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Selective colorimetric sensing of Co(II) in aqueous media with a spiropyran–amide–dipicolylamine linkage under UV irradiation†

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A spiropyran–amide–dipicolylamine linkage behaves as a colorimetric receptor for selective Co^{2+} sensing in aqueous media under UV irradiation. This is promoted by strong coordination of Co^{2+} with amide oxygens of the receptors and efficient photoisomerization of the spiropyran moieties.

Co^{2+} plays many important roles in biological systems. It is a main component of vitamin B_{12}, essential for folate and fatty acid metabolism.[1] The deficiency of Co^{2+} leads to anemia, retarded growth, and loss of appetite. However, excess dose causes diarrhea and cancer; the maximum tolerable level of Co is *ca.* 10 ppm (170 μM).[2] Co^{2+} is also essential in industry for manufacturing pigments, batteries, and alloys.[3] Selective and quantitative detection of trace levels of Co^{2+} is therefore necessary. Many analytical techniques such as flame atomic absorption and flow injection detect low levels of Co^{2+}, but require either tedious sample pretreatments or expensive instrumentation.

The design of chemosensors for metal cations has attracted much attention since they facilitate rapid detection of targeted cation by simple optical measurements.[4] Several successful receptors for Cu^{2+}, Zn^{2+}, and Hg^{2+} have been proposed, but the design of Co^{2+} receptor has been unsuccessful. All reported fluorometric[5] or colorimetric[6] Co^{2+} receptors act only in organic media[5a,b] or exhibit poor selectivity.[5c–f,6a–c] There is only one system enabling selective Co^{2+} sensing in aqueous media,[6d] but this is based on an aggregation of Ag particles by interaction with Co^{2+}, and suffers from handling difficulty and poor quantitative capability.

Here we report a molecular receptor enabling selective and quantitative Co^{2+} sensing. We employ a spiropyran dye that changes color upon UV irradiation due to the isomerization from the spirocyclic (SP) form to the spirocycle-opened merocyanine (MC) form.[7] The receptor, a spiropyran–amide–dipicolylamine linkage (**1**), exists as a colorless SP form in the dark or under UV irradiation. UV irradiation of **1** with Co^{2+}, however, leads

to coloration. This is promoted by strong coordination of Co^{2+} with amide oxygen, leading to efficient photoisomerization of the spiropyran moieties.

The receptor **1** was obtained in 49% yield as a red solid, by the reaction of an amino-substituted spiropyran derivative with 2-chloroacetyl chloride followed by condensation with di-2-picolylamine. The materials were characterized by ^{1}H, ^{13}C NMR and FAB-MS analysis (Fig. S1–S6, ESI†).

Fig. 1 shows the absorption spectra of **1** measured in a buffered water–MeCN mixture (1/1 v/v; HEPES 100 mM; pH 7.4) after stirring for 1 h at 25 °C. As shown in (a), without cation in the dark, **1** shows almost no absorption at >400 nm, indicating that **1** exists as a SP form. As shown in (b), UV irradiation (280 nm) of the solution creates an absorption band at 472 nm, although at a very weak level. This is assigned to the MC form of **1** by *ab initio* calculation (Gaussian 03). The singlet electronic excitation ($S_0 \rightarrow S_1$) of **1**(MC) is mainly contributed by HOMO → LUMO transition (Table S1, ESI†). Its energy is 2.64 eV (469 nm), which is close to the observed spectrum (472 nm). The π electrons on both HOMO and LUMO
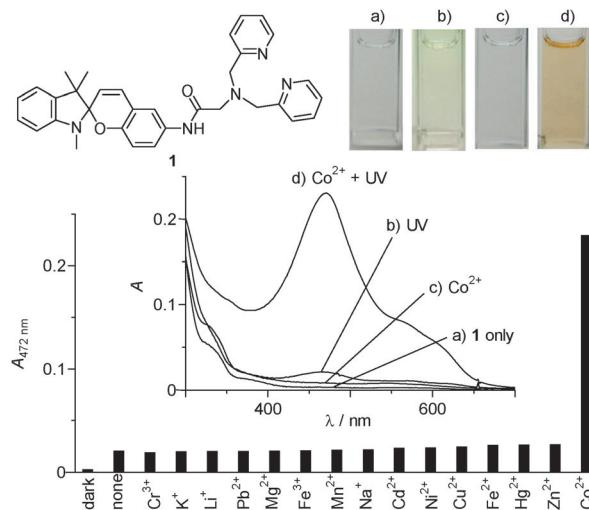

Fig. 1 Absorption spectra of **1** (20 μM) measured in a water–MeCN mixture (1/1 v/v; pH 7.4) after stirring for 1 h (a) in the dark, (b) under UV irradiation (280 nm), (c) with Co^{2+} (1 equiv.) in the dark, and (d) with Co^{2+} (1 equiv.) under UV irradiation. The bar graph shows the absorbance of solutions at 472 nm measured with and without each metal cation after UV irradiation. The detailed spectra are shown in Fig. S7 (ESI†).

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† Electronic supplementary information (ESI) available: Experimental, supplementary data (Table S1–S3 and Fig. S1–S16), and Cartesian coordinates for compounds. See DOI: 10.1039/c2cc30258f

are delocalized on the spiropyran moiety (Table S2, ESI†), indicating that the 472 nm absorption is assigned to the charge transfer band of **1**(MC).[8]

As shown in (c), the solution containing **1**, when treated with Co^{2+} (1 equiv.) in the dark, shows no absorption. UV irradiation of the solution, however, creates a strong MC band (d), where the solution changes from colorless to yellow. As shown by the bar graph, other metal cations do not promote coloration, indicating that Co^{2+} selectively promotes SP → MC isomerization of **1**. Note that this isomerization is unaffected by other cations (Fig. S8, ESI†), although addition of Cu^{2+} leads to significant decrease in the MC band due to the strong coordination of the receptor with Cu^{2+}.[9] This suggests that **1** enables selective Co^{2+} sensing in the presence of many other cations. It is also noted that the Co^{2+}-induced isomerization terminates within 1 h (Fig. S9, ESI†), indicating that 1 h assay time is required for sensing. In addition, the isomerization occurs at pH 7–12 (Fig. S10, ESI†), suggesting that **1** enables Co^{2+} sensing in neutral–basic media.

Absorption titration of **1** (20 μM) with Co^{2+} under UV irradiation shows a linear relationship between the absorbance and Co^{2+} amount at 1.0–10 μM (Fig. 2). This indicates that **1** enables quantification of Co^{2+} over this range. The detection limit (1.0 μM) is lower than that of the reported receptors.[5,6] The increase in MC band is saturated with 0.5 equiv. of Co^{2+}. Job's plot analysis (Fig. S11, ESI†) shows a maximum absorption at X ($= [Co^{2+}]/([Co^{2+}] + [\mathbf{1}])$) = 0.33, indicative of 2 : 1 interaction for **1** with Co^{2+}. This is further confirmed by ESI-MS analysis (Fig. S12, ESI†): the solution shows a peak at m/z 1220.7, assigned to the $[\mathbf{1} + \mathbf{1} + Co^{2+} + ClO_4^-]^+$ ion.

The Co^{2+}-induced coloration of **1** is due to the formation of the 2 : 1 **1**(SP)–Co^{2+} complex (Scheme 1c) and photoisomerization of its spiropyran moieties, producing the 2 : 1 **1**(MC)–Co^{2+} complex (d).[10] The formation of 2 : 1 **1**(SP)–Co^{2+} complex is confirmed by MS analysis (Fig. S13, ESI†): **1** treated with Co^{2+} in the dark shows a peak at m/z 1220.3.[11] It has an 8-coordinated structure with a symmetry of bicapped trigonal antiprism (D_{3d}),[12] involving two amide O, two amine N, and four pyridine N. *Ab initio* calculation (Scheme 1c) reveals that four pyridine N and two amide O are located at the corners of trigonal antiprism, and two amine N are at the top and bottom of trigonal faces. The average distances for Co–N (2.457 Å) and Co–O (2.190 Å) are shorter than the sum of van der Waals
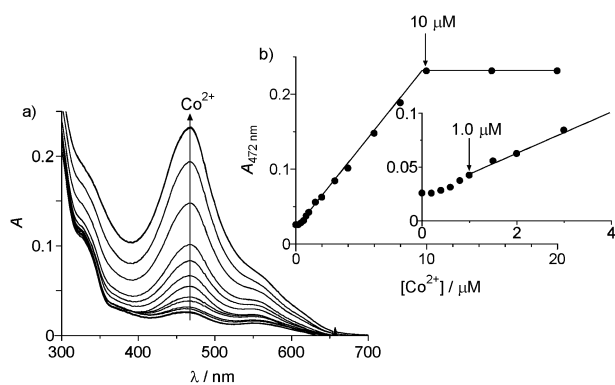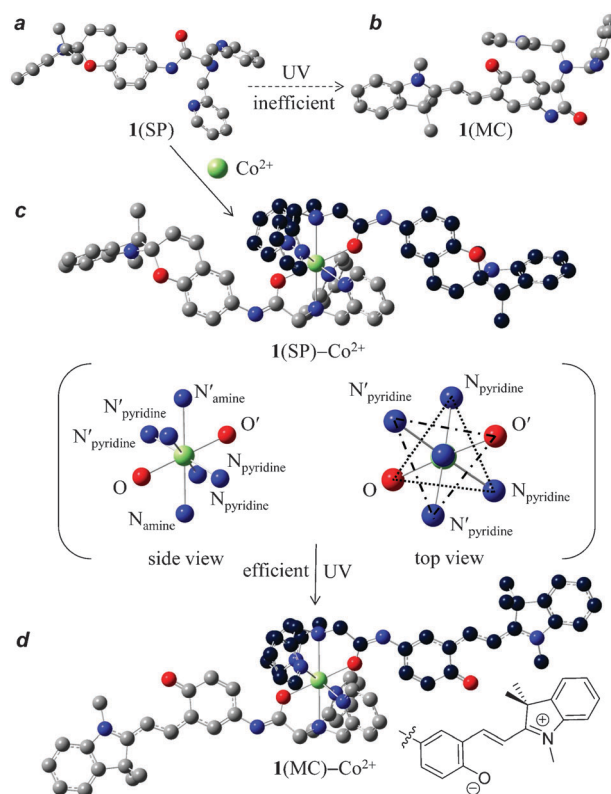

Scheme 1 Proposed mechanism for Co^{2+}-induced SP → MC isomerization of **1**. All structures were optimized at the DFT level (B3LYP/3-21G). The gray (black), blue, red, and green balls are C, N, O, and Co atoms, respectively. The bond lengths are summarized in Table S3 (ESI†).

radii of Co and N (3.14 Å) and Co and O (2.93 Å), respectively.[13] This supports the 8-coordinated structure of the 2 : 1 **1**(SP)–Co^{2+} complex.

UV irradiation of **1** without Co^{2+} (Fig. 1b) scarcely promotes isomerization. This is because, as reported,[7] electron donation by the amide N strengthens the spiro C–O bond and suppresses its cleavage (Scheme 1a→b). UV irradiation of **1**(SP)–Co^{2+}, however, promotes isomerization. Coordination of Co^{2+} with amide O leads to withdrawal of electrons on amide O and decreases the electron density of amide N due to the amide resonance (Fig. 3).[14] This suppresses the electron donation from the amide N and promotes isomerization. The decreased electron density of amide N is confirmed by natural population analysis (NPA).[15] The NPA charge of amide N for **1**(SP) is −0.629, but that for **1**(SP)–Co^{2+} complex is more positive (−0.284), indicating that coordination of amide O with Co^{2+} indeed decreases the electron donation ability of amide N. This thus weakens the spiro C–O bond and promotes SP → MC photoisomerization (Scheme 1c→d).

The Co^{2+}-selective SP → MC isomerization of **1** is due to the strong coordination of Co^{2+} with amide O. FT-IR analysis confirms this. **1** shows a C=O stretching band at 1653 cm^{-1} (Fig. 3a). Addition of Co^{2+} shifts the band to lower frequency ($\Delta = 19\ cm^{-1}$, Fig. 3g) due to the coordination with Co^{2+}. Alkali or alkaline-earth metal cations, especially Mg^{2+}, associate with C=O more strongly than transition metal cations;[16] however, addition of Mg^{2+} scarcely shifts the band (Fig. 3b). A dipicolylamine (DPA) unit scarcely coordinates with Mg^{2+},[17]

Fig. 2 (a) Result of absorption titration of **1** (20 μM) with Co^{2+} in a water–MeCN mixture (1/1 v/v; pH 7.4). Each spectrum was obtained after UV irradiation for 1 h. (b) Change in absorbance at 472 nm.
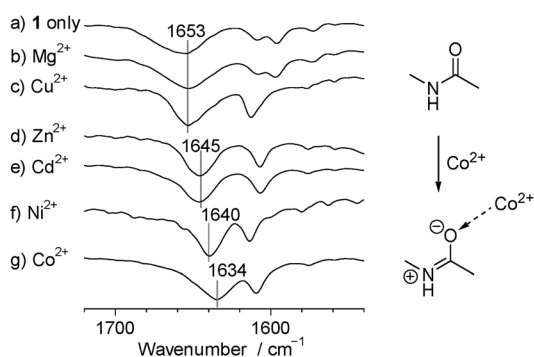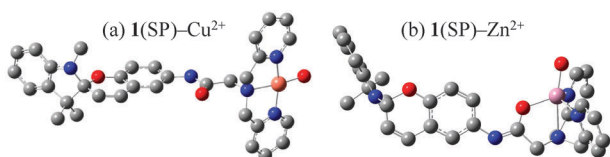
Fig. 3 FT-IR spectra of **1** (10 mM) measured in a D_2O–MeCN (1/1 v/v) mixture with each metal cation (1 equiv.) after stirring for 1 h in the dark.

Scheme 2 Optimized structures of (a) 1:1 **1**(SP)–Cu^{2+} and (b) 1:1 **1**(SP)–Zn^{2+} complexes (B3LYP/3-21G), where OH^- is attached to the metal centers. The orange and purple balls are Cu and Zn atoms, respectively.

implying that assisted coordination by the DPA unit of **1** is important for strong coordination of Co^{2+} with amide O.

Cu^{2+} coordinates with the DPA unit more strongly than Co^{2+},[9] but scarcely shifts the C=O band (Fig. 3c). An amide–DPA linkage coordinates with Cu^{2+} in a 1:1 stoichiometry,[18] as confirmed by MS analysis (Fig. S14, ESI†). Absence of interaction of Cu^{2+} with amide O is because, as shown in Scheme 2a and reported,[18] Cu^{2+} coordinates with the DPA unit and scarcely interacts with amide O. As shown in Fig. 3d–f, coordination of Zn^{2+}, Cd^{2+}, and Ni^{2+} with amide O is also weaker than that of Co^{2+}. MS analysis (Fig. S14, ESI†) suggests the formation of 1:1 complexes for these cations,[18] indicative of a structure involving two pyridine N, amine N, and amide O (Scheme 2b). As summarized in Table S3 (ESI†), the amide C=O length for the Zn, Cd, and Ni complexes (1.271, 1.271, and 1.270 Å) is shorter than that for the Co complex (1.290 Å), which is consistent with the FT-IR data. The NPA charge of amide N for the Zn, Cd, and Ni complexes (−0.564, −0.568, and −0.569) is more negative than that for the Co complex (−0.284). These suggest that strong coordination of Co^{2+} with amide O indeed decreases the electron density of amide N and promotes Co^{2+}-selective isomerization of spiropyran moieties. In contrast, the average cation–N distance for the Zn, Cd, and Ni complexes (2.239, 2.405, and 2.123 Å) is shorter than that for the Co complex (2.457 Å). This suggests that in the Zn, Cd, and Ni complexes, strong cation–N coordination probably results in relatively weaker cation–O interaction. This implies that *weak* Co^{2+}–N coordination creates a suitable structure for strong coordination of Co^{2+} with amide O and promotes SP → MC photoisomerization (Scheme 1c→d).

Note that the **1**(MC)–Co^{2+} complex does not revert to the SP form by visible light irradiation (Fig. S15, ESI†). This is probably because the MC form is stabilized in aqueous media by

H bonding interaction.[19] This suggests that Co^{2+} sensing can be performed even under room lighting. In contrast, addition of EDTA to the solution followed by extraction with CH_2Cl_2 enables successful recovery of **1** as a SP form (Fig. S16, ESI†). The obtained **1** shows Co^{2+}-induced coloration similar to the virgin **1**, indicating that **1** reversibly coordinates with Co^{2+} and is reusable for sensing.

In summary, we found that a spiropyran-based receptor (**1**) enables selective detection of low levels of Co^{2+} in aqueous media. The molecular design presented here, based on the spirocycle-opening by specific interaction of metal cations with ligands, may lead to a new strategy towards the development of more selective and efficient receptors for metal cations.

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