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Extremely high stereoselectivity of novel helical ruthenium(II) complexes for photoinduced reduction of racemic-[Co(acac)$_3$] (Hacac = pentane-2,4-dione)

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Abstract

A photocatalyst $M(C_3)$-Δ-[Ru(menbpy)$_3$]$^{2+}$ (menbpy = 4,4′-bis{(1R,2S,5R)-(−)-methoxycarbonyl}-2,2′-bipyridine; $M(C_3)$ = minus (counterclockwise) helical arrangement along the C_3 symmetry axis) possessing a long lifetime τ and the low quantum yield of photoracemization Φ(rac) (τ = 1500 ns and Φ(rac) = 4.0×10^{-6} in EtOH at 298 K) facilitated the asymmetric reduction of racemic Δ,Λ-[Co(acac)$_3$] (Hacac = pentane-2,4-dione) at 298 K in deaerated 90% v/v EtOH–H_2O; it exhibited extremely high stereoselectivity with the enantiomer rate ratio $k(\Delta)/k(\Lambda)$ = 14.79 (in the absence of Hacac) – 91.9 (in the presence of Hacac).

Keywords: Asymmetric photocatalysis; Helical ruthenium(II) complex; Stereoselective photoreduction; Photoinduced kinetic resolution

Although photoinduced asymmetric reactions catalyzed by chiral transition-metal complexes are of interest and significance in the field of photochemistry, they have, hitherto, been the subject of only limited investigation. This may, in part, be due to the difficulty in the molecular design of efficient chiral photocatalysts possessing long lifetimes (τ) without photoracemization or photodecomposition. The previously reported photocatalyst Δ-[Ru(bpy)$_3$]$^{2+}$ (bpy = 2,2′-bipyridine; τ = 790 ns in EtOH at 298 K [1]; photoactivated oxidation potential $E(3+/2+^*) = -0.81$V and $E(3+/2+) = +1.29$ V in MeCN [2]) used for the stereoselective photoreduction of racemic-[Co(acac)$_3$] was not effective, because it racemizes easily (the quantum yield of photoracemization Φ(rac) = 2.88×10^{-4} in EtOH [3]; Φ(dec) = 1.0×10^{-5} in H_2O [4]), leading to the low stereoselectivity (enantiomer pseudo-first-order rate ratio $k(\Delta)/k(\Lambda)$ = 1/1.08 [5]). This paper describes the extremely high stereoselectivity of a photocatalyst Δ-[Ru(menbpy)$_3$]$^{2+}$ (**1**; menbpy = 4,4′-bis{(1R,2S,5R)-(−)-menthoxycarbonyl}-2,2′-bipyridine) [6,7] for the asymmetric reduction of racemic-[Co(acac)$_3$] (**2**; **2a** for Δ-[Co(acac)$_3$], and **2b** for Λ-[Co(acac)$_3$], respectively) in the presence or absence of Hacac (Scheme 1). The photocatalyst **1** was obtained by optical resolution of diastereomeric [Ru(menbpy)$_3$]$^{2+}$ 2Cl$^-$ complexes by silica gel column chromatography (eluent: $CHCl_3$–MeOH), as previously described [6]. This exhibits a metal-to-ligand charge transfer band at $\lambda_{max}(\epsilon)$ = 466 nm (27200 mol^{-1} dm^{-3} cm^{-1}), τ = 1550 ns in EtOH at 298 K, and the low quantum yields of Φ(rac) = 4.0×10^{-6} and Φ(dec) = 1.9×10^{-5} in EtOH at 298 K. The Rehm–Weller relation [2] between the reduction potentials $E^0(Q/Q^-)$ of aromatic quenchers and oxidative quenching rate constants (see Fig. 1) gave the oxidation potentials of **1** as $E^0(3+/2+^*) = -0.45$ V and $E^0(3+/2+) = E^0(3+/2+^*) + E(0-0) = +1.55$ V vs. SCE; $E(0-0)$ is the one electron potential (2.00 V) corresponding to the zero–zero spectroscopic energy. Moreover, molecular mechanics (MM2) calculations with the energy minimized conformation of the chiral menbpy ligand adopted a minus (counterclockwise) helical arrangement of M(C_3) for **1** along the C_3 symmetry axis [7]. When deaerated 90% v/v EtOH–H_2O solutions including **1** (32 μmol dm^{-3}), **2** (2.4 mmol dm^{-3}), and Hacac (0–24.0 mmol dm^{-3}) were irradiated at 298 K by a 500 W xenon lamp (λ > 400 nm), the photoreduction of **2** by **1** produced only [Co(acac)$_2$(H_2O)$_2$] and acac$^-$ as reduction products. This reaction proceeded stereoselectively and was accelerated by Hacac with turnover numbers of 38 ([Hacac] = 0) – 54 ([Hacac]/[**2**] = 10) for 300 min (Fig. 2). The turnover numbers of **1** were evaluated on the basis of the reacted amount of **2** with respect to the initial concentration of **1**. The total concentration ([**2a**] + [**2b**]) and the concentration difference

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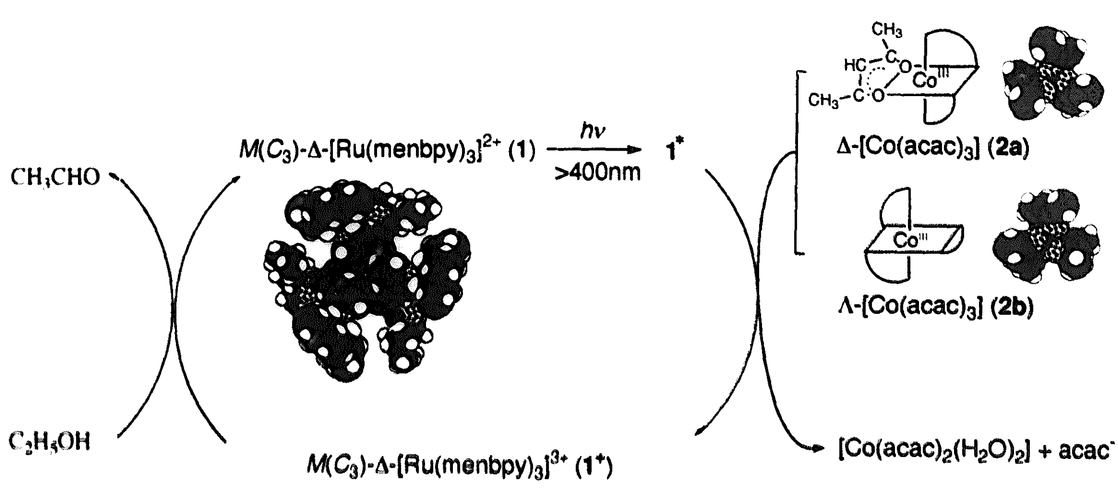

Scheme 1.

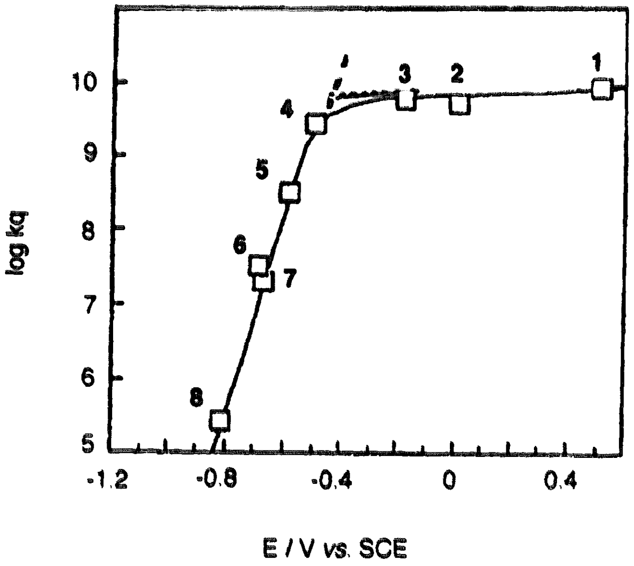

Fig. 1. Rehm–Weller relation between oxidative quenching rate (log kq) of **1** and reduction potentials (E) of quenchers in MeCN at 298 K; **1**: 3,3-dichloro-3,5-dicyanoquinon, **2**: chloranyl, **3**: 2,6-dichlorobenzoquinon, **4**: p-quinon, **5**: 2-methylbenzoquinon, **6**: p-dinitrobenzene, **7**: 2,6-dimethylbenzoquinon, **8**: o-dinitrobenzene.

([**2a**] − [**2b**]) were determined, respectively, using $\Delta\epsilon = 133\ \mathrm{mol^{-1}\ dm^3\ cm^{-1}}$ and $\lambda\mathrm{max} = 595$ nm for **2a–b** and $\Delta\epsilon = -8.11$ (**2a**) and $+8.11$ (**2b**) $\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$ at $\lambda(\mathrm{CD}) = 574$ nm and $\Delta\epsilon = +1.73$ (**2a**) and -1.73 (**2b**) at $\lambda(\mathrm{CD}) = 585$ nm.

The present photoreaction obeyed a pseudo-first-order rate law with different pseudo-first-order rate constants ($k(\Delta)$ and $k(\Lambda)$). During the initial stages of the reaction, up to ca. 30% conversion was realized (Fig. 3). The accumulation of the unreacted enantiomer **2b** after ca. 30% conversion predominated the reaction of **1** with **2b** so that pseudo-first-order kinetics were no longer observed, and EtOH (and/or acac-) was found to act as a reductant of Δ-[Ru(menbpy)$_3$]$^{3+}$ (**1+**) for the formation of catalytic cycle because the accumulation of acetone was detected in the present reaction system. It is worth emphasizing here that both of the rate was detected in the present reaction system. It is worth emphasizing here that both of the rate ratio $k(\Delta)/k(\Lambda)$ and the quantum yield of the reaction Φ(react) monotonously increased with the amount of Hacac (Table 1). The extremely large values of $k(\Delta)/k(\Lambda) = 14.7$ ([Hacac]/[2] = 0) − 91.9 ([Hacac]/[2] = 10), as compared with $k(\Delta)/k(\Lambda) = 1/1.08$ (under [Hacac]/[2] = 0) obtained with Δ-[Ru(bpy)$_3$]$^{2+}$ taking P(C$_3$) helicity, at least indicate that M(C$_3$)-**1** is able to exhibit more efficient asymmetric photocatalysis than P(C$_3$)-Δ-[Ru(bpy)$_3$]$^{2+}$, probably due to the effective molecular extension of its chiral and helical ligand in the direction of the C$_3$ symmetry axis along which P(C$_3$)-**2a** or M(C$_3$)-**2b** might approach to **1** (see Fig. 4).

Table 1
Stereoselective photoreduction of racemic **2** catalyzed by **1** [a]

[Hacac]/[2]	$10^2\ \Phi$(react)	$10^n\ k(\Delta)/s^{-1}$	$10^n\ k(\Lambda)/s^{-1}$	$k(\Delta)/k(\Lambda)$
0	0.55	74	5.0	14.7
0.63	1.1	137	8.3	16.5
1.1	1.6	205	8.0	25.8
2.0	1.7	217	5.4	40.1
5.8	1.8	209	2.9	70.8
10	1.7	204	2.2	91.9

[a] [1] = 32 μmol dm^{-3} and [2] = 2.1 mmol dm^{-3} in deaerated 90% v/v EtOH–H$_2$O at 298 K.

Moreover, the rate ratio $k(\Delta)/k(\Lambda)$ falling in the range 14.7–91.9 is considerably larger than the quenching rate ratio ($kq(\Delta/kq(\Lambda) = 1.28$) obtained with **1** under the same reaction conditions. This implies that the present photocatalytic reaction involves an asymmetric amplification process during the initial stages of the reaction; one of the expected process is the asymmetric amplification during the back electron-transfer from [Co(acac)$_3$]-(**2−**) to Δ-[Ru(menbpy)$_3$]$^{3+}$ (**1+**). As Fig. 5 indicates, the photoreduction of enantiomer **2a** (or **2b**) by **1** under the same reaction conditions resulted in the isomerization product of **2b** (or **2a**) with the isomerization occuring predominantly from **2a** to **2b** rather than **2b**

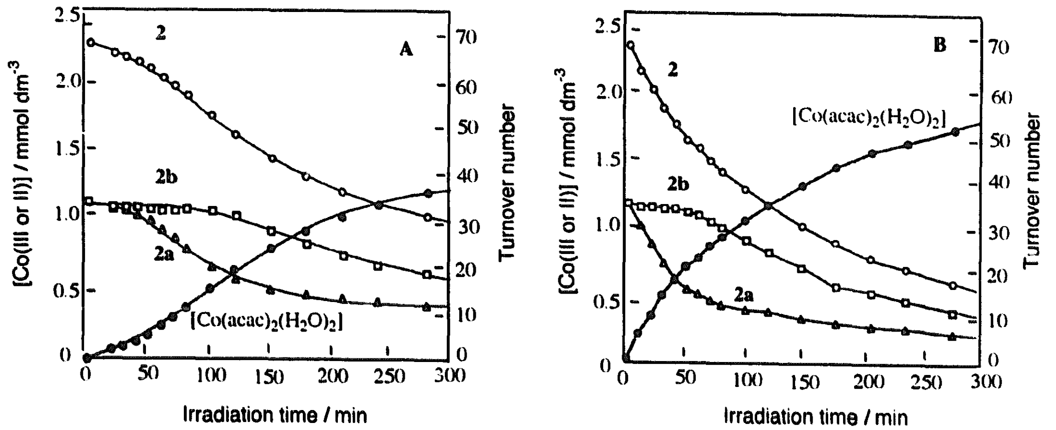

Fig. 2. Photoreduction of racemic **2** by **1** in deaerated 90% v/v EtOH–H_2O at 298 K under [Hacac]/[**2**] = 0 (**A**) or 10 (**B**); [**1**] = 32 μmol dm^{-3} and [**2**] = 2.4 mmol dm^{-3}.

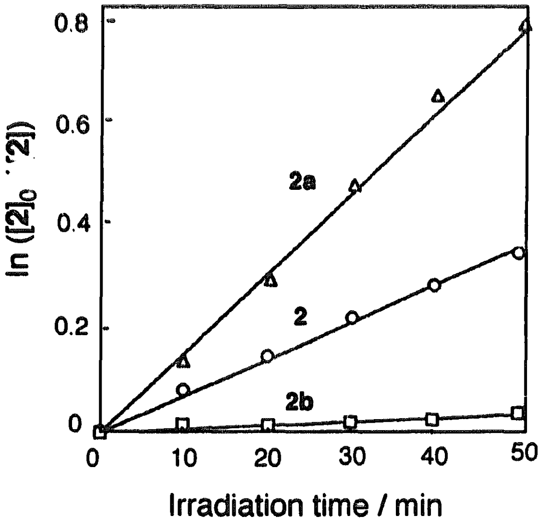

Fig. 3. Pseudo-first-order plots for the photoreduction of **2** by **1** in deaerated 90% v/v EtOH–H_2O at 298 K under [Hacac]/[**2**] = 10; [**1**] = 32 μmol dm^{-3} and [**2**] = 2.4 mmol dm^{-3}.

to **2a**. The increase of [Hacac] with respect to [enantiomer **2a** or **2b**] enhanced the extent of isomerization from **2a** to **2b** in the catalysed reduction of **2a**; but did not considerably change the rate of isomerization from **2b** to **2a** in the reduction of **2b**. Therefore, the isomerization between **2a** and **2b** through the back electron-transfer from **2a**− (or **2b**−) to **1**+ was also stereoselective. So was the stereoselective electron-transfer from photoactivated **1** to **2a**−**b**. Presumably, the back electron-transfer from $[Co(acac)_2(acac^-)]$ (generated from **2**−) to $M(C_3)-$**1**+ caused the prevailed isomerization of **2a** via the short-lived species $[Co(acac)_2(acac^{\bullet})]$ and the excess amount of Hacac facilitated the isomerization from **2a** to **2b**, probably through the suppression of the complete dissociation of $[Co(acac)_2(acac^-)]$. The novel photocatalyst of **1** was found highly effective for the stereoselective reduction of racemic substrates **2a**−**b**. This was predominantly through the electron-transfer from the photoactivated **1** to **2a** and facilitated isomerization from **2a** to **2b** during the back electron-transfer from the reduced **2a** (**2a**−) to the oxidized **1** (**1**+).

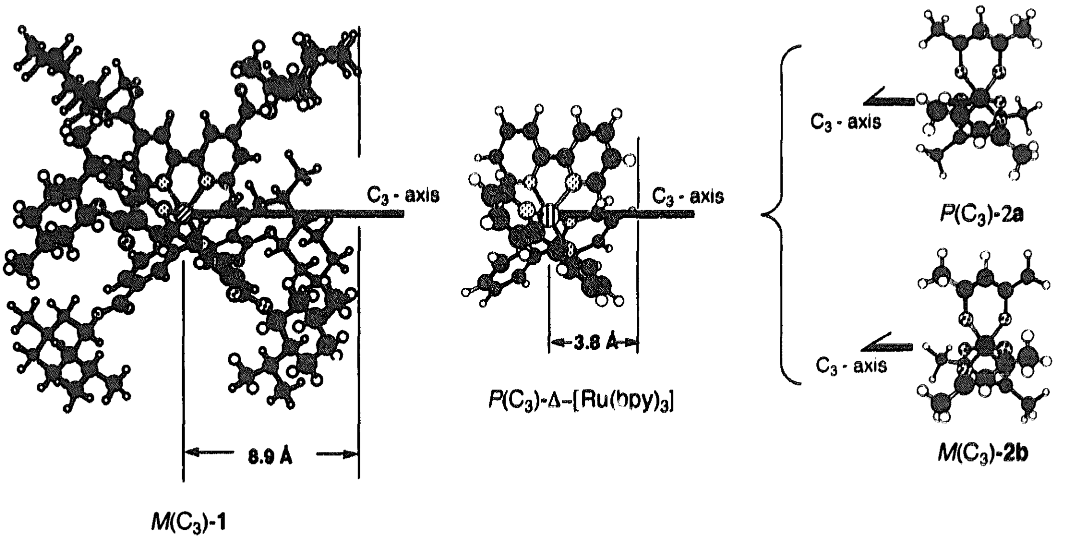

Fig. 4. Molecular extension of $M(C_3)$-**1** or $P(C_3)$-Δ-$[Ru(bpy)_3]$ in the direction of C_3 symmetry axis for the reaction with **2a**−**b**.

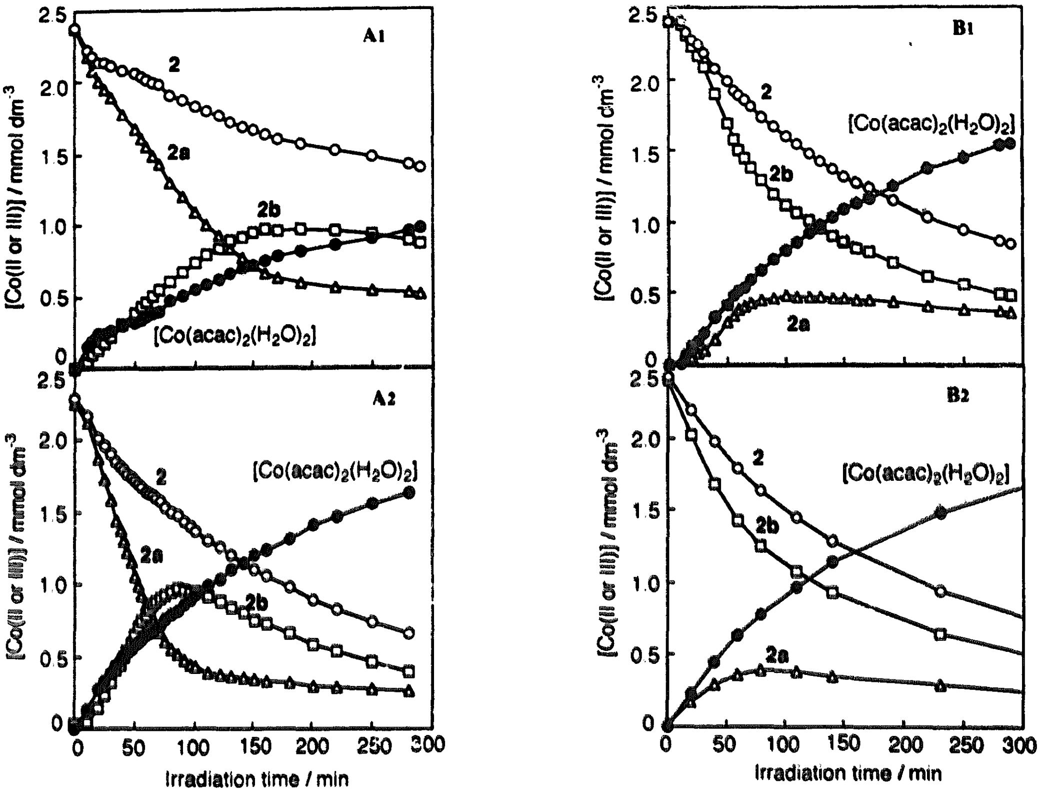

Fig. 5. Photoreduction of enantiomer **2a** (**A1** and **A2**) or **2b** (**B1** and **B2**) by **1** in deaerated 90% v/v EtOH–H_2O at 298 K under [Hacac]/[**2a** or **2b**] = 0 (**A1** or **B1**) or 10 (**A2** or **B2**); [**1**] = 32 μmol dm^{-3} and [**2a** or **2b**] = 2.4 mmol dm^{-3}.

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