

CRITICAL REVIEW

View Article Online  
View Journal | View Issue



CrossMark  
click for updates

Cite this: *Environ. Sci.: Processes Impacts*, 2016, **18**, 1381

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

Kristopher McNeill<sup>a</sup> and Silvio Canonica<sup>b</sup>

Excited triplet states of chromophoric dissolved organic matter ( $^3\text{CDOM}^*$ ) 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  $^3\text{CDOM}^*$ , 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  $^3\text{CDOM}^*$ . Information on  $^3\text{CDOM}^*$  relies mainly on the use of probe compounds because of the difficulties associated with directly observing  $^3\text{CDOM}^*$  using transient spectroscopic methods. Singlet molecular oxygen ( $^1\text{O}_2$ ), which is a product of the reaction between  $^3\text{CDOM}^*$  and dissolved oxygen, is probably the simplest indicator that can be used to estimate steady-state concentrations of  $^3\text{CDOM}^*$ . There are two major modes of reaction of  $^3\text{CDOM}^*$  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  $^3\text{CDOM}^*$  can be achieved.

Received 14th July 2016  
Accepted 21st September 2016

DOI: 10.1039/c6em00408c

rsc.li/process-impacts

## 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 ( $^3\text{CDOM}^*$ ), a form of electronically excited DOM. There has been a recent surge in the study of the properties and reactivity of  $^3\text{CDOM}^*$  and this review article is an attempt to organize and synthesize what has been discovered about  $^3\text{CDOM}^*$  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).<sup>1–4</sup> Triplet excited states of chromophoric dissolved organic matter ( $^3\text{CDOM}^*$ ) are an important subset of the larger pool of PPRI formed in sunlit waters that also include singlet oxygen ( $^1\text{O}_2$ ,  $^1\Delta_g$ ), superoxide ( $\text{O}_2^{\cdot-}$ ), hydrogen peroxide,

hydroxyl radical ( $\text{OH}^\cdot$ ), and others.<sup>1–4</sup>  $^3\text{CDOM}^*$  has been implicated in the degradation of contaminants, such as pesticides<sup>5</sup> and pharmaceuticals,<sup>6,7</sup> and holds a special position among the PPRI for at least two reasons. First,  $^3\text{CDOM}^*$  is known or suspected to be a precursor of other PPRI.<sup>1–4</sup> For example,  $^3\text{CDOM}^*$  is the primary source for  $^1\text{O}_2$  in sunlit natural waters.<sup>8,9</sup> Second, unlike other PPRI,  $^3\text{CDOM}^*$  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  $^3\text{CDOM}^*$  and to summarize what is known or can be reasonably inferred about both the triplet energy and redox potential of  $^3\text{CDOM}^*$ . In addition, some back-of-the-envelope calculations are presented that give rough answers to questions that often arise when discussing  $^3\text{CDOM}^*$ : why are triplet states more important than singlet states in CDOM-sensitized processes? And, what is the steady-state concentration of  $^3\text{CDOM}^*$ ?

<sup>a</sup>Institute for Biogeochemistry and Pollutant Dynamics, ETH Zurich, Universitaetstrasse 16, 8092 Zurich, Switzerland. E-mail: kris.mcneill@env.ethz.ch

<sup>b</sup>Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland



# Steady-state concentration of $^3\text{CDOM}^*$ in natural waters

Attempting to quantify the steady-state concentration of  $^3\text{CDOM}^*$  in an aquatic system would seem to be more challenging than other PPRI, due to the abovementioned problem that  $^3\text{CDOM}^*$  is a mixture of triplet states of diverse molecules. Therefore, it may seem surprising that we can actually estimate the steady-state concentration of  $^3\text{CDOM}^*$  within about a factor of two with a high degree of confidence. This is thanks to the inextricable link between  $^1\text{O}_2$  and  $^3\text{CDOM}^*$ .

To understand this, it is helpful to consider the simplified kinetic scheme that connects  $^3\text{CDOM}^*$  and  $^1\text{O}_2$  (Fig. 1). CDOM is excited by the absorption of a photon (symbolized by  $h\nu$ ) to form the excited singlet state of CDOM,  $^1\text{CDOM}^*$ . Under optically thin conditions, the rate of light absorbance ( $R_{\text{abs}}$ ), in units of  $\text{M s}^{-1}$ , is given by the product of the irradiance ( $\text{mmol photons cm}^{-2} \text{ s}^{-1}$ ), the Napierian absorption coefficient of CDOM (natural log-based absorption coefficient in units of  $\text{cm}^{-1}$ ), and a conversion factor ( $\text{mol L}^{-1} (\text{mmol cm}^{-3})^{-1} = 1$ ). The efficiency of the conversion of  $^1\text{CDOM}^*$  to  $^3\text{CDOM}^*$  (*i.e.*, the intersystem crossing efficiency) is given by  $\Phi_{\text{ISC}}$ . The rate constants for the  $\text{O}_2$ -independent and  $\text{O}_2$ -dependent deactivation pathways of  $^3\text{CDOM}^*$  are given by  $k_d^T$  and  $k_{\text{O}_2}[\text{O}_2]$ , respectively. Under normal air-saturated surface-water conditions,  $\text{O}_2$ -dependent relaxation almost certainly dominates over  $\text{O}_2$ -independent relaxation. Sharpless has estimated the  $\text{O}_2$ -independent lifetime of triplets through  $\text{O}_2$ -dependent formation kinetics of  $^1\text{O}_2$  using Suwannee River and Pony Lake isolates, and determined a lifetime around 20  $\mu\text{s}$  ( $k_d^T \approx 5 \times 10^4 \text{ s}^{-1}$ ).<sup>10</sup> Zepp has made a reasonable estimate of  $k_{\text{O}_2} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , based on  $\text{O}_2$  quenching rate constants of well-defined sensitizers.<sup>9</sup> While there is certainly some variation in the individual  $k_{\text{O}_2}$  values among the numerous sensitizers that comprise  $^3\text{CDOM}^*$ , they are all expected to be quite high and near the diffusion-controlled limit. For air-saturated freshwater at 25 °C (258  $\mu\text{M}$   $\text{O}_2$ ),  $k_{\text{O}_2}[\text{O}_2]$  is thus approximately  $5 \times 10^5 \text{ s}^{-1}$  ( $\tau = 2 \mu\text{s}$ ), which suggests that the  $\text{O}_2$ -dependent relaxation pathway is an order of magnitude more important than the  $\text{O}_2$ -independent pathway.

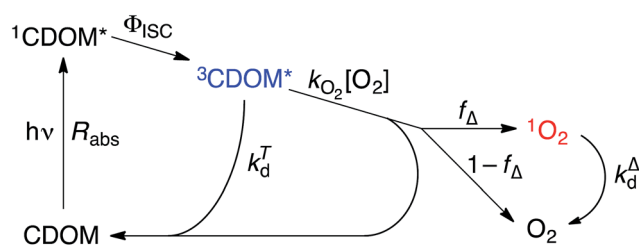


Fig. 1 Kinetic scheme illustrating the connection between  $^3\text{CDOM}^*$  and  $^1\text{O}_2$ . Definition of variables and symbols: CDOM, chromophoric dissolved organic matter;  $^1\text{CDOM}^*$ , singlet state dissolved organic matter;  $^3\text{CDOM}^*$ , triplet state dissolved organic matter;  $^1\text{O}_2$ , singlet oxygen ( $^1\Delta_g$ );  $h\nu$ , photon;  $R_{\text{abs}}$ , rate of light absorbance;  $\Phi_{\text{ISC}}$ , intersystem crossing quantum yield;  $k_{\text{O}_2}$ , bimolecular rate constant for the quenching of  $^3\text{CDOM}^*$  by  $\text{O}_2$ ;  $f_{\Delta}$ , fraction of  $\text{O}_2$ -dependent quenching that produces  $^1\text{O}_2$ ;  $k_d^T$ , rate constant for  $\text{O}_2$ -independent relaxation of  $^3\text{CDOM}^*$ ;  $k_d^A$ , rate constant for relaxation of  $^1\text{O}_2$  to  $\text{O}_2$ .

The quenching of triplet states by  $\text{O}_2$  produces  $^1\text{O}_2$ , but the yield for this process ( $f_{\Delta}$ ) is different for each sensitizer. It has often been assumed that  $f_{\Delta}$  is close to unity,<sup>9</sup> but studies with a range of well-defined triplet sensitizers have shown that this value can vary from near 0 (*e.g.*, coumarin<sup>11</sup>) to near 1 (*e.g.*, perinaphthenone<sup>12</sup>), depending on the sensitizer.<sup>11</sup> Indeed, the value of  $f_{\Delta}$  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  $^1\text{O}_2$  sensitizers.<sup>13,14</sup> Once formed,  $^1\text{O}_2$  mainly undergoes unimolecular deactivation,  $k_d^A$ .<sup>15</sup>

Expressions for the steady-state concentrations of  $^3\text{CDOM}^*$  and  $^1\text{O}_2$  based on the scheme depicted in Fig. 1 are given by eqn (1) and (2).

$$[^3\text{CDOM}^*]_{\text{ss}} = \frac{R_{\text{abs}}\Phi_{\text{ISC}}}{k_{\text{O}_2}[\text{O}_2] + k_d^T} \quad (1)$$

$$[^1\text{O}_2]_{\text{ss}} = \frac{[^3\text{CDOM}^*]_{\text{ss}} k_{\text{O}_2}[\text{O}_2] f_{\Delta}}{k_d^A} \quad (2)$$

One can rearrange eqn (2) to arrive at an expression for the ratio of the steady-state concentrations of  $^1\text{O}_2$  and  $^3\text{CDOM}^*$  (eqn (3)).

$$\frac{[^1\text{O}_2]_{\text{ss}}}{[^3\text{CDOM}^*]_{\text{ss}}} = \frac{k_{\text{O}_2}[\text{O}_2] f_{\Delta}}{k_d^A} \quad (3)$$

Substituting values for  $k_d^A$  ( $2.5 \times 10^5 \text{ s}^{-1}$  for  $\text{H}_2\text{O}$ ),<sup>15</sup>  $k_{\text{O}_2}$  ( $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>9</sup> and  $[\text{O}_2]$  (258  $\mu\text{M}$  at 298 K), one arrives at eqn (4).

$$\frac{[^1\text{O}_2]_{\text{ss}}}{[^3\text{CDOM}^*]_{\text{ss}}} \approx 2f_{\Delta}; \quad 25^\circ\text{C}, \text{ air-saturated water} \quad (4)$$

This result indicates that for 25 °C, air-saturated water, the ratio of  $^1\text{O}_2$  to  $^3\text{CDOM}^*$  is linearly dependent on the yield of  $^1\text{O}_2$  from the  $\text{O}_2$ -dependent quenching of  $^3\text{CDOM}^*$  ( $f_{\Delta}$ ) with a maximum  $[\text{O}_2]_{\text{ss}}$  value of two times  $[\text{O}_2]_{\text{ss}}$ . While we do not know the value of  $f_{\Delta}$  for  $^3\text{CDOM}^*$ , eqn (4) nevertheless suggests a useful rule-of-thumb of  $[\text{O}_2]_{\text{ss}} \approx [\text{O}_2]_{\text{ss}}$ . To reiterate, this will hold when the value for  $k_{\text{O}_2}$  is close to the estimate of  $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and the average  $f_{\Delta}$  value is near 0.5. Under noon-time clear summer sky conditions,  $[\text{O}_2]_{\text{ss}}$  has been found to be between  $10^{-14}$  and  $10^{-12} \text{ M}$  in natural waters, depending on the concentration of DOM (1–100  $\text{mg}_C \text{ L}^{-1}$ ; see for example Peterson *et al.*<sup>16</sup>). Based on the above argumentation, we can therefore adopt this same concentration range for  $[\text{O}_2]_{\text{ss}}$ .

## Why triplet states and not singlet states?

Could singlet excited state CDOM moieties ( $^1\text{CDOM}^*$ ) act as reactive intermediates in a similar manner to  $^3\text{CDOM}^*$ ? After



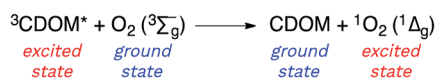
all, the lowest lying singlet excited state of a given sensitizer is higher in energy than its lowest lying triplet state and would therefore be expected to be more reactive than the triplet. While this is true, it is counteracted by the fact that the steady-state concentration of  $^1\text{CDOM}^*$  is much lower than that of  $^3\text{CDOM}^*$ .

To determine exactly how much lower  $[^1\text{CDOM}^*]_{\text{ss}}$  is than  $[^3\text{CDOM}^*]_{\text{ss}}$ , we need estimates of the relative formation and decay rate constants for both species. Formation quantum yields for  $^3\text{CDOM}^*$  have been estimated to be in the range of 1–2%,<sup>9,17</sup> but could be as high as 6% or higher for some DOM samples, based on  $^1\text{O}_2$  quantum yield measurements.<sup>16,18</sup> This indicates that  $^1\text{CDOM}^*$  formation rates are 15–100 times faster than those for  $^3\text{CDOM}^*$ . On the decay side, the  $^1\text{CDOM}^*$  lifetime is much shorter than that of  $^3\text{CDOM}^*$ , which has a lifetime of about 2  $\mu\text{s}$  (*i.e.*, the inverse of  $k_{\text{O}_2}[\text{O}_2]$ ; see previous section). Fluorescence lifetime studies give a direct measurement of the decay of  $^1\text{CDOM}^*$ , and, as expected, the mixture of fluorophores do not display a single lifetime. Rather, the data suggest a dominant pool of short lifetime  $^1\text{CDOM}^*$  species ( $\tau < 150$  ps), with contributions from two other pools of  $^1\text{CDOM}^*$  ( $\tau \approx 1$  and 3 ns).<sup>19</sup> For simplicity, we consider 100 ps to be the typical lifetime of  $^1\text{CDOM}^*$ .

Taken together, we see that while  $^1\text{CDOM}^*$  is formed 15–100 times faster than  $^3\text{CDOM}^*$ , it decays approximately 20 000 times faster, giving 200- to 1300-fold lower steady-state concentrations than  $^3\text{CDOM}^*$ . This corresponds to  $[^1\text{CDOM}^*]_{\text{ss}}$  of  $10^{-17}$  to  $10^{-14}$  M in sunlit surface waters, compared to  $[^3\text{CDOM}^*]_{\text{ss}}$  of  $10^{-14}$  to  $10^{-12}$  M. To put this into context of another PPRI,  $[^1\text{CDOM}^*]_{\text{ss}}$  is expected to be similar to  $[\text{OH}^*]_{\text{ss}}$ . Thus,  $^3\text{CDOM}^*$  is expected generally to be the more important species, but  $^1\text{CDOM}^*$  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  $^3\text{CDOM}^*$  production) or when the rate constant for reaction with  $^1\text{CDOM}^*$  is orders of magnitude faster than with  $^3\text{CDOM}^*$ . Another case where  $^1\text{CDOM}^*$  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,<sup>20,21</sup> reactions involving  $^1\text{O}_2$  with a highly hydrophobic probe molecule,<sup>22,23</sup> and the  $^3\text{CDOM}^*$ -sensitized degradation of amoxicillin.<sup>24</sup>

## 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  $^1\text{O}_2$  from the interaction of triplet ground state  $\text{O}_2$  with  $^3\text{CDOM}^*$ , which was first reported by Zepp in 1977.<sup>8</sup>



The energy required to promote ground state  $\text{O}_2$  to  $^1\text{O}_2$  is 94 kJ mol<sup>-1</sup> (980 meV).<sup>11</sup> Since most triplet excited states of organic chromophores are much higher (typically 180–320 kJ mol<sup>-1</sup>),  $\text{O}_2$

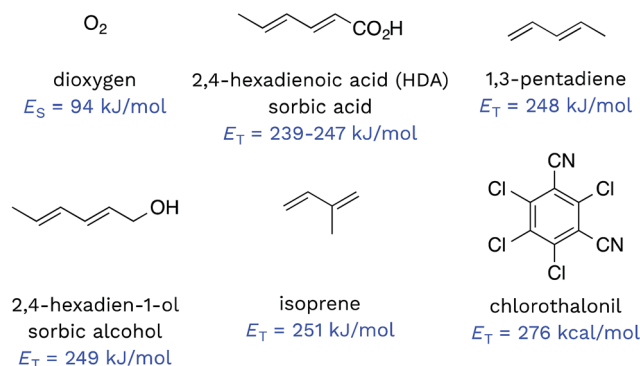


Fig. 2 Compounds that have been shown to act as energy acceptors with  $^3\text{CDOM}^*$ . Triplet energies ( $E_T$ ) are given for each compound, except in the case of  $\text{O}_2$ , where the lowest singlet energy ( $E_S$ ) is given.

has been proposed to be a universal energy acceptor, capable of accepting energy from all  $^3\text{CDOM}^*$  moieties.<sup>9</sup> This is an oversimplification as discussed above in the section on the concentration of  $^3\text{CDOM}^*$  in natural waters, but to a first approximation, it is a reasonable statement.

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

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

## Triplet energy of $^3\text{CDOM}^*$

Given the heterogeneous nature of the components of  $^3\text{CDOM}^*$ , 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  $^3\text{CDOM}^*$  and either  $\text{O}_2$  ( $E_S = 94 \text{ kJ mol}^{-1}$ )<sup>11</sup> or dienes 1,3-pentadiene ( $E_T = 248 \text{ kJ mol}^{-1}$ )<sup>25</sup> and 2,4-hexadien-1-ol ( $E_T = 249 \text{ kJ mol}^{-1}$ ),<sup>25</sup> Zepp concluded that  $^3\text{CDOM}^*$  comprised both high-energy triplets ( $E_T \geq 250 \text{ kJ mol}^{-1}$ ) and low-energy triplets ( $94 \leq E_T \leq 250 \text{ kJ mol}^{-1}$ ).<sup>9</sup> The high-energy triplets were able to sensitize the isomerization of the 1,3-pentadiene and produce  $^1\text{O}_2$ , while the low energy triplets could only produce  $^1\text{O}_2$ . 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.<sup>9</sup> To visualize this result, a hypothetical normal (Gaussian) distribution of triplet energies with 37% of the triplet energies being greater than or equal to  $250 \text{ kJ mol}^{-1}$  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,<sup>51,52</sup> while coumarins typically have poor triplet yields.<sup>53</sup>

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.<sup>9</sup> This

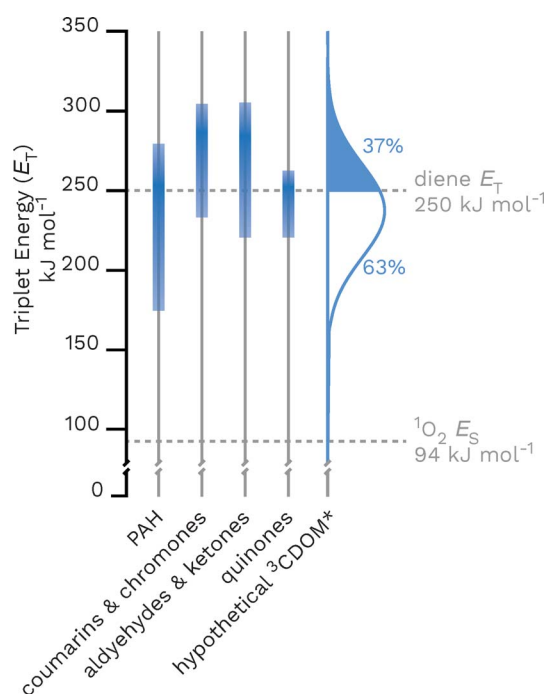


Fig. 3 Distributions of triplet energies found for different classes of organic molecules containing functional groups that are thought to be present in CDOM and a hypothetical normal distribution of  $^3\text{CDOM}^*$  triplet energies that fit the observation of 37% having  $E_T \geq 250 \text{ kJ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

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  $250 \text{ kJ mol}^{-1}$ .<sup>9</sup> Similar experiments conducted with functionalized carbon nanotubes<sup>41</sup> and petroleum<sup>54</sup> found the apparent  $E_T$  values to be lower and higher than CDOM, respectively. The petroleum value was estimated to be  $288\text{--}303 \text{ kJ mol}^{-1}$ , suggesting that the triplet photochemistry relevant to oil spills may differ substantially from CDOM-based photochemistry.<sup>54</sup> 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)<sup>55,56</sup> are dominating the sensitization of the diene probes.

At least two spectroscopic estimates of the  $E_T$  value of  $^3\text{CDOM}^*$  have been made. Brucoleri *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 ( $714 \text{ nm}$ ;  $14\,000 \text{ cm}^{-1}$ ) corresponded to an energy of  $170 \text{ kJ mol}^{-1}$ .<sup>57,58</sup> Mazhul *et al.* used room temperature phosphorescence spectroscopy to identify the opposite transition ( $T_1 \rightarrow S_0$ ), with an onset near  $405 \text{ nm}$ , corresponding to the highest energy (phosphorescing) triplets having an  $E_T$  value of  $300 \text{ kJ mol}^{-1}$ .<sup>59</sup> 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  $^3\text{CDOM}^*$  components in their mixture.<sup>59</sup> 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.

### $^3\text{CDOM}^*$ oxidation reactions

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

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  $^3\text{CDOM}^*$ . Excluded from this group are compounds that are suspected to be reactive toward  $^3\text{CDOM}^*$ , based on their reactivity toward model sensitizers (e.g., anthraquinone-2-sulfonate; AQ2S), but that have not yet been investigated with CDOM.<sup>61–65</sup>

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  $^3\text{CDOM}^*$ . This includes simple aniline structures, such as *N,N*-dimethylaniline,<sup>66</sup> *p*-aminobenzoic acid,<sup>67</sup> and





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

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

<sup>a</sup> Balance is H<sub>2</sub>O when a percentage co-solvent is specified. <sup>b</sup> 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<sub>3</sub>. <sup>c</sup> Matrix not specified. <sup>d</sup> No reported value found.



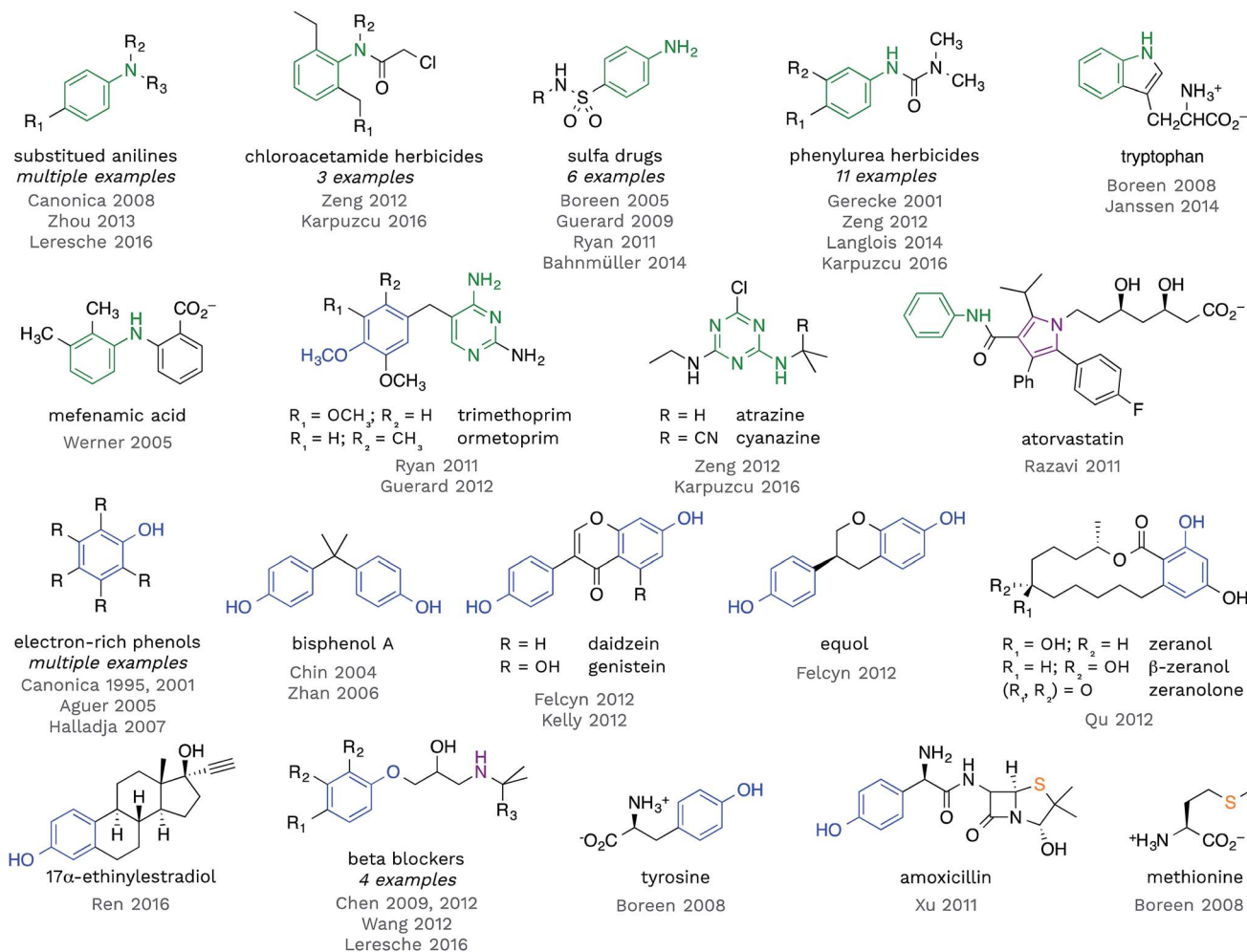


Fig. 4 Selected compounds that have been shown to react with  $^3\text{CDOM}^*$ . Aniline (and other aminoarene), phenol (and aryl ether), sulfide and related substructures are highlighted.

*p*-cyano-*N,N*-dimethylaniline,<sup>68</sup> but also more complex structures, such as found in phenylurea herbicides,<sup>28,69–72</sup> sulfa drugs,<sup>45,46,73–75</sup> chloroacetamide herbicides,<sup>28,72</sup> diarylamines (e.g., mefenamic acid<sup>44</sup>), and arguably within the structure of tryptophan<sup>47,76</sup> and indole<sup>77</sup> (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  $^3\text{CDOM}^*$ , and both of these compounds contain a diamino-triazine functional group.<sup>28,72</sup> The structurally similar diaminopyrimidine group in trimethoprim<sup>45</sup> and ormetoprim<sup>78</sup> may be responsible for the reactivity of these compounds toward  $^3\text{CDOM}^*$ , but these compounds also contain electron-rich methoxy-substituted benzene rings that could instead be the locus of reactivity.  $^3\text{CDOM}^*$  is capable of oxidizing both electron-rich and electron-poor anilines, although the rates of aniline oxidation are clearly modulated by their electron-richness.<sup>60,69</sup> By contrast, only electron-rich phenols appear to be susceptible to oxidation by  $^3\text{CDOM}^*$ .

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

$^3\text{CDOM}^*$  (Fig. 4).<sup>47,79–81</sup> This reactivity has been found in more complicated phenol-containing compounds, including the polycarbonate constituent bisphenol A,<sup>82,83</sup> the oral contraceptive 17 $\alpha$ -ethinylestradiol,<sup>42</sup> agricultural hormones zeranone,  $\beta$ -zeranol, and zeranone,<sup>84</sup> and phytoestrogens daidzein, genistein, and equol<sup>32,85</sup> (Fig. 4). Presumably, the phenol functionality is the site of reactivity toward  $^3\text{CDOM}^*$  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.<sup>86</sup> Canonica found weak isotope effects for oxidation of phenols by  $^3\text{CDOM}^*$ , favoring a two-step electron transfer-proton transfer mechanism being operative.<sup>79</sup>

For some of the polyfunctional compounds shown in Fig. 4, the primary target of  $^3\text{CDOM}^*$  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.<sup>87</sup> Amoxicillin reacts with  $^3\text{CDOM}^*$  and contains both phenol and sulfide functional groups.<sup>24</sup> While the reaction could be occurring at the phenol, S-containing compounds, such as methionine,<sup>47</sup> are also believed to be oxidized by  $^3\text{CDOM}^*$ . Beta blockers, atenolol, metoprolol, nadolol, and propranolol, have all been shown to react with  $^3\text{CDOM}^*$ .<sup>29,68,88</sup> 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.<sup>88,89</sup>

We have focused on the oxidation of organic molecules, but there is also evidence that  $^3\text{CDOM}^*$  can also oxidize inorganic species. Canonica demonstrated that triplet ketone sensitizers with similar reactivity to  $^3\text{CDOM}^*$  were capable of oxidizing carbonate,  $\text{CO}_3^{2-}$ , to carbonate radical,  $\text{CO}_3^{\cdot-}$ .<sup>90</sup> Recent work by Parker and Mitch has implicated  $^3\text{CDOM}^*$  in the oxidation of halides to dihalogen radical anions,  $\text{X}_2^{\cdot-}$  ( $\text{X} = \text{Cl}, \text{Br}$ ).<sup>48</sup> 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  $\text{X}_2^{\cdot-}$  from  $\text{Br}^-$  and  $\text{Cl}^-$ , using AQ2S as a sensitizer.<sup>91,92</sup> 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.<sup>48,91,92</sup>

### $^3\text{CDOM}^*$ 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 ( $\text{RB}^{2-}$ ).  $\text{RB}^{2-}$  in its triplet state has been shown to act as both a reductant and an oxidant.<sup>93</sup> The potential associated with  $\text{RB}^{2-}$  as a reductant,  $E^\circ(\text{RB}^{\cdot-}/\text{RB}^{2-})$ , decreases by 1.77 V (from 1.33 to  $-0.44$  V SHE) upon excitation to its triplet state,  $^3\text{RB}^{2-}$ .<sup>93</sup> The potential associated with  $\text{RB}^{2-}$  as an oxidant,  $E^\circ(\text{RB}^{2-}/\text{RB}^{\cdot 3-})$ , increases by 1.77 V (from  $-0.54$  to  $1.23$  V SHE).<sup>93</sup> The value 1.77 V is the triplet energy converted to potential,  $E_T(\text{RB}^{2-})/F = 1.77$  V, and the reason this is combined

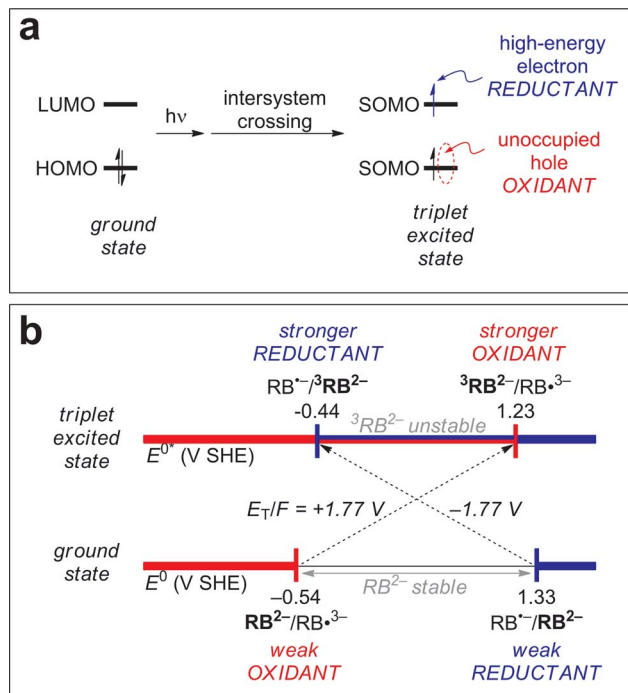


Fig. 5 (a) Frontier orbital occupancy diagram showing the difference between the ground state and its lowest triplet excited state, illustrating that the triplet state is both a stronger reductant and oxidant. HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital; SOMO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

with the ground state potential is discussed further in the next section. Note that  $\text{RB}^{2-}$  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  $\text{RB}^{2-}$  is thermodynamically unstable with respect to oxidation above  $-0.44$  V SHE and to reduction below  $1.23$  V SHE. Between these values,  $^3\text{RB}$  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  $^3\text{CDOM}^*$  is almost certainly reduction of  $\text{O}_2$  ( $E^\circ(\text{O}_{2,1\text{M}}/\text{O}_2^{\cdot-}) = -0.18$  V)<sup>94</sup> to superoxide ( $\text{O}_2^{\cdot-}$ ). Superoxide production has not been definitively linked to  $^3\text{CDOM}^*$ , but it is logical that a subset of these  $^3\text{CDOM}^*$  species would reduce dissolved  $\text{O}_2$ , given the foregoing discussion and the fact that  $\text{O}_2$  is the dominant oxidant present in surface waters. A sense of the maximum quantum yield for such a process comes from  $\text{H}_2\text{O}_2$  production quantum yields, since the primary formation pathway involves dismutation of  $\text{O}_2^{\cdot-}$ .  $\text{H}_2\text{O}_2$  production quantum yields are strongly wavelength dependent,<sup>95-97</sup> but are in the range of  $0.5 \times 10^{-4}$  to  $10^{-3}$ , with typical quantum yields being about  $10^{-4}$ .<sup>95-99</sup> Considering that two equivalents of  $\text{O}_2^{\cdot-}$  are needed to produce  $\text{H}_2\text{O}_2$  and that only a fraction of  $\text{O}_2^{\cdot-}$



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

How strong are these  $^3CDOM^*$  reductants? Some information potentially comes from Krogh who examined the photo-reduction of a suite of halogenated compounds sensitized by CDOM.<sup>104</sup>  $CCl_4$  ( $E^\circ(CCl_4/CCl_3^{\cdot -}, Cl^-) \approx -0.1$  V)<sup>105</sup> underwent facile photoreduction sensitized by Christina River water ( $18 \text{ mg}_C \text{ L}^{-1}$ ) exposed to 310 nm radiation. This makes sense given that  $CCl_4$  is thermodynamically easier to reduce than  $O_2$  ( $-0.18$  V).<sup>94</sup> Importantly, however, tetrachloroethylene (PCE) ( $E^\circ(PCE/C_2Cl_3^{\cdot -}, Cl^-) \approx -0.60$  V)<sup>105</sup> 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 $^3CDOM^*$

Returning to the topic of  $^3CDOM^*$  as an oxidant, the excited state reduction potential of  $^3CDOM^*$  ( $E^\circ(^3S^*/S^{\cdot -})$ ) is a critical value that determines not only the thermodynamics, but also the kinetics of its electron transfer reactions.<sup>105</sup> 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  $E^\circ(^3S^*/S^{\cdot -})$ , 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 ( $F = 96.485 \text{ kJ V}^{-1}$ ) to convert from energy to potential (eqn (5)).

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

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 ( $E^\circ(S/S^{\cdot -}) = -1.50$  V), the excited-state reaction is favorable ( $E^\circ(^3S^*/S^{\cdot -}) = +1.64$  V), and the difference between the two is the triplet energy of the ketone ( $E_T = 303 \text{ kJ mol}^{-1}$ ;  $E_T/F = 3.14$  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  $^3CDOM^*$ .<sup>79,106</sup> 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).<sup>79</sup> 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

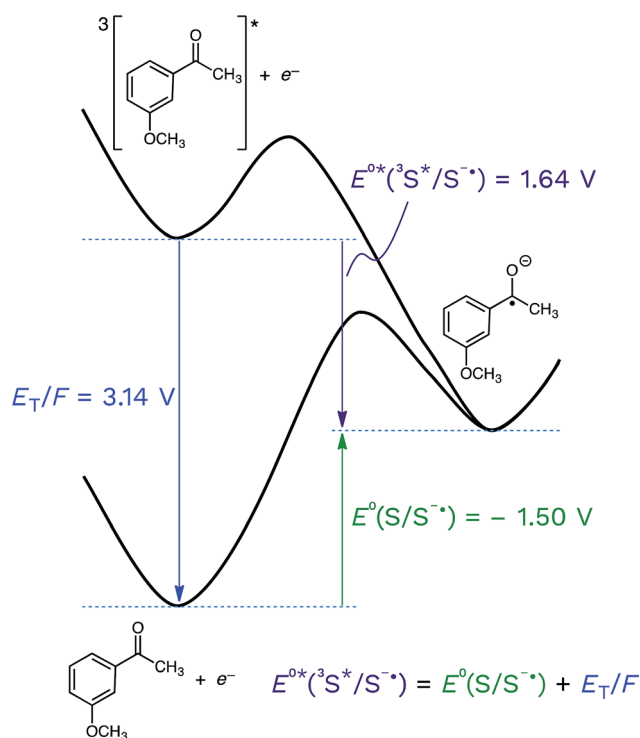


Fig. 6 Schematic representation of the half-wave reduction reactions of 3-methoxyacetophenone (3MAP) in its ground state and its triplet excited state, showing the relationship between the ground-state reduction potential ( $E^\circ(S/S^{\cdot -}) = -1.50$  V vs. the standard hydrogen electrode, SHE),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

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 ( $E^\circ(^3S^*/S^{\cdot -}) = 1.64$  V SHE) compared to GSW, the slope was approximately 1, indicating equal selectivity. However, with BP ( $E^\circ(^3S^*/S^{\cdot -}) = 1.69$  V SHE), the slope was lower than 1, indicating lower selectivity than  $^3CDOM^*$ , and with 2AN ( $E^\circ(^3S^*/S^{\cdot -}) = 1.10$  V SHE), the slope was higher than 1, indicating higher selectivity than  $^3CDOM^*$ . Insofar as the kinetics of the phenol oxidation reaction are controlled by the  $E^\circ(^3S^*/S^{\cdot -})$  value of the oxidant (see following section), this argues that the reduction potentials for the  $^3CDOM^*$  systems are centered near 1.64 V.<sup>79</sup> In a second study, in which the kinetics of phenol photooxidation by 2AN, 3MAP, and BP were followed using transient absorbance spectroscopy,  $E^\circ(^3CDOM^*/CDOM^{\cdot -})$  was estimated to be between 1.36 and 1.90 V.<sup>106</sup> Parker and Mitch came to a similar conclusion using the sensitized photoproduction of halide radicals from bromide and chloride ions.<sup>48</sup> They found Suwannee River DOM to have halide radical production rates consistent with model ketone sensitizers in the  $E^\circ(^3S^*/S^{\cdot -})$  range of 1.6 to 1.8 V.<sup>48</sup>

## Connecting excited state reduction potential to electron transfer kinetics

To assess whether or not  $^3CDOM^*$  will oxidize a substrate molecule at an appreciable rate, the standard molar Gibbs free





energy change for the electron transfer reaction ( $\Delta_r G_{\text{et}}^0$ ) can be taken as a proxy. As a rough estimate, the reaction will be relevant when  $\Delta_r G_{\text{et}}^0 \leq 0$ . 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  $^3\text{CDOM}^*$ ) second-order rate constants,  $k_{\text{et}}$ , depend on  $\Delta_r G_{\text{et}}^0$  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.<sup>105</sup> We consider here the Rehm–Weller relationship (eqn (6)),<sup>105–107</sup> which was found to be successful in explaining fluorescence quenching data:

$$k_{\text{et}} = \frac{k_d}{1 + \frac{k_d}{K_d Z} \left\{ \exp(x) + \exp\left(\frac{\Delta_r G_{\text{et}}^0}{RT}\right) \right\}} \quad (6)$$

$$x = \frac{\sqrt{\left(\frac{\Delta_r G_{\text{et}}^0}{2}\right)^2 + \left(\frac{\lambda}{4}\right)^2} + \left(\frac{\Delta_r G_{\text{et}}^0}{2}\right)}{RT}$$

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  $6 \times 10^{11} \text{ s}^{-1}$  for solution reactions<sup>105</sup>), and  $\lambda$  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  $\lambda$  can vary over a broad range (20 to several hundreds of  $\text{kJ mol}^{-1}$ ).<sup>105</sup> The reader should be aware that analogous relationships derived from Marcus' theory of electron transfer,<sup>105</sup> or Sandros–Boltzmann type relationships<sup>108,109</sup> could also be used.

Both  $\Delta_r G_{\text{et}}^0$  and  $\lambda$  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,  $k_{\text{et}}$  approaches the diffusion-controlled rate constant  $k_d$ . For highly endergonic reactions, the denominator of eqn (6) simplifies and  $\log k_{\text{et}}$  decreases linearly with increasing  $\Delta_r G_{\text{et}}^0$ , 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  $25^\circ\text{C}$ ). 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.<sup>106,110</sup> Moreover, in the case of electron-rich phenols as the electron donor quenchers, such triplet quenching rate constants<sup>106</sup> were almost equal to the second-order rate constants measured for phototransformation.<sup>79</sup> 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  $E^\circ(^3\text{S}^*/\text{S}^-)$  of  $^3\text{CDOM}^*$  that have been made so far<sup>79,106</sup> suffer from the simplification that  $^3\text{CDOM}^*$  is assigned a single “average” value of  $E^\circ(^3\text{S}^*/\text{S}^-)$ , that is determined by comparison with the  $E^\circ(^3\text{S}^*/\text{S}^-)$  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  $^3\text{CDOM}^*_i$  ( $i = 1 \dots N$ ), contributes to the photo-sensitized oxidation of a target compound (TC). The pseudo-first-order rate constant for this reaction,  $k_{\text{TC}}^{\text{sens}}$ , can then be expressed as:

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

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

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

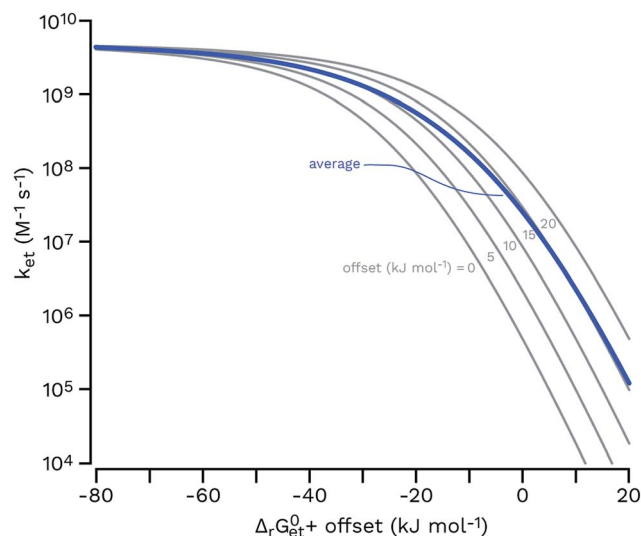


Fig. 7 Rehm–Weller plots (gray thin curves) for a set of five functions having the same parameters (eqn (6);  $k_d = 6.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_d/(K_d Z) = 0.1$ ;  $\lambda = 65 \text{ kJ mol}^{-1}$ ; values from a typical fit in ref. 106 were used) and an offset of 0, 5, 10, 15 and  $20 \text{ kJ mol}^{-1}$  (from left to right) for  $\Delta_r G_{\text{et}}^0$ . 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  $k_{TC}^{sens}$ . Let us assume that  $k_{et}$  for the electron transfer reaction between TC and  ${}^3\text{CDOM}^*_i$  can be expressed by eqn (6) using constant values for  $k_d$  and  $\lambda$ . In Fig. 7, Rehm–Weller plots are shown for five hypothetical  ${}^3\text{CDOM}^*_i$  having  $F \times E^\circ({}^3\text{CDOM}^*_i/\text{CDOM}^-_i)$  that differ by 5 kJ mol<sup>−1</sup> ( $\Delta E^\circ = 52$  mV). Assuming equal  $[{}^3\text{CDOM}^*_i]_{ss}$  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  $E^\circ({}^3\text{S}^*/\text{S}^-)$  for CDOM will remain fuzzy.

A possible approach to empirically determine the shape of the pseudo-Rehm–Weller curve for  ${}^3\text{CDOM}^*$  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.<sup>111</sup> Thereby, it is suitable to define an “effective” concentration of  ${}^3\text{CDOM}^*$  capable of oxidizing a given PC by dividing an experimentally determined  $k_{PC}^{sens}$  through the best guess for the maximum second-order rate constant for the electron-transfer reaction from the PC to  ${}^3\text{CDOM}^*$  (e.g.,  $\approx 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , but an optimized value might be obtained from a consistent set of quenching data for model photosensitizers in aqueous solution). The “effective” concentration of  ${}^3\text{CDOM}^*$  obviously decreases with increasing PC oxidation potential. In such a way, a function of  $[{}^3\text{CDOM}^*]$  vs. oxidation potential of PC can be constructed and used for the prediction of the “effective” concentration of  ${}^3\text{CDOM}^*$ , and consequently of a pseudo-first-order transformation rate constant, for the transformation of any TC by  ${}^3\text{CDOM}^*$  (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.<sup>112,113</sup> Thereby, the difference in triplet energy between donor and acceptor assumes the same role as  $\Delta_r G^\circ_{et}$  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  $E^\circ({}^3\text{S}^*/\text{S}^-)$

values for a series of compounds that have structures that could plausibly be similar to constituents of CDOM. These  $E^\circ({}^3\text{S}^*/\text{S}^-)$  values come from the compounds triplet energies ( $E_T$ ) and ground state reduction potentials ( $E^\circ(\text{S}/\text{S}^-)$ ) (eqn (5)), which are also listed in Table 1. These data are visualized in Fig. 8, with a plot of  $E_T$  vs.  $E^\circ({}^3\text{S}^*/\text{S}^-)$ .

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.<sup>105</sup> 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.*<sup>114</sup> 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  $E^\circ({}^3\text{S}^*/\text{S}^-)$ , 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  $E^\circ({}^3\text{S}^*/\text{S}^-)$  values of different functional group classes are somewhat distinct, with polycyclic aromatic hydrocarbons having the lowest reduction potentials (*i.e.*, relatively weak oxidants,  $E^\circ({}^3\text{S}^*/\text{S}^-) \leq 0.69$  V) of this set and quinones having the highest (*i.e.*, strong oxidants,  $E^\circ({}^3\text{S}^*/\text{S}^-) \geq 2.19$  V). Indeed, excited state triplet quinones are such strong oxidants that they are above the one-electron reduction potential for water at pH 7 ( $E^\circ(\text{OH}^\bullet/\text{OH}^-) = 2.18$  V), which is actually the oxidation of hydroxide ion ( $E^\circ(\text{OH}^\bullet/\text{OH}^-) = 1.77$  V) corrected for its activity at pH 7.<sup>115,116</sup> Incidentally, the one-electron oxidation of water itself requires a much higher potential of  $E^\circ(\text{H}_2\text{O}^+/\text{H}_2\text{O}) = 2.65$  V.<sup>117</sup> This makes quinones one of the prime suspects in the CDOM-sensitized formation of hydroxyl radical or lower-energy hydroxyl radical-like species.<sup>118–120</sup> Whether or not quinones actually oxidize hydroxide ion (or water) to produce hydroxyl radical has been a controversial topic.<sup>118,121–124</sup> To give just two concrete examples, both methylbenzoquinone and



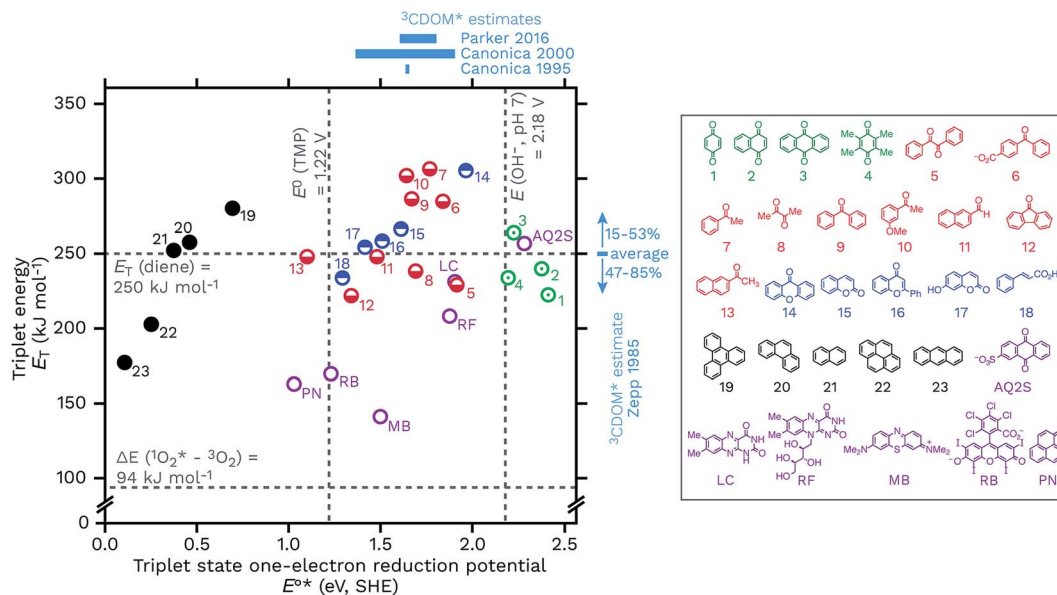


Fig. 8 Triplet energies ( $E_T$ ,  $\text{kJ mol}^{-1}$ ) vs. triplet state one-electron reduction potentials ( $E^\circ(^3\text{S}^*/\text{S}^-)$ , V SHE) for a selection of 23 DOM-like model compounds and a selection of widely used sensitizers. The horizontal lines correspond to the triplet excited state energy of a typical diene energy transfer probe and the singlet state energy of  $\text{O}_2$ . The vertical lines correspond to the one-electron oxidation potentials of TMP,  $E^\circ(\text{ArOH}^{+}/\text{ArOH})$ , and hydroxide at pH 7,  $E^\circ(\text{OH}^+/\text{OH}^-)$ . Selected estimates for  $^3\text{CDOM}^*$  values from Zepp,<sup>9</sup> Canonica,<sup>79,106</sup> and Parker and Mitch<sup>48</sup> 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.<sup>118,119,124,125</sup>

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.<sup>9,10,60,70,79,98,106,126–128</sup>

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.<sup>128</sup> Similarly, Sharpless showed that borohydride-treated DOM formed  $^1\text{O}_2$  at lower rates than (but with the same quantum efficiency as) untreated DOM.<sup>10</sup> In most cases, treatment with borohydride led to incomplete loss of photosensitization ability, suggesting that non-ketone and -aldehyde photosensitizers are also involved.<sup>10,128</sup> 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<sup>129</sup> 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,  $E^\circ(\text{ArOH}^{+}/\text{ArOH})$ ,<sup>106</sup> which is

a popular probe molecule for  $^3\text{CDOM}^*$ .<sup>130</sup> 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  $E^\circ(^3\text{S}^*/\text{S}^-) < 1.22$  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 ( $E^\circ(^3\text{S}^*/\text{S}^-) = 1.10$ ) 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  $\text{D}_2\text{O}$  was 3.4 times slower than in  $\text{H}_2\text{O}$ , which can be interpreted as a result of the phenolic O–H/D bond being broken in the rate-determining step.<sup>79</sup> When Suwannee River fulvic acid or Fluka humic acid was used as the sensitizer for TMP photooxidation, isotope effects of only  $k_{\text{H}}/k_{\text{D}} = 1.1 \pm 0.1$  and  $1.2 \pm 0.1$ , respectively, were observed.<sup>79</sup> 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  $E^\circ(^3\text{S}^*/\text{S}^-)$  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  $^3CDOM^*$  (Elliot Soil humic and fulvic acid, in this case) have a sufficiently high  $E^\circ(^3S^*/S^{*-})$  to oxidize TMP.<sup>81</sup>

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  $E^\circ(^3S^*/S^{*-})$  ranging from 1.03 to 1.50 V (Table 1). Flavin-type photosensitizers, such as riboflavin ( $E^\circ(^3S^*/S^{*-}) = 1.88$  V) and lumichrome ( $E^\circ(^3S^*/S^{*-}) = 1.91$  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 ( $E^\circ(^3S^*/S^{*-}) = 2.28$  V), which has been reported to give very low yields of either  $^1O_2$  or hydroxyl radical.<sup>125</sup> Thus AQ2S might model some of the most oxidizing triplet states found in  $^3CDOM^*$ , but is a considerably stronger oxidant than the average  $^3CDOM^*$  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  $n\pi^*$  triplet (strong sensitizer) or  $\pi\pi^*$  triplet (weak sensitizer).<sup>114,131</sup> The difference has to do with the electronic configuration of the triplet, in which the lower energy SOMO has more non-bonding (n) or  $\pi$ -bonding ( $\pi$ ) character. For example, many triplet aromatic ketones are classified as  $n\pi^*$ , while triplet PAHs are  $\pi\pi^*$ . We have not included discussion of  $n\pi^*$  and  $\pi\pi^*$  classifications in this review for a few reasons. First, and foremost, we are mostly concerned with  $^3CDOM^*$  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  $n\pi^*$  and  $\pi\pi^*$  triplets in  $^3CDOM^*$  is beyond the currently visible horizon. Second, assigning a triplet as  $n\pi^*$  or  $\pi\pi^*$  is not trivial, as the SOMO in question may have mixed character. For example, duroquinone has been taken as a prototypical  $n\pi^*$  triplet and  $\pi\pi^*$  triplet in different studies.<sup>114,132</sup> Finally, while some have found the  $n\pi^*/\pi\pi^*$  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  $n\pi^*/\pi\pi^*$  concept (where  $\pi\pi^*$  triplet states give higher  $^1O_2$  yields),<sup>132</sup> but also in terms of  $E_T$  and excited state oxidation potential ( $E^\circ(^3S^*/S^{+*})$ ) (where low  $E_T$  and low  $E^\circ$  triplet states give higher  $^1O_2$  yields), without considering the electronic configuration.<sup>13,14,133</sup>

## Outlook

Despite the importance of  $^3CDOM^*$  in the transformation of organic molecules, its study has lagged behind other important PPRI, especially  $^1O_2$ ,  $^{\bullet}OH$ ,  $H_2O_2$ , and  $O_2^{*-}$ . This is clearly because  $^3CDOM^*$  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  $^3CDOM^*$  are outlined below along with some of the most pressing research problems.

A critical strategy for studying a complex mixture like  $^3CDOM^*$  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  $^3CDOM^*$ . 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  $^3CDOM^*$  formation quantum yields. Additionally, the steady-state concentrations of  $^1O_2$  and  $^3CDOM^*$  must be within a factor of two of each other (when  $0.25 < f_{\Delta} < 1$ ; see eqn (4)).

While  $O_2$  quenching of  $^3CDOM^*$  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  $^3CDOM^*$ . 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.<sup>48</sup> At the moment, there is a large gap between the energy of  $^1O_2$  (94 kJ mol<sup>-1</sup>) and the diene quenchers that have been employed ( $E_T \approx 250$  kJ mol<sup>-1</sup>; 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<sup>-1</sup>), anthracene (178 kJ mol<sup>-1</sup>), ferrocene (167 kJ mol<sup>-1</sup>), azulene (163 kJ mol<sup>-1</sup>), and tetracene (123 kJ mol<sup>-1</sup>), 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  $^3CDOM^*$  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  $^3CDOM^*$ . This will hopefully change in the future as a more nuanced and detailed view of  $^3CDOM^*$  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.<sup>111</sup>

Finally, the composition of  $^3CDOM^*$  is clearly different for different sources of organic matter. In particular, there has been growing evidence of significant variability in the nature of  $^3CDOM$  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).<sup>134</sup> 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 photo-transformation.<sup>45,46,73,74,135,136</sup> 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).<sup>73,135</sup> Arnold found that sulfamethoxazole degraded much more rapidly in the presence of effluent organic matter than with CDOM from other sources.<sup>45</sup> Canonica found that sulfadiazine undergoes more rapid degradation when sensitized by PLFA than SRFA.<sup>74</sup> In each case, convincing evidence that <sup>3</sup>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.<sup>66,137,138</sup> Another possibility is that the PLFA-derived <sup>3</sup>CDOM\* is a stronger oxidant (higher  $E^\circ(*^3S^*/S^-)$ ) than the SRFA-derived <sup>3</sup>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 <sup>3</sup>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<sub>2</sub> and HDA) and oxidation-based probe methods (e.g., TMP) will only further our understanding of the scope, reactivity, and variability of <sup>3</sup>CDOM\*. There is an especially important link between <sup>1</sup>O<sub>2</sub> and <sup>3</sup>CDOM\* that makes <sup>1</sup>O<sub>2</sub> 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 <sup>3</sup>CDOM\* and their reactivity patterns will come into view, which will in turn allow a better understanding of the role of <sup>3</sup>CDOM\* in the photochemical fate of contaminants and sunlight-driven biogeochemical processes.

## Acknowledgements

We thank Caroline Davis, Paul Erickson, Elisabeth Janssen, Douglas Latch, Vivian Lin, Rachele Ossola, Kimberly Parker, Fernando Rosario-Ortiz, and Markus Schmitt for helpful feedback on the manuscript. We gratefully acknowledge funding

from the Swiss National Science Foundation (Grant number 200021\_156198).

## References

- O. C. Zafriou, Marine organic photochemistry previewed, *Mar. Chem.*, 1977, **5**(4), 497–522.
- O. C. Zafriou, J. Joussot-Dubien, R. G. Zepp and R. G. Zika, Photochemistry of natural waters, *Environ. Sci. Technol.*, 1984, **18**(12), 358A–371A.
- N. V. Blough and R. G. Zepp, Reactive oxygen species in natural waters, in *Active oxygen in chemistry*, Springer, 1995, pp. 280–333.
- D. Vione, M. Minella, V. Maurino and C. Minero, Indirect photochemistry in sunlit surface waters: photoinduced production of reactive transient species, *Chem.-Eur. J.*, 2014, **20**(34), 10590–10606.
- C. K. Remucal, The role of indirect photochemical degradation in the environmental fate of pesticides: a review, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 628–653.
- J. K. Challis, M. L. Hanson, K. J. Friesen and C. S. Wong, A critical assessment of the photodegradation of pharmaceuticals in aquatic environments: defining our current understanding and identifying knowledge gaps, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 672–696.
- S. Yan and W. Song, Photo-transformation of pharmaceutically active compounds in the aqueous environment: a review, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 697–720.
- R. G. Zepp, N. L. Wolfe, G. L. Baughman and R. C. Hollis, Singlet oxygen in natural waters, *Nature*, 1977, **267**(5610), 421–423.
- R. G. Zepp, P. F. Schlotzhauer and R. M. Sink, Photosensitized transformations involving electronic energy transfer in natural waters: role of humic substances, *Environ. Sci. Technol.*, 1985, **19**(1), 74–81.
- C. M. Sharpless, Lifetimes of triplet dissolved natural organic matter (DOM) and the effect of NaBH<sub>4</sub> reduction on singlet oxygen quantum yields: implications for DOM photophysics, *Environ. Sci. Technol.*, 2012, **46**(8), 4466–4473.
- F. Wilkinson, W. P. Helman and A. B. Ross, Quantum yields for the photosensitized formation of the lowest electronically excited singlet state of molecular oxygen in solution, *J. Phys. Chem. Ref. Data*, 1993, **22**(1), 113–262.
- R. Schmidt, C. Tanielian, R. Dunsbach and C. Wolff, Phenalenone, a universal reference compound for the determination of quantum yields of singlet oxygen O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>) sensitization, *J. Photochem. Photobiol., A*, 1994, **79**(1), 11–17.
- M. Bodesheim, M. Schütz and R. Schmidt, Triplet state energy dependence of the competitive formation of O<sub>2</sub> (<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>) and O<sub>2</sub> (<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) in the sensitization of O<sub>2</sub> by triplet states, *Chem. Phys. Lett.*, 1994, **221**(1), 7–14.
- C. Schweitzer, Z. Mehrdad, A. Noll, E.-W. Grabner and R. Schmidt, Mechanism of photosensitized generation of singlet oxygen during oxygen quenching of triplet states



- and the general dependence of the rate constants and efficiencies of  $O_2 (^1\Sigma_g^+)$ ,  $O_2 (^1\Delta_g)$ , and  $O_2 (^3\Sigma_g^-)$  formation on sensitizer triplet state energy and oxidation potential, *J. Phys. Chem. A*, 2003, **107**(13), 2192–2198.
- 15 F. Wilkinson, W. P. Helman and A. B. Ross, Rate constants for the decay and reactions of the lowest electronically excited singlet state of molecular oxygen in solution. An expanded and revised compilation, *J. Phys. Chem. Ref. Data*, 1995, **24**(2), 663–677.
  - 16 B. M. Peterson, A. M. McNally, R. M. Cory, J. D. Thoenke, J. B. Cotner and K. McNeill, Spatial and temporal distribution of singlet oxygen in Lake Superior, *Environ. Sci. Technol.*, 2012, **46**(13), 7222–7229.
  - 17 J. E. Grebel, J. J. Pignatello and W. A. Mitch, Sorbic acid as a quantitative probe for the formation, scavenging and steady-state concentrations of the triplet-excited state of organic compounds, *Water Res.*, 2011, **45**(19), 6535–6544.
  - 18 S. L. H. Sandvik, P. Bilski, J. D. Pakulski, C. F. Chignell and R. B. Coffin, Photogeneration of singlet oxygen and free radicals in dissolved organic matter isolated from the Mississippi and Atchafalaya River plumes, *Mar. Chem.*, 2000, **69**(1), 139–152.
  - 19 E. S. Boyle, N. Guerriero, A. Thiallet, R. D. Vecchio and N. V. Blough, Optical properties of humic substances and CDOM: relation to structure, *Environ. Sci. Technol.*, 2009, **43**(7), 2262–2268.
  - 20 S. E. Burns, J. P. Hassett and M. V. Rossi, Binding effects on humic-mediated photoreaction: intrahumic dechlorination of mirex in water, *Environ. Sci. Technol.*, 1996, **30**(10), 2934–2941.
  - 21 S. E. Burns, J. P. Hassett and M. V. Rossi, Mechanistic implications of the intrahumic dechlorination of mirex, *Environ. Sci. Technol.*, 1997, **31**(5), 1365–1371.
  - 22 D. E. Latch and K. McNeill, Microheterogeneity of singlet oxygen distributions in irradiated humic acid solutions, *Science*, 2006, **311**(5768), 1743–1747.
  - 23 M. Grandbois, D. E. Latch and K. McNeill, Microheterogeneous concentrations of singlet oxygen in natural organic matter isolate solutions, *Environ. Sci. Technol.*, 2008, **42**(24), 9184–9190.
  - 24 H. Xu, W. J. Cooper, J. Jung and W. Song, Photosensitized degradation of amoxicillin in natural organic matter isolate solutions, *Water Res.*, 2011, **45**(2), 632–638.
  - 25 R. E. Kellogg and W. T. Simpson, Perturbation of Singlet–Triplet Transition Energies, *J. Am. Chem. Soc.*, 1965, **87**(19), 4230–4234.
  - 26 R. G. Zepp, M. M. Gumz, W. L. Miller and H. Gao, Photoreaction of valerophenone in aqueous solution, *J. Phys. Chem. A*, 1998, **102**(28), 5716–5723.
  - 27 J. Morrison, H. Osthoff and P. Wan, Photoredox, photodecarboxylation, and photo-retro-aldol chemistry of *p*-nitrobiphenyls, *Photochem. Photobiol. Sci.*, 2002, **1**(6), 384–394.
  - 28 T. Zeng and W. A. Arnold, Pesticide photolysis in prairie potholes: probing photosensitized processes, *Environ. Sci. Technol.*, 2013, **47**(13), 6735–6745.
  - 29 L. Wang, H. Xu, W. J. Cooper and W. Song, Photochemical fate of beta-blockers in NOM enriched waters, *Sci. Total Environ.*, 2012, **426**, 289–295.
  - 30 S. L. Rosado-Lausell, H. Wang, L. Gutiérrez, O. C. Romero-Maraccini, X.-Z. Niu, K. Y. Gin, J.-P. Croué and T. H. Nguyen, Roles of singlet oxygen and triplet excited state of dissolved organic matter formed by different organic matters in bacteriophage MS2 inactivation, *Water Res.*, 2013, **47**(14), 4869–4879.
  - 31 J. E. Grebel, J. J. Pignatello and W. A. Mitch, Impact of halide ions on natural organic matter-sensitized photolysis of 17 $\beta$ -estradiol in saline waters, *Environ. Sci. Technol.*, 2012, **46**(13), 7128–7134.
  - 32 J. R. Felcyn, J. C. Davis, L. H. Tran, J. C. Berude and D. E. Latch, Aquatic photochemistry of isoflavone phytoestrogens: degradation kinetics and pathways, *Environ. Sci. Technol.*, 2012, **46**(12), 6698–6704.
  - 33 B. A. Cottrell, S. A. Timko, L. Devera, A. K. Robinson, M. Gonsior, A. E. Vizenor, A. J. Simpson and W. J. Cooper, Photochemistry of excited-state species in natural waters: a role for particulate organic matter, *Water Res.*, 2013, **47**(14), 5189–5199.
  - 34 O. C. Romero-Maraccini, N. J. Sadik, S. L. Rosado-Lausell, C. R. Pugh, X.-Z. Niu, J.-P. Croué and T. H. Nguyen, Sunlight-induced inactivation of human Wa and porcine OSU rotaviruses in the presence of exogenous photosensitizers, *Environ. Sci. Technol.*, 2013, **47**(19), 11004–11012.
  - 35 K. M. Parker, J. J. Pignatello and W. A. Mitch, Influence of ionic strength on triplet-state natural organic matter loss by energy transfer and electron transfer pathways, *Environ. Sci. Technol.*, 2013, **47**(19), 10987–10994.
  - 36 W. A. Arnold, One electron oxidation potential as a predictor of rate constants of N-containing compounds with carbonate radical and triplet excited state organic matter, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 832–838.
  - 37 S. A. Timko, C. Romera-Castillo, R. Jaffé and W. J. Cooper, Photo-reactivity of natural dissolved organic matter from fresh to marine waters in the Florida Everglades, USA, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 866–878.
  - 38 M. Antonopoulou, C. G. Skoutelis, C. Daikopoulos, Y. Deligiannakis and I. K. Konstantinou, Probing the photolytic–photocatalytic degradation mechanism of DEET in the presence of natural or synthetic humic macromolecules using molecular-scavenging techniques and EPR spectroscopy, *J. Environ. Chem. Eng.*, 2015, **3**(4), 3005–3014.
  - 39 A. P. S. Batista, A. C. S. Teixeira, W. J. Cooper and B. A. Cottrell, Correlating the chemical and spectroscopic characteristics of natural organic matter with the photodegradation of sulfamerazine, *Water Res.*, 2016, **93**, 20–29.
  - 40 C. Prasse, J. Wenk, J. T. Jasper, T. A. Ternes and D. L. Sedlak, Co-occurrence of photochemical and microbiological transformation processes in open-water unit process wetlands, *Environ. Sci. Technol.*, 2015, **49**(24), 14136–14145.



- 41 C.-Y. Chen and R. G. Zepp, Probing photosensitization by functionalized carbon nanotubes, *Environ. Sci. Technol.*, 2015, **49**(23), 13835–13843.
- 42 D. Ren, B. Huang, T. Bi, D. Xiong and X. Pan, Effects of pH and dissolved oxygen on the photodegradation of 17 $\alpha$ -ethynylestradiol in dissolved humic acid solution, *Environ. Sci.: Processes Impacts*, 2016, **18**(1), 78–86.
- 43 R. S. H. Liu, N. J. Turro and G. S. Hammond, Mechanisms of Photochemical Reactions in Solution. XXXI. Activation and Deactivation of Conjugated Dienes by Energy Transfer, *J. Am. Chem. Soc.*, 1965, **87**(15), 3406–3412.
- 44 J. J. Werner, K. McNeill and W. A. Arnold, Environmental photodegradation of mefenamic acid, *Chemosphere*, 2005, **58**(10), 1339–1346.
- 45 C. C. Ryan, D. T. Tan and W. A. Arnold, Direct and indirect photolysis of sulfamethoxazole and trimethoprim in wastewater treatment plant effluent, *Water Res.*, 2011, **45**(3), 1280–1286.
- 46 A. L. Boreen, W. A. Arnold and K. McNeill, Triplet-Sensitized Photodegradation of Sulfa Drugs Containing Six-Membered Heterocyclic Groups: Identification of an SO<sub>2</sub> Extrusion Photoproduct, *Environ. Sci. Technol.*, 2005, **39**(10), 3630–3638.
- 47 A. L. Boreen, B. L. Edlund, J. B. Cotner and K. McNeill, Indirect photodegradation of dissolved free amino acids: the contribution of singlet oxygen and the differential reactivity of DOM from various sources, *Environ. Sci. Technol.*, 2008, **42**(15), 5492–5498.
- 48 K. M. Parker and W. A. Mitch, Halogen radicals contribute to photooxidation in coastal and estuarine waters, *Proc. Natl. Acad. Sci. U. S. A.*, 2016, **113**(21), 5868–5873.
- 49 J. Porras, J. J. Fernández, R. A. Torres-Palma and C. Richard, Humic Substances Enhance Chlorothalonil Phototransformation via Photoreduction and Energy Transfer, *Environ. Sci. Technol.*, 2014, **48**(4), 2218–2225.
- 50 S. Bouchama, P. de Sainte-Claire, E. Arzoumanian, E. Oliveros, A. Boulkamh and C. Richard, Photoreactivity of the fungicide chlorothalonil in aqueous medium, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 839–847.
- 51 A. A. Lamola and G. S. Hammond, Mechanisms of photochemical reactions in solution. XXXIII. Intersystem crossing efficiencies, *J. Chem. Phys.*, 1965, **43**(6), 2129–2135.
- 52 P. J. Wagner and G. S. Hammond, Mechanisms of Photochemical Reactions in Solution. XXXVIII. 1 Quenching of the Type II Photoelimination Reaction, *J. Am. Chem. Soc.*, 1966, **88**(6), 1245–1251.
- 53 N. A. Kuznetsova and O. L. Kaliya, The photochemistry of coumarins, *Russ. Chem. Rev.*, 1992, **61**(7), 683–696.
- 54 P. Z. Ray and M. A. Tarr, Formation of organic triplets from solar irradiation of petroleum, *Mar. Chem.*, 2015, **168**, 135–139.
- 55 D. E. Nicodem, C. L. Guedes, M. C. Z. Fernandes, D. Severino, R. J. Correa, M. C. Coutinho and J. Silva, Photochemistry of petroleum, *Prog. React. Kinet. Mech.*, 2001, **26**(2–3), 219–238.
- 56 J. R. Payne and C. R. Phillips, Photochemistry of petroleum in water, *Environ. Sci. Technol.*, 1985, **19**(7), 569–579.
- 57 A. Bruccoleri, C. H. Langford and C. Arbour, Pulsed photo acoustic evaluation of intersystem crossing quantum yields in fulvic acid, *Environ. Technol.*, 1990, **11**(2), 169–172.
- 58 A. Bruccoleri, B. C. Pant, D. K. Sharma and C. H. Langford, Evaluation of primary photoproduct quantum yields in fulvic acid, *Environ. Sci. Technol.*, 1993, **27**(5), 889–894.
- 59 V. M. Mazhul, L. S. Ivashkevich, D. G. Shcherbin, N. A. Pavlovskaya, G. V. Naumova and T. F. Ovchinnikova, Luminescence properties of humic substances, *J. Appl. Spectrosc.*, 1997, **64**(4), 503–508.
- 60 S. Canonica, Oxidation of aquatic organic contaminants induced by excited triplet states, *Chim. Int. J. Chem.*, 2007, **61**(10), 641–644.
- 61 D. Vione, P. R. Maddigapu, E. De Laurentiis, M. Minella, M. Pazzi, V. Maurino, C. Minero, S. Kouras and C. Richard, Modelling the photochemical fate of ibuprofen in surface waters, *Water Res.*, 2011, **45**(20), 6725–6736.
- 62 E. De Laurentiis, S. Chiron, S. Kouras-Hadef, C. Richard, M. Minella, V. Maurino, C. Minero and D. Vione, Photochemical fate of carbamazepine in surface freshwaters: laboratory measures and modeling, *Environ. Sci. Technol.*, 2012, **46**(15), 8164–8173.
- 63 B. Sur, E. De Laurentiis, M. Minella, V. Maurino, C. Minero and D. Vione, Photochemical transformation of anionic 2-nitro-4-chlorophenol in surface waters: laboratory and model assessment of the degradation kinetics, and comparison with field data, *Sci. Total Environ.*, 2012, **426**, 296–303.
- 64 G. Marchetti, M. Minella, V. Maurino, C. Minero and D. Vione, Photochemical transformation of atrazine and formation of photointermediates under conditions relevant to sunlit surface waters: laboratory measures and modelling, *Water Res.*, 2013, **47**(16), 6211–6222.
- 65 E. De Laurentiis, C. Prasse, T. A. Ternes, M. Minella, V. Maurino, C. Minero, M. Sarakha, M. Brigante and D. Vione, Assessing the photochemical transformation pathways of acetaminophen relevant to surface waters: transformation kinetics, intermediates, and modelling, *Water Res.*, 2014, **53**, 235–248.
- 66 S. Canonica and H.-U. Laubscher, Inhibitory effect of dissolved organic matter on triplet-induced oxidation of aquatic contaminants, *Photochem. Photobiol. Sci.*, 2008, **7**(5), 547–551.
- 67 L. Zhou, Y. Ji, C. Zeng, Y. Zhang, Z. Wang and X. Yang, Aquatic photodegradation of sunscreen agent *p*-aminobenzoic acid in the presence of dissolved organic matter, *Water Res.*, 2013, **47**(1), 153–162.
- 68 F. Leresche, U. von Gunten and S. Canonica, Probing the photosensitizing and inhibitory effects of dissolved organic matter by using *N,N*-dimethyl-4-cyanoaniline (DMABN), *Environ. Sci. Technol.*, DOI: 10.1021/acs.est.6b02868.
- 69 A. C. Gerecke, S. Canonica, S. R. Müller, M. Schärer and R. P. Schwarzenbach, Quantification of dissolved natural organic matter (DOM) mediated phototransformation of



- phenylurea herbicides in lakes, *Environ. Sci. Technol.*, 2001, **35**(19), 3915–3923.
- 70 S. Canonica, B. Hellrung, P. Müller and J. Wirz, Aqueous oxidation of phenylurea herbicides by triplet aromatic ketones, *Environ. Sci. Technol.*, 2006, **40**(21), 6636–6641.
- 71 M. C. Langlois, L. K. Weavers and Y.-P. Chin, Contaminant-mediated photobleaching of wetland chromophoric dissolved organic matter, *Environ. Sci.: Processes Impacts*, 2014, **16**(9), 2098–2107.
- 72 M. E. Karpuzcu, A. J. McCabe and W. A. Arnold, Phototransformation of pesticides in prairie potholes: effect of dissolved organic matter in triplet-induced oxidation, *Environ. Sci.: Processes Impacts*, 2016, **18**(2), 237–245.
- 73 J. J. Guerard, Y.-P. Chin, H. Mash and C. M. Hadad, Photochemical fate of sulfadimethoxine in aquaculture waters, *Environ. Sci. Technol.*, 2009, **43**(22), 8587–8592.
- 74 S. Bahn Müller, U. von Gunten and S. Canonica, Sunlight-induced transformation of sulfadiazine and sulfamethoxazole in surface waters and wastewater effluents, *Water Res.*, 2014, **57**, 183–192.
- 75 Y. Li, J. Chen, X. Qiao, H. Zhang, Y. Zhang and C. Zhou, Insights into photolytic mechanism of sulfapyridine induced by triplet-excited dissolved organic matter, *Chemosphere*, 2016, **147**, 305–310.
- 76 E. M.-L. Janssen, P. R. Erickson and K. McNeill, Dual roles of dissolved organic matter as sensitizer and quencher in the photooxidation of tryptophan, *Environ. Sci. Technol.*, 2014, **48**(9), 4916–4924.
- 77 E. M. Janssen, E. Marron and K. McNeill, Aquatic photochemical kinetics of benzotriazole and structurally related compounds, *Environ. Sci.: Processes Impacts*, 2015, **17**(5), 939–946.
- 78 J. J. Guerard and Y.-P. Chin, Photodegradation of ormetoprim in aquaculture and stream-derived dissolved organic matter, *J. Agric. Food Chem.*, 2012, **60**(39), 9801–9806.
- 79 S. Canonica, U. Jans, K. Stemmler and J. Hoigné, Transformation kinetics of phenols in water: photosensitization by dissolved natural organic material and aromatic ketones, *Environ. Sci. Technol.*, 1995, **29**(7), 1822–1831.
- 80 J.-P. Aguer and C. Richard, Humic substances mediated phototransformation of 2,4,6-trimethylphenol: a catalytic reaction, *Photochem. Photobiol. Sci.*, 2005, **4**(6), 451–453.
- 81 S. Halladja, A. Ter Halle, J.-P. Aguer, A. Boulkamh and C. Richard, Inhibition of humic substances mediated photooxygenation of furfuryl alcohol by 2,4,6-trimethylphenol. Evidence for reactivity of the phenol with humic triplet excited states, *Environ. Sci. Technol.*, 2007, **41**(17), 6066–6073.
- 82 Y.-P. Chin, P. L. Miller, L. Zeng, K. Cawley and L. K. Weavers, Photosensitized degradation of bisphenol A by dissolved organic matter, *Environ. Sci. Technol.*, 2004, **38**(22), 5888–5894.
- 83 M. Zhan, X. Yang, Q. Xian and L. Kong, Photosensitized degradation of bisphenol A involving reactive oxygen species in the presence of humic substances, *Chemosphere*, 2006, **63**(3), 378–386.
- 84 S. Qu, E. P. Kolodziej and D. M. Cwiertny, Phototransformation rates and mechanisms for synthetic hormone growth promoters used in animal agriculture, *Environ. Sci. Technol.*, 2012, **46**(24), 13202–13211.
- 85 M. M. Kelly and W. A. Arnold, Direct and indirect photolysis of the phytoestrogens genistein and daidzein, *Environ. Sci. Technol.*, 2012, **46**(10), 5396–5403.
- 86 D. R. Weinberg, C. J. Gagliardi, J. F. Hull, C. F. Murphy, C. A. Kent, B. C. Westlake, A. Paul, D. H. Ess, D. G. McCafferty and T. J. Meyer, Proton-coupled electron transfer, *Chem. Rev.*, 2012, **112**(7), 4016–4093.
- 87 D. Eskiköy, Z. Durmuş and E. Kiliç, Electrochemical oxidation of atorvastatin and its adsorptive stripping determination in pharmaceutical dosage forms and biological fluids, *Collect. Czech. Chem. Commun.*, 2012, **76**(12), 1633–1649.
- 88 Y. Chen, C. Hu, X. Hu and J. Qu, Indirect photodegradation of amine drugs in aqueous solution under simulated sunlight, *Environ. Sci. Technol.*, 2009, **43**(8), 2760–2765.
- 89 Y. Chen, H. Li, Z. Wang, H. Li, T. Tao and Y. Zuo, Photodegradation of selected  $\beta$ -blockers in aqueous fulvic acid solutions: kinetics, mechanism, and product analysis, *Water Res.*, 2012, **46**(9), 2965–2972.
- 90 S. Canonica, T. Kohn, M. Mac, F. J. Real, J. Wirz and U. von Gunten, Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds, *Environ. Sci. Technol.*, 2005, **39**(23), 9182–9188.
- 91 E. De Laurentiis, M. Minella, V. Maurino, C. Minero, G. Mailhot, M. Sarakha, M. Brigante and D. Vione, Assessing the occurrence of the dibromide radical ( $\text{Br}_2^{\cdot-}$ ) in natural waters: measures of triplet-sensitized formation, reactivity, and modelling, *Sci. Total Environ.*, 2012, **439**, 299–306.
- 92 M. Brigante, M. Minella, G. Mailhot, V. Maurino, C. Minero and D. Vione, Formation and reactivity of the dichloride radical ( $\text{Cl}_2^{\cdot-}$ ) in surface waters: a modelling approach, *Chemosphere*, 2014, **95**, 464–469.
- 93 C. R. Lambert and I. E. Kochevar, Electron transfer quenching of the rose bengal triplet state, *Photochem. Photobiol.*, 1997, **66**(1), 15–25.
- 94 W. H. Koppenol, D. M. Stanbury and P. L. Bounds, Electrode potentials of partially reduced oxygen species, from dioxygen to water, *Free Radical Biol. Med.*, 2010, **49**(3), 317–322.
- 95 W. J. Cooper, R. G. Zika, R. G. Petasne and J. M. Plane, Photochemical formation of hydrogen peroxide in natural waters exposed to sunlight, *Environ. Sci. Technol.*, 1988, **22**(10), 1156–1160.
- 96 L. C. Powers and W. L. Miller, Blending remote sensing data products to estimate photochemical production of hydrogen peroxide and superoxide in the surface ocean, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 792–806.
- 97 D. J. Kieber, G. W. Miller, P. J. Neale and K. Mopper, Wavelength and temperature-dependent apparent





- quantum yields for photochemical formation of hydrogen peroxide in seawater, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 777–791.
- 98 C. M. Sharpless and N. V. Blough, The importance of charge-transfer interactions in determining chromophoric dissolved organic matter (CDOM) optical and photochemical properties, *Environ. Sci.: Processes Impacts*, 2014, **16**(4), 654–671.
  - 99 N. M. Scully, D. J. McQueen, D. R. S. Lean and W. J. Cooper, Photochemical formation of hydrogen peroxide in lakes: effects of dissolved organic carbon and ultraviolet radiation, *Can. J. Fish. Aquat. Sci.*, 1995, **52**(12), 2675–2681.
  - 100 Y. Zhang and N. V. Blough, Photoproduction of one-electron reducing intermediates by chromophoric dissolved organic matter (CDOM): relation to  $O_2^-$  and  $H_2O_2$  photoproduction and CDOM photooxidation, *Environ. Sci. Technol.*, DOI: 10.1021/acs.est.6b02919.
  - 101 R. G. Petasne and R. G. Zika, Fate of superoxide in coastal sea water, *Nature*, 1987, **325**, 516–518.
  - 102 S. Garg, A. L. Rose and T. D. Waite, Photochemical production of superoxide and hydrogen peroxide from natural organic matter, *Geochim. Cosmochim. Acta*, 2011, **75**(15), 4310–4320.
  - 103 Y. Zhang, K. A. Simon, A. A. Andrew, R. Del Vecchio and N. V. Blough, Enhanced photoproduction of hydrogen peroxide by humic substances in the presence of phenol electron donors, *Environ. Sci. Technol.*, 2014, **48**(21), 12679–12688.
  - 104 D. R. Letourneau, C. G. Gill and E. T. Krogh, Photosensitized degradation kinetics of trace halogenated contaminants in natural waters using membrane introduction mass spectrometry as an *in situ* reaction monitor, *Photochem. Photobiol. Sci.*, 2015, **14**(11), 2108–2118.
  - 105 L. Eberson, *Electron transfer reactions in organic chemistry*, Springer-Verlag, 1987.
  - 106 S. Canonica, B. Hellrung and J. Wirz, Oxidation of phenols by triplet aromatic ketones in aqueous solution, *J. Phys. Chem. A*, 2000, **104**(6), 1226–1232.
  - 107 D. Rehm and A. Weller, Kinetics of fluorescence quenching by electron and H-atom transfer, *Isr. J. Chem.*, 1970, **8**(2), 259–271.
  - 108 S. Farid, J. P. Dinnocenzo, P. B. Merkel, R. H. Young and D. Shukla, Bimolecular Electron Transfers That Follow a Sandros–Boltzmann Dependence on Free Energy, *J. Am. Chem. Soc.*, 2011, **133**(13), 4791–4801.
  - 109 S. Farid, J. P. Dinnocenzo, P. B. Merkel, R. H. Young, D. Shukla and G. Guirado, Reexamination of the Rehm–Weller data set reveals electron transfer quenching that follows a Sandros–Boltzmann dependence on free energy, *J. Am. Chem. Soc.*, 2011, **133**(30), 11580–11587.
  - 110 P. R. Erickson, N. Walpen, J. J. Guerard, S. N. Eustis, J. S. Arey and K. McNeill, Controlling factors in the rates of oxidation of anilines and phenols by triplet methylene blue in aqueous solution, *J. Phys. Chem. A*, 2015, **119**(13), 3233–3243.
  - 111 F. Rosario-Ortiz and S. Canonica, Probe molecules to assess the photochemical activity of natural organic matter, *Environ. Sci. Technol.*, in revision.
  - 112 K. Sandros, Transfer of triplet state energy in fluid solutions III. Reversible energy transfer, *Acta Chem. Scand.*, 1964, **18**(10), 2355–2374.
  - 113 V. Balzani, F. Bolletta and F. Scandola, Vertical and “nonvertical” energy transfer processes. A general classical treatment, *J. Am. Chem. Soc.*, 1980, **102**(7), 2152–2163.
  - 114 I. Loeff, J. Rabani, A. Treinin and H. Linschitz, Charge transfer and reactivity of  $n\pi^*$  and  $\pi\pi^*$  organic triplets, including anthraquinonesulfonates, in interactions with inorganic anions: a comparative study based on classical Marcus theory, *J. Am. Chem. Soc.*, 1993, **115**(20), 8933–8942.
  - 115 W. H. Koppenol and J. F. Liebman, The oxidizing nature of the hydroxyl radical. A comparison with the ferryl ion ( $FeO^{2+}$ ), *J. Phys. Chem.*, 1984, **88**(1), 99–101.
  - 116 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $^{\bullet}OH/^{\bullet}O^-$ ) in aqueous solution, *J. Phys. Chem. Ref. Data*, 1988, **17**(2), 513–886.
  - 117 H. A. Schwarz, Free radicals generated by radiolysis of aqueous solutions, *J. Chem. Educ.*, 1981, **58**(2), 101.
  - 118 A. Pochon, P. P. Vaughan, D. Gan, P. Vath, N. V. Blough and D. E. Falvey, Photochemical oxidation of water by 2-methyl-1,4-benzoquinone: evidence against the formation of free hydroxyl radical, *J. Phys. Chem. A*, 2002, **106**(12), 2889–2894.
  - 119 D. Gan, M. Jia, P. P. Vaughan, D. E. Falvey and N. V. Blough, Aqueous photochemistry of methyl-benzoquinone, *J. Phys. Chem. A*, 2008, **112**(13), 2803–2812.
  - 120 S. E. Page, W. A. Arnold and K. McNeill, Assessing the contribution of free hydroxyl radical in organic matter-sensitized photohydroxylation reactions, *Environ. Sci. Technol.*, 2011, **45**(7), 2818–2825.
  - 121 O. Brahmia and C. Richard, Phototransformation of 1,4-naphthoquinone in aqueous solution, *Photochem. Photobiol. Sci.*, 2003, **2**(10), 1038–1043.
  - 122 H. Görner, Photoprocesses of *p*-benzoquinones in aqueous solution, *J. Phys. Chem. A*, 2003, **107**(51), 11587–11595.
  - 123 J. von Sonntag, E. Mvula, K. Hildenbrand and C. von Sonntag, Photohydroxylation of 1,4-Benzoquinone in Aqueous Solution Revisited, *Chem.–Eur. J.*, 2004, **10**(2), 440–451.
  - 124 D. Vione, M. Ponzo, D. Bagnus, V. Maurino, C. Minero and M. E. Carloti, Comparison of different probe molecules for the quantification of hydroxyl radicals in aqueous solution, *Environ. Chem. Lett.*, 2010, **8**(1), 95–100.
  - 125 P. R. Maddigapu, A. Bedini, C. Minero, V. Maurino, D. Vione, M. Brigante, G. Mailhot and M. Sarakha, The pH-dependent photochemistry of anthraquinone-2-sulfonate, *Photochem. Photobiol. Sci.*, 2010, **9**(3), 323–330.
  - 126 J. Wenk, S. N. Eustis, K. McNeill and S. Canonica, Quenching of excited triplet states by dissolved natural organic matter, *Environ. Sci. Technol.*, 2013, **47**(22), 12802–12810.



- 127 J. Ma, R. Del Vecchio, K. S. Golanoski, E. S. Boyle and N. V. Blough, Optical properties of humic substances and CDOM: effects of borohydride reduction, *Environ. Sci. Technol.*, 2010, **44**(14), 5395–5402.
- 128 K. S. Golanoski, S. Fang, R. Del Vecchio and N. V. Blough, Investigating the mechanism of phenol photooxidation by humic substances, *Environ. Sci. Technol.*, 2012, **46**(7), 3912–3920.
- 129 K. Pratibha, Poonam and S. M. S. Chauhan, Efficient cobalt(II) phthalocyanine-catalyzed reduction of flavones with sodium borohydride, *Chem. Commun.*, 2009, **42**, 6397–6399.
- 130 S. Canonica and M. Freiburghaus, Electron-rich phenols for probing the photochemical reactivity of freshwaters, *Environ. Sci. Technol.*, 2001, **35**(4), 690–695.
- 131 J. N. Moore, D. Phillips, N. Nakashima and K. Yoshihara, Photophysics and photochemistry of sulphonated derivatives of 9,10-anthraquinone. “Strong” versus “weak” sensitizers, *J. Chem. Soc., Faraday Trans. 2*, 1987, **83**(8), 1487–1508.
- 132 A. P. Darmanyan and C. S. Foote, Solvent effects on singlet oxygen yield from  $n\pi^*$  and  $\pi\pi^*$  triplet carbonyl compounds, *J. Phys. Chem.*, 1993, **97**(19), 5032–5035.
- 133 K. Gollnick, T. Franken, G. Schade and G. Dörhöfer, Photosensitized oxygenation as a function of the triplet energy of sensitizers, *Ann. N. Y. Acad. Sci.*, 1970, **171**(1), 89–107.
- 134 L. C. Bodhipaksha, C. M. Sharpless, Y.-P. Chin, M. Sander, W. K. Langston and A. A. MacKay, Triplet Photochemistry of Effluent and Natural Organic Matter in Whole Water and Isolates from Effluent-Receiving Rivers, *Environ. Sci. Technol.*, 2015, **49**(6), 3453–3463.
- 135 J. J. Guerard, P. L. Miller, T. D. Trouts and Y.-P. Chin, The role of fulvic acid composition in the photosensitized degradation of aquatic contaminants, *Aquat. Sci.*, 2009, **71**(2), 160–169.
- 136 P. R. Tentscher, S. N. Eustis, K. McNeill and J. S. Arey, Aqueous oxidation of sulfonamide antibiotics: aromatic nucleophilic substitution of an aniline radical cation, *Chem.–Eur. J.*, 2013, **19**(34), 11216–11223.
- 137 J. Wenk, U. Von Gunten and S. Canonica, Effect of dissolved organic matter on the transformation of contaminants induced by excited triplet states and the hydroxyl radical, *Environ. Sci. Technol.*, 2011, **45**(4), 1334–1340.
- 138 J. Wenk and S. Canonica, Phenolic antioxidants inhibit the triplet-induced transformation of anilines and sulfonamide antibiotics in aqueous solution, *Environ. Sci. Technol.*, 2012, **46**(10), 5455–5462.
- 139 Y. A. Ilan, G. Czapski and D. Meisel, The one-electron transfer redox potentials of free radicals. I. The oxygen/superoxide system, *Biochim. Biophys. Acta, Bioenerg.*, 1976, **430**(2), 209–224.
- 140 J. Goodman and L. E. Brus, Distant intramolecular interaction between identical chromophores: the  $n-\pi^*$  excited states of *p*-benzoquinone, *J. Chem. Phys.*, 1978, **69**(4), 1604–1612.
- 141 A. E. Alegria, A. Ferrer, G. Santiago, E. Sepúlveda and W. Flores, Photochemistry of water-soluble quinones. Production of the hydroxyl radical, singlet oxygen and the superoxide ion, *J. Photochem. Photobiol., A*, 1999, **127**(1), 57–65.
- 142 I. Loeff, S. Goldstein, A. Treinin and H. Linschitz, Interactions of formate ion with triplets of anthraquinone-2-sulfonate, 1,4-naphthoquinone, benzophenone-4-carboxylate and benzophenone-4-sulfonate, *J. Phys. Chem.*, 1991, **95**(11), 4423–4430.
- 143 T. Vo-Dinh and U. P. Wild, Luminescence of 1,4-naphthoquinone and the vitamin K system in Shpol'skii matrices at 4 K, *Spectrochim. Acta, Part A*, 1984, **40**(5), 411–418.
- 144 S. Hayano and M. Fujihira, The effect of water on the reduction potentials of some aromatic compounds in the DMF–water system, *Bull. Chem. Soc. Jpn.*, 1971, **44**(8), 2051–2055.
- 145 C. A. Parker and C. G. Hatchard, The possibilities of phosphorescence measurement in chemical analysis: tests with a new instrument, *Analyst*, 1962, **87**(1037), 664–676.
- 146 W. G. Herkstroeter, A. A. Lamola and G. S. Hammond, Mechanisms of Photochemical Reactions in Solution. XXVIII. 1 Values of Triplet Excitation Energies of Selected Sensitizers, *J. Am. Chem. Soc.*, 1964, **86**(21), 4537–4540.
- 147 I. Gutiérrez, S. G. Bertolotti, M. A. Biasutti, A. T. Soltermann and N. A. García, Quinones and hydroxyquinones as generators and quenchers of singlet molecular oxygen, *Can. J. Chem.*, 1997, **75**(4), 423–428.
- 148 J. Nafisi-Movaghar and F. Wilkinson, Photochemical reactions of duroquinone. Part 2—Flash photolytic investigations, *Trans. Faraday Soc.*, 1970, **66**, 2268–2278.
- 149 A. J. G. Barwise, A. A. Gorman, R. L. Leyland, P. G. Smith and M. A. J. Rodgers, A pulse radiolysis study of the quenching of aromatic carbonyl triplets by norbornadienes and quadricyclenes. The mechanism of interconversion, *J. Am. Chem. Soc.*, 1978, **100**(6), 1814–1820.
- 150 P. B. Merkel and J. P. Dinnocenzo, Thermodynamic energies of donor and acceptor triplet states, *J. Photochem. Photobiol., A*, 2008, **193**(2), 110–121.
- 151 W. M. Nau and J. C. Scaiano, Oxygen quenching of excited aliphatic ketones and diketones, *J. Phys. Chem.*, 1996, **100**(27), 11360–11367.
- 152 J. K. Hurley, H. Linschitz and A. Treinin, Interaction of halide and pseudohalide ions with triplet benzophenone-4-carboxylate: kinetics and radical yields, *J. Phys. Chem.*, 1988, **92**(18), 5151–5159.
- 153 P. J. Wagner, R. J. Truman, A. E. Puchalski and R. Wake, Extent of charge transfer in the photoreduction of phenyl ketones by alkylbenzenes, *J. Am. Chem. Soc.*, 1986, **108**(24), 7727–7738.
- 154 A. A. Gorman and M. A. J. Rodgers, The quenching of aromatic ketone triplets by oxygen: competing singlet oxygen and biradical formation?, *J. Am. Chem. Soc.*, 1986, **108**(17), 5074–5078.



- 155 R. A. Day Jr and R. E. Biggers, Polarography of *p*-Chlorobenzophenone and Xanthone, *J. Am. Chem. Soc.*, 1953, **75**(3), 738–739.
- 156 Y. E. Orlov, Polarography of Coumarins (Chromen-2-ones), *Russ. Chem. Rev.*, 1977, **46**(7), 671.
- 157 W. W. Mantulin and P.-S. Song, Excited states of skin-sensitizing coumarins and psoralens. Spectroscopic studies, *J. Am. Chem. Soc.*, 1973, **95**(16), 5122–5129.
- 158 T. A. Geissman and S. L. Friess, Flavanones and related compounds. VI. The polarographic reduction of some substituted chalcones, flavones and flavanones, *J. Am. Chem. Soc.*, 1949, **71**(12), 3893–3902.
- 159 S. Criado, S. G. Bertolotti, A. T. Soltermann, V. Avila and N. A. Garcia, Effect of flavonoids on the photooxidation of fats. A study on their activity as singlet molecular oxygen [ $O_2(^1\Delta)$ ] generators and quenchers, *Fat Sci. Technol.*, 1995, **97**(7–8), 265–269.
- 160 M. Tsuda, S. Oikawa and R. Miyake, Phosphorescence and Excitation Spectra of Cinnamic Acid, *Bull. Soc. Sci. Photogr. Jpn.*, 1972, **35**(2), 90–93.
- 161 R. S. Ruoff, K. M. Kadish, P. Boulas and E. C. M. Chen, Relationship between the electron affinities and half-wave reduction potentials of fullerenes, aromatic hydrocarbons, and metal complexes, *J. Phys. Chem.*, 1995, **99**(21), 8843–8850.
- 162 D. S. McClure, Triplet–Singlet Transitions in Organic Molecules. Lifetime Measurements of the Triplet State, *J. Chem. Phys.*, 1949, **17**(10), 905–913.
- 163 A. A. Abdel-Shafi and F. Wilkinson, Charge transfer effects on the efficiency of singlet oxygen production following oxygen quenching of excited singlet and triplet states of aromatic hydrocarbons in acetonitrile, *J. Phys. Chem. A*, 2000, **104**(24), 5747–5757.
- 164 S. Wawzonek and H. A. Laitinen, The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. II. Aromatic Polynuclear Hydrocarbons, *J. Am. Chem. Soc.*, 1942, **64**(10), 2365–2368.
- 165 W. G. Herkstroeter and G. S. Hammond, Mechanisms of Photochemical Reactions in Solution. XXXIX. 1 Study of Energy Transfer by Kinetic Spectrophotometry, *J. Am. Chem. Soc.*, 1966, **88**(21), 4769–4777.
- 166 P. Wardman, Reduction potentials of one-electron couples involving free radicals in aqueous solution, *J. Phys. Chem. Ref. Data*, 1989, **18**(4), 1637–1755.
- 167 I. Loeff, A. Treinin and H. Linschitz, Photochemistry of 9,10-anthraquinone-2-sulfonate in solution. 1. Intermediates and mechanism, *J. Phys. Chem.*, 1983, **87**(14), 2536–2544.
- 168 P. F. Heelis, B. J. Parsons, G. O. Phillips, E. J. Land and A. J. Swallow, Pulse-radiolysis study of the effect of pH on the one-electron reduction potentials of lumichrome derivatives, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**(5), 1225–1235.
- 169 R. W. Chambers and D. R. Kearns, Triplet states of some common photosensitizing dyes, *Photochem. Photobiol.*, 1969, **10**(3), 215–219.
- 170 C. K. Remucal and K. McNeill, Photosensitized amino acid degradation in the presence of riboflavin and its derivatives, *Environ. Sci. Technol.*, 2011, **45**(12), 5230–5237.
- 171 D. Meisel and P. Neta, One-electron reduction potential of riboflavine studied by pulse radiolysis, *J. Phys. Chem.*, 1975, **79**(23), 2459–2461.
- 172 S. O. Kelley, J. K. Barton, N. M. Jackson and M. G. Hill, Electrochemistry of methylene blue bound to a DNA-modified electrode, *Bioconjugate Chem.*, 1997, **8**(1), 31–37.
- 173 R. W. Redmond and J. N. Gamlin, A compilation of singlet oxygen yields from biologically relevant molecules, *Photochem. Photobiol.*, 1999, **70**(4), 391–475.
- 174 P. Beckmann, A Polarographic Investigation of Perinaphthenone, *Aust. J. Chem.*, 1961, **14**(2), 229–236.
- 175 A. J. Wain, L. Drouin and R. G. Compton, Voltammetric reduction of perinaphthenone in aqueous and non-aqueous media: an electrochemical ESR investigation, *J. Electroanal. Chem.*, 2006, **589**(1), 128–138.
- 176 T. Okutsu, S. Noda, S. Tanaka, A. Kawai, K. Obi and H. Hiratsuka, Nature of excited singlet and non-phosphorescent triplet states of perinaphthenone, *J. Photochem. Photobiol., A*, 2000, **132**(1), 37–41.

