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# Synthesis and Spectral Properties of 5,5′-Di(4-pyridyl)-2,2′-bithienyl as a New Fluorescent Compound

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**Synopsis.** A new type of fluorescent compound, 5,5′-di(4-pyridyl)-2,2′-bithienyl, has been synthesized and its fluorescence intensity measured at 510 nm in a 40% aqueous methanol (pH<3.0) with excitation at 425 nm. The quantum yield was found to be 0.52. The thienylpyridine skeleton was found for the first time as a new fluorophore.

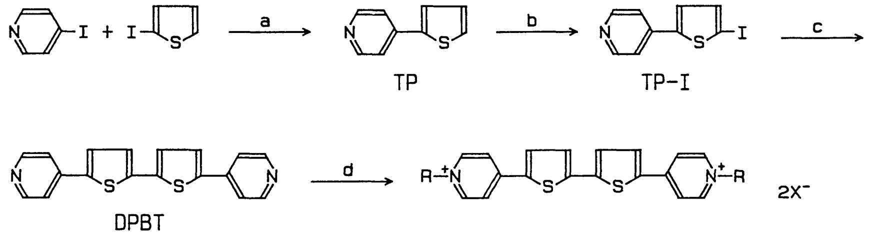
In the course of an investigation of new viologen derivatives, 5,5′-di(1-alkyl-4-pyridinio)-2,2′-bithienyl dihalides according to the procedure outlined in Scheme 1, we have found that an intermediate, 5,5′-di(4-pyridyl)-2,2′-bithienyl (DPBT), is an intensely fluorescent compound and that the thienylpyridine skeleton is a new fluorophore. Being very stable and intensely fluorescent, some of the new thienylpyridine derivatives may be utilized as laser dyes, electrochromic compounds, analytical reagents,[1,2] etc. Especially, the quaternary salts of DPBT can be expected to be useful redox materials which become nonfluorescent when they are reduced chemically or electrochemically. We report here the synthesis and spectral properties of DPBT.

## Results and Discussion

DPBT was prepared from 4-iodopyridine and 2-iodothiophene as outlined in Scheme 1. No convenient methods for the preparation of 4-(2-thienyl)pyridine (TP) had been reported[3–8] previously and the Busch-type reaction is a convenient method for the preparation of pure biaryls.[9] The new compounds, 4-(5-iodo-2-thienyl)pyridine (TP-I) and DPBT, were characterized by mass and NMR spectra, and by elemental analysis.

UV-vis absorption and fluorescence spectroscopy was employed to evaluate DPBT. Absorption spectra of DPBT varied with change of pH in 40% aqueous methanol; the wave length of the absorption maxima was 381 nm ($\varepsilon$=39500) at pH above 7.0, where DPBT is present as the free base, and 425 nm ($\varepsilon$=50600) at pH below 3.0, where it is present as the diprotonated form. The behavior of the spectra in the range of pH 3.0 to 7.0 was very similar to that of a monoacidic base such as pyridine and TP. Fluorescence spectra of DPBT in 40% aqueous methanol at both pH 1.44 and 10.10 are shown in Fig. 1. The fluorescence spectra of TP were also determined since pyridine and thiophene showed no luminescence.[10] The fluorescence quantum efficiencies of these free bases and their protonated forms were calculated and are shown in Table 1. The values of absorption maxima and molar absorptivities of TP are in good agreement with those reported by Wynberg et al.[4] TP and DPBT are very stable, and their acidic and basic aqueous methanol solutions do not exhibit a significant change in the fluorescence intensity even after deaeration with nitrogen or elapse of two years.

It is therefore concluded that the thienylpyridine skeleton is a new fluorophore, which exhibits excellent fluorescence emission characteristics such as a high quantum efficiency, relative narrow emission band, and high absorption efficiency. Similar fluorescence has been found in 4-(5-methyl-2-thienyl)-



Scheme. 1. a) $N_2H_4 \cdot H_2O$, PdHg, NaOH, $H_2O$; b) $HIO_4 \cdot 2H_2O$, $I_2$, 80% HOAc; c) $N_2H_4 \cdot H_2O$, PdHg, NaOH, 50% MeOH; d) RX, $CHCl_3$.

Table 1. Spectroscopic Properties of DPBT and TP[a]

| Compound | Form | Absorption | | Emission | |
|---|---|---|---|---|---|
| | | $\lambda_{max}$/nm | $\varepsilon$ | $\lambda_{max}$/nm | $\phi_f$ |
| DPBT | Diprotonated | 425 | $5.06\times10^4$ | 510 | 0.52[b] |
| | Nonprotonated | 381 | $3.95\times10^4$ | 455 | 0.10[c] |
| TP | Monoprotonated | 334 | $2.12\times10^4$ | 395 | 0.07[d] |
| | Nonprotonated | 295 | $1.60\times10^4$ | 353 | 0.21[d] |

a) 40% Aqueous methanol. b—d) Detrermined relative to the fluorescence quantum efficiencies of b) uranin ($\phi_f$=0.90, $\lambda_{ex}$=436 nm), c) quinine hydrogensulfate in 0.05 mol dm$^{-3}$ $H_2SO_4$ ($\phi_f$=0.55, $\lambda_{ex}$=365 nm), and d) 1,2-dihydroacenaphthylene ($\phi_f$=0.39, $\lambda_{ex}$=313 nm).

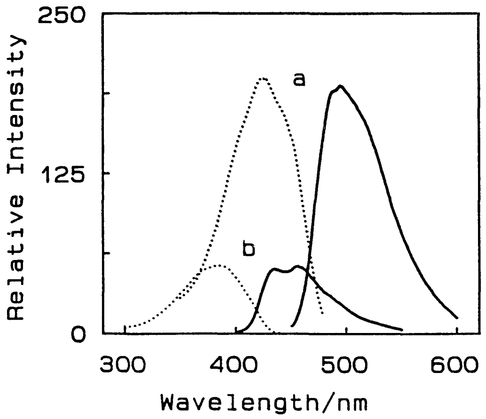


Fig. 1. Excitation (······) and emission (——) spectra of $6.56\times10^{-8}$ mol dm$^{-3}$ DPBT (corrected).
(a) pH=1.44, $\lambda_{ex}$=426 nm, $\lambda_{em}$=495 nm. (b) pH=10.10, $\lambda_{ex}$=384 nm, $\lambda_{em}$=455 nm.

pyridine and 5-(4-pyridyl)thiophene-2-carbaldehyde.$^{1)}$ Some of 5,5′-di(alkyl-4-pyridinio)-2,2′-bithienyl dibromides are under investigation.

## Experimental

Melting points were not corrected. $^1$H NMR spectra were recorded on a Jeol JNM-GX400 FT spectrometer in $CDCl_3$ or $CD_3OD$ using TMS as the internal standard. High-resolution mass spectra were taken with a Hitachi M-80B mass spectrometer. UV-vis spectra and fluorescence spectra were obtained on a Shimadzu UV-265 spectrophotometer or a Hitachi 850 spectrofluorophotometer, respectively.

**Preparation of TP.** A mixture of 4-iodopyridine$^{11)}$ (50 mmol), 2-iodothiophene$^{12)}$ (50 mmol), hydrazine hydrate (60 mmol), palladium amalgam$^{9)}$ (PdHg, 1.2 mmol), and NaOH (0.50 mol) in $H_2O$ (64 ml) was refluxed with stirring for 6 h. The resulting mixture was filtered and the residual amalgam was washed with chloroform, and subsequently with water. A mixture of TP and 4,4′-bipyridyl was extracted into dilute hydrochloric acid from the separated organic layer, back-extracted into $CHCl_3$ after the solution was made alkaline, isolated by ball-tube distillation, and chromatographed on silica gel with acetone as an eluent to give TP as the first fraction (15.1 mmol, 30%). Mp 93.0—94.0 °C, lit,$^{4)}$ 92.5—93.5 °C. Found: C, 67.30; H, 4.21; N, 8.73%.

**Preparation of TP-I.** A mixture of TP (16.3 mmol), iodine (14.3 mmol), periodic acid dihydrate (9.45 mmol), and 80%HOAc (30 ml) was heated at 80 °C for 8 h. The mixture was then made alkaline. $Na_2S_2O_3$ was added and the product extracted with hot $CH_3Cl$, and distilled in vacuo (230 °C/0.5 kPa, 13.2 mmol, 81%). White solid, mp 200.0—201.0 °C, Found: C, 37.92; H, 2.10; N, 5.00%, *m/z* 286.9255. Calcd for $C_9H_6NSI$: C, 37.65; H, 2.11; N, 4.88%; M, 286.9266. $^1$H NMR (400MHz, $CDCl_3$) $\delta$=8.59 (2H, dd, $J$=4.5 and 1.7 Hz, H-2 and H-6 in pyridine ring), 7.38 (2H, dd, $J$=4.5 and 1.7 Hz, H-3 and H-5 in pyridine ring), 7.28 (1H, d, $J$=3.8 Hz, H-4 in thiophene ring), and 7.16 (1H, d, $J$=3.8 Hz, H-3 in thiophene ring).

**Preparation of DPBT.** A mixture of TP-I (10 mmol), NaOH (50 mmol), PdHg (0.5 mmol), and 50% MeOH (6.4 ml) containing hydrazine hydrate (6 mmol) was refluxed for 10h. The mixture was filtered and the residual amalgam washed with $CH_3Cl$ and $H_2O$. The organic layer was concentrated, distilled in vacuo to remove TP, and the residue sublimed at 230 °C/0.4 kPa to give DPBT in a 46% yield (2.31 mmol). Yellow crystals, mp 241.0—242.0 °C, Found: C, 67.78; H, 3.95; N, 8.72%; *m/z* 320.0414. Calcd for $C_{18}H_{12}N_2S_2$: C, 67.48; H, 3.77; N, 8.74%; M, 320.0440. $^1$H NMR ($CD_3OD$, 50 °C) $\delta$=8.53 (4H, dd, $J$=4.6 and 1.8 Hz, H-2 and H-6 in pyridine ring), 7.65—7.68 (6H, m, H-3 and H-5 in pyridine ring, and thiophene ring protons), and 7.40 (2H, d, $J$=4.0 Hz, thiophene ring protons).

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