# Revisiting the Laser Dye Styryl-13 As a Reference Near-Infrared Fluorophore: Implications for the Photoluminescence Quantum Yields of Semiconducting Single-Walled Carbon Nanotubes

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The near-infrared (NIR) polymethine dye Styryl-13 emitting at ~925 nm has recently been suggested as a reference fluorophore for determining the quantum yield (QY) of the NIR photoluminescence of dispersed single-walled carbon nanotubes (SWNTs). Ju et al. reported the QY for SWNTs to be as high as 20% on the basis of 11% QY for Styryl-13 in methanol (*Science* **2009**, *323*, 1319). We directly compared the fluorescence of Styryl-13 and Styryl-20 (emitting at ~945 nm) with that of the standard fluorophore Rhodamine 6G using a spectrometer with a broad visible-NIR detection range. QYs of 2.0 (4.5) and 0.52 (0.80)% were determined for Styryl-13 and Styryl-20 in methanol (propylene carbonate), respectively. Correspondingly, the above-mentioned photoluminescence efficiency of SWNTs appears to be strongly overestimated. We also discuss singlet oxygen as an alternative NIR reference. A total QY of 1.4% was measured for the emission of singlet oxygen at 1275 nm, as photosensitized by $C_{70}$ fullerene in air-saturated carbon tetrachloride.

The fluorescence of molecules and nanostructures emitting light in the near-infrared (NIR) spectral range above ~800 nm has been increasingly studied in recent years. This development has been driven partially by the emergence of new classes of NIR emitters such as quantum dots and single-walled carbon nanotubes (SWNTs), which have interesting properties and promising applications. An important parameter of a fluorophore is its emission efficiency or quantum yield (QY), that is, the ratio of photons emitted to photons absorbed. In solution, QYs are conveniently measured relative to a reference emitter with a known QY.[1] Typical references such as quinine sulfate, some polycyclic aromatic hydrocarbons, and Rhodamine and Coumarine dyes are well-characterized compounds with bright emissions (QY ≈ 0.5 to 1) in the UV−visible spectral range, high photochemical stability, and good solubility in common solvents.[1]

In principle, NIR fluorescence can be quantified by direct comparison with these "standard" reference emitters using a spectrometer covering an adequately broad visible-near-infrared emission range (see below).[2−4] This is, in our opinion, the most flexible and accurate approach. Recently developed NIR photomultipliers[5] sensitive up to ~1700 nm are detectors that are especially well suited for such measurements. This approach is, however, not feasible for many commercial NIR spectrometers with a limited detection range, which are practically "blind" in the UV−visible spectral region. In this case, selected NIR emitters such as NIR laser dyes[6] may serve as a (secondary) reference. Unfortunately, although numerous NIR dyes have been synthesized and tested for lasing in different pumping schemes (with the main interest being their tuning wavelength range, energy conversion, and photostability), their emission efficiencies have remained scarcely documented.[6,7] Calibration measurements against a "standard" fluorophore have been performed for only a few NIR dyes emitting above ~800 nm.[4,8] Note that the QYs of NIR dyes are typically much less than unity and typically decrease along a series of compounds as emission wavelength increases.

Recently, Crochet et al. have suggested the polymethine dye Styryl-13 as a reference emitter for dispersed single-walled carbon nanotubes (SWNTs) because its absorption maximum at ~580 nm and emission maximum at ~925 nm are close to those of some semiconducting SWNT species.[9] These authors found a QY of up to 0.01 for SWNTs in water−surfactant dispersions on the basis of 0.11 QY for Styryl-13 dissolved in methanol. Unfortunately, no details of the source of the emission efficiency measurement for Styryl-13 were provided. Very recently, using the same Styryl-13 reference, Ju et al. reported the QY to be as high as 0.2 for SWNTs dispersed in toluene and wrapped with an aliphatic analog of flavin mononucleotide.[10]

Because an accurate QY value is crucial for a reference emitter, we measured the fluorescence of Styryl-13 relative to that of the well-known fluorophore Rhodamine 6G and found the QY of Styryl-13 in methanol to be $(2.0 \pm 0.2) \times 10^{-2}$. Consequently, the reported emission efficiencies[9,10] of SWNTs appear to be overestimated by a factor of 5.5. The fluorescence of Styryl-13 is brighter and red-shifted when it is dissolved in propylene carbonate. For comparison, we also determined the fluorescence QY of the polymethine dye Styryl-20, which emits at ~945 nm, as well as the phosphorescence QY of singlet oxygen $^1O_2$ ($a^1\Delta_g$) at 1275 nm as photosensitized by $C_{70}$ fullerene in air-saturated carbon tetrachloride. We propose singlet oxygen as an alternative NIR reference emitter.

The laser dyes Rhodamine 6G (Sigma-Aldrich), Styryl-13 (LDS925, Exciton), and Styryl-20 (LC9440, Lambda Physik) and solvents (Merck, analytical or HPLC grade) were used as received. The structures and nomenclature of the NIR dyes are listed in Figure S1 (Supporting Information). Fullerene $C_{70}$ was produced and chromatographically purified (>99%) in this lab.

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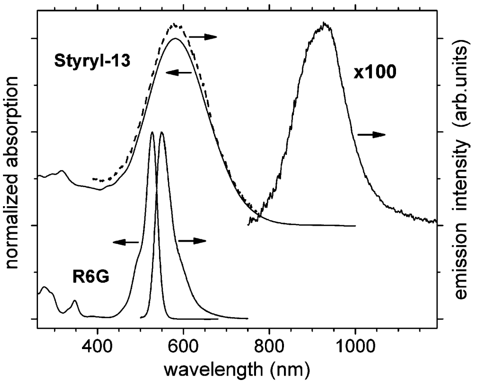

**Figure 1.** Absorption and fluorescence spectra of Rhodamine 6G and Styryl-13 solutions in methanol (vertically shifted for clarity). The emission spectra were recorded under the same conditions for dilute solutions of Rhodamine 6G and Styryl-13 (optical density 0.031 and 0.048 at the excitation wavelength of 527 nm, respectively) and corrected for the spectrometer response. (See the text.) The fluorescence excitation spectrum of Styryl-13 (dashed line) was acquired at the emission wavelength of 940 nm.

**TABLE 1: Fluorescence Quantum Yields and Absorption/Emission Maxima of Styryl-13 and Styryl-20 in Methanol and Propylene Carbonate**

| solvent | Styryl-13 | Styryl-20 |
|---|---|---|
| MeOH | $(2.0 \pm 0.2) \times 10^{-2}$<br>581/925 nm | $(5.2 \pm 1.0) \times 10^{-3}$<br>628/960 nm |
| PC | $(4.5 \pm 0.4) \times 10^{-2}$<br>579/941 nm | $(8.0 \pm 1.0) \times 10^{-3}$<br>626/978 nm |

Absorption spectra were recorded on a Varian Cary 500 spectrometer. Note that the red or near-infrared absorption of NIR dyes is quite characteristic and allows an easy and reliable control of their quality, stability, or both. The absorption spectra and molar peak absorptivity of Styryl-13 and Styryl-20 ((5.25 and 4.62) × $10^4$ $M^{-1}$ $cm^{-1}$ in methanol, respectively) were found to be in good agreement with literature data.[11−13] Fluorescence was measured in 90° geometry on a Spex Fluorolog-3 spectrometer equipped with double excitation and emission monochromators. Diffraction gratings (Thorlabs) ruled at 600 lines/mm and blazed at 750 nm as well as a Hamamatsu R5509 photomultiplier were applied in one emission channel of the Fluorolog-3. This combination provided a detection range of ~400−1390 nm, with the lower and upper limits defined by the gratings and photomultiplier, respectively. For QY measurements, solutions were diluted to an absorption of <0.05 (in 10 mm cuvettes) at the excitation wavelength of 527 nm (absorption maximum of Rhodamine 6G). The emission of a sample solution was recorded versus that of Rhodamine 6G at the same geometry and spectrometer parameters. Excitation and emission slit widths were typically set to 3 nm. Freshly prepared solutions of Styryl-20 were used to preclude their photodegradation. (See below.) Emission spectra were corrected for wavelength-dependent spectrometer and detector response in relative photon flux units per wavelength interval (Figure S2, Supporting Information). We measured the latter by using a standard tungsten halogen lamp (LOT-Oriel) and a Spectralon integrating sphere (Labsphere) for reducing light intensity, as illustrated in Figure S3 (Supporting Information).[8] All preparations and measurements were done at ambient temperature (22 °C).

Figure 1 compares absorption and fluorescence spectra of Rhodamine 6G and Styryl-13 dissolved in methanol. The QY of a sample fluorophore (Styryl), $\varphi_s$, was calculated according to

$$\varphi_s = \varphi_{ref} \times (I_s/I_{ref}) \times (A_{ref}/A_s) \times (n_s/n_{ref})^2 \qquad (1)$$

where $\varphi_{ref}$ is the QY of the reference (Rhodamine 6G), $I$ is the integrated emission intensity (area of the corrected emission spectrum), $A$ is the absorption at the excitation wavelength (proportional to the relative amount of the absorbed excitation light at $A \leq 0.05$), and $n$ is the refractive index of the solvent for the sample (s) and reference (ref), respectively.[1] The emission efficiency of Rhodamine 6G in methanol was taken to be 0.95.[14] For Styryl-13 in methanol, we obtained a QY of $(2.0 \pm 0.2) \times 10^{-2}$ as averaged from several measurements. The experimental uncertainty includes an estimated error due to the emission correction and background subtraction. Absorption and fluorescence spectra of Styryl-13 in propylene carbonate and Styryl-20 in methanol and propylene carbonate as well as the corresponding emission quantum yields are collected in Figure S4 (Supporting Information) and Table 1, respectively. Note that the QY of Styryl-20 in propylene carbonate ($\varphi = 8 \times 10^{-3}$) coincides with our earlier result.[8] That value was also referenced to Rhodamine 6G but was measured in a tedious procedure using three different photodetectors (Hamamatsu R928 and R5108 photomultipliers and an Edinburgh Instruments Ge-photodiode) to cover the required visible-NIR emission range.[8] The agreement between the two experiments indicates the accuracy of our procedure for determining the spectrometer and detector spectral response.

Characteristic for both NIR dyes are broad absorption and emission bands and a large Stokes shift of up to ~6500 $cm^{-1}$ between the absorption and emission maxima (Figure 1 and Figure S4 in the Supporting Information). The measurements also demonstrate significant solvatochromic effects: the fluorescence is red-shifted by 16−18 nm in propylene carbonate relative to methanol solutions (Table 1). These features appear to be common for unsymmetric polymethine dyes having different (charged) functional groups at the ends of a polymethine chain. The highly polar character of the electronic ground state in these dyes induces a large orientational polarization of the solvent, which explains pronounced Stokes shifts.[15] The low emission efficiency of a few percent or less can be attributed to the structural (rotational) flexibility of polymethine dyes, resulting in efficient nonradiative relaxation pathways. This correlates with a picosecond lifetime of the fluorescence.[4,6,15] The QYs of Styryl-13 and Styryl-20 increase by a factor of 2 in propylene carbonate as compared with methanol solutions (Table 1). This trend has also been observed for other polymethine dyes and assigned to specific dye-solvent interactions in aprotic (propylene carbonate) versus protic (methanol) media.[4]

According to our QY determination for Styryl-13 in methanol (Table 1), the emission efficiencies of SWNTs presented in refs 9 and 10 have to be corrected downward by a factor of 5.5 to $\sim 2 \times 10^{-3}$ and $\sim 3.5 \times 10^{-2}$, respectively. These last values approach those reported earlier for SWNTs in water−surfactant ($\varphi \approx 1 \times 10^{-3}$) and polymer−toluene ($\varphi \approx 1 \times 10^{-2}$) dispersions.[16−18] Note that ~1% QY in polymer−toluene dispersions has also been demonstrated by nanotube species emitting light at wavelengths as large as 1350 nm.[18] In particular, above ~1000 nm, SWNTs are, in fact, more efficient emitters than NIR laser dyes.[4,8,15] This justifies the continued interest in SWNTs as potential luminescent markers for analytical applications.

Apart from the limited photophysical data available, NIR dyes have some other disadvantages as reference NIR emitters. For instance, most of them, including Styryl-13 and Styryl-20, are

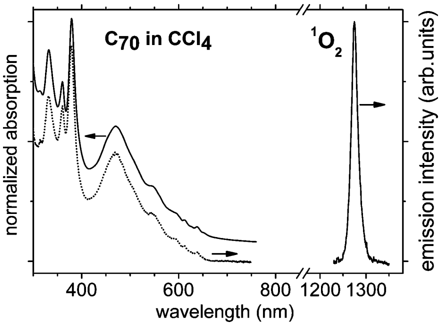

**Figure 2.** Emission of singlet oxygen at 1275 nm as photosensitized by $C_{70}$ fullerene in air-saturated carbon tetrachloride solution irradiated at 527 nm. The excitation spectrum of the singlet oxygen emission (dotted line) follows well the absorption of the photosensitizer (vertically shifted for clarity). The half-bandwidths of the excitation and emission monochromators corresponded to 3 nm.

rare and quite expensive chemicals. Furthermore, NIR dyes are often only moderately photostable.[6] Whereas no photodegradation of Styryl-13 was observed in our experiments, solutions of Styryl-20 in methanol and propylene carbonate showed a significant decrease in the absorption band at ~628 nm after absorption of only ~$10^5$ photons per dye molecule (irradiation at 633 nm). Such degradation is consistent with our observation of complete photobleaching of moderately concentrated solutions of Styryl-20 after exposure to daylight for only a few days (Figure S5, Supporting Information).

Therefore, we propose the phosphorescence of photosensitized singlet oxygen $^1O_2$ ($a^1\Delta_g$) as a possible alternative NIR reference. Its characteristic narrow peak at ~1275 nm can be readily detected and precisely integrated, in contrast with the broad and long-tailed emission bands of NIR dyes. The total QY of the photosensitized emission, $\varphi_{PE}$, (ratio of photons emitted by singlet oxygen to photons absorbed by the photosensitizer) is determined not only by the rate of radiative deactivation of $^1O_2$ (strongly dependent on the solvent) but also by the efficiency of $^1O_2$ formation via quenching of the triplet excited state of a photosensitizer by dissolved oxygen. The phosphorescence of $^1O_2$ is especially bright in solvents such as carbon tetrachloride, carbon disulfide, and chlorofluorocarbons.[2] Fullerene $C_{70}$ is an efficient singlet oxygen sensitizer with a relatively smooth absorption spectrum in the visible spectral range of ~400−700 nm.[19] Figure 2 shows the emission spectrum of $^1O_2$ photosensitized by $C_{70}$ in air-saturated carbon tetrachloride. Note that the excitation spectrum of the emission at 1275 nm is quite consistent with the absorption spectrum of $C_{70}$ (Figure 2; the deviation between the spectra below ~350 nm is due to the silicon photodiode used for correction of the excitation light intensity). This indicates that the intersystem crossing in photoexcited $C_{70}$ (and generation of $^1O_2$) is independent of the excitation wavelength, at least in the range of ~350−700 nm.

In a similar procedure as that used for the NIR dyes, we determined the total emission efficiency for the $C_{70}/^1O_2$ (air-saturated $CCl_4$) system to be $\varphi_{PE} = (1.4 \pm 0.1) \times 10^{-2}$. It is lower than $\varphi_{PE} = 4.9 \times 10^{-2}$, as found by Schmidt et al.[2] for tetraphenylporphine/$^1O_2$ ($CCl_4$), but higher than $\varphi_{PE} = 1.38 \times 10^{-3}$, as reported by Shimizu et al.[3] for phenalenone/$^1O_2$ ($CCl_4$). The discrepancy is probably due to different efficiencies of the generation of $^1O_2$ by these photosensitizers and is subject to ongoing investigations. To establish singlet oxygen as a versatile and reliable reference NIR emitter in future, it will be necessary to quantify its emission for several commonly available photosensitizers in carbon tetrachloride and other solvents.

In conclusion, we have determined fluorescence quantum yields of two polymethine NIR laser dyes in methanol and propylene carbonate, respectively, as well as the phosphorescence quantum yield of singlet oxygen photosensitized by $C_{70}$ in air-saturated $CCl_4$. The accuracy of our method is based on a direct comparison of the NIR emitters with a well-characterized “standard” UV−visible fluorophore (Rhodamine 6G in this work) by using a spectrometer sensitive over a broad visible-NIR detection range. The NIR dyes can now be applied as benchmarks for other NIR emitters such as dispersions of quantum dots and single-walled carbon nanotubes. The bright and characteristic emission of singlet oxygen in carbon tetrachloride (photosensitized, for instance, by $C_{70}$ fullerene) can provide an alternative reference for determining the efficiency of NIR fluorophores.

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**Supporting Information Available:** Structures and nomenclature of the NIR laser dyes used, spectral response of the spectrometer, schematic setup for spectrometer calibration, absorption and fluorescence spectra of Styryl-13 in propylene carbonate and Styryl-20 in methanol and propylene carbonate, and photodegradation of Styryl-20 in propylene carbonate. This material is available free of charge via the Internet at http://pubs.acs.org.

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