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Absolute Measurements of Photoluminescence Quantum Yields of 1-Halonaphthalenes in 77 K Rigid Solution Using an Integrating Sphere Instrument

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A new apparatus to determine the absolute luminescence quantum yield of organic molecules in 77 K rigid solution is developed by using an integrating sphere (IS). Using this apparatus the fluorescence and phosphorescence quantum yields of 1-halogenated naphthalenes in 77 K rigid solutions are measured to determine the rate constants for the spin-forbidden radiative and nonradiative transitions.

Fluorescence (Φ_f) and phosphorescence (Φ_p) quantum yields are important photophysical quantities which can be used to evaluate the emissive properties of organic molecules and to obtain various rate parameters involved in the excited singlet and triplet states.[1] Over the past several decades considerable efforts have been made to develop reliable methods for determining luminescence quantum yield.[2] Absolute (primary) methods using a solid or solution scatterer to calibrate the detector/excitation system give luminescence quantum yields without the need of reference compounds. In the absolute quantum yield measurements, however, various complex corrections are required: they include polarization effects, refractive index effects, reabsorption/reemission effects, internal reflection effects, and the spectral sensitivity of the detection system. Therefore, in most laboratories relative (secondary) methods have been used to determine quantum yields. In the relative methods, the quantum yield of sample compounds is determined in comparison with the value of suitable standards. In the case of low-temperature rigid solutions, polarization effects and refractive index effects as well as the temperature change in absorbance have to be considered to obtain accurate quantum yield. In addition very few standards are available for use at low temperature.

Recently, we have developed a simple and reliable method to determine the absolute luminescence quantum yields of solutions[3] and solid-state films.[4] The same apparatus has also been applied to evaluate the Φ_f of organic crystals.[5] Our method was based on a spectrometer using an IS and a back-thinned CCD (BT-CCD) detector. Using this system we reevaluated the Φ_f values of some standard solutions reported in the literature.[3] There was excellent agreement between our Φ_f and the values given in the literature.

In this present study, we have modified the IS to permit observation of rigid solution at 77 K as shown in Figure 1. A quartz tube with an inner diameter of 6 mm was used as the sample cell and situated in a quartz liquid nitrogen dewar. By utilizing a BT-CCD as photodetector, high sensitivity from the ultraviolet to near-infrared region was achieved for the spectrophotometer. The whole system was fully calibrated for spectral sensitivity. Monochromatized light was introduced into the IS so as to hit the internal surface coated with high reflectance material (Spectralon). After multiple reflections on the internal surface, much of the optical anisotropy was eliminated. The detector first monitored the excitation light profile when a quartz tube without sample solution was set at the position above the center of the IS and then recorded the excitation light profile and the luminescence spectrum when a quartz tube with sample solution was set at the same position. From these spectral data, the luminescence quantum yield was calculated according to eq 1 in ref 3.

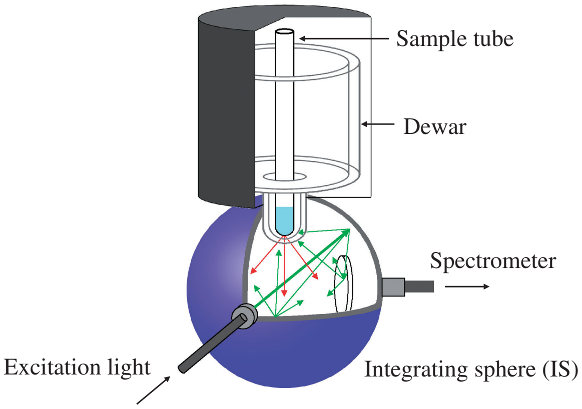

Figure 1. Schematic diagram of an IS instrument for absolute measurements of luminescence quantum yields at 77 K.

In order to evaluate the reliability of the luminescence quantum yield obtained by the modified apparatus, we first measured the fluorescence quantum yield of 9,10-diphenylanthracene in ethanol at 296 and 77 K. The Φ_f value of 9,10-diphenylanthracene in solution is known to be close to unity and almost constant between room temperature and 77 K.[6] Based on our method, we obtained the Φ_f values of 9,10-diphenylanthracene in ethanol at 296 K to be 0.95 and that at 77 K to be 0.97, which were in good agreement with the values determined by Huber et al.[6] on the basis of a relative method taking into account the corrections for the temperature dependence of the refractive index and absorbance. We also measured the Φ_p of benzophenone in ethanol at 77 K and obtained the value to be 0.88. This value was very close to the Φ_p value (0.85) of benzophenone in EPA (ether:isopentane:alcohol = 5:5:2 by volume) at 77 K obtained by Gilmore et al.[7] based on an absolute method performing complex corrections.

Using the modified apparatus we measured the Φ_f and Φ_p of naphthalene (NA) and 1-halonaphthalenes in ethanol at 77 K to examine quantitatively the internal heavy atom effects of halogens on spin-forbidden transitions. Figure 2 shows the fluorescence (blue) and phosphorescence (red) spectra of NA and its 1-halogenated derivatives in ethanol at 77 K, together with their absorption spectra at room temperature. It is apparent

Table 1. Photophysical parameters of naphthalene and 1-halonaphthalenes (2×10^{-4} M) in ethanol at room temperature (rt) and 77 K ($\lambda_{ex} = 270$ nm)

Compounds	77 K						rt[c]				
	Φ_f	Φ_p	Φ_{isc}	τ_p /s	k_p /s^{-1}	k_{isc}' /s^{-1}	Φ_f	Φ_{isc}	τ_f /ns	k_f /10^6 s^{-1}	k_{isc} /10^7 s^{-1}
NA	0.38	0.024 (0.051)[a]	0.62	1.3	0.030	0.74	0.20	0.83	97	2.1	0.86
1F-NA	0.41	0.026 (0.056)[a]	0.59	0.8	0.055	1.2	0.20	0.84	40	5.0	2.1
1Cl-NA	0.023	0.09 (0.30)[a]	0.98	0.31	0.297	2.9	0.014	0.98	2.7	5.2	36
1Br-NA	0.0034	0.14 (0.27)[a]	1.0	0.02	7.024	43	0.0005[b]	0.97	0.078	6.3	1.2×10^3
1I-NA	<0.0022	0.14 (0.38)[a]	1.0	0.0026	54	3.3×10^2	—	—	—	—	—

[a] In an ethanol/ether glass at 77 K, from Ref. 8. [b] Determined by the relative method using Φ_f of 1Cl-NA. [c] The quantum yields and τ_f of 1I-NA could not be determined by occurrence of photodecompositions (ref 9).

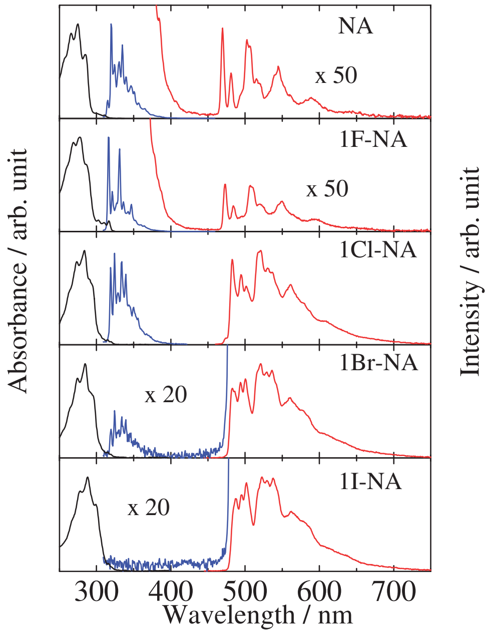

Figure 2. Room-temperature absorption and 77 K luminescence spectra of naphthalene derivatives in ethanol.

from Figure 2 that the relative phosphorescence intensity increases rapidly in the sequence of fluoro- (1F-NA), chloro- (1Cl-NA), bromo- (1Br-NA), and iodonaphthalenes (1I-NA). Our IS instrument enables us to measure simultaneously the absolute fluorescence and phosphorescence quantum yields as well as the corrected luminescence spectra. In Table 1, the Φ_f and Φ_p values of NA and its 1-haloganated derivatives in ethanol at 77 K obtained by using our apparatus are presented together with the quantum yields reported by Ermolaev and Svitashev.[1,8,10] They determined the Φ_p values in Table 1 based on the relative method in which the Φ_f value (0.55)[7] of NA in EPA at 77 K was used as the standard. Our Φ_p values are much smaller than their values. This is due at least partly to the fact that their Φ_f value (0.55) of the reference sample (NA) was larger than our value (0.38). In a subsequent paper,[11] however, Ermolaev used 9,10-di-*n*-propylanthracene in rigid ethanol/ether solution at 77 K as standard in the quantum yield measurements of NA, 1Cl-NA, 1Br-NA, and 1I-NA and reported much smaller Φ_p values (0.16, 0.14, and 0.20 for 1Cl-NA, 1Br-NA, and 1I-NA, respectively).

It can be seen from Table 1 that in the 1-halonaphthalenes the fluorescence quantum yield decreases and the phosphorescence quantum yield increases as the atomic number of the halogens increases. Assuming that the quantum yield of intersystem crossing (Φ_{isc}) of these compounds is given by $(1 - \Phi_f)$ at 77 K, one can derive the values for the $T_1 \rightarrow S_0$ radiative (k_p) and nonradiative (k_{isc}') rate constants by substituting the Φ_p, Φ_{isc} and the phosphorescence lifetime (τ_p) into the following equations: $k_p = \Phi_p/(\Phi_{isc}\tau_p)$ and $k_{isc}' = 1/\tau_p - k_p$. Table 1 clearly indicates that both k_p and k_{isc}' increases as the atomic number of the substituent increases because of the enhancement in spin–orbit coupling.

The Φ_f and Φ_p of 1-halonaphthalenes in Table 1 also suggest that the rate of $S_1 \rightarrow T_1$ intersystem crossing (k_{isc}) is enhanced by internal heavy atom effects due to halogen susbtitution. In fact, the k_{isc} values of NA and 1-halonaphthalenes calculated from the fluorescence lifetime (τ_f) and the Φ_{isc} determined by photoacoustic measurements at room temperature (rt) significantly increased by heavy atom substitution (Experimental procedure is shown in Supporting Information.).[12] Our results suggest that in 1-halonaphthalenes k_{isc} is more sensitive to spin–orbit coupling than are k_p and k_{isc}'.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.