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Connecting BINOL and terpyridine: the electronic effects of the linkage

Zeng Huang[a], Xi Chen[a], Jing Zhang[a], Xiao-Qi Yu[a,*], Lin Pu[b,*]

[a] Department of Chemistry, Key Laboratory of Green Chemistry and Technology (Ministry of Education), Sichuan University, Chengdu 610064, China
[b] Department of Chemistry, University of Virginia, Charlottesville, VA 22904-4319, USA

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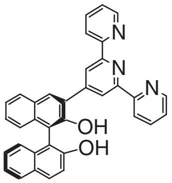
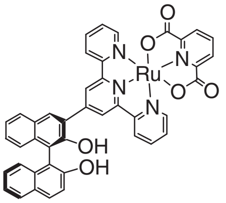
ABSTRACT

1,1′-Bi-2-naphthol and terpyridine are covalently connected either directly or through different linkers. It is found that in contrast to the directly connected one, when the saturated methyleneoxy linker is used, there is inefficient electronic communication between the BINOL and terpyridine units and the fluorescence of the BINOL unit cannot be completely quenched by the coordination of terpyridine unit with a Cu^{2+} ion. However, a phenylene linker allows an efficient electronic communication between the BINOL and terpyridine units and the fluorescence of the BINOL is almost completely quenched upon Cu^{2+} coordination. The interaction of these compounds with valinol is studied and large fluorescence enhancements are observed for those with efficient electronic communication between the BINOL and terpyridine units.

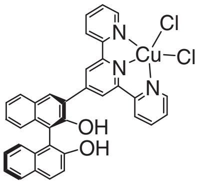
1,1′-Bi-2-naphthol (BINOL) represents a class of chiral molecules that has found broad applications in asymmetric catalysis, molecular recognition and materials.[1] In the meantime, multipyridine-based ligands such as terpyridine have been used extensively as metal coordinating ligands.[2] Recently, we and others have covalently linked BINOL and terpyridine together to build new materials for various applications.[3,4] For example, we have prepared the BINOL-terpyridine compound (*R*)-**1** and found that this compound in combination with $ZnEt_2$ and $Ti(O^iPr)_4$ is a highly enantioselective catalyst for the asymmetric reaction of methyl propiolate with aromatic aldehydes to generate γ-hydroxy-α,β-acetylenic esters.[3a] When terpyridine unit of (*R*)-**1** is coordinated to a Ru(II) metal center, the resulting complex (*R*)-**2** is a multi-task catalyst for the tandem oxidation of benzylic alcohols to aldehydes and asymmetric alkylzinc addition to generate chiral alcohols.[3b] We also studied the application of the Cu(II) complex (*R*)-**3** in chiral discrimination. This complex forms a gel in chloroform upon sonication which exhibits enantioselective gel collapsing in the presence of chiral amino alcohols.[3c] The solution of (*R*)-**3** also shows enantioselective fluorescent responses toward phenylglycinol. These discoveries demonstrate that joining the BINOL and terpyrdine units together can afford them new and promising properties for diverse applications. In (*R*)-**1**, the BINOL and terpyridine units are directly connected. We have also prepared compounds that contain two different types of linkers between BINOL and terpyridine. Herein, we report the synthesis and study of these compounds and their Cu(II) complexes. It is found that the type of linkers between the BINOL and terpyridine units has great effects on their electronic properties.



(*R*)-**1**



(*R*)-**2**



(*R*)-**3**

We first introduced a saturated methyleneoxy linker between the BINOL and terpyridine units of (*R*)-**1**. As shown in Scheme 1, from the reaction of (*R*)-**4**[5] with **5** in the presence of K_2CO_3, compound (*R*)-**6** was obtained. The MOM groups of (*R*)-**6** were removed by treatment with CF_3CO_2H to give the BINOL-terpyridine compound (*R*)-**7**. The UV spectrum of (*R*)-**7** shows $\lambda_{max}(\varepsilon) = 230$ (9.09×10^4), 277 (2.9×10^4), 323 (6.6×10^3) nm. Its fluorescence spectrum gives emission at λ = 371 nm. Treatment of (*R*)-**7** with $CuCl_2$ gave the corresponding Cu(II) complex (*R*)-**8**.

The conversion from (*R*)-**7** to (*R*)-**8** was investigated by using UV and fluorescence spectroscopic methods. As shown by the UV spectra in Figure 1a, titration of a solution of (*R*)-**7** with $CuCl_2$ led to a decrease in absorption at λ = 230 nm and an increase at λ = 323 nm. These changes are similar to those observed for the reaction of (*R*)-**1** with $CuCl_2$ (Fig. 2a).[3c] However, the change at λ = 277 nm for (*R*)-**7** is small when treated with Cu^{2+} which is quite different from (*R*)-**1**. Upon interaction with Cu^{2+}, (*R*)-**1** exhibited

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* Corresponding authors.
E-mail addresses: xqyu@tfol.com (X.-Q. Yu), lp6n@virginia.edu (L. Pu).

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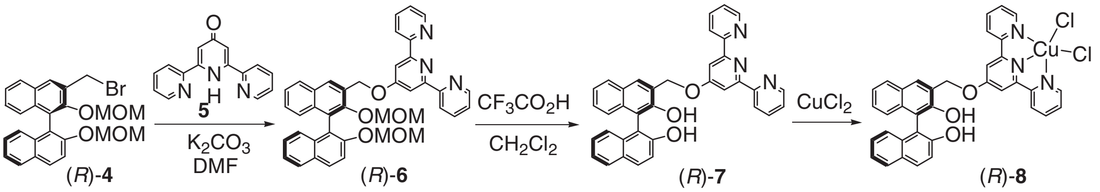


Scheme 1. Synthesis of the BINOL-terpyridine compound (*R*)-**7** and its Cu(II) complex (*R*)-**8**.

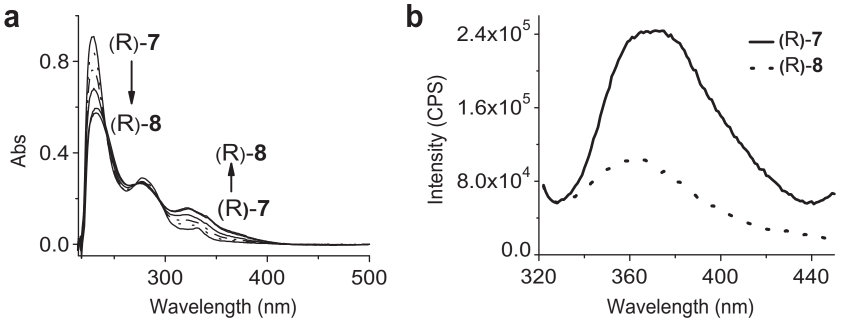


Figure 1. (a) UV titration of (*R*)-**7** (1.0×10^{-5} M in CH_2Cl_2/*n*-hexane = 2:3) with 0.2, 0.4, 0.6, 0.8, and 1.0 equiv $CuCl_2$ to Generate (*R*)-**8**. (b) Fluorescence spectra of (*R*)-**7** and (*R*)-**8** (5.0×10^{-7} M in CH_2Cl_2/*n*-hexane = 2:3, λ_{exc} = 334 nm, slits: 2 nm/5 nm).

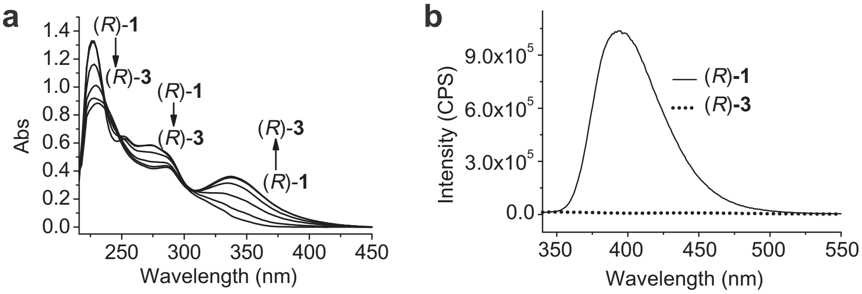


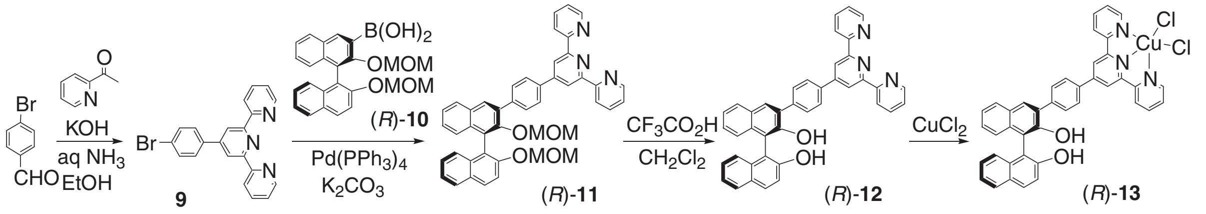
Figure 2. (a) UV titration of (*R*)-**1** (1.0×10^{-5} M in CH_2Cl_2/*n*-hexane = 2:3) with 0.2, 0.4, 0.6, 0.8, and 1.0 equiv $CuCl_2$ to generate (*R*)-**3**. (b) Fluorescence spectra of (*R*)-**1** and (*R*)-**3** (5.0×10^{-7} M in CH_2Cl_2/*n*-hexane = 2:3, λ_{exc} = 289 nm, slits: 2 nm/5 nm).

significantly greater decrease in absorption at λ = 273 nm. The observed changes at λ = ~230 and ~330 nm for compounds (*R*)-**1** and (*R*)-**7** in the presence of Cu^{2+} can be attributed to the increased conjugation within their terpyridine units upon coordination with Cu^{2+}. Unlike those in (*R*)-**1**, the BINOL and terpyridine units of (*R*)-**7** are not electronically conjugated. Thus, the coordination of its terpyridine unit to a Cu^{2+} should have much smaller effect on its BINOL unit which could explain its much smaller change for the absorption at λ = 277 nm. Figure 1b compares the fluorescence spectra of (*R*)-**7** and (*R*)-**8**. It shows that the coordination of a Cu^{2+} to (*R*)-**7** significantly reduces its fluorescence. However, unlike (*R*)-**3** whose Cu^{2+} almost completely quenches its fluorescence due to a ligand to metal electron or energy transfer process (Fig. 2b),[3c] (*R*)-**8** still shows significant fluorescence at λ = 363 nm. This demonstrates that because of the saturated methyleneoxy linkage between the BINOL and terpyridine units in (*R*)-**8**, the fluorescence of its BINOL unit cannot be completely quenched by the coordinated Cu^{2+}. The electronic communication between the BINOL and terpyridine units in (*R*)-**8** is not as efficient as that in (*R*)-**3**.

We also introduced a phenylene linker between the BINOL and terpyridine units of (*R*)-**1**. As shown in Scheme 2, from the reaction of *p*-bromobenzaldehyde with 2-acetylpyridine in the presence of KOH and NH_3, the terpyridine compound **9** was obtained.[6] The Suzuki coupling of **9** with the BINOL-boronic acid (*R*)-**10** gave (*R*)-**11**.[7] The MOM groups of (*R*)-**11** were removed by treatment with CF_3CO_2H to produce (*R*)-**12**. The UV spectrum of (*R*)-**12** shows $\lambda_{max}(\varepsilon)$ = 226 (7.03×10^4), 283 (4.16×10^4), 339 (7.3×10^3) nm. Its fluorescence spectrum gives strong emission at λ = 384 nm. Treatment of (*R*)-**12** with $CuCl_2$ gave the corresponding Cu(II) complex (*R*)-**13**.

The conversion of (*R*)-**12** to (*R*)-**13** was investigated by using UV and fluorescence spectroscopic methods. As shown by the UV spectra in Figure 3a, titration of a solution of (*R*)-**12** with $CuCl_2$ led to decrease in absorptions at λ = 228 and 283 nm and an increase at λ = 339 nm. The fluorescence spectra in Figure 3b show that the coordination of a Cu^{2+} from (*R*)-**12** to (*R*)-**13** almost completely quenches the emission. Thus, the effects of the coordination of a Cu^{2+} to (*R*)-**12** are very similar to those of (*R*)-**1**. The phenylene linker in (*R*)-**12** and (*R*)-**13** allows an efficient electronic communication between the BINOL unit and the coordinated Cu^{2+}, leading to the efficient fluorescent quenching.

Figure 4 compares the fluorescence spectra of the BINOL-terpyridine compounds. It shows that the introduction of the methyleneoxy unit in (*R*)-**7** gives significantly reduced fluorescence intensity as well as a blue-shifted emission wavelength. However, the emissions of compounds (*R*)-**1** and (*R*)-**12** without the saturated linker



Scheme 2. Synthesis of the BINOL-terpyridine (*R*)-**12** and its Cu(II) complex (*R*)-**13**.

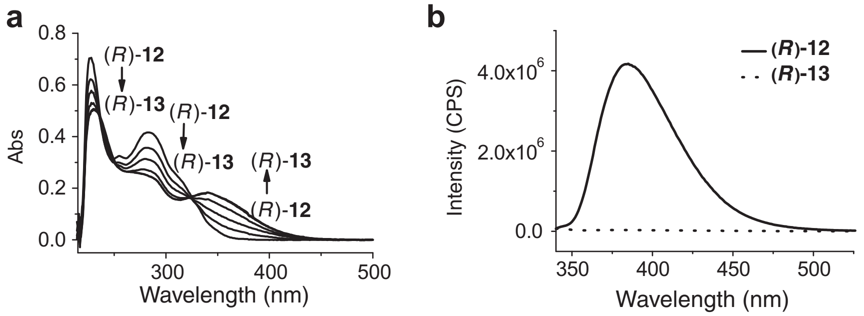


Figure 3. (a) UV titration of (*R*)-**12** (1.0×10^{-5} M in CH_2Cl_2/*n*-hexane = 2:3) with 0.2, 0.4, 0.6, 0.8, and 1.0 equiv $CuCl_2$ to generate (*R*)-**13**. (b) Fluorescence spectra of (*R*)-**12** and (*R*)-**13** (5.0×10^{-7} M in CH_2Cl_2/*n*-hexane = 2:3, λ_{exc} = 312 nm, slits: 2 nm/5 nm).

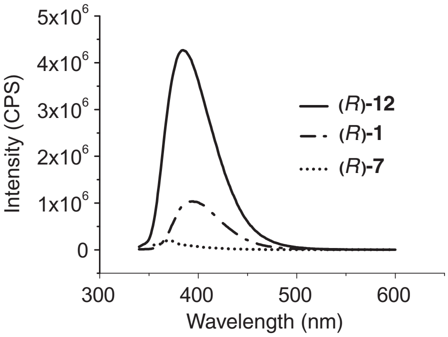


Figure 4. Comparison of the fluorescence spectra of (*R*)-**1** (λ_{exc} = 289 nm), (*R*)-**7** (λ_{exc} = 334 nm) and (*R*)-**12** (λ_{exc} = 312 nm) at 5.0×10^{-7} M in CH_2Cl_2/*n*-hexane = 2:3 (silts: 2 nm/5 nm).

are significantly enhanced. These strong fluorescence and their efficient quenching by Cu^{2+} coordination have suggested their potentials as fluorescent sensors.

We have studied the fluorescence responses of the BINOL-terpyridine-Cu(II) complexes toward valinol, an amino alcohol. As shown in Figure 5, both (*R*)-**3** and (*R*)-**13** exhibit large fluorescence enhancement in the presence of L-valinol with I/I_0 = 106.1 and 142.7, respectively. However, only very small fluorescence enhancement is observed for (*R*)-**8** when treated with D-valinol with I/I_0 = 1.25. These compounds also interacted with D-valinol which shows fluorescence enhancements similar to those in the presence of L-valinol with small enantioselectivity. The fluorescence enhancements of these compounds in the presence of the amino alcohol are attributed to a possible displacement of the Cu^{2+} ion off terpyridine unit. These results demonstrate that the Cu^{2+} complexes (*R*)-**3** and (*R*)-**13** are highly sensitive fluorescent sensors toward the amino alcohol, but the methyleneoxy linkage in (*R*)-**8** makes this molecule unsuitable for the fluorescent recognition of the amino alcohol.

Acknowledgments

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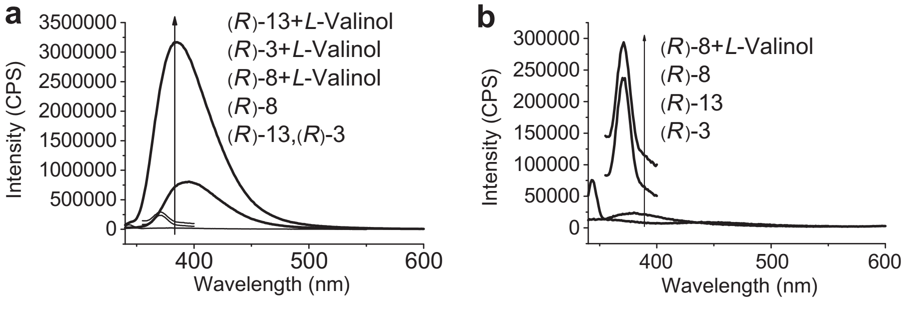

Figure 5. (a) Fluorescence responses of (*R*)-**3** (λ_{exc} = 289 nm, silts: 2 nm/5 nm), (*R*)-**8** (λ_{exc} = 334 nm, silts: 5 nm/5 nm) and (*R*)-**13** (λ_{exc} = 312 nm, silts: 2 nm/5 nm) (each at 5.0×10^{-7} M in CH_2Cl_2/*n*-hexane = 2:3) toward L-valinol (5.0×10^{-4} M). (b) A portion of (a) is amplified.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.08.068.

References and notes

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