Short Communication

9,10-Diphenylanthracene as a fluorescence quantum yield standard

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The indirect method highly recommended by Parker and Rees [1] for measuring absolute fluorescence quantum yields [2] and the fact that versatile self-correcting absolute spectrofluorimeters are now commercially available, makes the measurement of absolute fluorescence quantum yields a routine procedure. In view of these aspects a measured fluorescence quantum yield is only as good as the certainty of the quantum yield of the fluorescence standard. The most widely used and generally accepted fluorescence standard for room temperature is quinine sulfate in 1.0 N sulfuric acid with Melhuish's value of 0.546 [2]. Another frequently used fluorescence standard for room temperature is 9,10-diphenylanthracene [3 - 8] which was reported by several authors to have a fluorescence quantum yield of unity.

However, there are contradictory results for the value of the fluorescence quantum yield of 9,10-diphenylanthracene leading to some dispute in the literature [8].

Owing to the importance of having a fluorescence standard with a fluorescence quantum yield of unity as a check for the quality of the absolute value of quinine sulfate we made a careful quantitative study of the photophysical data of 9,10-diphenylanthracene, measuring the fluorescence quantum yields at different temperatures and exciting wavelengths, the fluorescence lifetimes, with and without oxygen, as well as the triplet–triplet absorption in different solvents.

Experimental

The fluorescence quantum yield measurements were carried out with degassed and air-saturated solutions using a self-correcting recording spectro-fluorimeter. The fluorescence lifetimes were measured with a pulse sampling fluorometer and the triplet–triplet absorptions were investigated by flash spectroscopy. All instruments have been constructed in this laboratory [9, 10].

The fluorescence efficiencies were evaluated from the areas under the emission spectra with respect to the area of the fluorescence spectrum of

quinine bisulfate in $1.0\ N$ H_2SO_4 ($Q = 0.55$ at 298 K), taking into account the different refractive indices of the solvents. The concentration of the samples was carefully adjusted to give the same absorbance of quinine bisulfate at the exciting wavelength at the chosen temperature. Care was taken to insure that the concentration of the samples was well below 10^{-5} mol/l to avoid re-absorption of fluorescence emission [7] in the 1 cm cell at the right angle illumination-viewing geometry. The reproducibility of our data is excellent and gives a standard deviation in the fluorescence quantum yield and lifetime measurements of ± 2%.

The concentrations of the solutions for triplet–triplet absorption were lower than 10^{-4} mol/l. Degassing was performed by five freeze–evacuation–thaw cycles to a pressure of less than 10^{-5} Torr.*

9,10-Diphenylanthracene (EGA-Chemie) was purified by two dimensional thin-layer chromatography and finally recrystallized from cyclohexane. n-Heptane, benzene and cyclohexane (Merck), all of quality Uvasol für die Fluoreszenzspektroskopie, did not show any fluorescence and were used without purification. Ethanol (Merck), diethyl ether (Merck) and isopentane (Fluka) were carefully purified by distillation over a column of 1.50 m length.

Results and Discussion

The fluorescence quantum yield of 9,10-diphenylanthracene published in the literature (Table 1) covers a range between 0.60 and 1.18. Great discrepancies exist in the most common solvents, benzene and ethanol, showing values from 0.80 to 1.08 and from 0.76 to 1.00. The fluorescence efficiencies of 9,10-diphenylanthracene in various solvents from literature data are summarized in Table 1.

Bowen and Sahu [12] assume a fluorescence quantum yield of unity independent of the solvent, temperature and concentration. For 9,10-diphenylanthracene in cyclohexane, which was used as a fluorescence standard solution by Berlman [7], only one fluorescence quantum yield actually measured by Eastman [18] exists with a value 9% higher than unity. Birks [19, 20] simply used a mean value of the fluorescence quantum yield for cyclohexane from data published in the literature measured in different solvents. With the exception of the fluorescence efficiencies measured by Eastman [18] the quantum yields in EPA are within the small range of between 0.95 and 1.00 (Table 1).

The great difficulties involved in performing fluorescence quantum yield measurements are certainly responsible for the large discrepancies of the values in Table 1. The sources of error may be a result of impurity of solution,

*The use of the Schlenk type spectrofluorimeter cells with stopcock and/or stopper of polytetrafluoroethylene (PTFE) should be handled with precaution. We found that aromatic compounds tend to absorb onto the PTFE. Especially in low boiling solvents such as EPA these aromatic compounds may subsequently be redissolved and lead to unwanted effects, e.g. triplet–triplet energy transfer etc.

TABLE 1

Fluorescence quantum yields of 9,10-diphenylanthracene

Solvent	Temperature (K)	τ (ns)	Q	$\lambda_{exc.}$ (nm)	Method[a]	Ref.
acetone	293		0.99	365	A/b (0.24)	11
	203 - 293		1.00	366	A/b (0.29)	12
benzene	273 - 333		0.80	365	A/b (0.24)	11
	203 - 293		1.00	366	A/b (0.29)	12
	298		0.84[d]	366	Q (0.51)	13
	RT	7.3	0.85[d]		D/b (0.85)	3
	298	7.37	0.84[d]		value of ref. 13	14
	293		0.81[d]	366	Q (0.55)	15
	298	13.0	0.84[d]		value of ref. 13	16
	RT		0.84		Q (0.55)	17
	298		1.08	378	absolute	18
chloroform	273 - 333		0.65	365	A/b (0.24)	11
	203 - 293		1.00	366	A/b (0.29)	12
cyclohexane	298		1.09	376	absolute	18
	RT	9.35	1.00[d]	265	D/c (1.00)	7, 8
	RT		0.83		mean value	19, 20
EPA[b]	77		1.00	254, 366	D/EPA (1.00)	4
	110		1.12	374	absolute	18
	298		1.16	374	absolute	18
	77 - 300	8.0	1.00		Q (0.55)	21
	77 - 300	8.0	0.95	320, 370	A/e (0.28), Q (0.55)	22
ethanol	RT	6.8	0.84		A/e (0.22)	23
	203 - 293		1.00	366	A/b (0.29)	12
	298		0.81[d]	366	Q (0.51)	13
	293		0.76[d]	366	Q (0.55)	15
	293		0.89		A/e (0.30)	24
	298		0.93[d]	254	Q (0.55)	25
	RT		0.89		value of ref. 22	26
	150		1.00			27
	300		~0.9			27
	RT		0.95	350 - 375	A/e (0.28), Q (0.55)	22
ethyl acetate	203 - 293		1.00	366	A/b (0.29)	12
isobutanol	170		0.92	394	absolute	18
	298		1.18	376	absolute	18
isopentane	120		1.15	376	absolute	18
kerosene	293		0.60	365	A/b (0.24)	11
paraffin	293		0.81[d]	366	Q (0.55)	15
	293		0.81[d]		value of ref. 15	28
petroleum ether	203 - 293		1.00	366	A/b (0.29)	12
	298		0.83[d]	366	Q (0.51)	13
PMMA[c]	298		0.99	366	Q (0.51)	29
			0.83[d]	366	Q (0.51)	29
toluene	203 - 293		1.00	366	A/b (0.29)	12

[a] Values refer to quantum yields for the following standard solutions: A/b anthracene in benzene; A/e, anthracene in ethanol; D/b, 9,10-diphenylanthracene in benzene; D/c, 9,10-diphenylanthracene in cyclohexane; D/EPA, 9,10-diphenylanthracene in EPA; Q, quinine bisulfate in dilute H_2SO_4.

[b] EPA = diethyl ether, isopentane and ethanol, 5:5:2 by vol.

[c] PMMA = poly(methyl methacrylate).

[d] Values corrected for re-absorption or measurements with dilute solutions.

TABLE 2

Fluorescence decay times τ_0, fluorescence quantum yields Q_0 and Q^*, triplet–triplet absorption wavelengths λ_{max} and triplet decay times τ_0' of 9,10-diphenylanthracene in degassed solutions

Solvent	Temperature	Fluorescence			Triplet–triplet absorption	
	T (K)	τ_0(ns)	Q_0	Q	λ_{max}(nm)	τ_0' (ms)
n-heptane	298	8.0	0.89	0.60 (254)	~450	2.5 ± 50%
ethanol	298	8.1	0.94	0.68 (254, 366)	~440	3 ± 50%
	77		1.00	1.00 (254)		
benzene	298	6.8	0.96	0.72 (366)	~450	5 ± 50%
cyclohexane	298	7.6	1.00	0.77 (254, 366)	no absorption	
EPA**	298	8.0	1.00	0.83 (254, 366)	no absorption	
	77		1.00	1.00 (254)	no absorption	

*Q is the quantum yield of the air-saturated solution. The excitation wavelengths are given in parenthesis.
**Diethyl ether, isopentane and ethanol, 5:5:2 by volume.

concentration quenching, oxygen quenching, incorrect fluorescence standard quantum yield, incorrect adjustment of the absorbance at the exciting wavelength at the chosen temperature, re-absorption and re-emission of the solution and systematic instrumentation error. Further details are discussed in the literature [2, 7].

Our experimental results of the quantitative fluorescence study of 9,10-diphenylanthracene are summarized in Table 2 and discussed together with the literature data of Table 1.

Our data for the fluorescence lifetimes of 9,10-diphenylanthracene agree quite well with those obtained by Birks and Dyson [3], Ware and Baldwin [14], and Huber et al. [21, 22]. The fluorescence quantum yield of 9,10-diphenylanthracene depends on the temperature in those solvents, in which the room temperature value is lower than unity. Furthermore, it strongly depends on oxygen quenching but does not depend on the exciting wavelength. The fluorescence quantum yield in n-heptane shows the smallest value of all solvents measured (Table 2). As to ethanol, its value increases to 0.94 which is in good agreement with those of Parker and Joyce [24], Huber et al. [21, 22] and Schulte-Frohlinde et al. [25], and the estimate based on delayed fluorescence measurements by Ferguson and Mau [27] (see Table 1). At lower temperatures in ethanol the fluorescence quantum yield of 9,10-diphenylanthracene reaches unity in degassed and even in air-saturated solutions in accordance with the data of Mantulin and Huber [21]. In benzene the fluorescence quantum yield is 0.96. Finally, only in cyclohexane and EPA does the fluorescence quantum yield reach unity at room temperature, supporting the results of Lim et al. [4], Huber et al. [21, 22] and Berlman [7]. Our flash spectroscopic measurements on the same solutions unequiv-

ocally show that the fluorescence quantum yields in n-heptane, ethanol and benzene are lower than unity. In these solvents we find a weak triplet–triplet absorption at room temperature with a maximum between 440 and 450 nm and a triplet decay time of less than 10 ms. Both values are in good agreement with the triplet–triplet absorption data of anthracene and 9,10-diphenylanthracene [15] and the triplet lifetime determined by Parker and Joyce [24]. The concentration of our solutions for $T_1 - T_x$ absorption ($< 10^{-4}$ mol/l) is lower by two orders of magnitude than those in which electronic processes as singlet–singlet interactions could give rise to additional triplet population.

We do not observe any triplet–triplet absorption in cyclohexane at 298 K and in EPA at 298 K and 77 K, thus, supporting the fluorescence quantum yield of unity for 9,10-diphenylanthracene in these two solvents.

Assuming the absence of a radiationless S_1–S_0 transition in 9,10-diphenylanthracene, the quantum yields of the intersystem crossing in n-heptane, ethanol and benzene at room temperature are 0.11, 0.06 and 0.04, respectively. In cyclohexane and EPA the probability for intersystem crossing is zero, which is in agreement with theoretical calculations [30].

For the benefit of standardizing luminescence data [31, 32] we suggest 9,10-diphenylanthracene in EPA as a fluorescence standard for low temperature fluorescence and phosphorescence quantum yield measurements [33]. Since the value of unity is only valid for carefully degassed solutions and 9,10-diphenylanthracene is susceptible to re-absorption errors [7], it is certainly not an ideal fluorescence standard for measurements carried out at room temperature. In view of the available data [2] and the present study, quinine sulfate with a value of 0.55 at 25 °C is still the highly recommended room temperature fluorescence quantum yield standard.

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