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Synthesis and Fluorescence Properties of 2,6-Diaryl-4-(2-substituted thienyl-5-yl)pyridines

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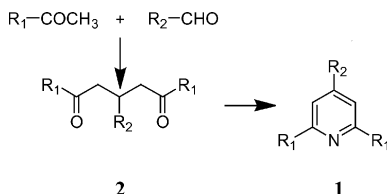
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INTRODUCTION

The structure of fluorescent compounds is important in designing luminescent materials for organic light-emitting diodes and dye lasers, fluorescent labeling reagents for HPLC or CE, and so forth. In our earlier work, 2,5-di(4-pyridyl)thiophene and 4-(5-substituted 2,2'-bithienyl-5'-yl)pyridines were shown to be useful materials as a nitrogen laser dye and labeling reagents, respectively, because of their strong fluorescence and photostability.

RESULTS

2,6-Diphenyl- and 2,6-di(2-thienyl)-4-(2-substituted thienyl-5-yl)pyridines (**1**) were prepared from the corresponding 1,5-diaryl-3-(2-substituted thienyl-5-yl)-1,5-pentadiones (**2**).



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TABLE I

	R ₁	R ₂	Yield (%)	
			1	2
a	phenyl	2-thienyl	53	72
b	phenyl	2,2'-bithienyl-5-yl	13	25
c	2-thienyl	2-thienyl	22	50
d	2-thienyl	2,2'-bithienyl-5-yl	11	24

¹H and ¹³C NMR, HRMS-FAB spectra, and elemental analysis of compounds **1a–d** and **2a–d** were found in good agreement with their structures. As shown in Table II, the wavelengths of maximum absorption of **1b–d** in 60% MeOH were similar to those of the corresponding 2,6-unsubstituted 4-(2-thienyl)pyridine (**1e**) and 4-(2,2'-bithienyl-5-yl)pyridine (**1f**); Both molar absorptivities and fluorescence intensities of **1a–d** were larger than those of the corresponding **1e** and **1f**, respectively. On the other hand, in strong acidic 60% MeOH, no shift in the absorption maximum based on the protonated form for **1c** and **1d** was observed.

TABLE II Absorption and Fluorescence Properties of **1a–1f** in 60% MeOH

	λ_{abs} (nm)	ε	pK _a	λ_{ex} (nm) ^a	λ_{em} (nm) ^a	RFI ^{a,b}	τ (ns)
1a	263	35700	2.87	310	370	285	0.87 ± 0.08, 3.21 ± 0.01
1b	353	31000	3	362	443	624	1.31 ± 0.01
1c	298	40600		306	402	193	1.55 ± 0.01
1d	357	37000		367	449	838	1.37 ± 0.01
1e	295	16000	4.48	304	359	101	0.80 ± 0.05, 2.00 ± 0.48
1f	354	27400	4.44	359	438	17	1.14 ± 0.01

^aObtained from uncorrected spectra.

^bRelative fluorescence intensity.