Photophysical Characterization of Phenalenone Derivatives

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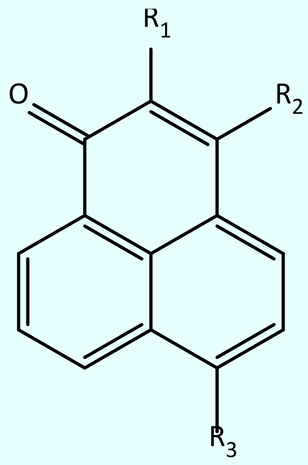
Introduction

Phenalenone has been extensively studied due to its photophysical behavior and because it can be used on interesting applications from the scientific and technological point of view, however fewer are the articles referring to the phenalenone derivatives as singlet oxygen generators. The incorporation of substituents on the phenalenone ring at fitterent positions rearranges the molecular electronic states changing its photophysical behavior. In order to rationalize the effect of the presence substituents on different positions of the phenalenone ring, we prepared and studied several derivatives and their corresponding hydroxyl precursor, and we have also included a benzoxazole ring as an electron-aceptor. Benzoxazole-phenalenone derivative shows a shifted absorption with a larger molar extinction coefficient when compared to the other phenalenones presented here, and shows $O_2(^1\Delta_g)$ quantum yields close to the unity in different solvents.



Molecule	R1	R2	R3
OXA2PN	Benzoxazole	-H	-H
3OHPN	-H	-OH	-H
3OEtPN	-H	-OEt	-H
6CGalPN	-H	$-O(CH_2)_6Gal$	-H
6CManPN	-H	$-O(CH_2)_6Man$	-H
6OHPN	-H	-H	-OH
6OEtPN	-H	-H	-OEt

Figure 1. Phenalenone derivatives studied in this work.

UV-Vis absorption and emission

Table 1. Molar extinction coefficients and maximum UV-Vis absorption wavelengths of studied phenalenone derivatives.

Solvent	ε / 10^3 $M^{-1}cm^{-1}$ (λ_{max} / nm)						
	3OHPN	3OEtPN	6CGalPN	6CManPNn	60HPN	6OEtPN	OXA2PN
Acetonitrile	9.0 (349)	12.7 (324)	11.0 (325)	11.4 (332)	5.8 (425)	9.7 (427)	17.5 (411)
Benzene	9.1 (334)	11.5 (351)	10.4 (332)	9.0 (332)	4.5 (428)	10.1 (422)	19.8 (411)
Chloroform	9.7 (333)	12.0 (328)	11.7 (329)	11.0 (329)	5.0 (440)	9.6 (433)	18.3 (417)
Methanol	11.3 (338)	12.9 (328)	12.3 (329)	13.7 (325)	4.5 (455)	9.2 (436)	15.9 (414)

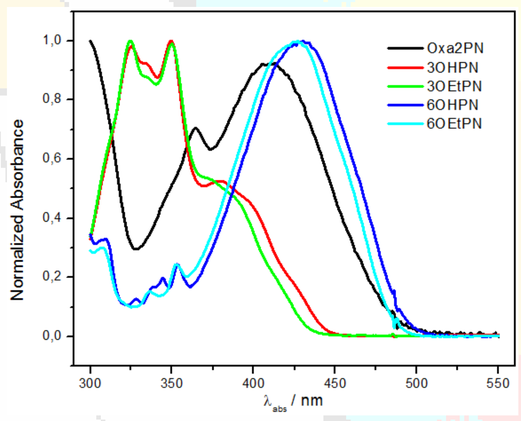


Figure 2. Normalized absorption spectra of the different phenalenone derivatives studied in this work

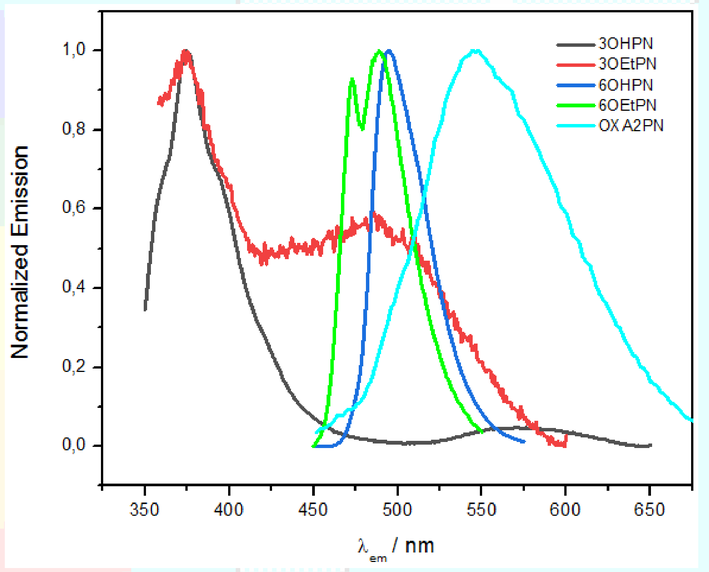


Figure 3. Normalized emission spectra of the different phenalenone derivatives studies in this work.

Singlet oxygen generation

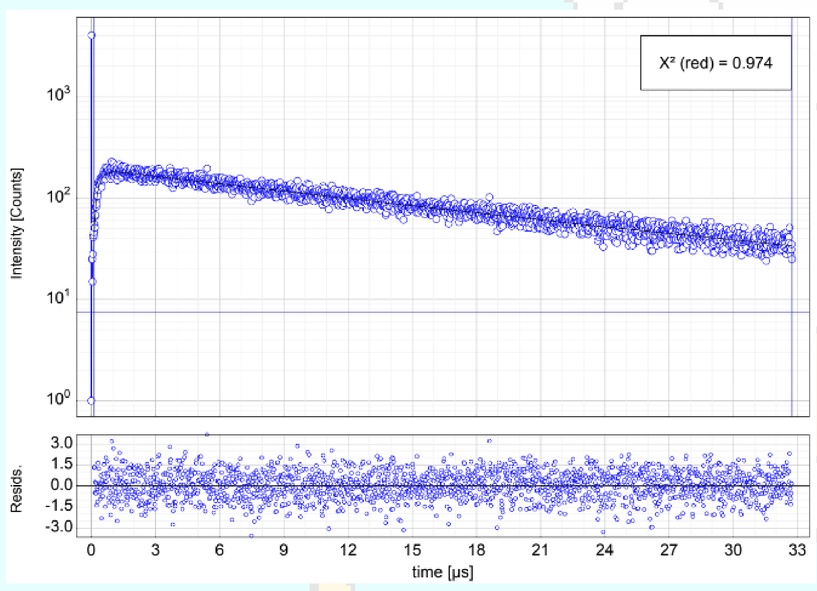


Figure 2. Time resolved infrared emission of $O_2(^1\Delta_g)$ (1270 nm) obtained upon excitation of **OXA2PN** at 355 nm in air-saturated toluene.

Table 2. $O_2(^1\Delta_g)$ quantum yields for PN derivatives in several solvents, determined values are referred to phenalenone as actinometer, with excitation at 355 nm under air.

Solvent	Φ_Δ						
	3OHPN	3OEtPN	6CGalPN	6CManPN	6OHPN	6OEtPN	OXA2PN
Acetonitrile	0.83 ± 0.06	0.52 ± 0.02	1.17 ± 0.11	1.01 ± 0.02	0.66 ± 0.03	0.62 ± 0.03	0.75 ± 0.04
Benzene	0.33 ± 0.01	0.74 ± 0.03	0.60 ± 0.02	0.61 ± 0.03	0.07 ± 0.01	0.86 ± 0.06	1.07 ± 0.07
Chloroform	0.65 ± 0.02	N.H.D.	N.H.D.	1.03 ± 0.05	0.16 ± 0.01	1.07 ± 0.09	0.88 ± 0.09

Table 3. Triplet lifetimes for PN derivatives in several solvents under air, determined from the growth of singlet oxygen emission.

Solvent	τ_T / ns					
	3OEtPN	6CGalPN	6CManPN	6OHPN	6OEtPN	OXA2PN
Acetonitrile	270	270	240	290	288	200
Benzene	346	300	330	328	301	167
Chloroform	407	N.H.D.	450	464	430	N.A.

Conclusion

As consequence of this study, we can state that the presence of benzoxazole, hydroxy and alkoxy substituents on the **PN** framework promotes significant changes on their photophysical properties and ground state behavior. For phenalenone derivatives with hydroxy or ethoxy substitution, as new deactivation pathways are opened, a lowered but still significative singlet oxygen generation quantum yield, is observed, but this behavior reverts with ethoxy chains. Benzoxazole-phenalenone derivatives acts like a electron-aceptor substituent and exhibits larger molar extinction coeffcients and shows $O_2(^1\Delta_g)$ quantum yields values close to the unit in different solvents. This benzoxazole based phenalenone could be used in the photosensitized singlet oxygen generation.

References

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