



Photophysical Characterization of Phenalenone Derivatives

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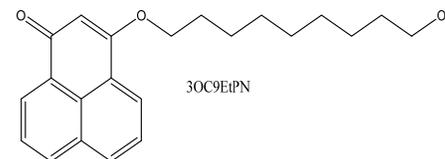
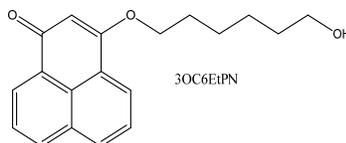
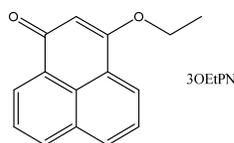
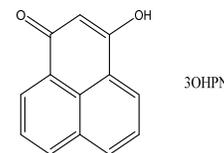
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Introduction

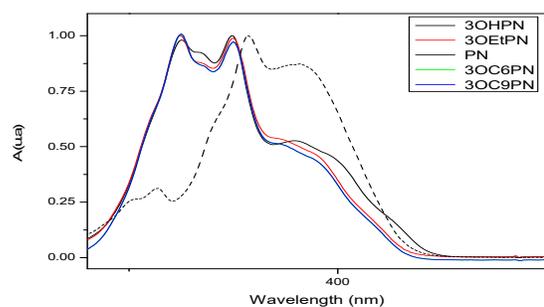
Phenalenone has been extensively studied due to its photophysical behavior and because it can be used on interesting applications from the scientific and technological point of view, however fewer are the articles referring to the phenalenone derivatives as singlet oxygen generators. The incorporation of substituents on the phenalenone ring rearranges the molecular electronic states changing its photophysical behavior. In order to rationalize the effect of the presence of electron-donor substituents on the position 3 of phenalenone ring, we prepared and studied several alkoxy derivatives and their corresponding hydroxyl precursor. Shorter alkyl chain on derivatives promotes a reduction of singlet oxygen quantum yield values compared with phenalenone. 3-Hydroxyphenalenone showed a low emission quantum yield with two emission bands, which can be related with equilibria between diketo and enol tautomers.



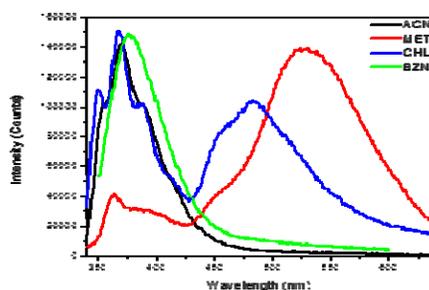
UV-Vis absorption and emission

Solvent	$\epsilon / 10^3 \text{ M}^{-1}\text{cm}^{-1} (\lambda_{\text{max}} / \text{nm})$			
	3OHPN	3OEtPN	3OC6PN	3OC9PN
Acetonitrile	9.0 (349)	12.7 (324)	10.8 (325)	10.2 (325)
Benzene	9.1 (334)	11.5 (351)	10.2 (326)	9.5 (351)
Chloroform	9.7 (333)	12.0 (328)	11.4 (328)	10.1 (329)
Methanol	11.3 (338)	12.9 (328)	12.0 (329)	11.5 (328)

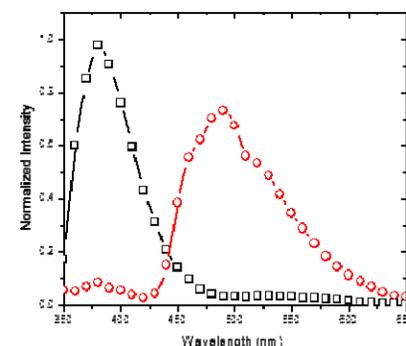
Molar extinction coefficients (ϵ , $10^3 \text{ M}^{-1}\text{cm}^{-1}$) of phenalenone derivatives. Standard error for the data was below 6%.



Normalized absorption spectra of PN and PN derivatives in ACN.



Emission spectra of 3-hydroxyphenalenone (3OHPN) in several solvents, excitation 330 nm.

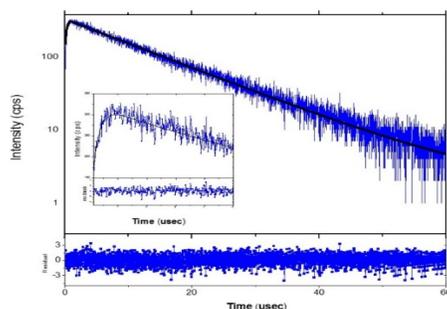


TRES showing two components in MET after excitation at 330 nm.

Lifetimes of singlet excited states of 3OHPN in several solvents, excited at 330 nm and two decays were fitted, at 375 and 500 nm. All lifetimes were obtained from fitting of at least 20 decays obtained in TRES mode. Standard error for the data is below 4%.

Solvent	Lifetime / ns			
	Air		Argon	
Acetonitrile	1.79		1.81	
Benzene	2.26		2.41	
Chloroform	1.07	0.17	1.10	0.20
Methanol	1.65	0.22	1.70	0.20

Singlet oxygen generation



Time resolved infrared emission of $\text{O}_2(^1\Delta_g)$ (1270 nm) obtained upon excitation of 3OHPN at 355 nm in air-saturated ethanol. Inset corresponds to initial scale of decay, fitting residuals are given.

$\text{O}_2(^1\Delta_g)$ quantum yields values 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	3OC6PN	3OC9PN
Acetonitrile	0.833 ± 0.062	0.519 ± 0.021	0.965 ± 0.072	0.975 ± 0.068
Benzene	0.332 ± 0.012	0.735 ± 0.032	0.935 ± 0.047	0.981 ± 0.055
Chloroform	0.655 ± 0.027	--	0.832 ± 0.045	0.602 ± 0.029

Solvent	τ_T / ns			
	3OHPN	3OEtPN	3OC6PN	3OC9PN
Acetonitrile		270	290	288
Benzene		346	328	301
Chloroform		407	464	430

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

Conclusion

As consequence of this study, we can state that the presence of hydroxy and alkoxy substituents on the PN framework promotes significant changes on their photophysical properties and ground state behavior. Fluorescence is modified when compared with the non-fluorescent phenalenone. Singlet excited state deactivation of these PN derivatives is mainly controlled by non-radiative processes (ISC to triplet excited state or IC to ground state singlet). 3OHPN, despite its low emission efficiency, shows two emission in several solvents, bands probably originated in the existence of a tautomeric equilibria in the first singlet excited state. For phenalenone derivatives with hydroxy or ethoxy substitution, as new deactivation pathways are opened, a lowered but still significant singlet oxygen generation quantum yield, is observed. This behavior reverts with longer alkyl chains with a terminal hydroxy group.

References

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Acknowledgments

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