Synthesis and Fluorescent Properties of Oligopyridines Containing Pyrene Units

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1. Introduction
Molecular tweezers which were investigated as the intercalators for DNA[1] have been correcting much attention for their ability to make the inclusion complexes.[2] We tried to synthesize a novel fluorescent reagent (1) which has two pyrene subunits at 6- and 6"-positions of a terpyridine unit as fluorescent functional groups. The terpyridine unit is a π-electron rich unit and can associate with the π-electron deficient guests similarly to ether units.[3] On the other hands, once the unit is protonated by acidic guests, the formed anion could be interact with the protonated terpyridine unit.

This formed contact ion pair will be stabilized by π-stacking interactions caused by conformational changes of the terpyridine unit to a syn-syn conformation from an anti-anti conformation as shown in the schematic figure. In a syn-syn conformation compound 1 hold the distances between two pyrene subunits being ca. 7 Å, suitable for sandwiching the aromatic guest. This species could be expected to show the exciplex-like emission, detectable by spectral methods.[4] So, aromatic substances which have donative protons are the most suitable candidate for the guest for molecular tweezers 1. We selected the benzenesulfonic acid as a guest compound and investigated the complex formation between the protonated 1 and the benzenesulfonate anion by spectroscopic methods.

2. Synthesis
Compound 1 was prepared by condensation between the 2,6-bis[3,3-bis(n-propylthio)-1-oxoprophen-1-y1]pyridine prepared by described procedure[5] and 2 equivalent of the enolate of 1-acetylpyrene prepared from pyrene by reaction with the acetic anhydride.[6] 1 was isolated from the complex mixture by silica gel column chromatography with eluent of hexane-chloroform and then recrystallization from chloroform or ethylacetate. The products were identified by 1H NMR and mass spectroscopic procedures.

3. Results and Discussion
The absorption spectrum of 1 is different from those of pyrene and terpyridine in chloroform, and the band at the longest wavelength showed the 20 nm red shift compared with that of pyrene. This...
result indicates the pyrene and terpyridine units have through bond interactions among the units. The conformational changes would induce the spectral changes.

The fluorescence spectrum of 1 was measured in chloroform at the concentration range between \(1 \times 10^3\) and \(1 \times 10^6\)M. The shape of the emission bands didn't change in the measured range and the emissions were assigned to the monomer emissions. The intensity of the spectrum was larger than that of pyrene at the same concentrations. The relative quantum yield of 1 estimated at \(1 \times 10^6\)M was 0.59 with the reference to the quinine sulfate.

The addition of the benzenesulfonic acids to chloroform solution of 1 changed the absorption spectrum. The absorption spectra of 1 before and after the addition of 10 equivalent of benzenesulfonic acid were shown in Fig. 1. The new absorption maximum was observed at 400 nm and the absorption was assigned to the species protonated to the pyridine ring, because the similar absorption was observed in case the addition of tetrafluoroboric acid to 1.

The emission spectral change of 1 on addition of benzenesulfonic acid monohydrate (bsa) in chloroform at 25°C. \(A_{ex} = 350\) nm. (a) \([1]=1 \times 10^5\)M; (b) \([1]=1 \times 10^5\)M, \([bsa]=1 \times 10^4\)M; (c) \([1]=1 \times 10^5\)M, \([bsa]=1 \times 10^3\)M.

emissions could not be observed in the fluorescence spectra. These results indicate the interaction between protonated cation of 1 and benzenesulfonate anion was not observed.

4. Conclusion

The fluorescent receptor 1 was synthesized and showed the fluorescence spectral decrease at 400 nm, assigned to the monomer emission and increase emission at 520 nm on addition of benzenesulfonic acids. As the any changes of emission didn't observed in case of addition of trifluoroacetic acid, the emission at 520 nm was ascribed to the interaction between protonated cation of 1 and benzenesulfonate anion.

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References