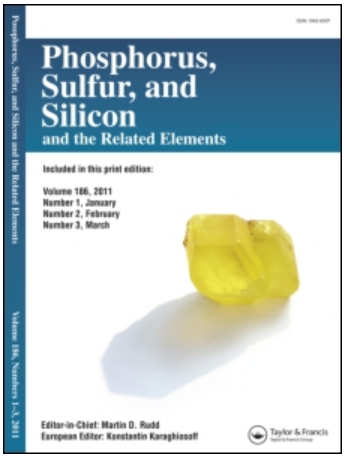

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Properties of New Laser Dyes Containing 4-(2-Thienyl)Pyridine Skeleton

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To cite this Article Nakajima, Riichiro , Ise, Takashi , Takahashi, Yoshiyuki , Yoneda, Hideo , Tanaka, Kanya and Hara, Tadashi(1994) 'Synthesis and Properties of New Laser Dyes Containing 4-(2-Thienyl)Pyridine Skeleton', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 535 — 536
To link to this Article: DOI: 10.1080/10426509408034306
URL: http://dx.doi.org/10.1080/10426509408034306

Phosphorus, Sulfur, and Silicon, 1994, Vol. 95-96, pp. 535-536
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SYNTHESIS AND PROPERTIES OF NEW LASER DYES CONTAINING 4-(2-THIENYL)PYRIDINE SKELETON

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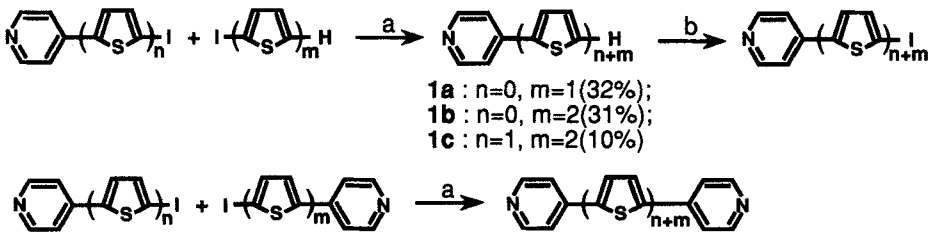
Abstract Three 4-(oligothienyl)pyridines and four α,ω-di(4-pyridyl)oligothiophenes were prepared and the effect of conjugated thiophene rings on their fluorescence properties were examined. 4-(2,2'-Bithienyl-5-yl)pyridine and 2,5-di(4-pyridyl)thiophene exhibited laser dye emission upon pumping with a nitrogen laser and the conversion efficiency of the latter was 1.5 times as great as that of a commercial laser dye PBBO at 400 nm.

INTRODUCTION

Various laser dyes have been so far reported and used, but there has still been a demand for ideal laser dyes because of the requirements for the dyes used in various fields. The commercially available UV laser dyes such as *p*-oligophenylenes, 2,5-diaryloxazoles, 2,5-diaryl-1,3,4-oxadiazoles, and 1,2-diarylethylenes are not adequate for the ideal dyes with respect to tuning range, conversion efficiency, photochemical stability, etc. 4-(2-Thienyl)pyridine skeleton has been interested in designing fluorescent labeling reagents for CZE or HPLC,[1] and electrochromic materials.[2] In order to design the new reagents with different fluorescent color as well as laser dyes, it is required particularly to understand the fluorescent properties relating to arenes conjugated with its skeleton.

RESULTS AND DISCUSSION

Three 4-(oligothienyl)pyridines(**1**) and four α,ω-di(4-pyridyl)oligothiophenes(**2**) including four new compounds were prepared by a modified Busch reaction,[3] as shown in Scheme 1, characterized by both mass and ^{1}NMR spectra as well as by elemental analyses, and the effect of conjugated thiophene rings on their fluorescence properties were examined. The wavelengths of their absorption and fluorescence maxima were found to be 295 to 480 nm and 353 to 648 nm, respectively, in 60%MeOH(or MeOH); the molar absorptivities and quantum yields were calculated to be 1.60×10^4 to 5.06×10^4



1a : n=0, m=1(32%);
1b : n=0, m=2(31%);
1c : n=1, m=2(10%)

2a : n=1, m=0(18%); **2b** : n=1, m=1(46%);
2c : n=1, m=2(3%); **2d** : n=2, m=2(20%)

Scheme 1. a) PdHg, $NH_2NH_2 \cdot H_2O$, NaOH, solvent(H_2O, 50%MeOH, or C_5H_5N); b) I_2, $HIO_4 \cdot 2H_2O$, 80%HOAc (added with CCl_4, if necessary).

and 0.02 to 0.52. The wavelengths of their observed absorption and fluorescence maxima for protonated and non-protonated forms agreed with the values estimated by a PPP-MO method using a new parameter set within an error of 8%.

Compound **1b** and **2a** exhibited laser dye emission upon pumping with a nitrogen laser(LN120C, Laser Photonics, Inc.) at 438 and 396 nm, respectively, and the conversion efficiency of the latter was 1.5 times as great as that of a commercial laser dye PBBO at 400 nm as shown in Figure 1. No decrease in the output energy was observed during 48h of continuous operation(1.728 x 10^6 shots).

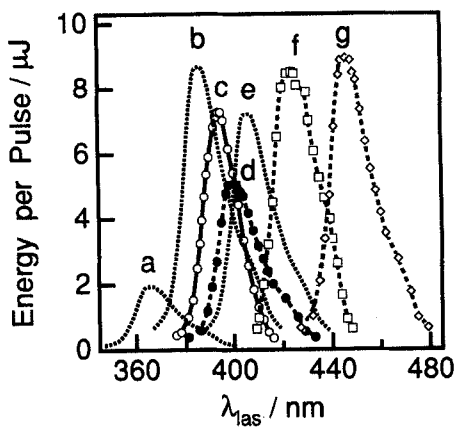


FIGURE 1. Tuning curves for (a) PBD,[4] (b)BBQ,[4] (c)**2a**(1.0×10^{-3}M, Toluene /EtOH =1:1), (d)PBBO, (e)DPS,[4] (f) Stilbene-420, and (g)Coumarin-450.

AKNOWLEDGMENT: This work was partially supported by the Aid of Doshisha University's Research Promotion Fund(1992 and 1993).

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