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Malachite Green as a Sensitive Free-Volume Probe

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Malachite green acts as a highly sensitive free-volume probe due to the delicate dependence of its mechanism of internal conversion on the environment. A strong contrast is observed between the temperature dependence of the fluorescence decays in the adsorbed state and in solid matrix.

Free-volume in polymer matrix and at interfaces, allowing the rotation of dissolved or adsorbed organic molecules, or of molecular constituents, is of considerable interest for the characterization of surfaces and for the construction of engineered molecular assemblies. Among the few free-volume probes known at present are N,N-dimethylaminobenzonitrile and its derivatives, which are able to monitor free-volume in polymer matrix1) and in the adsorbed state,2) by formation of the twisted internal charge-transfer state. Xanthene dyes like rhodamine B can serve as probes for free-volume at distorted adsorption sites,3) and cyanine dyes can indicate large-amplitude motions, as occurring in cis-trans isomerization of molecules in the adsorbed state.4) Malachite green is a very sensitive probe for free-volume and has the additional advantage over the above mentioned aminobenzonitriles that its absorption and emission spectra are located in the visible region of the spectrum, allowing easy discrimination from matrix background signals. Malachite green in the adsorbed state displays a short, temperature-independent fluorescence lifetime, which had been interpreted as indication of a barrierless, all-downhill

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potential surface, due to sufficient free-volume near the surface, allowing the unhindered rotation of its phenyl rings.4)

This paper examines the temperature dependence of the fluorescence lifetime of malachite green in homogeneous matrix and demonstrates a large variation of free-volume when the mixed solvent EPA (diethylether, isopentane, ethanol, 5:5:2) passes through its glass transition. Figure 1 compares the behaviour of malachite green in a matrix of varying degree of viscosity and free-volume with that in the adsorbed state. Figure 1a displays the strongly temperature-dependent fluorescence decays of malachite green in EPA matrix and contrasts it with the fluorescence decays of a submonolayer of malachite green adsorbed on quartz. The lifetime of the dominant fast component (> 90%) in latter case is 46 ± 5 ps, independent of temperature in the range 298 - 4 K,4) as shown in Fig. 1b.

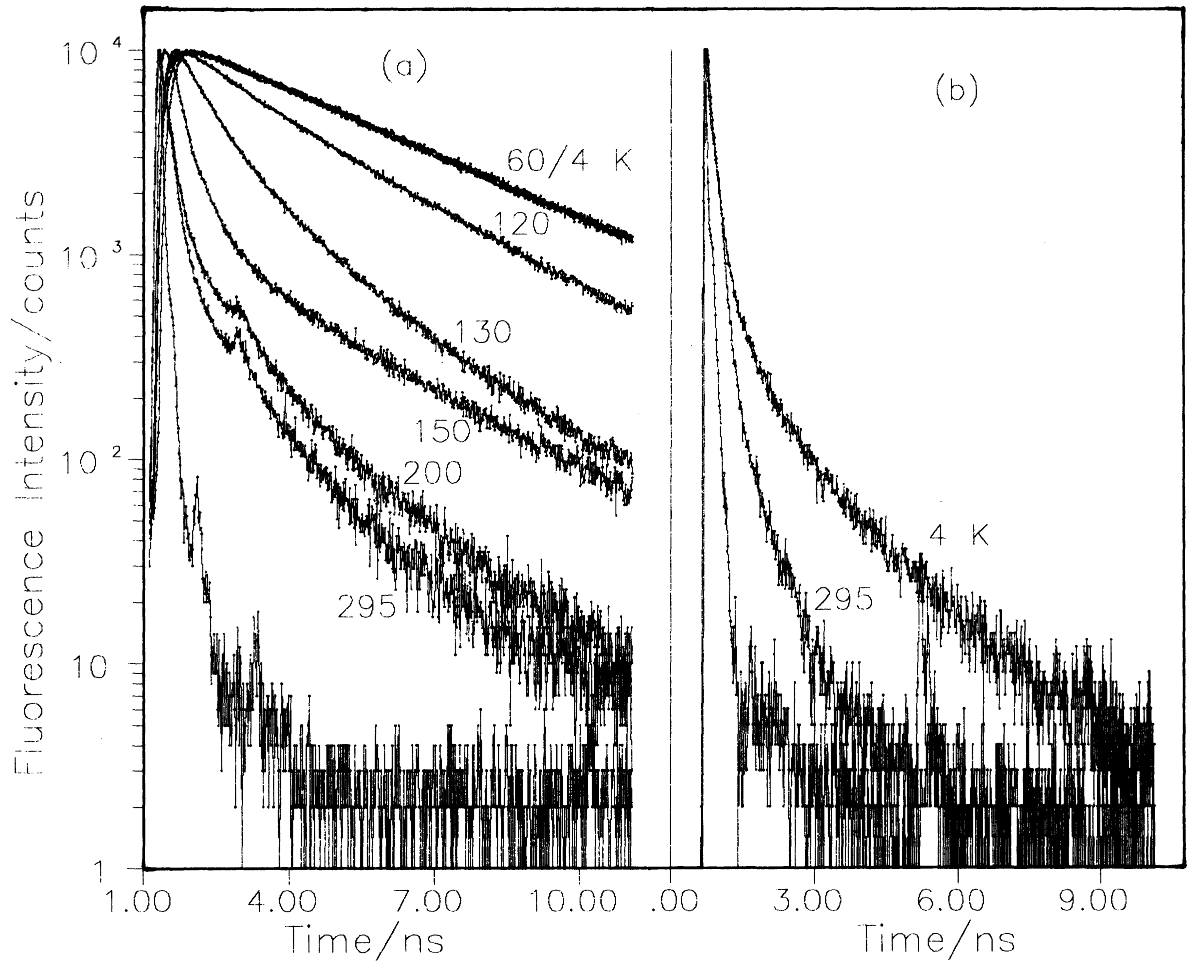

Fig. 1. a) Temperature-dependent fluorescence decay of 1×10^{-6} M malachite green in EPA and b) of 1/10th monolayer adsorbed on quartz, acquired by time-correlated single photon counting techniques.4)

Table 1. Fluorescence decay analysis of malachite green in EPA, lifetimes, τ_i, in ps and preexponential factors, A_i, in %

T	τ_1	τ_2	τ_3	A_1	A_2	A_3
298	≤15	160	1240	80.0	18.2	1.8
200	≤15	170	1430	79.9	17.7	2.4
150	290	820	3090	83.8	8.7	7.5
130	480	1160	2720	51.7	33.6	14.7
120	-	1280	3340	-	31.6	68.4
60	-	-	4050	-	-	100.0
4	-	-	4070	-	-	100.0

Table 1 presents the three-exponential analysis of the fluorescence decays in EPA matrix of Fig. 1a according to $I(t) = \Sigma_i A_i \exp(-t/\tau_i)$.

Malachite green in low viscosity solvents shows extremely short fluorescence lifetimes on the order of a few picoseconds,[5) due to very efficient internal conversion after a synchronized twist motion of its three phenyl rings, as indicated by the arrows in Fig. 2a. Figure 2b describes internal conversion after excitation to the excited potential surface S_1, followed by activated or activationless twist, and fast consecutive internal conversion to the closely spaced ground state potential surface.[6)

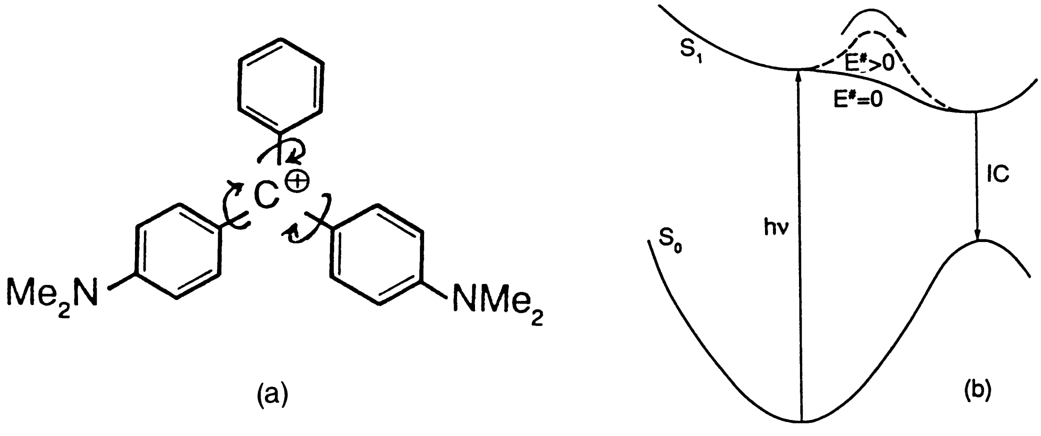

Fig. 2. (a) Molecular structure of malachite green and (b) ground and excited state potential surfaces and internal conversion after crossing the free-volume dependent activation barrier $E^{\#}$.

Figure 1a and Table 1 clearly demonstrate the dramatic effect of temperature on the fluorescence kinetics of malachite green in EPA. From room temperature down to about 160

K the fluorescence decay is dominated by a fast component of less than 15 ps, accompanied by about 20% contribution of lifetime close to 200 ps. Such double-exponential behaviour had been observed also in water5) and in glycerol.7) The slow component of about 1300 ps and 2% contribution (Table 1), however, had not been observed in the above polar solvents, and is attributed to the fluorescence of ion pairs formed in the nonpolar solvent EPA ($\epsilon \approx 7$). Formation of ion pairs with fluorescence lifetimes different from that of the dissociated ions had been observed in weakly or nonpolar solvents in case of xanthene monomers and dimers,8) and for polymethine dyes,9) though an alternative mechanism might be seen in an equilibrium between short-lived ionic species and long-lived leuco-dye.10)

At temperatures below 160 K a sudden increase of the lifetime of the fast component by more than 20 times is observed, as is the development of a very long lived component of about 3 ns. At about 130 K the decays become two-exponential and finally single-exponential with a lifetime of 4 ns below about 100 K. Below 100 K the matrix is absolutely rigid without any free-volume and the temperature-independent 4 ns decay is thought to be mainly due to the radiative decay channel.

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