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Unique blue shift due to the formation of static pyrene excimer: highly selective fluorescent chemosensor for Cu^{2+}

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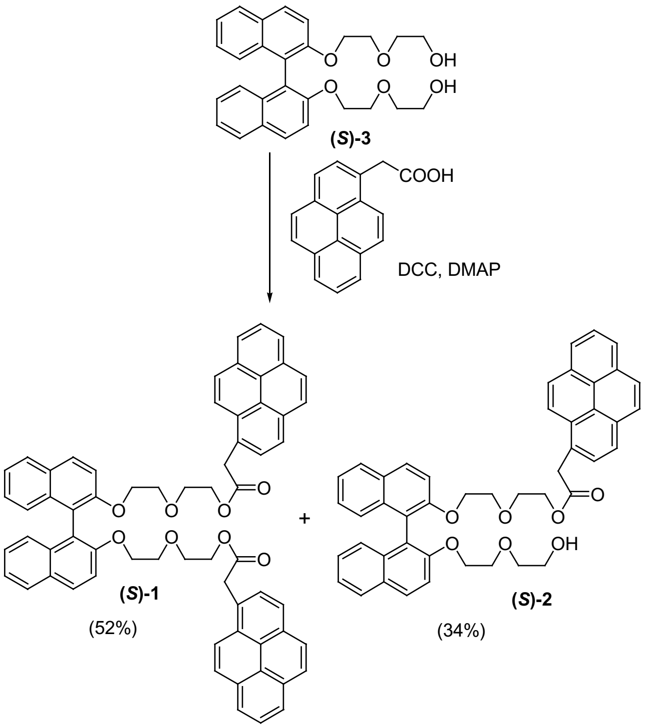
Abstract—New binaphthyl derivatives bearing pyrene groups have been synthesized and studied as fluorescent chemosensors for Cu^{2+} ions. A unique blue shift along with fluorescent enhancement in pyrene excimer emission was observed, which were induced by the formation of a static pyrene excimer.

Fluorescent chemosensors for the detection and measurement of metal ions, especially for cations with biological interest such as Na^+, Ca^{2+}, Cu^{2+}, and Zn^{2+}, are actively investigated.[1] In particular, Cu^{2+} is the third in abundance among the essential heavy metal ions in human body and plays an important role in various biological processes. Accordingly, the design and synthesis of fluorescent chemosensors for copper ions has become a very active area of research.[2–4] However, the fluorescent chemosensors, which display fluorescence enhancements are relatively few.[3,4]

We report herein a new binaphthyl-crown ether-bis(pyrene) system [(***S***)-**1**] as a selective fluorescent chemosensor for Cu^{2+}. A unique blue shift along with fluorescent enhancement in pyrene excimer emission of (***S***)-**1** was observed upon the addition of Cu^{2+}. The blue-shifted excimer peak attributes to the formation of the static pyrene excimer.

Compound (***S***)-**3** was synthesized from (***S***)-binaphthol by following the reported procedure,[5] which was then reacted with pyrene acetic acid. The crude product was purified by column chromatography using ethyl acetate and hexane (1:1, v/v) to give analytically pure compound **1** in 52% yield. Under this reaction condition, mono-pyrene derivative (***S***)-**2** was also obtained in 34% yield (Scheme 1).



Scheme 1. Synthesis of compounds **1** and **2**.

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Ca^{2+}, Cd^{2+}, Co^{2+}, Cs^{+}, Cu^{2+}, Hg^{2+}, K^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} ions were used to evaluate the metal ion binding properties of (***S***)-**1** and (***S***)-**2**. All fluorescent studies were conducted in acetonitrile, using a 1 μM concentration of compounds. The fluorescence emission changes of (***S***)-**1** upon the addition of various metal ions (100 equiv) are illustrated in Figure 1. Compound (***S***)-**1** effectively recognized Cu^{2+} among the metal ions examined. With excitation at 342 nm, (***S***)-**1** exhibits monomer and excimer emissions at 376 and 477 nm, respectively. As shown in Figure 1, a unique blue shift ($\Delta\lambda = 30$ nm) and an intensity enhancement (3-fold) were observed upon the addition of Cu^{2+}. In contrast, other metal ions gave almost no changes either in fluorescent intensities or in wavelength. From the fluorescence titration (Fig. 2), the association constant of (***S***)-**1** with Cu^{2+} was observed to be 65,600 M^{-1} (errors < 15%).[6] An intensity maximum was observed upon the addition of 5 equiv of Cu^{2+}; however, the addition of large amounts of Cu^{2+} (>50 equiv) caused the reduced intensity of (***S***)-**1**. For the calculation of association constant, the fluorescence data between 0.1 and 5 equiv of Cu^{2+} were used. As reported by Yang et al.,[3] fluorescence quenching could be attributed to the unbound Cu^{2+}. In the presence of excess Cu^{2+}, the net increase of the stronger fluorescent (***S***)-**1**·Cu^{2+} is too low to compensate for the fluorescence quenching by the additional unbound Cu^{2+}.[1d,7]

Pyrenes are known to display relatively efficient excimer emission peaks.[8] Depending on the origin of the pyrene dimer, a dynamic and a static excimer is defined.[8] The former is emitted from a pyrene dimer formed in the excited state, whereas the latter is emitted from that in the ground state.[8]

The blue shifted peak at 447 nm in the fluorescent emission of (***S***)-**1**·Cu^{2+} can be attributed to the formation of static pyrene excimer, as shown in Figure 2. We also observed a carbonyl group shift (1736–1729 cm^{-1}) in its IR spectrum upon the addition of Cu^{2+} (5 equiv), which confirms the participation of carbonyl oxygen in the binding with Cu^{2+}. A useful method to differentiate a dynamic excimer from a static one is to check the excitation spectrum.[3,8,9] Excitation spectrum at both the monomer wavelength (376 nm) and the excimer wavelength (477 nm) were almost identical, which indicates that the emission at 477 nm arises from the dynamic excimer.[3,8,9] On the other hand, the excitation spectrum of (***S***)-**1** with Cu^{2+} monitored at 447 nm is remarkably red-shifted ($\Delta\lambda = 15$ nm) in comparison to that recorded at 376 nm as well as at decreased monomer emission, which means that the 447 nm emission is from a static excimer (Fig. 3).[3,8,9] In the UV absorption spectra of (***S***)-**1** (Fig. 4), a unique red-shift (~20 nm) upon the addition of Cu^{2+} was also observed. This result explains that the pyrene moiety of (***S***)-**1**·Cu^{2+} forms a dimer within more efficient Py–Py interaction in the ground state, too.

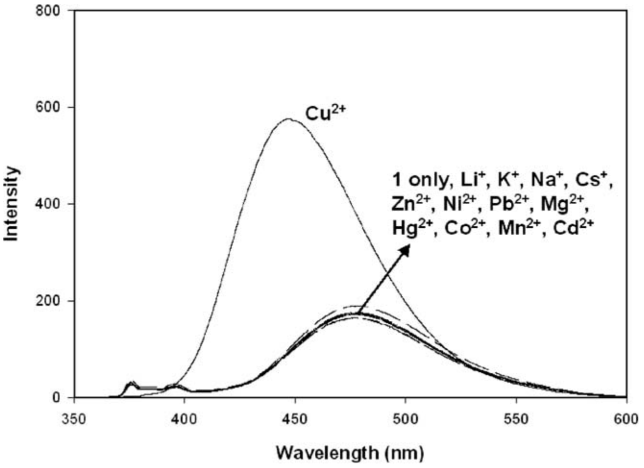
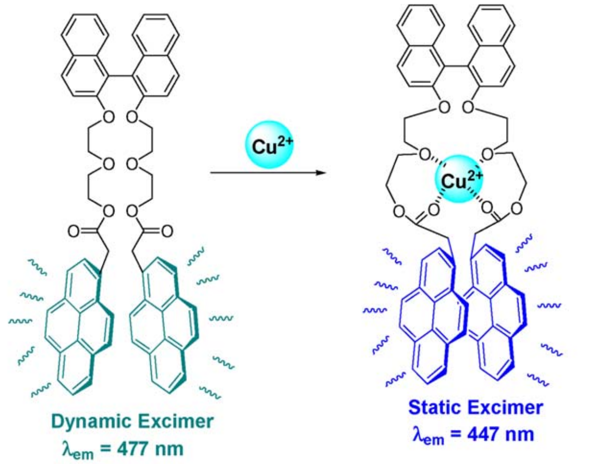


Figure 1. Fluorescence spectra of (***S***)-**1** (1 μM) upon the addition of various metal ions (100 equiv, 300 μM) in CH_3CN (excitation at 342 nm).



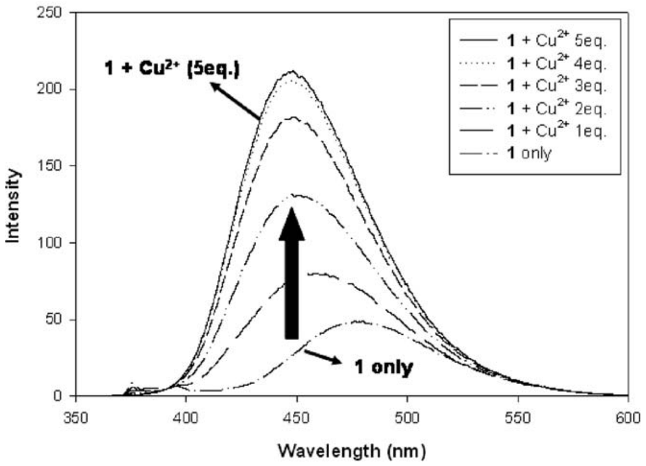


Figure 2. Fluorescent titrations of (***S***)-**1** (3 μM) with $Cu(ClO_4)_2$ in CH_3CN (excitation at 342 nm).

The formation of (***S***)-**1**·Cu^{2+} caused a new emitting static excimer, which displays an enhanced fluorescence compared to that of a dynamic excimer. Beyond the critical point (~5 equiv of Cu^{2+}), the fluorescence quenching effect by an additional unbound Cu^{2+} dominates the enhanced fluorescent effect by the formation of a static excimer.[3]

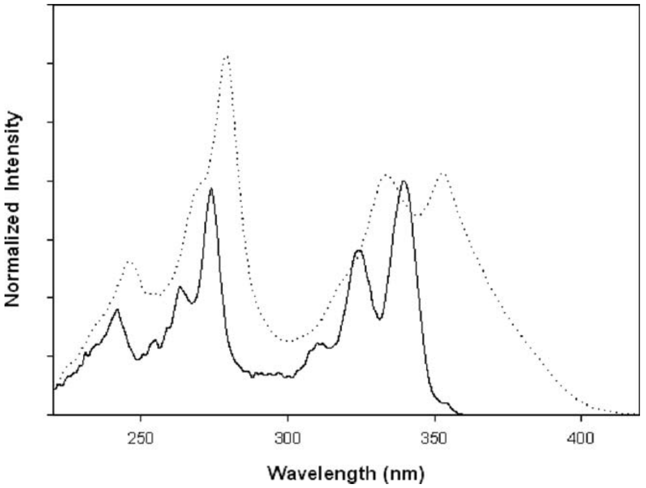


Figure 3. Excitation spectra (normalized) of (***S***)-**1** (1 μM) monitored at 376 nm (solid line) and 447 nm (dashed line) in the presence of Cu^{2+} (5 equiv) in CH_3CN.

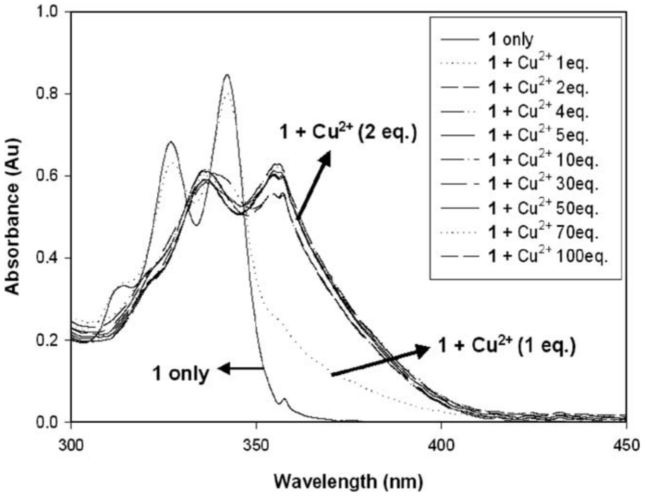


Figure 4. UV absorption spectra of (***S***)-**1** (10 μM) with $Cu(ClO_4)_2$ in CH_3CN (excitation at 342 nm).

The monopyrene derivative, (***S***)-**2**, also displayed a selective fluorescent change with Cu^{2+} among the metal ions examined (Fig. 5). However, there was only a moderate fluorescent quenching effect upon the addition of Cu^{2+}. From the fluorescence titration, the association constant of (***S***)-**2** with Cu^{2+} was observed to be 41,100 M^{-1} (errors < 15%).[6] The fluorescent quenching effect of (***S***)-**2**·Cu^{2+} can be productively compared with that of (***S***)-**1**.

Unfortunately, (***S***)-**1** did not display any fluorescent changes with chiral guests, such as (*R*)- and (*S*)-2-phenylglycinol hydrochloride and (*R*)- and (*S*)-2-phenylglycine methyl ester hydrochloride in acetonitrile. There was not any significant fluorescent change by changing the excitation wavelength (280 and 290 nm), which corresponds to the absorption of binaphthyl group, or using different solvent systems, such as toluene–DMSO and $CHCl_3$–DMSO (9:1, v/v, respectively).

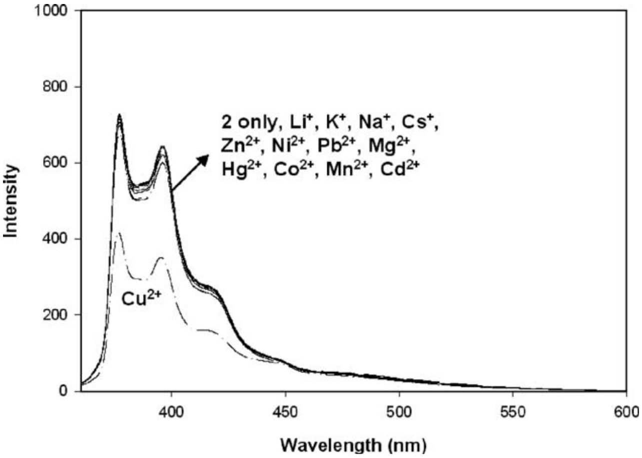


Figure 5. Fluorescence spectra of (***S***)-**2** (1 μM) upon the addition of various metal ions (100 equiv, 300 μM) in CH_3CN (excitation at 343 nm).

In conclusion, we synthesized new binaphthyl-crown derivatives bearing pyrene groups as potential fluorescent chemosensors for Cu^{2+}. A unique blue shift along with fluorescent enhancement in pyrene excimer emission of (***S***)-**1**·Cu^{2+} was observed, which was induced by the formation of a static pyrene excimer.

Acknowledgments

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Supplementary data

Experimental sections including syntheses and characterizations of (***S***)-**1** and (***S***)-**2** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.04.143.

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