Photoasymmetric Synthesis of $[Co(edta)]^-$ from Co(II) Salt and L_4edta ($L=H^+$ or Na^+), Using a Chiral Cu(I) Complex

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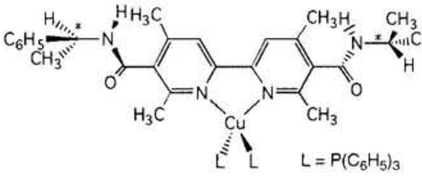
$[Co(edta)]^-$ was photochemically synthesized from CoX_2 ($X=NO_3^-$ or OAc^-) and L_4edta ($L=H^+$ or Na^+) with a chiral Cu(I) complex, under irradiation of near UV light (350 - 370 nm). Λ-$[Co(edta)]^-$ was produced in excess (7% e.e.) from $Co(OAc)_2$ and H_4edta, while Δ-$[Co(edta)]^-$ was produced in excess (7%e.e.) from $Co(OAc)_2$ and Na_4edta. When $Co(NO_3)_2$ was used, Λ-$[Co(edta)]^-$ was yielded from either H_4edta or Na_4edta.

Photoinduced electron transfer reaction of transition metal complexes is an interesting subject of research. However, enantioselective photoinduced electron transfer reactions have been sparse, so far.[1-6] Its application to photochemical synthesis is much more limited; for instance, only one example reported is photoasymmetric synthesis of $Co(acac)_3$ from $Co(acac)_2$ and Hacac with a chiral ruthenium(II) complex, to our best knowledge.[7] Since photochemical synthesis is expected to be potentially useful, various efforts must be made to utilize a photoinduced electron transfer reaction for photochemical synthesis. In this communication, we wish to report novel photoasymmetric synthesis of $[Co(edta)]^-$ from CoX_2 ($X=NO_3^-$ or OAc^-) and L_4edta ($L=H^+$ or Na^+), using $[Cu\{(-)\text{-tmdcbpy}\}(PPh_3)_2](ClO_4)$ **1** {(−)-tmdcbpy=4,4',6,6'-tetramethyl-5,5'-bis[(s)-(−)-1-phenylcarbamoyl]-2,2'-bipyridine; see Scheme 1} as a chiral photosensitizer,[8] under irradiation of near UV light which corresponds to the MLCT absorption of **1**.



Scheme 1.

In all the reactions, **1** (1.0 mM), PPh_3 (1.0 mM),[9] CoX_2 (1.0 mM), and L_4edta (1.0 mM) was irradiated with near UV light (350 - 370 nm) at 30° C in DMSO under oxygen atmosphere, where a high pressure mercury-arc lamp (Toshiba H400-P) was used with cut-off filters (Toshiba UV-35 and UV-D35). $[Co(edta)]^-$ concentration was spectroscopically determined, and the enantiomeric excess was measured with a circular dichroism spectrometer (JASCO J-500C).

Enantioselective photoreduction of $[Co(edta)]^-$ by **1** successfully occurs under irradiation of near UV light in $EtOH/H_2O$ (60/40 or 75/25 v/v).[4b] However, when investigating solvent effects in this reaction, we found that this reaction did not occur in DMSO. From this result, one might expect that the oxidation of CoX_2 to $[Co(edta)]^-$ with $\mathbf{1}^+$ would take place in DMSO, where $\mathbf{1}^+$ represents $[Cu(II)\{(-)\text{-tmdcbpy}\}(PPh_3)_2]^{2+}$ (a counter ion is ClO_4^- and/or X^-). $\mathbf{1}^+$ would be easily produced by irradiation of **1** in the presence of molecular oxygen, since oxidative quenching of **1*** with molecular oxygen rapidly occurs to yield $\mathbf{1}^+$ and O_2^- (remember that **1*** is in the triplet MLCT excited state).[4b] Actually, when the DMSO solution involving **1**, $Co(OAc)_2$, and H_4edta was irradiated with near UV light (350 - 370 nm) under oxygen atmosphere, the absorption spectrum of $[Co(edta)]^-$ appeared around 540 nm, as expected (the absorption of $[Co(edta)]^-$ around 360 nm overlaps with the MLCT absorption of **1**). The quantum yield for $[Co(edta)]^-$ formation is rather low (4.9×10^{-3}). Interestingly, however, CD spectra of the reaction solution exhibited a positive peak around 515 nm and a negative one around 590 nm, as shown in Figure 1. These spectral changes clearly show that Λ-$[Co(edta)]^-$ is photoasymmetrically synthesized, where the enantiomeric excess (e.e.) is 7%. After the reaction, the absorption of **1** around 360 nm little changed. This indicates that **1** does not decompose and the reaction is catalytic. Although the enantiomeric excess is not high due to the essential feature of electron transfer, this reaction is worthy of note, since this is the second example of asymmetric synthesis utilizing a photoinduced electron transfer reaction of a transition metal complex.

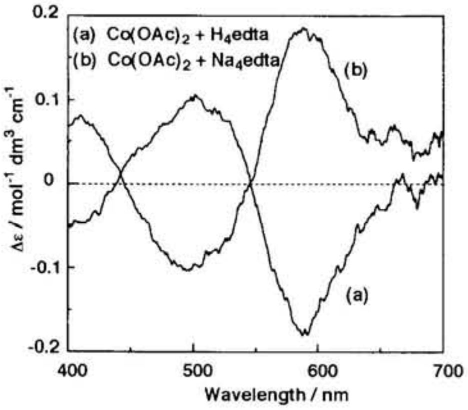


Figure 1. CD Spectra of the reaction solutions after photoirradiation (24 h).

This photosynthetic reaction could occur only in DMSO, and this reaction did not take place in such solvent as DMF, $EtOH/H_2O$, $MeOH/H_2O$, and acetone/H_2O. Even in DMSO/H_2O (90/10 v/v), the reaction was considerably suppressed ($[Co(edta)]^-$ yield was only 3%) and no stereoselectivity was observed. One plausible reason is shift of redox potential in DMSO. In fact, the reduction potential of $[Co(edta)]^-$ shifts to a more negative value upon going to DMSO from $EtOH/H_2O$

(60/40 v/v) by ca. 0.45 V, while the oxidation potential of **1** shifts to a less positive value upon going to DMSO from EtOH/H_2O (60/40 v/v) by ca. 0.15 V.[10] These results suggest that DMSO is favorable for $[Co(edta)]^-$ formation from Co(II).

Since similar photoasymmetric synthesis of $[Co(acac)_3]$ with a chiral Ru(II) complex was recently reported,[7] we tried to perform photoasymmetric synthesis of $[Co(edta)]^-$ with the chiral Ru(II) complex, $[Ru(menbpy)_3]^{2+}$,[11] in DMSO/H_2O (95/5 v/v), where 5 vol.% of H_2O must be added to the solvent to suppress the photodecomposition of $[Ru(menbpy)_3]^{2+}$. $[Co(edta)]^-$ was produced as expected, but no stereoselectivity was observed. Thus, H_2O in the solvent completely suppresses the stereoselectivity, probably due to hydrogen bond with chiral tmdcbpy and menbpy ligands. **1** is only one efficient photosensitizer for this asymmetric reaction, at the moment.

When Na_4edta and $Co(OAc)_2$ were adopted as raw materials, $[Co(edta)]^-$ was synthesized similarly, as shown in Table 1. However, the CD spectra of the reaction solution clearly indicate that Δ-$[Co(edta)]^-$ is produced in excess (Figure 1), where the enantiomeric excess is similar (Table 1). When $Co(NO_3)_2$ was used instead of $Co(OAc)_2$, Λ-$[Co(edta)]^-$ was produced in excess from either H_4edta or Na_4edta. The stereoselectivity slightly increased to about 10% in H_4edta, but decreased to 5% in Na_4edta. When $CoCl_2$ was used, $[Co(edta)]^-$ was yielded a little from Na_4edta, where no stereoselectivity was observed. But, $[Co(edta)]^-$ was not produced at all from H_4edta. These results indicate that the reactivity and the selectivity significantly depend on the counter anion of Co(II) and an edta species.

Table 1. Yield of $[Co(edta)]^-$, enantiomeric excess (e.e.), and configuration of excess enantiomer[a]

CoX_2	L_4edta	Yield	e.e.(%)	Conf.[b]
$Co(OAc)_2$	H_4edta	28	7	Λ
	Na_4edta	32	7	Δ
$Co(NO_3)_2$	H_4edta	22	9	Λ
	Na_4edta	36	5	Λ
$CoCl_2$	H_4edta	0	–	
	Na_4edta	5	0	

[a] After 24 h at 30° C. [**1**]=[CoX_2]=[L_4edta]=1.0 mM.
[b] Configuration of excess enantiomer of $[Co(edta)]^-$

1 exhibits CD spectrum around 355 nm (Δε =−0.177 M^{-1} cm^{-1}) in DMSO (Figure 2), which arises from the MLCT absorption. This CD spectrum changes upon addition of CoX_2, H_4edta, and Na_4edta. Moreover, the change depends on the kinds of counter anion of Co(II) and an edta species (H_4edta or Na_4edta), as shown in Figure 2. All these results suggest that **1**, CoX_2, and the edta species interact with each other to form a ternary complex and that the photoexcitation of **1**, the oxidative quenching of **1*** by molecular oxygen, and the Co(II) oxidation to $[Co(edta)]^-$ occur in the ternary complex, as shown in Scheme 2. Here, we mention that O_2^- formed by the quenching reaction would change into either HO_2 when H_4edta is used or NaO_2 when Na_4edta is used, since O_2^- would be stabilized as a salt, as well known.

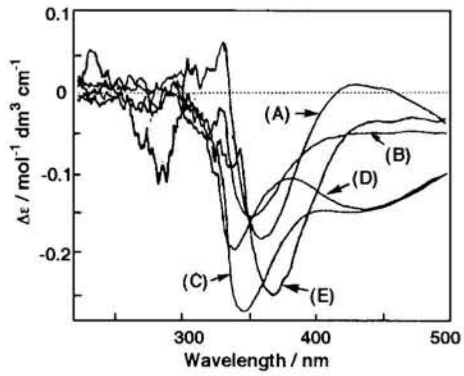
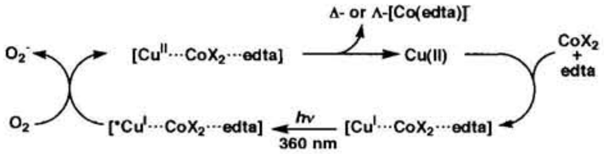


Figure 2. DMSO solution involving **1**, CoX_2, and L_4edta (before irradiation).[a]
a (A) **1**, (B) **1** + $Co(OAc)_2$, (C) **1** + $Co(OAc)_2$ + H_4edta, (D) **1** + $Co(OAc)_2$ + Na_4edta, (E) **1** + $Co(NO_3)_2$ + Na_4edta.



Scheme 2.

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References and Notes

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8 See ref. 4b for synthesis of **1**.
9 Excess phosphine was added to suppress PPh_3 dissociation from **1**.
10 Working electrode: either glassy carbon or Pt. Reference electrode: Ag/AgCl. Supporting electrolyte: $[N(C_4H_9)_4](PF_6)$.
11 See ref. 5 for $[Ru(menbpy)_3]^{2+}$.