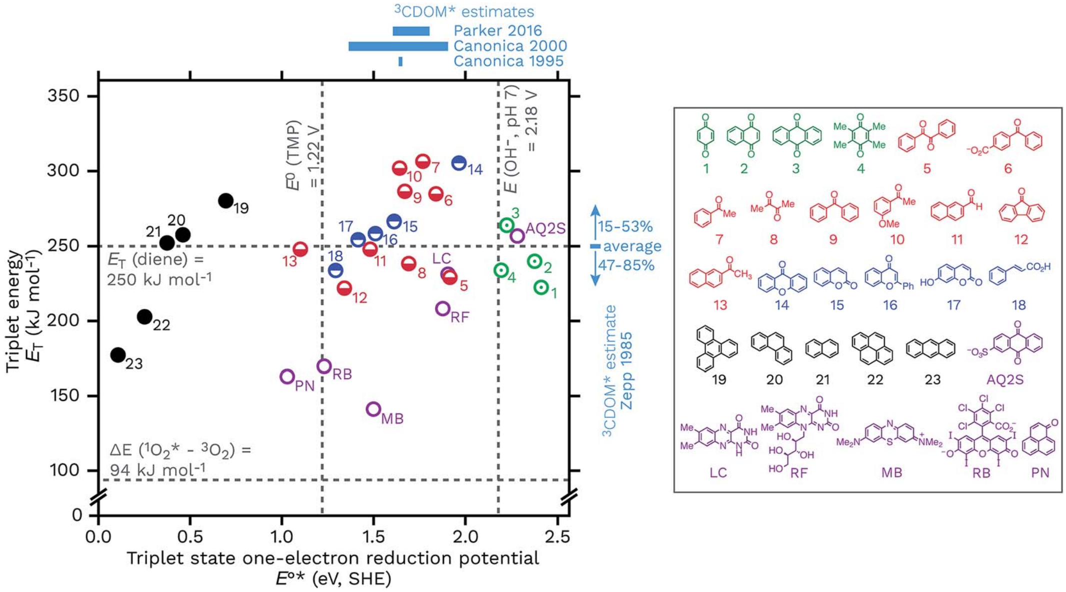

Fig. 8 Triplet energies (E_T, kJ mol^{-1}) *vs.* triplet state one-electron reduction potentials ($E°*(^3S*/S^{-•})$, V SHE) for a selection of 23 DOM-like model compounds and a selection of widely used sensitizers. The horizontal lines correspond to the triplet excited state energy of a typical diene energy transfer probe and the singlet state energy of O_2. The vertical lines correspond to the one-electron oxidation potentials of TMP, $E°(ArOH^{+•}/ArOH)$, and hydroxide at pH 7, $E°'(OH^•/OH^-)$. Selected estimates for ^{3}CDOM* values from Zepp,[9] Canonica,[79,106] and Parker and Mitch[48] are also shown. The data used for this figure is compiled in Table 1 along with the abbreviation definitions.

AQ2S give positive results when challenged with hydroxyl radical probes, but deeper investigations suggest very little if any free hydroxyl radical involvement in these processes.[118,119,124,125]

Carbonyl-containing compounds fill the middle of the series with potentials ranging from 1.10 V (**13**, 2AN) to 1.96 V (**14**, xanthone). Among the carbonyl-containing compounds, aromatic ketones and aldehydes in particular, represented by compounds **5–13** in Table 1 and Fig. 8, have been considered an especially important sensitizer type in CDOM.[9,10,60,70,79,98,106,126–128]

Further support for the importance of ketone- and aldehyde-containing sensitizers in CDOM comes from experiments in which the CDOM-sensitized photooxidation rates of trimethylphenol (TMP, a probe molecule for triplet oxidants) were significantly reduced following removal of the ketone and aldehyde functional groups by treatment of the CDOM samples with sodium borohydride.[128] Similarly, Sharpless showed that borohydride-treated DOM formed $^1O_2$ at lower rates than (but with the same quantum efficiency as) untreated DOM.[10] In most cases, treatment with borohydride led to incomplete loss of photosensitization ability, suggesting that non-ketone and -aldehyde photosensitizers are also involved.[10,128] Quinones, which are reduced by borohydride but quickly revert under aerated conditions, are candidates for a part of this other pool of photosensitizers. Flavones, which are not easily reduced by borohydride[129] and have similar triplet state properties to aromatic ketones (Table 1 and Fig. 8), are also possible candidates.

A second observation concerns a potential noted in Fig. 8 as a vertical line at 1.22 V. The line corresponds to the one-electron oxidation potential for TMP, $E°(ArOH^{+•}/ArOH)$,[106] which is a popular probe molecule for ^{3}CDOM*.[130] One-electron transfer reactions between TMP and any of the triplets to the right of this line are exergonic. This does not necessarily forbid reactions between TMP and the triplets with $E°*(^3S*/S^{-•}) < 1.22$ V, but rather means that strict one-electron transfer oxidations of TMP by these sensitizers will be thermodynamically unfavorable. The way around this problem for weaker oxidants is to oxidize TMP *via* hydrogen atom transfer or some other proton-coupled electron transfer (PCET) reaction that yields a phenoxy radical directly. For example, 2AN ($E°*(^3S*/S^{-•}) = 1.10$) oxidizes TMP and one strong piece of evidence favoring PCET as the oxidation mechanism comes from the isotope effect on this reaction. Photooxidation of TMP by 2AN in D_2O was 3.4 times slower than in H_2O, which can be interpreted as a result of the phenolic O–H/D bond being broken in the rate-determining step.[79] When Suwannee River fulvic acid or Fluka humic acid was used as the sensitizer for TMP photooxidation, isotope effects of only $k_H/k_D = 1.1 \pm 0.1$ and 1.2 ± 0.1, respectively, were observed.[79] This suggests that the majority of the oxidants responsible for the oxidation of TMP in these two DOM isolates did not undergo PCET, and the most obvious reason is that their $E°*(^3S*/S^{-•})$ values were significantly greater than 1.22 V.

Another observation is that triplet quenchers based on energy transfer, such as isoprene, HDA, and other dienes, are only able to capture a subset of the total triplet pool. One might be tempted to conclude from eqn (5) that using a diene quencher would lead to preferential quenching of the highly oxidizing triplets, but even with the small set of triplet states shown in Fig. 8, it is clear that some highly oxidizing triplets could be missed. For example, low-energy triplet species that are strong oxidants include benzil (**5**), diacetyl (**8**), and 9-

fluorenone (**12**). On the other hand, the data in Fig. 8 suggest that energy transfer quenching by O_2 is thermodynamically feasible for essentially all triplet states. If this is true, a potentially surprising finding was that high concentrations of TMP were shown to inhibit the production of $^1O_2$ completely, indicating that nearly all of the $^1O_2$-sensitizing triplets in ^{3}CDOM* (Elliot Soil humic and fulvic acid, in this case) have a sufficiently high $E^\circ*(^3S*/S^{-\bullet})$ to oxidize TMP.[81]

A final set of observations regards the sensitizers that are commonly used in laboratory studies. Perinaphthenone (PN), rose bengal (RB), and methylene blue (MB) are widely employed for generating $^1O_2$, but all three have also been found to be triplet oxidants, with $E^\circ*(^3S*/S^{-\bullet})$ ranging from 1.03 to 1.50 V (Table 1). Flavin-type photosensitizers, such as riboflavin ($E^\circ*(^3S*/S^{-\bullet}) = 1.88$ V) and lumichrome ($E^\circ*(^3S*/S^{-\bullet}) = 1.91$ V), are even stronger triplet oxidants, with potentials near the most oxidizing triplet ketone sensitizers. Near the far end of the spectrum is AQ2S, a powerful triplet oxidant ($E^\circ*(^3S*/S^{-\bullet}) = 2.28$ V), which has been reported to give very low yields of either $^1O_2$ or hydroxyl radical.[125] Thus AQ2S might model some of the most oxidizing triplet states found in ^{3}CDOM*, but is a considerably stronger oxidant than the average ^{3}CDOM* species.

It would be remiss not to mention that there is often a discussion in the chemistry of triplet excited states of whether the triplet is an nπ* triplet (strong sensitizer) or ππ* triplet (weak sensitizer).[114,131] The difference has to do with the electronic configuration of the triplet, in which the lower energy SOMO has more non-bonding (n) or π-bonding (π) character. For example, many triplet aromatic ketones are classified as nπ*, while triplet PAHs are ππ*. We have not included discussion of nπ* and ππ* classifications in this review for a few reasons. First, and foremost, we are mostly concerned with ^{3}CDOM* and, while there seems to be some hope in the near term of determining the average and spread of excited state energies (E_T) and excited state reduction potentials ($E^\circ*$), assessing the distribution of nπ* and ππ* triplets in ^{3}CDOM* is beyond the currently visible horizon. Second, assigning a triplet as nπ* or ππ* is not trivial, as the SOMO in question may have mixed character. For example, duroquinone has been taken as a prototypical nπ* triplet and ππ* triplet in different studies.[114,132] Finally, while some have found the nπ*/ππ* framework useful for interpreting reactivity, other models have also been used. For instance, the variation in $^1O_2$ yields from O_2 quenching of triplet states has not only been interpreted using the nπ*/ππ* concept (where ππ* triplet states give higher $^1O_2$ yields),[132] but also in terms of E_T and excited state oxidation potential ($E^\circ*(^3S*/S^{+\bullet})$) (where low E_T and low $E^\circ*$ triplet states give higher $^1O_2$ yields), without considering the electronic configuration.[13,14,133]

Outlook

Despite the importance of ^{3}CDOM* in the transformation of organic molecules, its study has lagged behind other important PPRI, especially $^1O_2$, $^\bullet$OH, H_2O_2, and $O_2^{-\bullet}$. This is clearly because ^{3}CDOM* is a complex mixture, and its complexity confounds both direct (*i.e.*, spectroscopic) and indirect (*i.e.*, molecular probe methods) methods to observe and/or quantify these states. While this certainly provides a challenge, the situation is far from hopeless. Some strategies for attaining a clearer picture of ^{3}CDOM* are outlined below along with some of the most pressing research problems.

A critical strategy for studying a complex mixture like ^{3}CDOM* is to use methods that integrate the disparate signals arising from the mixture's components and give a single signal that is more easily detected. The best and most accessible example is the use of $^1O_2$ as a proxy for ^{3}CDOM*. As mentioned above, quenching of triplet states by O_2 to yield $^1O_2$ is not quantitative, but it is the best universal triplet detection method of any available. Singlet oxygen formation quantum yields provide solid lower bounds for ^{3}CDOM* formation quantum yields. Additionally, the steady-state concentrations of $^1O_2$ and ^{3}CDOM* must be within a factor of two of each other (when $0.25 < f_\Delta < 1$; see eqn (4)).

While O_2 quenching of ^{3}CDOM* gives a picture of essentially all of the component triplets, using energy transfer quenchers of different energies is a clear way to probe the distribution of triplet energies in ^{3}CDOM*. For example, HDA (sorbic acid), being a diene, is an excellent probe for quantifying the high energy triplet states capable of transferring energy to diene-containing contaminants such as domoic acid.[48] At the moment, there is a large gap between the energy of $^1O_2$ (94 kJ mol^{-1}) and the diene quenchers that have been employed ($E_T \approx$ 250 kJ mol^{-1}; see Fig. 2), giving us only a rudimentary idea of the distribution (*e.g.*, Fig. 3). While triplet energy acceptors with intermediate energies are certainly known, such as 1,3-cyclohexadiene (E_T = 221 kJ mol^{-1}), anthracene (178 kJ mol^{-1}), ferrocene (167 kJ mol^{-1}), azulene (163 kJ mol^{-1}), and tetracene (123 kJ mol^{-1}), they pose technical challenges including long wavelength absorbance, poor aqueous solubility, and/or susceptibility to photooxidation. All of these challenges can and will eventually be overcome.

The use of HDA isomerization and TMP oxidation as probe reactions for ^{3}CDOM* is gaining in popularity. The fact that these methods are based on different mechanisms (energy transfer and oxidation, respectively) is not widely discussed in the aquatic photochemistry literature. This is potentially problematic as energy transfer- and oxidation-based probe methods are reporting on different, but overlapping, subpopulations of ^{3}CDOM*. This will hopefully change in the future as a more nuanced and detailed view of ^{3}CDOM* is brought into focus by further research. This also brings up the larger issue of the correct use of probe molecules and quenchers in photochemical studies. As essentially all probe molecules react by different pathways (*e.g.*, with triplet states and with $^1O_2$), care must be taken in both conducting the proper control experiments and in interpreting the outcome. We refer the interested reader to a recent review on the use of molecular probes for studying PPRI.[111]

Finally, the composition of ^{3}CDOM* is clearly different for different sources of organic matter. In particular, there has been growing evidence of significant variability in the nature of ^{3}CDOM in DOM of terrestrial origin (*e.g.*, surface waters with input from soil organic matter) and of microbial origin (*e.g.*, surface waters dominated by algal DOM or wastewater effluent DOM).[134] The photochemistry of sulfa drugs serves to illustrate the point. Sulfa drugs are widespread contaminants in wastewater-impacted surface waters that have been the subject of several recent studies seeking to understand their phototransformation.[45,46,73,74,135,136] In three separate studies, with three different sulfa drugs, significantly better photosensitization by autochthonous (algal) than allochthonous (terrestrial) CDOM has been observed. Chin observed that sulfadimethoxine undergoes enhanced degradation when sensitized by Pony Lake (Antarctica) fulvic acid (PLFA, a standard for microbially derived organic matter) and eutrophic lake water, but not terrestrial isolates (*e.g.*, Suwannee River fulvic acid, SRFA).[73,135] Arnold found that sulfamethoxazole degraded much more rapidly in the presence of effluent organic matter than with CDOM from other sources.[45] Canonica found that sulfadiazine undergoes more rapid degradation when sensitized by PLFA than SRFA.[74] In each case, convincing evidence that ^{3}CDOM was responsible for the indirect transformation was obtained.

Why do autochthonous-dominated DOM samples (*e.g.*, PLFA) seem to show increased reactivity compared to SRFA and other terrestrially derived organic matter samples? One possibility is that both PLFA and SRFA photooxidize compounds similarly, but SRFA contains many more antioxidants which repair some of the photooxidation damage (intermolecular or intramolecular) and slow down the macroscopic transformation rate. This idea definitely has support from studies showing the antioxidant properties of DOM in photoreactions.[66,137,138] Another possibility is that the PLFA-derived ^{3}CDOM* is a stronger oxidant (higher $E^\circ{}^*(^3S^*/S^{-\bullet})$) than the SFRA-derived ^{3}CDOM*. The only way to answer the question is to determine the fundamental photophysical properties of both terrestrially derived and microbially (algal) derived CDOM.

It is clear that the study of ^{3}CDOM* is both important and difficult. Despite the challenges, a fair amount of information about its reactivity, steady-state concentrations, and physical properties can already be inferred from existing data. Future studies, taking advantage of energy transfer-based probe methods (*e.g.*, O_2 and HDA) and oxidation-based probe methods (*e.g.*, TMP) will only further our understanding of the scope, reactivity, and variability of ^{3}CDOM*. There is an especially important link between $^1O_2$ and ^{3}CDOM* that makes $^1O_2$ probe methods (both spectroscopic and reaction-based) particularly useful in this regard. With additional study, a clearer and more detailed picture of the components contributing to ^{3}CDOM* and their reactivity patterns will come into view, which will in turn allow a better understanding of the role of ^{3}CDOM* in the photochemical fate of contaminants and sunlight-driven biogeochemical processes.

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