

Electronic Supporting Information

Study of the Fenton-mediated Oxidation of Methylene Blue - Cucurbit[*n*]uril Complexes

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1. Absorption spectra for MB⁺ during oxidation by the Fenton process in the dark

The evolution of the absorption spectrum for MB⁺ in the absence of CB[*n*] during the Fenton-mediated oxidation is shown on figure S1.

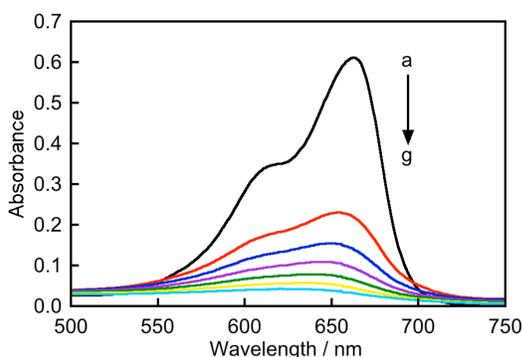


Figure S1. Absorption spectra for MB⁺ (8.3 μM) during oxidation by the Fenton process in the dark. Samples were measured after 0 (a), 5 min (b), 10 min (c), 15 min (d), 20 min (e), 25 min (f) and 30 min (g). Experimental conditions: [Fe²⁺] = 20 μM, [H₂O₂] = 500 μM, pH = 3.0.

2. Absorption spectra for MB⁺ in the presence of CB[7] during oxidation by the Fenton process in the dark

The evolution of the absorption spectrum for MB⁺ in the presence of CB[7] during the Fenton-mediated oxidation is shown on figure S2.

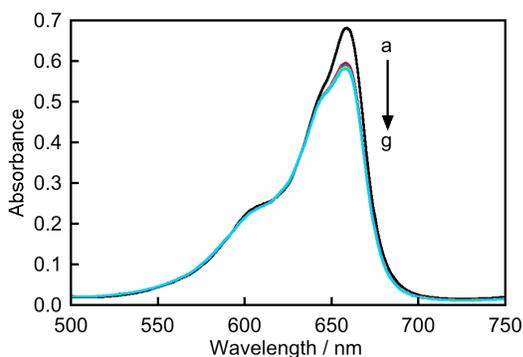


Figure S2. Absorption spectra for MB⁺ (8.3 μM) in the presence of CB[7] (100 μM) during oxidation by the Fenton process in the dark. Samples were measured after 0 (a), 5 min (b), 10 min (c), 15 min (d), 20 min (e), 25 min (f) and 30 min (g). Experimental conditions: [Fe²⁺] = 20 μM, [H₂O₂] = 500 μM, pH = 3.0.

3. Absorption spectra for MB⁺ in the presence of CB[8] during oxidation by the Fenton process in the dark

The evolution of the absorption spectrum for MB⁺ in the presence of CB[8] during the Fenton-mediated oxidation is shown on figure S3.

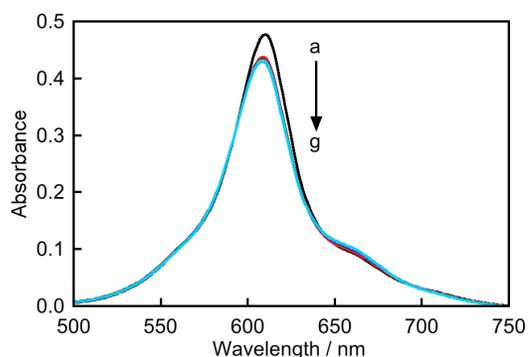


Figure S3. Absorption spectra for MB⁺ (8.3 μM) in the presence of CB[8] (100 μM) during oxidation by the Fenton process in the dark. Samples were measured after 0 (a), 5 min (b), 10 min (c), 15 min (d), 20 min (e), 25 min (f) and 30 min (g). Experimental conditions: [Fe²⁺] = 20 μM, [H₂O₂] = 500 μM, pH = 3.0.

4. Competitive kinetics analysis

The initial rate of MB⁺ oxidation in the absence of CB[7] is given by equation S1 ($k_1 = 2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$).

$$\frac{d[\text{MB}_{\text{ox}}^+]}{dt} = k_1 [\text{MB}^+][\text{HO}^*] \quad (\text{S1})$$

In the presence of CB[7], the reaction of HO^{*} radicals with CB[7] competes with the reaction of HO^{*} radicals with MB⁺. Assuming steady-state conditions for the concentration of HO^{*} radicals, the initial rate of MB⁺ oxidation in the presence of CB[7] is proportional to the fraction of HO^{*} radicals that react with MB⁺ (*f*). This fraction is given by equation S2, where *k*' corresponds to the apparent bimolecular rate constant for the reaction of HO^{*} radicals with CB[7].

$$f = \frac{k_1 [\text{MB}^+]_i}{k_1 [\text{MB}^+]_i + k' [\text{CB}[7]]_i} \quad (\text{S2})$$

Therefore, a linear relationship can be established between the inverse of the concentration of MB⁺ oxidized at initial times

and the concentration of CB[7] as written in equation S3, where b is a proportionality constant.

$$\frac{1}{[\text{MB}_{\text{ox}}^+]} = b \left(1 + \frac{k' [\text{CB}[7]]_i}{k_1 [\text{MB}^+]_i} \right) \quad (\text{S3})$$

From the plot of $1/[\text{MB}_{\text{ox}}^+]$ vs $[\text{CB}[7]]$ (see inset in figure 2 in the paper), we estimated that the value of the rate constant k' is $6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

5. Emission spectra for hydroxylated terephthalate in the absence and presence of CB[n]

The evolution of the emission spectra for hydroxylated terephthalate in the absence and presence of CB[n] is shown on figure S4.

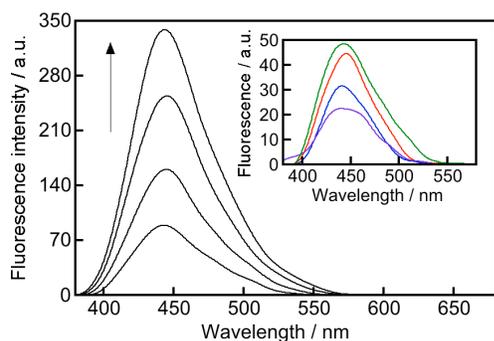


Figure S4. Emission spectra for hydroxylated terephthalate generated by the reaction of Fenton generated hydroxyl radicals with terephthalate. The arrow indicates the increase in the formation of the product at 5, 10, 15 and 20 min of reaction. Inset: Emission spectra for hydroxylated terephthalate generated after 20 min of reaction in the presence of CB[5] (red), CB[6] (blue), CB[7] (purple) and CB[8] (green). Experimental conditions: [Terephthalate] = 100 μM , $[\text{Fe}^{2+}] = 20 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 500 \mu\text{M}$, $\text{pH} = 3.0$, $\lambda_{\text{ex}} = 320 \text{ nm}$.

6. Control experiments irradiated in the visible region at lower irradiances

Samples were irradiated using a PTI equipment with a 150 W Xe lamp and the wavelength was selected with a monochromator. Samples containing MB^+ , $\text{MB}^+@\text{CB}[7]$ or $\text{MB}^+@\text{CB}[8]$ were irradiated at 664 nm, 659 nm or 610 nm, respectively. The irradiance was adjusted between 30-35 W m^{-2} according to the absorbance of the samples at the different irradiation wavelengths, so that the amount of absorbed photons was the same. The results show that MB^+ in the presence of CB[7] is degraded slowly over time, while for CB[8] there is no change in the oxidation with the irradiation. These results are consistent with the observations at higher irradiances using polychromatic visible light.

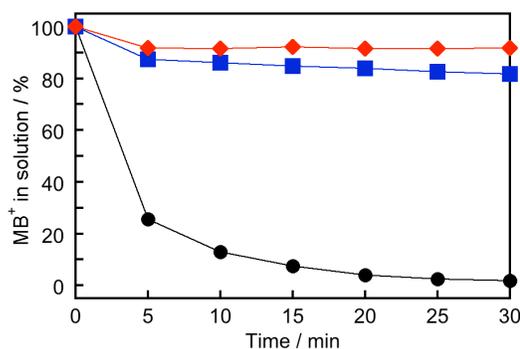
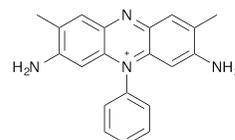


Figure S5. Oxidation of MB^+ (8.3 μM) by the photo-Fenton process with visible light (monochromatic) in the absence (black circles) or in the presence of CB[7] (blue squares) and CB[8] (red diamonds). The samples were irradiated at their absorption maxima. Experimental conditions: $[\text{Fe}^{2+}] = 20 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 500 \mu\text{M}$, $\text{CB}[7] = 100 \mu\text{M}$, $\text{CB}[8] = 100 \mu\text{M}$, $\text{pH} = 3.0$.

7. Binding of SF^+ to CB[7]

The structure for SF^+ is shown below on scheme S1.



Scheme S1. SF^+ structure.

The addition of 100 μM CB[7] to an 8.3 μM SF^+ solution showed no appreciable changes in the absorption or fluorescence spectra of the molecule, suggesting there is no formation of an inclusion complex at this concentration of the macrocycle. Weak interactions with SF^+ and/or the formation of an exclusion complex cannot be discarded.

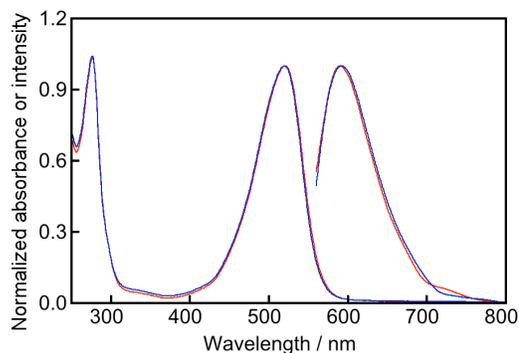


Figure S6. Absorption and fluorescence spectra for SF^+ (8.3 μM) in the absence (red) or presence (blue) of CB[7] (100 μM). The spectra are normalized to unity at the maxima for comparison.

8. Oxidation of SF^+ by the Fenton process under UVA light irradiation in the absence and presence of CB[7]

As can be seen in figure S7, the protection achieved for SF^+ is lower than for MB^+ , which is consistent with the results observed in the dark.

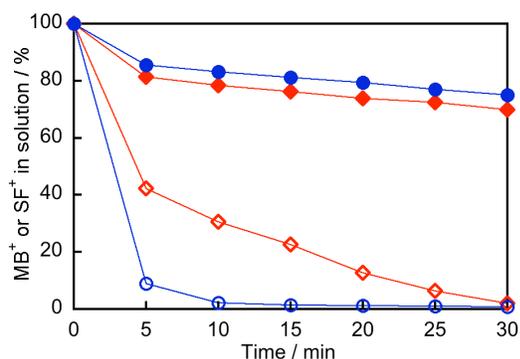


Figure S7. Oxidation of SF⁺ (8.3 μM) by the Fenton process irradiated with UVA light in the absence (open red diamonds) and presence of CB[7] (solid red diamonds). The data for MB⁺ in the absence (open blue circles) and presence of CB[7] (close blue circles) is included for comparison with SF⁺. Experimental conditions: [Fe²⁺] = 20 μM, [H₂O₂] = 500 μM, CB[7] = 100 μM, pH = 3.0.

9. Oxidation of a mixture of SF⁺ and MB⁺ by the Fenton process under UVA light irradiation in the absence and presence of CB[7]

Figure S8 shows that the protection achieved for SF⁺ in the mixture is lower than for MB⁺, similar to the behavior observed for the oxidation of each dye in separate solutions as shown above.

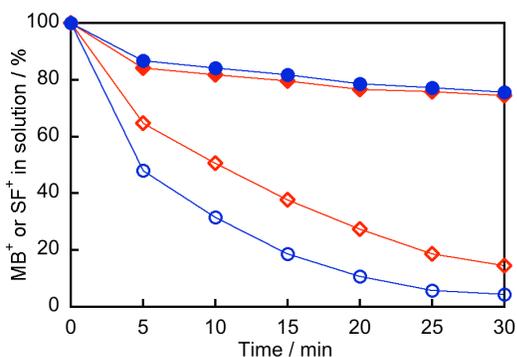


Figure S8. Fenton oxidation of a mixture of 8.3 μM MB⁺ (blue circles) and 8.3 μM SF⁺ (red diamonds) irradiated with UVA light in the absence (open symbols) or in the presence of CB[7] (solid symbols). Experimental conditions: [Fe²⁺] = 20 μM, [H₂O₂] = 500 μM, CB[7] = 100 μM, pH = 3.0.

10. Evaluation of the relative contributions from direct reaction of CB[7] with HO[•] radicals and the effect of encapsulation

Calculations of the fraction of dye oxidized at initial times were carried out from the data in figure 6 in the paper, under the particular conditions specified in the caption of the figure. The fraction of MB⁺ oxidized in the presence of CB[7] at 5 min of reaction is 6.4 times lower than in the absence of CB[7], which we can write as follows:

$$\frac{k_1 [\text{MB}^+]_i}{k_1 [\text{MB}^+]_i + k' [\text{CB}[7]]_i} = \frac{1}{6.4} \quad (\text{S4})$$

We can consider that k' corresponds to the sum of contributions from the reaction of CB[7] with HO[•] radicals (k'_r) and from the effect of encapsulation (k'_e).

On the other hand, the fraction of SF⁺ oxidized in the presence of CB[7] is 2.9 times lower than in the absence of CB[7], which we can write as follows:

$$\frac{k_2 [\text{SF}^+]_i}{k_2 [\text{SF}^+]_i + k'_r [\text{CB}[7]]_i} = \frac{1}{2.9} \quad (\text{S5})$$

In this case, only the contribution from the reaction of CB[7] with HO[•] radicals (k'_r) is considered since there is no encapsulation for SF⁺. Combining equations S4 and S5, we can write:

$$\frac{k'_r + k'_e}{k'_r} = \frac{5.4 k_1 [\text{MB}^+]_i}{1.9 k_2 [\text{SF}^+]_i} \quad (\text{S6})$$

Knowing that in the absence of CB[7], SF⁺ is oxidized 1.5 times slower than MB⁺ and that the initial concentrations of both dyes are the same (*i.e.* $k_1 = 1.5 k_2$), we can estimate the relative contributions of k'_r and k'_e . The contribution of k'_e is 3.3 times the contribution of k'_r indicating that encapsulation plays a major role in the protection of MB⁺ from oxidation.