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Mixed-Metal Complexes Incorporating Platinum and Lanthanide Centers for Selective Binding and Chirality Sensing of Succinates

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Supporting Information

ABSTRACT: A chromophoric platinum complex was combined with a nonacoordinated cyclen−lanthanide complex to give a new series of mixed-metal receptors. They specifically formed 1:1 complexes with dicarboxylates and offered selective chirality sensing of succinates.

Metal receptors are a family of programmed metal complexes exhibiting specific molecular recognition based on their characteristic coordination chemistry.[1] In addition to various transition-metal complexes,[2] lanthanide complexes have recently been recognized as effective receptors with selective sensing properties available for bioanalytical applications.[3] To generate more sophisticated complex functions, two or more types of metal centers have been elegantly arranged in designed three-dimensional spaces.[4] Several d−f mixed-metal complexes exhibited particularly excellent luminescent, magnetic, and receptor properties.[5] We report below the combination of platinum(II) and lanthanide(III) centers to develop a new series of mixed-metal receptors. Although similar d−f mixed-metal complexes commonly exhibit sensitized lanthanide luminescence,[6] these newly designed metal complexes provide unique recognition and chirality sensing of biologically interesting succinate anions.[7]

Square-planar platinum(II) complexes with oligopyridine ligands are well-characterized effective building blocks for DNA intercalators, supramolecular assemblies, and intelligent receptors.[8] As shown in Figure 1, we attached platinum complexes to the pyridine moieties of cyclen−lanthanide complexes and obtained a series of mixed-metal complexes in good yields (62% for **1a**, 63% for **1b**, 70% for **2a**, and 67% for **2b**).[9] The crystal structure of complex **2a** reveals that two different kinds of metal centers were successfully included as substrate binding sites in the single complex. The Lu^{3+} center was coordinated by an octadentate cyclen ligand and one water molecule to form a nonacoordinated complex, and the two attached platinum complexes adopted a common square-planar structure. This class of mixed-metal complexes possesses the following interesting features that enable them to behave as effective receptors for the binding of bifunctional substrates: (1) The nonacoordinated cyclen−lanthanide complex has one water molecule in an axial coordination site available for an external guest. (2) The introduced platinum complexes work as substrate binding sites as well as intense chromophores for CD detection. (3) The two different metal centers, e.g., Pt^{2+} and Yb^{3+}, allow chain-length selective binding of bifunctional substrates. Thus, the present mixed-metal

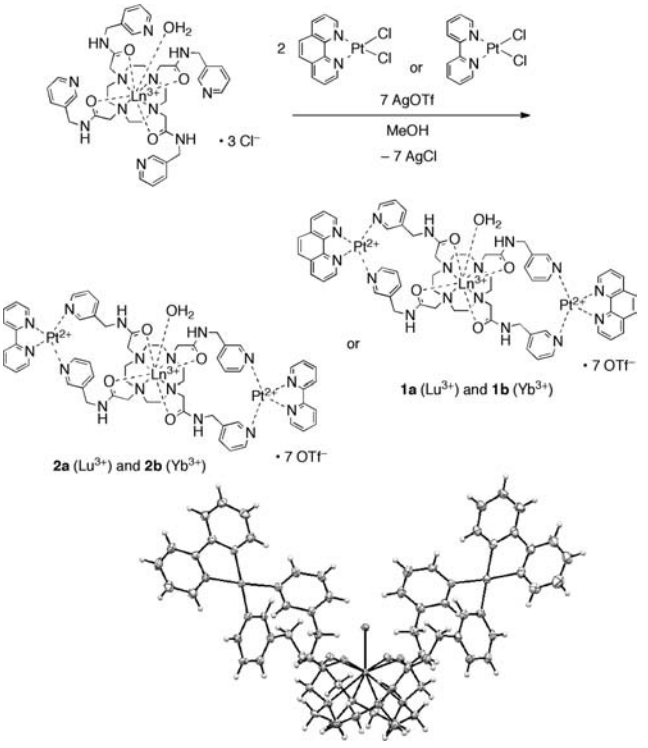

Figure 1. Synthesis of metal receptors and the crystal structure of metal receptor **2a**.

complexes can sense the chirality of specific substrates upon multiple-metal coordination.

Figure 2 shows the UV spectral changes of metal receptor **1b** (Ln^{3+} = Yb^{3+}) upon the stepwise addition of a succinate dianion.[10] When succinate was added to a CH_3CN solution of receptor **1b**, intense UV peaks appeared around 350 and 367 nm, which corresponded to the absorption region of the platinum complex chromophore. The plot of the observed UV change against the mole ratio of dianion/receptor indicates that receptor **1b** bound one succinate dianion. Because this receptor has two Pt^{2+} centers and one Yb^{3+} center, "hetero" and "homo" binding modes are assumed for 1:1 complexation with the succinate dianion (Figure 2). Both Yb^{3+} and Pt^{2+} centers bound $-CO_2^-$ groups of the succinate in the "hetero" mode, and two Pt^{2+}

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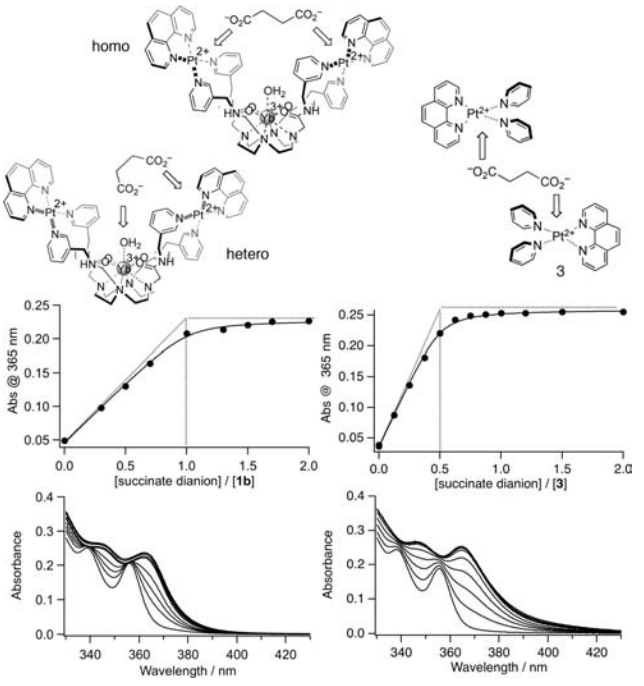

Figure 2. UV spectral changes of metal receptor **1b** and platinum complex **3** upon the addition of a succinate dianion (dicyclohexylamine salt) in CH_3CN. [**1b**] = 6.0×10^{-5} M, [**3**] = 1.2×10^{-4} M, cell length = 1 cm, and 25 °C.

centers bound $-CO_2^-$ groups of the succinate in the "homo" mode. Platinum complex **3**, supported by one phenanthroline and two pyridines, exhibited similar UV spectral changes, indicating that the two Pt^{2+} centers complexed one succinate dianon to form a 2:1 complex. These UV spectral changes were quantitatively analyzed to determine the stability constants for receptor−succinate complexes: log K = 5.9 ± 0.2 for the **1b**−succinate complex and log K_1 = log K_2 = 5.0 ± 0.1 for **3**−succinate complexes.[11] NMR experiments were performed with receptor **1a** (Ln^{3+} = Lu^{3+}) and **3** upon the addition of an equimolar succinate dianion in CD_3CN (Figure S1 in the Supporting Information). Proton signals for one free pyridine were observed with **3**, indicating that one of the two pyridine ligands was replaced by one $-CO_2^-$ group of the succinate dianion. The addition of a succinate dianion to receptor **1a** led to the NMR spectrum of a single species with no C_2 symmetry, indicating that only one of the four pyridine moieties coordinating the Pt^{2+} centers was replaced by one $-CO_2^-$ group of the succinate dianion. The UV absorption spectral change of **1a** was almost the same as that of **1b**, suggesting that Yb^{3+} and Lu^{3+} ions show only small differences in their guest binding behavior (Figure S2 in the Supporting Information). The succinate complex with **1a** or **1b** showed a UV spectrum that could be assumed to be the sum of the spectra of two different platinum complexes (Figure S3 in the Supporting Information). Thus, the observed UV spectral changes provided a good indication of the pyridine substitution on the Pt^{2+} center.

Chiral dicarboxylates **4a**−**4c** having different chain lengths of the $-CH_2-$ spacers between the two $-CO_2^-$ anions exhibited characteristic UV and CD spectral changes in the presence of an equimolar receptor **1b** (Ln^{3+} = Yb^{3+}; Figure 3). All of the examined dianions showed new UV bands around 350 and 367 nm upon complexation with receptor **1b**, indicating that

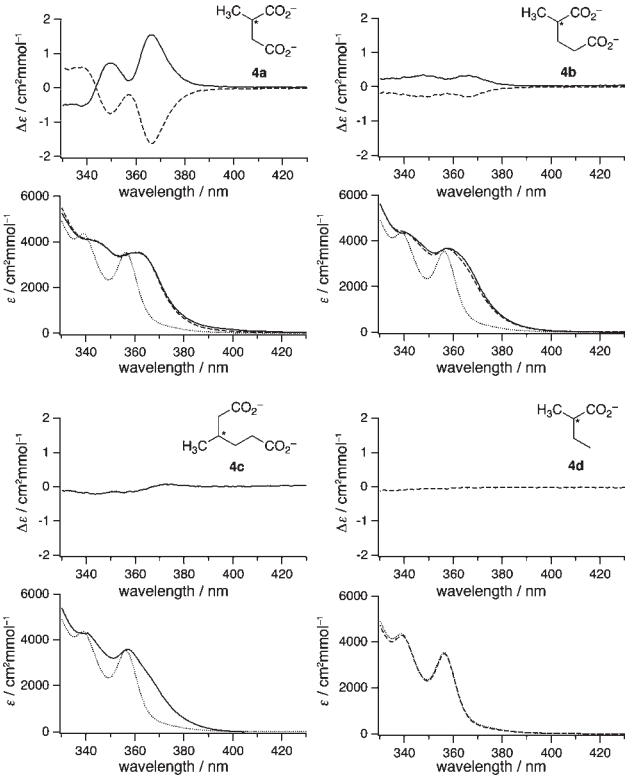

Figure 3. UV and CD spectral changes in platinum complex absorption of metal receptor **1b** (Ln^{3+} = Yb^{3+}) upon the addition of various carboxylates **4a**−**4d** in CH_3CN. [**1b**] = [chiral anion (dicyclohexylamine salt)] = 6.0×10^{-5} M and 25 °C. Dotted line: **1b** only. Solid line: **1b** + *R* isomer. Dashed line: **1b** + *S* isomer.

pyridine substitution occurred in each case. Among them, only chiral succinate **4a** gave rise to significant CD signals,[10] the signs of which were determined by the absolute stereochemistry of the succinate. Monocarboxylate anion **4d** barely induced UV spectral changes at the platinum complex chromophore, demonstrating that the $-CO_2^-$ group of the substrate did not coordinate with the Pt^{2+} center. As reported for related lanthanide complexes,[12] the $-CO_2^-$ group of monocarboxylate **4d** was strongly bound with the Yb^{3+} center, not the Pt^{2+} centers. Because dianions **4b** and **4c** having longer methylene spacers gave rise to smaller UV and CD spectral changes, the mixed-metal receptor **1b** exhibited chain-length selectivity in the "hetero" binding of carboxylates (see Figure 2). When platinum complex **3** was employed, both dianions and monoanion **4a**−**4d** gave rise to characteristic UV spectral changes upon pyridine substitution on Pt^{2+} centers (Figure S4 in the Supporting Information). Significant CD signals were observed with dianion **4a**, but their sign was opposite and their intensity lower than that of mixed-metal complex **1b**.[13]

CD is one of the most effective methods for determination of the absolute configuration and enantiomeric purity of substrates, but it is applicable only for chromophoric substrates. Several types of chirality probes have been developed to form CD-active species with nonchromophoric chiral substrates.[14] We characterized metal complexes **1a** and **1b** as a new class of CD chirality probes for determination of the enantiomeric excess (ee %) of chiral succinates. Figure 4 illustrates the typical relationship between ee % of the examined methylsuccinate dianion **4a** and

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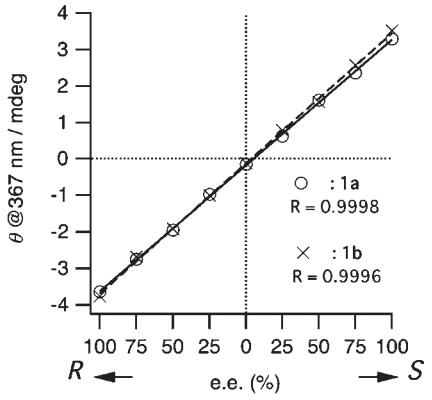

Figure 4. CD chirality probing of nonchromophoric methylsuccinate dianion **4a** (dicyclohexylamine salt) with metal receptors **1a**(Lu) and **1b**(Yb). [**1a**] = [**1b**] = [**4a**] = 6.0×10^{-5} M, cell length = 1 cm, and 25 °C.

the intensity of the induced CD signals with receptor **1a** or **1b**. Because linear relationships were confirmed, the present mixed-metal complexes worked as effective CD chirality probes for dicarboxylate substrates.

We have developed new mixed-metal receptors in which Pt^{2+} and Ln^{3+} centers effectively bound dicarboxylates. These receptors exhibited selective CD responses that were dependent on the chain length and chirality of the dicarboxylate substrates. Among the employed chiral anions, the methylsuccinate dianion specifically induced CD signals upon 1:1 complexation with mixed-metal receptors. Both stereochemistry and optical purity were easily determined by the CD probing method, which has the advantage of simplicity for amplifying enantiomeric purity information. Further combinations of various metal centers may have wide applications in the recognition and detection of multifunctional substrates.

■ ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data of **2a** in CIF format, synthesis of receptors **1** and **2**, ^{1}H NMR spectral changes of receptor **1b** upon the addition of succinate, estimated spectra of two platinum complexes in the **1b**—succinate complex, and UV/CD spectral changes of complex **3** with carboxylates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See the Supporting Information.

(10) We used a mixture of succinic acid and dicyclohexylamine (1:2 mole ratio) in CH_3CN as a source of the succinate dianion. Other anions were prepared as well. When a CD experiment with chiral methylsuccinic acid was carried out in the absence of dicyclohexylamine, no CD signal was induced by **1b**.

(11) Ligand exchange with a succinate anion on the platinum center was largely acceralated in **1b** by cooperative binding (required period to reach the equilibrium at room temperature: 10 h for **3** and 1 h for **1b**).

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(13) Complex **2b** similarly exhibited UV and CD spectral changes upon complexation with succinate **4a**. See Figure S5 in the Supporting Information.

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