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Phosphorescence and delayed fluorescence properties of fluorone dyes in bio-related films

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ABSTRACT

The phosphorescence and delayed fluorescence behaviour of the fluorone dyes disodium fluorescein (FL, uranine), 4,5-dibromofluorescein (DBF), eosin Y (EO), erythrosine B (ER), and rose bengal (RB) in bio-films of gelatine, starch, and chitosan at room temperature is studied. Phosphorescence and delayed fluorescence quantum yields and lifetimes were measured. The singlet–triplet dynamics is described and applied to the fluorone dyes for parameter extraction. For uranine films at room temperature no phosphorescence could be resolved. The efficiency of singlet–triplet intersystem crossing increased in the order ϕ_{ISC}(DBF) < ϕ_{ISC}(EO) < ϕ_{ISC}(ER) < ϕ_{ISC}(RB) due to the heavy atom effect on spin–orbit coupling. The phosphorescence quantum yields increased in the order ϕ_P(DBF) < ϕ_P(EO) < ϕ_P(RB) < ϕ_P(ER). The phosphorescence lifetimes followed the order τ_P(DBF) > τ_P(EO) > τ_P(ER) > τ_P(RB).

1. Introduction

Fluorone dyes are hydroxy-xanthene dyes (homologues of fluorescein). From this group the phosphorescence and delayed fluorescence behaviour of disodium fluorescein (uranine, FL), 4,5-dibromofluorescein (DBF), disodium-2,4,5,7-tetrabromofluorescein (eosin Y, EO), disodium-2,4,5,7-tetraiodofluorescein (erythrosine B, ER), and disodium-3′,4′,5′,6′-tetrachloro-2,4,5,7-tetraiodofluorescein (rose bengal, RB) in bio-films of gelatine, starch and chitosan is studied here. An absorption and fluorescence spectroscopic characterization of these fluorone dye doped bio-films was carried out previously [1].

The heavy-atom substituted fluorescein dyes with high quantum yield of triplet formation find application in the determination of rotational diffusion of macromolecules like proteins by phosphorescence depolarization measurement [2–4], in the concentration determination of phosphorescence quenchers like molecular oxygen and humidity by phosphorescence efficiency measurement [5–7], in optical limiting due to high effective third-order nonlinearity because of population accumulation in the triplet state [8–10], and in holographic recording [11–14].

Phosphorescence spectra measurements on fluorone dyes showed the occurrence of T_1–S_0 emission (phosphorescence) and time-delayed S_1–S_0 fluorescence (E-type delayed fluorescence [15,16]) due to thermal activated T_1–S_1 back intersystem crossing [3–6,17–20]. Phosphorescence decay time measurements on fluorone dyes in liquid solution revealed some concentration dependent lifetime shortening due to self-quenching (triplet–triplet annihilation, P-type delayed fluorescence [15,16]) [20,21]. The phosphorescence of aerobic liquid solutions is quenched by diffusion controlled dye-oxygen molecule collisions leading to singlet oxygen generation [15,16].

Reported data on the phosphorescence of the fluorone dyes studied here (wavelength of maximum phosphorescence emission $\lambda_{P,max}$, quantum yield of intersystem crossing ϕ_{ISC}, phosphorescence lifetime τ_P, phosphorescence quantum yield ϕ_P) in various liquid and solid hosts at room temperature and cryogenic temperatures are collected in Table 1. The table shows that the quantum yield of intersystem crossing and the quantum yield of phosphorescence rises with heavy atom substitution and the phosphorescence lifetimes shorten with heavy atom substitution. The phosphorescence efficiency increases with lowering the temperature, with changing from liquid solution to solid solution, and with de-aerating the samples (especially in the case of liquid solutions and porous sol–gel glasses).

In this paper for the selected fluorone dyes FL, DBF, EO, ER, and RB, fluorescence spectra, phosphorescence quantum distributions and quantum yields, delayed fluorescence quantum distributions and quantum yields, phosphorescence and delayed fluorescence lifetimes are measured. The phosphorescence and delayed fluorescence dynamics is described and applied to parameter extraction

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Table 1
Reported phosphorescence parameters of investigated fluorone dyes.

Dye	Solvent	T (K)	$\lambda_{P,max}$ (nm)	ϕ_{ISC}	τ_P (ms)	ϕ_P	Reference
FL							
	EPA	77	642	0.03			[31]
	EPA	80				0	[34]
	Ethanol	77	611		300	2.8×10^{-4}	[30]
	Ethanol, anaer	RT		0.035			[35]
	Ethanol, aer	RT		0.03			[36]
	Water, anaer	RT		0.032			[35]
	Water, pH 9, anaer	296		0.05			[37]
DBF							
	EPA	80	650		44	0.061	[34]
	PVA	RT	670		7.7	0.0024	[19]
	Ethanol, aer	RT		0.29			[36]
	Water, pH 9, anaer	296		0.49			[37]
EO							
	Glycerol	77			10.8	0.0553	[18]
	Glycerol	298			2.7	0.0124	[18]
	Ethanol	77			9.3	0.0224	[18]
	Ethanol	298			1.7	0.0039	[18]
	Ethanol	77	666		18.4		[38]
	Ethanol	77	641		30	0.017	[30]
	Water	RT			1.85		[38]
	Water, anaer	RT			2.4		[39]
	Water, anaer	RT		0.76			[35]
	Water, pH 9, anaer	296		0.71			[37]
	Methanol, aer	RT			0.0006		[40]
	Methanol, anaer	RT			0.0075		[40]
	EPA	80			9.4	0.033	[31]
	Gelatine	RT			4.2		[41]
	Gelatine	RT	685		2.96	0.025[a]	[42]
	Sol–gel silica	RT	678		0.76		[42]
	PVA	RT	686		4.1	0.0035	[19]
ER							
	EPA	77		0.69			[31]
	EPA	80	686		1.3	0.026	[34]
	Gelatine	RT			0.63		[41]
	Gelatine	RT	685		0.73	0.16[b]	[42]
	Sol–gel silica	RT	683		0.23	0.031[b]	[42]
	PVA	RT	691		0.65	0.019	[19]
	Water, pH 7.4, anaer	RT	689		0.30	0.007	[20]
	Ethanol, anaer	RT	694		0.94	0.013	[20]
	Ethanol, aer	RT			0.063		[21]
	PMMA		702		0.64		[20]
	Sol–gel glass, aer	RT				1.4×10^{-4}	[6]
	Water, aer	RT			0.0028		[43]
	Water, anaer	RT			0.0505		[43]
	Water, pH 9, anaer	296 K		0.98			[37]
RB							
	Ethanol	77	720		1.0		[38]
	Ethanol, aer	RT			0.09		[21]
	Ethanol, aer	RT		0.86			[36]
	Water	RT			0.145		[38]
	Gelatine	RT			0.32		[41]
	Water, pH 8	RT	716		0.135		[44]

[a] ϕ_F(eosin in gelatine) = 0.60 from [1] used.
[b] ϕ_F(erythrosine in gelatine) = 0.22 from [1] used. EPA: glass of diethyl ether, isopentane, and ethanol with volume ratio of 5:5:2. PVA = poly-vinylalcohol. PMMA = poly-methylmethacrylate. anaer = anaerobe. aer = aerobe. RT = room temperature.

like triplet radiative lifetime, τ_{rad,T_1}, intersystem crossing-rate, k_{ISC}, and back intersystem-crossing rate, k_{T_1,S_1}.

2. Experimental

The same samples were used as in [1]. Their preparation is described there. The fluorone dyes in gelatine, starch, and chitosan films on optical glass plates (microscope objective plates) were approximately 10 μm thick. The dye concentration in the films was adjusted to approximately 10^{-3} mol dm^{-3}.

Fluorescence spectra, phosphorescence spectra and phosphorescence lifetimes were measured with a commercial spectrofluorimeter (Cary Eclipse from Varian). The fluorescence spectra are measured during sample exposure (excitation with Xe pulse lamp of 2 μs duration). The phosphorescence is measured with a gated photomultiplier after sample excitation (adjustable delay time 100 μs–5 s, adjustable gate width 40 μs–10 s). Phosphorescence lifetimes are measurable in a collection time range from 1 ms to 1 h, with time delays from 0 ms to 100 ms, and with sampling gate widths of 1 μs–10 s. The excitation light was polarized to the vertical with a polarizer. The sample plates were put in vertically and tilted to an angle-of-light-incidence of 45° (reflected light opposite to luminescence detection spectrometer). The luminescence was collected at an angle of 90° to the excitation path under magic angle polarisation conditions (polarizer in luminescence path oriented under an angle of 54.7° to the polarisation of the