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A Chiral Molecular Square with Metallo-Corners for Enantioselective Sensing

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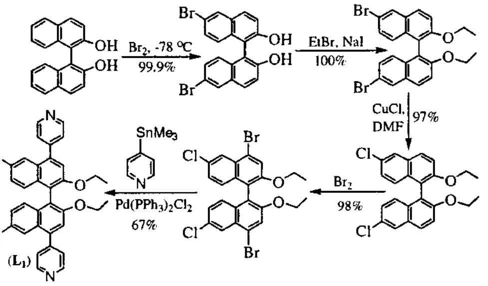
Metal-directed self-assembly has been widely used to construct supramolecular systems such as grids, helicates, boxes, and cylinders.[1] Compared to covalently bonded organic counterparts, metal−organic supramolecules can be assembled with much ease and higher efficiency.[2] The incorporation of metal centers can also impart novel functionalities such as host−guest recognition,[3] inclusion,[4] catalysis,[5] and fluorescence sensing.[6] Among many metal−organic supramolecular systems, the construction of molecular squares based on metallo-corners with ∼90 ° angles and linear bridging ligands has proven to be the most reliable strategy, as exemplified by successful design of numerous molecular squares based on the *cis*-$[M(phosphine)_2]^{2+}$ corners (M = Pd or Pt) by Stang et al.,[1d] the *cis*-$[M(en)]^{2+}$ corners (M = Pd and Pt, en is ethylenediamine) by Fujita et al.,[1e] and the *fac*-$(CO)_3ReX$ corners (X = halide) by Hupp et al.,[1g,1h] and the $M_2(carboxylate)_2$ corners by Cotton et al.[1i] Of particular interest to us are elegant studies by Hupp et al. that demonstrated the feasibility of constructing microporous molecular materials based on neutral Re-based molecular squares.[1g] We envision that the incorporation of axially chiral bridging ligands into such Re-based molecular squares could lead to enzyme-like chiral supramolecular systems exploitable for enantioselective recognition, sensing, separation, and catalysis.[7−9] Herein we wish to report the synthesis and characterization of a family of novel chiral molecular squares $[Cl(CO)_3Re(\mathbf{L_{1-4}})]_4$ (where $\mathbf{L_{1-4}}$ is enantiopure 4,4′-bis(pyridyl)-1,1′-binaphthyl) and the first observation of enantioselective luminescence sensing by a chiral metallocycle.

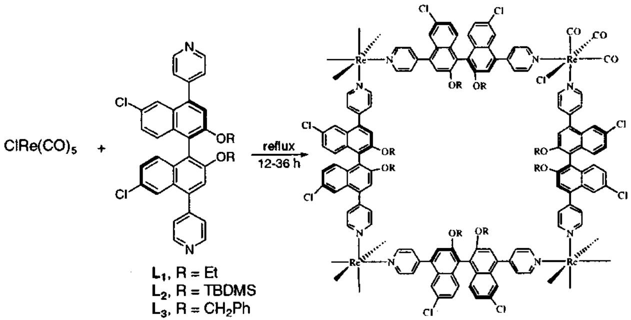
Enantiopure atropisomeric 6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthyl-4,4′-bipyridine $\mathbf{L_1}$ was synthesized in five steps starting from readily available 1,1′-bi-2-naphthol (BINOL) in 63.6% overall yield (Scheme 1). The bis(*tert*-butyldimethylsilyl) and bis(benzyl) analogues $\mathbf{L_2}$ and $\mathbf{L_3}$ were similarly prepared, while the bis(hydroxy) ligand $\mathbf{L_4}$ was obtained quantitatively by treating $\mathbf{L_2}$ with tetra(*n*-butyl)ammonium fluoride (TBAF) in THF. All these ligands have been characterized by ^1H and $^{13}C\{^1H\}$ NMR, UV−vis, and circular dichroism (CD) spectroscopies and high-resolution mass spectrometry.

Chiral molecular squares $[Cl(CO)_3Re(\mathbf{L_{1-4}})]_4$ (**1**−**4**) were prepared in very high yields by refluxing $ClRe(CO)_5$ and $\mathbf{L_{1-4}}$ in 1:1 molar ratio (Scheme 2). ^1H and $^{13}C\{^1H\}$ NMR spectra of **1**−**4** showed a single $\mathbf{L_{1-4}}$ ligand environment, suggesting the formation of cyclic species. FAB-MS showed the presence of molecular ions due to tetranuclear species for **1**−**3**,[10] and thus unambiguously established their cyclic tetrameric nature. The highest M/Z peak is due to the $[M - Cl]^+$ species in the FAB-MS of **4**. The formulations of **1**−**4** are supported by microanalysis results. Interestingly, **4** can also be prepared in high yields by treating **2** with TBAF, which provides further evidence for the tetrameric structure of **4**. The IR spectra of metallocycles **1**−**4** exhibit three carbonyl stretches, consistent with the formation of the *fac*-$[Cl(CO)_3Re]$ metallocorners that have local C_s symmetry.

Scheme 1



Scheme 2



1-4

The ^1H NMR spectra of **1**−**3** all exhibit well-resolved signals for a single ligand environment, indicative of diastereoselectivity in the assembly of chiral molecular squares based on $\mathbf{L_1}$−$\mathbf{L_3}$. On the basis of their single ligand environment, we believe that one single enantiomer has formed during the assembly of **1**−**3**, which possesses an approximate D_4 symmetry (Scheme 2). Available spectroscopic data cannot pinpoint the position of Cl atoms on the *fac*-$Re(CO)_3Cl$ corners, and this ambiguity has been fairly well-established among achiral cycles based on *fac*-$Re(CO)_3Cl$ metallocorners.[8] The ^1H signals of **4** appear very broad, probably a consequence of facile torsion motion of the atropisomeric $\mathbf{L_4}$ ligand. Numerous attempts have failed to produce X-ray diffraction-quality single crystals of **1**−**4**.

The electronic spectra of $\mathbf{L_{1-4}}$ are characterized by three $\pi \rightarrow \pi^*$ transitions at ∼240 nm, ∼300 nm, and ∼355 nm in the UV region. Metallocycles **1**−**4** exhibit all these three $\pi \rightarrow \pi^*$ transitions with slight bathochromic shifts (∼5 nm) for the absorptions near 360 nm. In addition, there are new bands around 325 nm for **1**−**4**, which are probably due to the MLCT excitations. CD spectra of ligands $\mathbf{L_{1-4}}$ exhibit three bisignate bands corresponding to the three $\pi \rightarrow \pi^*$ transitions. CD spectra of metallocycles **1**−**4** exhibit three major bands similar to those of atropisomeric bipyridine ligands, but with much higher intensities (Figure 1). The enhanced CD signals for **1**−**4** are consistent with the presence of multi-ligands in each metallocycle, while the similarity between the CD spectra of metallocycles **1**−**4** and atropisomeric bipyridine ligands L_{1-4}

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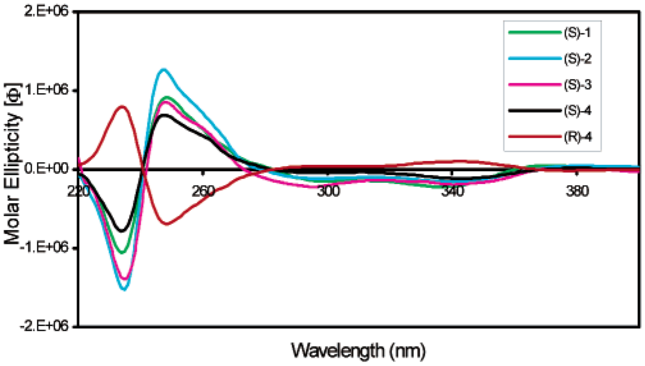

Figure 1. Circular dichroism spectra of (*S*)-**1**−**4** and (*R*)-**4** in acetonitrile at concentrations of 1.3−1.9 × 10^{-5} M.

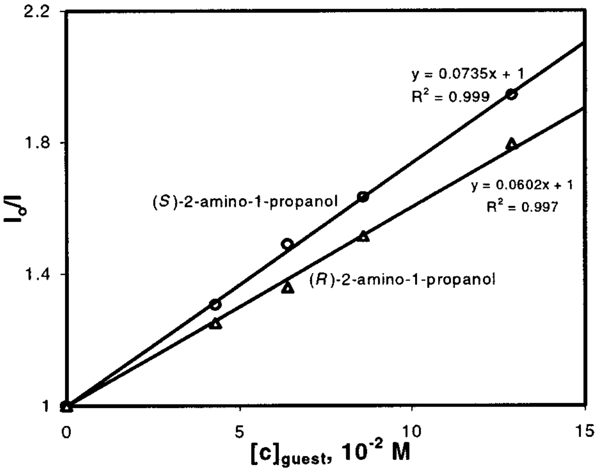

Figure 2. Stern-Völmer plots of (*R*)-**4** in the presence of (*S*)- and (*R*)-2-amino-1-propanol. The concentration of (*R*)-**4** is 2.2 × 10^{-6} M.

indicate that no chiral amplification has occurred during the self-assembly of enantiopure metallocycles.

While metallocycles **1**−**3** exhibit negligible luminescence signals, **4** shows two luminescence peaks around 412 and 536 nm in THF when excited at 360 nm at room temperature. The luminescence peak at 412 nm can be assigned to a ligand-localized $\pi \rightarrow \pi^*$ excited state, while the weaker luminescence at 536 nm can be attributed to a ^{3}MLCT excited state.[12]

We have studied the luminescence quenching of (*R*)- and (*S*)-**4** in the presence of chiral amino alcohols. The luminescence signal of enantiopure **4** at 412 nm can be quenched by both enantiomers of 2-amino-1-propanol, but at significantly different rates. Figure 2 shows the Stern−Völmer plots of **(R)-4** (2.2 × 10^{-6} M) in the presence of (*R*)- and (*S*)-2-amino-1-propanol in THF.[9] It is evident from Figure 2 that luminescence quenching of chiral metallocycle **4** by 2-amino-1-propanol is enantioselective. For (*R*)-**4**, the Stern−Völmer quenching constant K_{sv} is 7.35 M^{-1} in the presence of (*S*)-2-amino-1-propanol, and 6.02 M^{-1} in the presence of (*R*)-2-amino-1-propanol. (*R*)-**4** has an enantioselectivity factor $k_{sv}(R-S)/k_{sv}(R-R)$ of 1.22 for luminescence quenching in favor of (*S*)-2-amino-1-propanol. The opposite trend in enantioselectivity was observed for the quenching of (*S*)-**4** by 2-amino-1-propanol, which lends further support to a chirality-based luminescence-quenching selectivity. This magnitude of enantioselectivity for **4** is significantly higher that of free ligand $\mathbf{L_4}$ (1.04), suggesting a better-defined chiral environment conferred by metallocycle **4**.[14] Pu et al. has proposed that the formation of a nonemissive hydrogen-bonded complex and a poorly emissive excited-state proton-transfer complex is responsible for the luminescence quenching of phenylene-acetylene dendrimers with BINOL core by amino alcohols.[14,15] It is interesting to note that no enantioselectivity was observed for the luminescence quenching of **4** by 1-amino-2-propanol, which supports the involvement of amino groups in the formation of a ground-state hydrogen-bonded complex and an excited-state proton-transfer complex.[16]

In summary, a family of novel chiral molecular squares have been readily assembled using enantiopure atropisomeric bipyridyl bridging ligands and *fac*-Re(CO)$_3$Cl corners. Metallocycle **4** exhibits interesting enantioselective luminescence quenching by chiral amino alcohols. Higher enantioselectivity of **4** versus $\mathbf{L_4}$ is probably a consequence of a better-defined chiral environment in the metallocycle. Exploration of chiral metallocycles for applications in asymmetric catalysis is currently underway.

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Supporting Information Available: Experimental procedures, analytical data, one table, and 10 figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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