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Short Communication

Low temperature fluorescence quantum yield of 9,10-diphenylanthracene, 9,10-dichloroanthracene and phenanthrene in EPA solution

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Most of the quantum yields in solution reported in the literature have been determined by relative quantum yield measurements using a more or less well defined "standard" as a reference[1]. For room temperature conditions, numerous compounds are suggested as reference standards. The two most popular ones are probably quinine sulfate and anthracene[1]. It appears that reliable reference standards for solution work at room temperature are available. This situation is quite different at 77 K in glassy solutions. Owing to obvious experimental difficulties, a considerable uncertainty exists in the few low temperature quantum yield values published[2]. It seems desirable, therefore, to employ a different technique enabling one to establish Φ_f values at 77 K of compounds which appear to be good candidates for low temperature fluorescence standards.

We have recently developed a simple procedure (accurate to about $\pm$ 5%) for measuring the relative fluorescence quantum yield as a function of temperature for organic molecules in solution[3]. Φ_f at 77 K can be determined by knowing the Φ_f value at room temperature. Moreover, if the areas under the corrected fluorescence and phosphorescence spectra are compared, the former value also furnishes the phosphorescence quantum efficiency.

This communication reports the results of a study of the temperature dependence of the fluorescence quantum yield of 9,10-diphenylanthracene (DPA), 9,10-dichloroanthracene (DCA) and phenanthrene (P) in EPA solution** between 300 and 77 K, thus establishing the Φ_f values of these compounds at 77 K.

Following the procedure reported recently[3], the fluorescence quantum yield as a function of temperature, $\Phi_f(T)$, is determined relative to the value of Φ_f^0 at room temperature by means of the relationship:

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** Prior to its use: DPA (Aldrich Chemical Co.) was recrystallized 3 times from ethanol; DCA (Eastman Chemical Co.) was recrystallized 6 times from benzene; P (Aldrich Chemical Co.) was zone refined with 100 passes on a Fisher Zone Refiner.

$$\Phi_f(T) = \Phi_f^0 \frac{\int_0^\infty F(v,T)\,dv}{\int_0^\infty F_0(v)\,dv} \frac{D_0}{D(T)} \frac{n^2(T)}{n_0^2} \quad (1)$$

The index 0 refers to room temperature. The ratio $\frac{D_0}{D(T)}$ at the excitation wavelength must be measured over the same temperature range as the fluorescence spectrum $F(v,T)$ since the optical density, D, also changes with temperature. The refractive index ratio $n^2(T)/n_0^2$ can be expressed as[3]:

$$\frac{n(T)^2}{n_0^2} = \left\{ 1 + \frac{C}{n_0} \alpha (T - T_0) \right\}^2 \quad (2)$$

C is a solvent dependent proportionality constant relating the change in the index of refraction Δn to the change in density. The parameters used in eqn. (2) for EPA are: n_0 (293 K) = 1.3550, $\alpha = 1.005 \times 10^{-3}$ and $C = 0.52$[3].

Figure 1 summarizes the results of the temperature dependence of the Φ_f of DPA, DCA and P in EPA between 300 and 77 K*. Both DPA and P show—

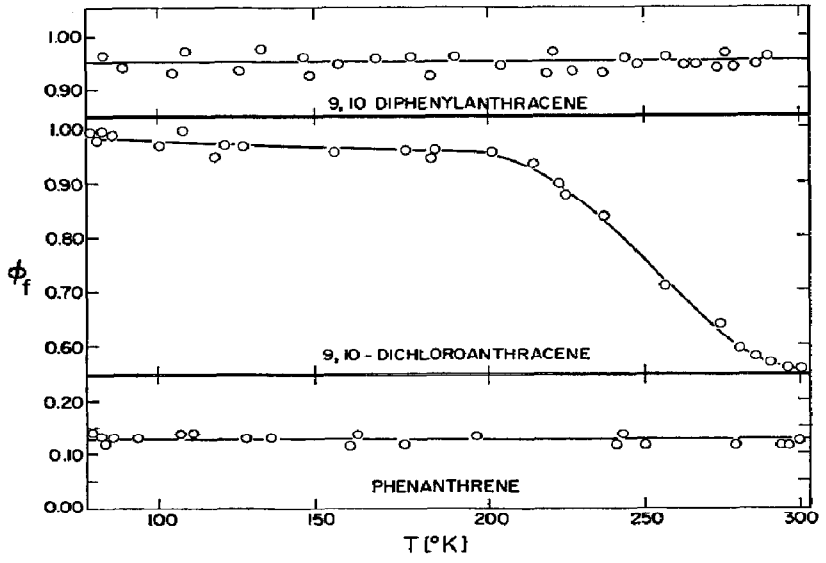

Fig. 1. The temperature dependence of the fluorescence quantum yield $\Phi_f(T)$ of 9,10-diphenylanthracene, 9,10-dichloroanthracene, and phenanthrene in EPA solution. Application of eqn. (1) in conjunction with eqn. (2).

* The excitation wavelengths were: 320 and 370 nm for DPA; 360, 370 and 378 nm for DCA; 334 and 330 nm for P. In each case, the spectral bandwidth at the excitation wavelength did not exceed 1.5 nm.

within experimental error—no temperature dependence of Φ_f, while DCA nearly doubles its value over this range.

The quantum yield at 77 K can be determined if the value at room temperature is known (*cf.* eqn. 1). In our earlier work[3] the Φ_f value given was the best *estimate* available. We have carefully re-evaluated the Φ_f of DPA in ethanol using anthracene ($\Phi_f = 0.28$)[1] and quinine sulfate ($\Phi_f = 0.55$)[1] as standards. The excitation wavelengths were 350, 355 and 360 nm when anthracene was used and 350, 360, 370 and 375 nm when quinine sulfate was the reference. Out of 6 independent series of Φ_f determinations, each consisting of 8 equally weighted measurements, the Φ_f value of DPA was found to be 0.95 ± 0.03 at room temperature. This value is slightly higher than the value reported by Parker[2]. Since it was found that the ratio between Φ_f values of DPA in ethanol and EPA is unity at room temperature, $\Phi_f(77\text{ K}) = 0.95 \pm 0.05$. Our value is in close agreement with a recently reported value. By means of an integrating sphere technique, Lim and coworkers[4] determined the $\Phi_f(77\text{ K})$ of DPA in EPA to be 1.00 ± 0.05. Moreover, the observed temperature independence of Φ_f for DPA is consistent with our recent fluorescence lifetime measurements[5]. At both 300 K and 77 K, the fluorescence lifetime was found to be 8.0 ± 0.1 ns.

The Φ_f of phenanthrene is also temperature independent (*cf.* Fig. 1). Based on the room temperature Φ_f value of 0.13 reported by Parker[2], our experiments yield a value $\Phi_f(77\text{ K}) = 0.13$. At 77 K, Li and Lim reported a Φ_f value of 0.13 based on a value $\Phi_f(77\text{ K}) = 1.00$ for DPA[6]. The 5% discrepancy in the DPA Φ_f value is hardly discernible in this case.

The strong temperature dependence of the fluorescence quantum yield of 9,10-dichloroanthracene is well known[4, 7, 8]. In EPA, the most dramatic change in Φ_f occurs between 280 K and 210 K (*cf.* Fig. 1). A much more gradual increase is observed between 210 K and 77 K. No change is manifested between the Φ_f value of DCA in ethanol and EPA at room temperature. Therefore, using the room temperature Φ_f value of 0.56* we obtain a value $\Phi_f(77\text{ K}) = 0.98 \pm 0.05$, which is again in excellent agreement with the reported value by Lim *et al.*[4].

Summarizing our results, we find the following fluorescence quantum yields in EPA glass at 77 K: DPA, $\Phi_f = 0.95 \pm 0.05$; DCA, $\Phi_f = 0.98 \pm 0.05$; P, $\Phi_f = 0.13 \pm 0.01$. The agreement between our values and those arrived at by other workers, using independent techniques, suggests that DPA and DCA can be reliably used as low temperature quantum yield standards.

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* The Φ_f value of 0.56 was obtained by averaging the values given in refs. 8a and 8b and the value derived from an additional determination relative to anthracene and quinine sulfate.

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