Experimental methodology to measure the reaction rate constants of processes sensitised by the triplet state of 4-carboxybenzophenone as proxy of the triplet states of chromophoric dissolved organic matter, under steady-state irradiation conditions

Marco Minella, a Lorenzo Rapa, a Luca Carena, a Marco Pazzi, a Valter Maurino, a Claudio Minero, a Marcello Brigante, b Davide Vione a,*

a Dipartimento di Chimica, Università di Torino, Via Pietro Giuria 5, 10125 Torino, Italy.
b Université Clermont Auvergne, CNRS, Sigma Clermont, Institut de Chimie de Clermont-Ferrand, F-63000 Clermont-Ferrand, France.

* Corresponding author. Tel. +39-011-6705296; Fax +39-011-6705242; E-mail: davide.vione@unito.it
Figure ESI1. Raw laser flash photolysis traces representing the decay of the triplet state of 4-carboxybenzophenone ($^3$CBBP*) in the presence of different FFA concentration values (varied in the range of 0-0.25 mmol L$^{-1}$). The laser emission wavelength was 266 nm (energy of 35-40 mJ pulse$^{-1}$), while $^3$CBBP* was detected at 550 nm.
Figure ESI2. Pseudo-first order decay constant of the excited triplet state of 4-carboxybenzophenone ($k_{\text{CBBP}*}$) as a function of the concentrations of quenchers: (a) oxygen, (b) phenol, (c) furfuryl alcohol (FFA), and (d) sodium azide, NaN$_3$ (Stern-Volmer plots). The concentration of oxygen was calculated on the basis of its water solubility at 25°C, for the three studied systems that were purged with Ar (no oxygen), equilibrated with air, and purged with pure oxygen. The $^3$CBBP* quenching rate constant in aerated solution in the absence of quenchers ($k_{\text{CBBP*}} = 6 \times 10^5$ s$^{-1}$) was derived as the average of the $k_{\text{CBBP*}}$ experimental values obtained with CBBP alone in aerated solution. The rate constant $k_{\text{CBBP*}}$ represents the deactivation kinetics of $^3$CBBP* by the joint processes of oxygen quenching and internal conversion. The value of the $^3$CBBP* deactivation rate constant in the absence of oxygen ($k_{\text{CBBP*},\Delta} = 2 \times 10^5$ s$^{-1}$) represents the $^3$CBBP* deactivation kinetics by internal conversion alone. In each plot the solid line represents the least-squares fit, while the dotted curves are the 95% confidence intervals of the fit.
**Figure ESI3.** Extracted ion chromatogram (m/z = 186) of a concentrated CH$_2$Cl$_2$ extract of a solution containing 66 µmol L$^{-1}$ 4-carboxybenzophenone (CBBP) and 100 µmol L$^{-1}$ phenol, irradiated for 8 h. Authentic standards were available for 2,2'-dihydroxybiphenyl, 4,4'-dihydroxybiphenyl and 4-phenoxyphenol, for which reliable identification could be achieved. Standard availability is highlighted as (STD) on the plot. In the cases of 2-phenoxyphenol and of 2,4'-dihydroxybiphenyl, tentative identification was carried out on the basis of mass spectra and chromatographic retention times (phenoxyphenols appeared to have shorter retention times than dihydroxybiphenyls, and the compound tentatively identified as 2,4'-dihydroxybiphenyl had intermediate retention time compared to 2,2' - and 4,4'-dihydroxybiphenyl).
Figure ESI4. MS spectrum of 4-carboxybenzophenone, and comparison with the library spectrum.
Figure ESI5. MS spectrum of 2,2'-dihydroxybiphenyl, and comparison with the library spectrum.
Figure ESI6. MS spectrum of 4,4'-dihydroxybiphenyl, and comparison with the library spectrum.
Figure ESI7. MS spectrum of 4-phenoxyphenol, and comparison with the library spectrum.
Figure ESI8. (a) Time trends of furfuryl alcohol (FFA, initial concentration 0.2-1.0 mmol L\(^{-1}\)) irradiated under the Philips TL-K 05 lamp in the presence of 66 µmol L\(^{-1}\) CBBP in H\(_2\)O. The experimental data were fitted with an exponential function with residual 
\[ \frac{C_i}{C_o} = 1 + A(e^{-kt} - 1) \].

(b) Time trends of FFA (initial concentration 0.1 mmol L\(^{-1}\)) irradiated under the Philips TL-K 05 lamp in the presence of 83 µmol L\(^{-1}\) CBBP, in both H\(_2\)O and D\(_2\)O. Each run was carried out in duplicate and the results of both couples of experiments are shown, with excellent agreement.
Figure ESI9. Time trends of FFA (left Y-axis, red circles, $C_0 = 0.1 \text{ mmol L}^{-1}$), furfural (right Y-axis, blue squares, peak area) and benzaldehyde (insert, peak area) upon irradiation of FFA in the presence of 66 µmol L$^{-1}$ CBBP.

Figure ESI10. GC-MS chromatogram of a solution containing 1 mmol L$^{-1}$ FFA and 66 µmol L$^{-1}$ CBBP, irradiated for 8h.
Figure ESI11. Experimental mass spectrum of FFA, compared with the spectral library.

Figure ESI12. Experimental mass spectrum of furfural, compared with the spectral library.
Figure ES113. Experimental mass spectrum of benzaldehyde, compared with the spectral library.
Figure ESI14. Time trends of FFA (initial concentration 0.2 mmol L$^{-1}$) upon irradiation in the presence of 66 μmol L$^{-1}$ CBBP, in air-equilibrated conditions as well as under N$_2$ and O$_2$ atmosphere.