Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Comparative Study of Singlet Oxygen Production by Photosensitiser Dyes Encapsulated in Silicone: Towards Rational Design of Antimicrobial Surfaces

Supplementary Information

Sacha Noimark, Enrico Salvadori, Rafael Gómez-Bombarelli, Alexander J. MacRobert, Ivan P. Parkin and Christopher W. M. Kay

Supplementary Information

1 DFT Studies

Table 1: TD-DFT singlet energies and experimental absorption wavelengths.

	Vertical Absorption (eV)						
	CAM-B3LYP	CAM-B3LYP	CAM-B3LYP	M062X	wB97xD	Experimental	
	Gas	PCM	PCM-Noneq	PCM	PCM	Solution	Catheter
TBO	2.72	2.29	2.67	2.29	2.28	1.97	2.01
AO	3.18	2.90	3.18	2.85	2.92	2.54	2.49
MB	2.64	2.22	2.60	2.20	2.20	1.88	1.91
CV	2.86	2.55	2.83	2.47	2.79	2.11	2.08
MG	2.75	2.34	2.71	2.27	2.36	2.02	2.00

Table 2: Ionisation potential and electron affinities with respect to the ground state B3LYP/cc-pVDZ.

	Energy (eV)			
	IP		EA	
	Gas	PCM	Gas	PCM
TBO	10.13	5.79	5.04	3.79
AO	9.78	5.54	4.22	2.96
MB	9.95	5.73	4.99	3.79
CV	9.08	5.43	4.27	3.29
MG	9.49	5.52	4.67	3.54

2 UV-Vis Spectroscopy

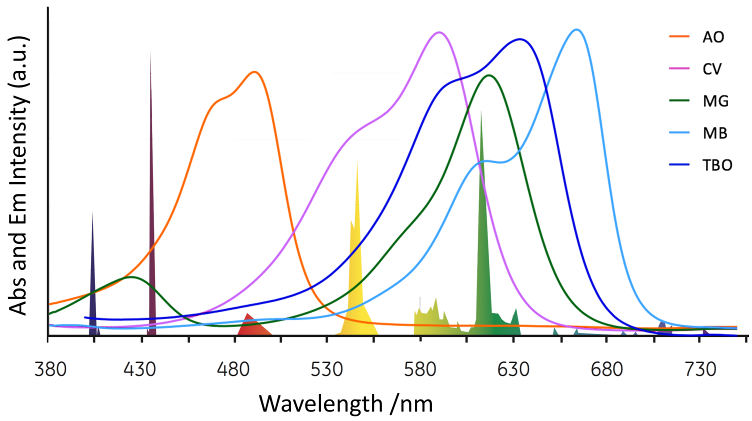

Figure 1: Hospital lighting emission spectrum of a 28 W fluorescent lamp overlayed to UV-Vis spectra of dye-encapsulated silicone polymers.

3 Singlet Oxygen Measurements

Equation 1 can be used to describe the key factors that determine the concentration of $^1O_2$ concentration, $[O_2(a^1\Delta_g)]$: [1]

$$[O_2(a^1\Delta_g)]_t \;=\; [^3\text{sens}^*]_0 \,\frac{k_\Delta^{O_2}\;[^3O_2]}{k_d^T \;+\; k_q^{O_2}\;[^3O_2]}\,\frac{\tau_\Delta}{\tau_T - \tau_\Delta}(e^{-t/\tau_T} - e^{-t/\tau_\Delta}) \qquad (1)$$

Where $k_{\Delta}^{O_2}$ is the rate constant of energy transfer between the excited triplet state of the photosensitiser and molecular oxygen, $k_{\mathrm{d}}^{\mathrm{T}}$ is the rate constant of the photosensitiser's triplet state decay by oxygen-independent processes, $k_{\mathrm{q}}^{O_2}$ is the rate constant for the photosensitiser's triplet state decay by quenching with molecular oxygen, τ_{T} is the photosensitiser triplet state lifetime and τ_{Δ} is the O_2 ($a^1\Delta_g$) lifetime.[1]

In Equation 1, [O_2 ($\mathrm{a}^1\Delta_g$)] is zero at time $t = 0$ after which the signal grows to a maximum, correlating to a steep rise in $^1O_2$ production upon laser excitation of the silicone encapsulated dye, preceding a decay. $^1O_2$ is a transient species; it is rapidly quenched, both chemically and physically, resulting in a decrease in the $^1O_2$ signal as a function of time.

References

[1] A. Jimenez-Banzo, X. Ragas, P. Kapusta and S. Nonell, *Photochemical & Photobiological Sciences*, 2008, **7**, 1003–1010.