

Electrochemical Tuning by Polarized UV Light Induced Molecular Orientation of Chiral Salen-type Mn(II) and Co(II) Complexes in an Albumin Matrix

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Abstract: The authors have prepared supramolecular systems as artificial metalloproteins composed of several chiral salen-type Mn(II) and Co(II) complexes in a HSA (human serum albumin) matrix. The docking was discussed by UV-vis spectral changes and a ligand-protein docking simulation program. After linearly polarized UV light irradiation, that anisotropy of molecular orientation of the complexes increased was confirmed by polarized IR spectra. The authors have observed that the electrochemical behavior of the aligned complexes incorporating diphenyl groups in HSA can be tuned without UV radiation damage of HSA higher structures.

Key words: Redox potential, Schiff base, Mn(II) complex, Co(II) complex, albumin.

1. Introduction

In recent years, metal complex-protein hybrid materials are attracted attention in view of bio-inspired catalysis [1] or bioinorganic photochemistry [2]. These materials have high eco-compatible, so are called artificial metalloenzymes as biohybrid materials, observed in bioinorganic chemistry and pharmacy fields and using biocatalysis and homogeneous (chiral) catalysis [3-5]. The report about the composition with protein and low molecular like complex was little due to the difficulty of crystallization of hybrid materials and the requirement of high technique [6].

Herein, the authors have prepared supramolecular systems as artificial metalloproteins composed of several chiral salen-type Mn(II) and Co(II) complexes in a HSA (human serum albumin) matrix [7]. After linearly polarized UV light irradiation, that anisotropy of molecular orientation of the complexes increased [8]

was confirmed by polarized IR spectra [9, 10]. The authors have observed that the electrochemical behavior of the aligned complexes incorporating diphenyl groups in HSA can be tuned without UV radiation damage of HSA higher structures.

2. Experiments

Chiral Schiff base complexes of (1*R*, 2*R*)-enantiomers (Fig. 1) (Mn-diphenyl, Mn-cyclo, and Co-diphenyl) were reported elsewhere [11-14]. For example, a new complex (Co-cyclo) was prepared and characterized as follows: To a solution of 3,5-dichlorosalicylaldehyde (0.0955 g, 0.500 mmol) dissolved in methanol (50 mL), (1*R*,2*R*)-(+)-1,2-diaminocyclohexane (0.0285 g, 0.250 mmol) was added dropwise and stirred at 313 K for 2 h to give yellow solution of ligand. Cobalt(II) acetate tetrahydrate (0.0623 g, 0.25 mmol) was added to the resulting solution to give brown solution of complex. After stirring for 4.5 h under N₂, brown solution was filtrated to obtain brown precipitates. Yield 0.0696 g

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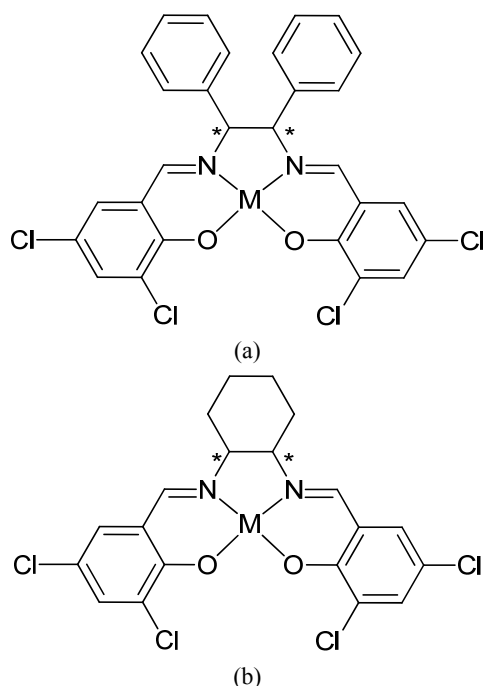


Fig. 1 Molecular structures of chiral salen-type (a) diphenyl; or (b) cyclo (M = Mn or Co) complexes.

(53.83%). Anal. Calcd. for $C_{20}H_{16}Cl_4CoN_2O_2$: C, 46.45; H, 3.12; N, 5.42. Found: C, 46.46; H, 3.01; N, 5.24%. IR (KBr (cm^{-1})): 1,637(C=N). In addition, cast films for spectral and electrochemical measurements were prepared [15, 16]. Commercially available HSA (0.0152 g) and acetone solution of the complexes (1 mM) were mixed in sodium citrate buffer (2 mL), and dropped onto a PMMA cast film and dried for 2 days at 298 K.

3. Results and Discussions

3.1 Spectral Interpretation and Docking

Absorption of UV light by metal complexes mainly was attributed to intra-ligand transitions and experimental UV-vis spectra was reasonably assigned by TD-DFT calculations with UCAM-B3LYP/6-31G(d) on Gaussian09. Co-cyclo: 221 nm HOMO-1 $\rightarrow$ LUMO+3, 266 nm, HOMO $\rightarrow$ LUMO+2, 278 nm HOMO-1 $\rightarrow$ LUMO+1, 335 nm HOMO-1 $\rightarrow$ LUMO; Co-diphenyl: 242 nm HOMO-5 $\rightarrow$ LUMO+1, 266.78 nm HOMO $\rightarrow$ LUMO+4, 278 nm HOMO-1 $\rightarrow$ LUMO (α), 336 nm HOMO-1 $\rightarrow$ LUMO (β).

The docking of metal complexes into HSA was discussed by UV-vis spectral changes (30 μ M of metal complexes in 0–8 mg of HSA solutions in pH 5.10 sodium citrate buffer at 273 K) (Fig. 2), corresponds to Stern-Volmer discussion by fluorescence spectra [7], and a CCDC GOLD program for ligand (TD-DFT optimized structure)–protein (PDB: 1BM0 crystal structure) docking simulation (Fig. 2). Both experimental results and theoretical data suggested that docking of Co-diphenyl + HSA was made adequately.

3.2 Irradiation of Polarized UV Light

Weigert effect by linearly polarized UV light causes dichroism due to anisotropic aligned metal complexes in a HSA matrix with photochemical reactions as well as interaction with highly polar molecules [8]. The magnitude of polarized light-induced anisotropy was Co-cyclo > Co-diphenyl > Mn-cyclo > Mn-diphenyl. The degree of photoinduced optical anisotropy of angular dependent changes of polarized IR spectra of C=N bands in metal complexes (1,653 cm^{-1} , 1,642 cm^{-1} , 1,654 cm^{-1} , and 1,652 cm^{-1} for Mn-diphenyl + HSA, Mn-cyclo + HSA, Co-diphenyl + HSA, and Co-cyclo + HSA, respectively) can be described by S and R parameters (Fig. 3 and Tables 1–4).

Where $A_{\text{perpendicular}}$ and A_{parallel} values denote absorbance measured with the measuring polarizer parallel (0°) or perpendicular (90°) to electric vector of irradiation polarized light. The ideal isotropic system of $S = 0$ and $R = 1$ both S and R parameters are changed as increasing dichroism by molecular alignment [15].

However, even strong synchrotron UV linearly polarized UV light irradiation (at 260 nm, 318 nm, and 380 nm of 10^2 mm^2 spot at 10 mW/cm^2 generated with an undulator at IMS UVSOR BL1U [17]) did not damage higher structure of HSA for Co-diphenyl + HSA or Co-cyclo + HSA. Little changes from the initial CD spectra in the range of 200–900 nm could be observed after 1 min, 3 min, and 5 min irradiation.

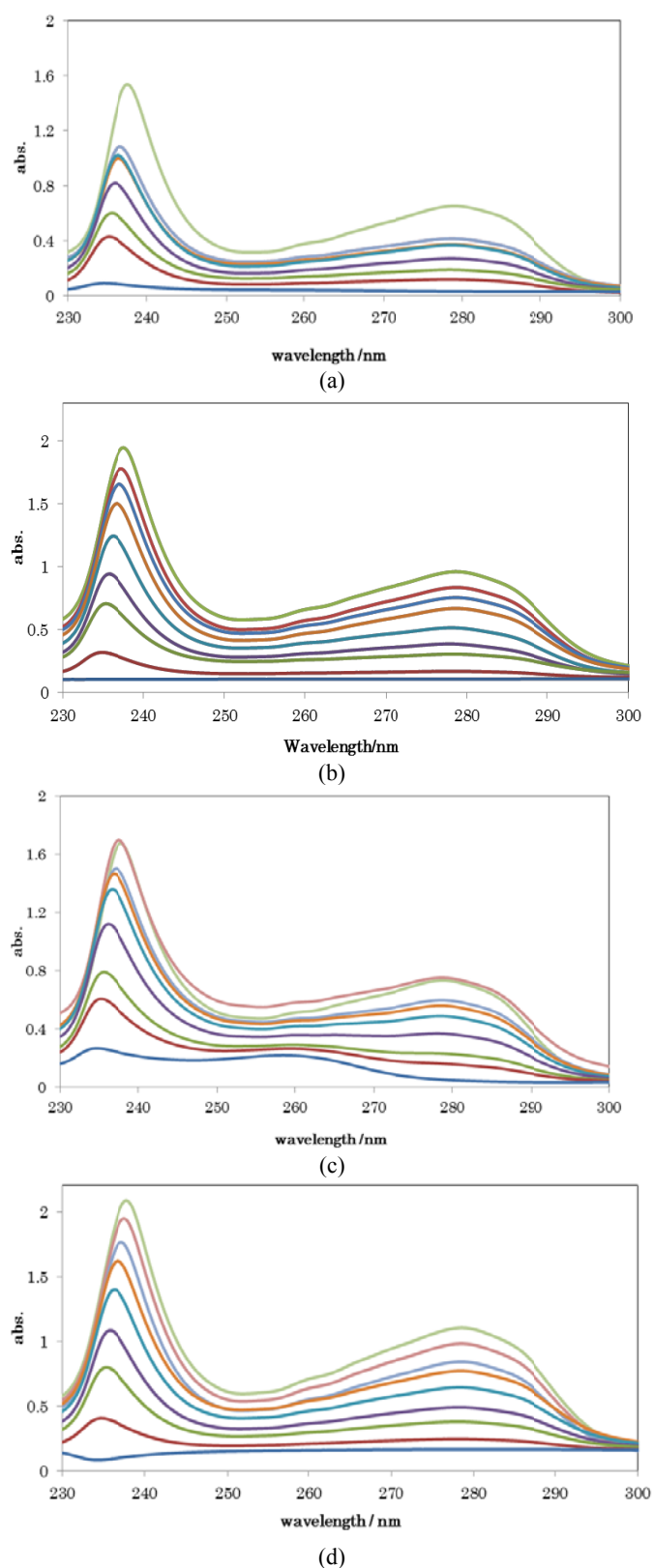


Fig. 2 Changes of UV-vis spectra by docking HSA and (a) Mn-diphenyl; (b) Co-diphenyl; (c) Mn-cyclo; and (d) Co-cyclo.

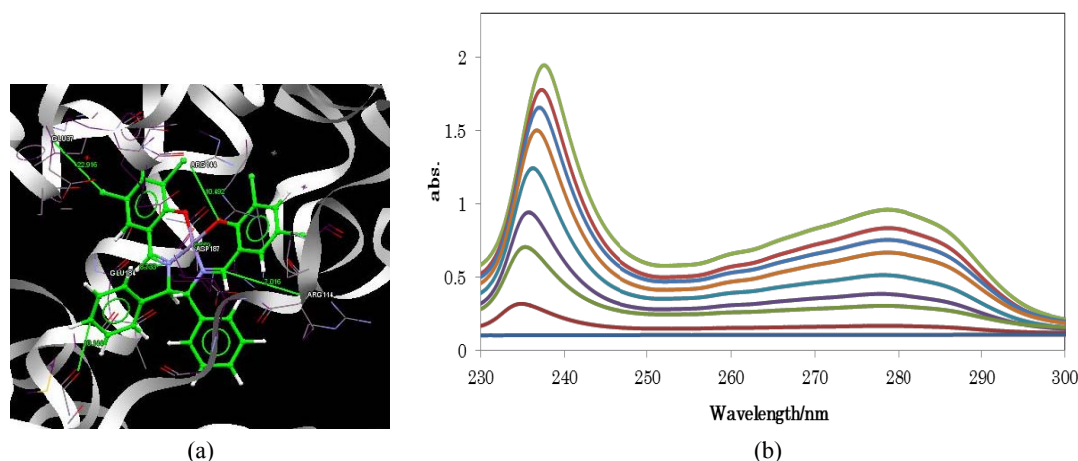


Fig. 3 (a) Changes of UV-vis spectra by docking Co-diphenyl and HAS; (b) Ligand-protein docking simulation by a GOLD program for Co-diphenyl + HSA.

Table 1 R and S parameters for Mn-diphenyl + HSA.

UV irradiation time /min.	R	S
initial	1.240216	0.074136
UV0.5	1.70117	0.189445
UV1	1.42665	0.124002
UV3	1.509487	0.145174
UV5	1.281971	0.085915
UV10	1.094364	0.030496

Table 2 R and S parameters for Co-diphenyl + HSA.

UV irradiation time /min.	R	S
initial	1.576484	0.161187
UV0.5	1.217963	0.067733
UV1	1.433377	0.126225
UV3	1.335905	0.100694
UV5	1.604287	0.167658
UV10	1.091833	0.029702

Table 3 R and S parameters for Mn-diphenyl + HSA.

UV irradiation time /min.	R	S
initial	1.246985	0.161187
UV0.5	1.204419	0.067733
UV1	1.14387	0.045762
UV3	1.217677	0.06765
UV5	1.199981	0.062494
UV10	1.168433	0.5316

Table 4 R and S parameters for Co-cyclo + HSA.

UV irradiation time /min.	R	S
initial	1.117181	0.037592
UV0.5	1.200079	0.062523
UV1	1.246687	0.075981
UV3	1.262976	0.080594
UV5	1.141254	0.044967
UV10	1.411156	0.120533

$$S = (A_{\text{parallel}} - A_{\text{perpendicular}}) / (2A_{\text{perpendicular}} + A_{\text{parallel}})$$

$$R = A_{\text{perpendicular}} / A_{\text{parallel}}$$

3.3 Electrochemical Effect

The CV measurements revealed the effects of UV light for not only metal complexes but also complex-HSA hybrids (Fig. 4). In contrast to relatively UV light-resistant complexes Mn-diphenyl and Co-diphenyl, Mn-cyclo and Co-cyclo exhibited CV changes after UV irradiation for 10 min, which may be in agreement with expectation based on the intra-ligand transitions or stable isolation [18] and O₂ oxidation during preparation from Mn(II) source [19] for the analogous Mn(III)-cyclo complexes. As complex-HSA hybrids, Co-diphenyl + HSA exhibited little CV changes, though only Mn-diphenyl + HSA exhibited significant CV changes (decreasing current) only after 1 min polarized UV irradiation (Fig. 5).

4. Conclusions

In conclusion, the authors have prepared supramolecular systems as artificial metalloproteins composed of several chiral salen-type Mn(II) and Co(II) complexes in a HSA matrix, and their docking features were confirmed experimentally. Polarized IR spectra indicated that anisotropic molecular orientation of metal complexes in HSA has been induced by irradiation linearly polarized UV light. Excluding unstable metal complexes and denying irradiation damage of HSA, the authors have successfully found that electrochemical tuning by polarized UV light

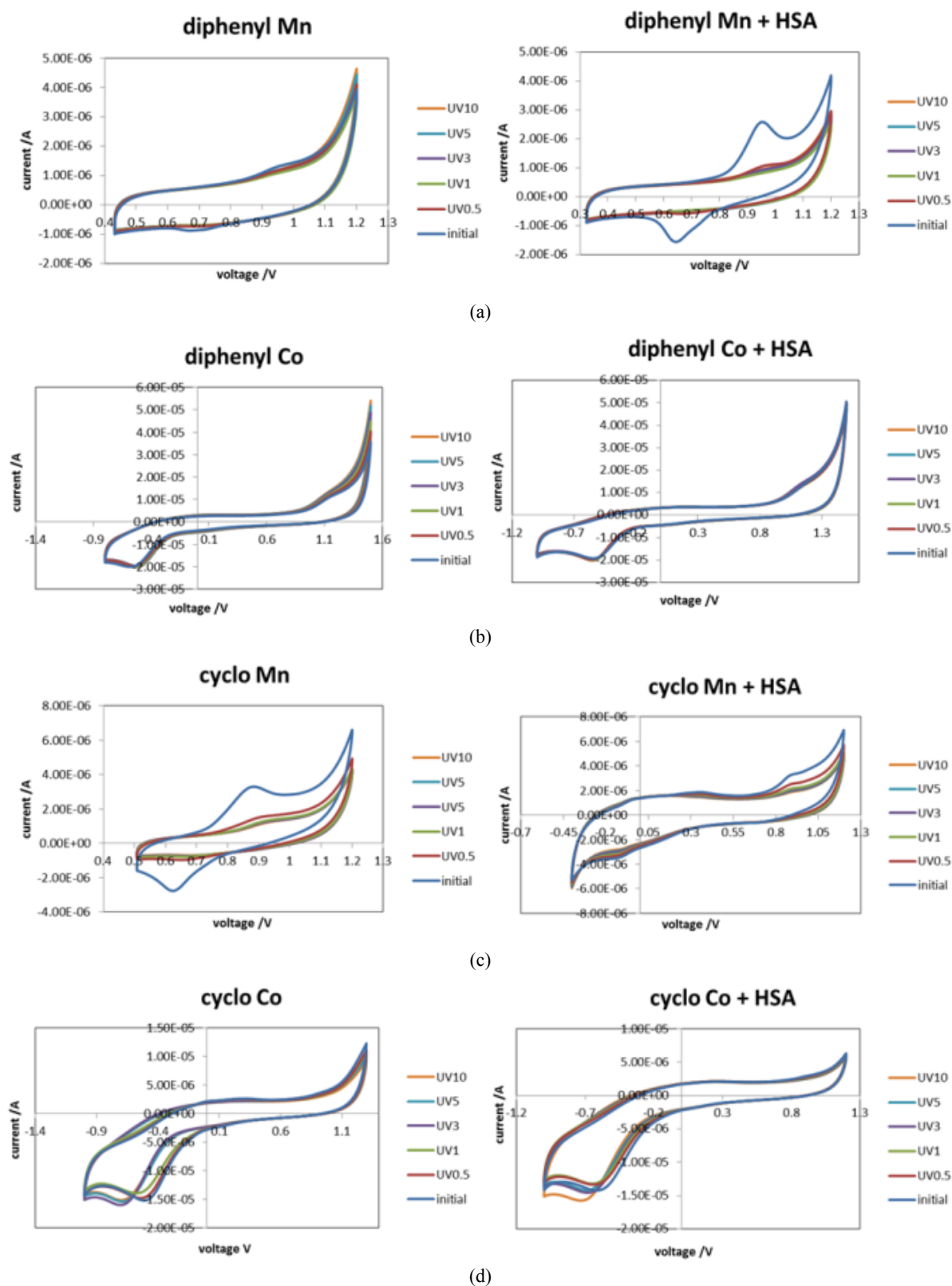


Fig. 4 Changes of CV after polarized UV light irradiation for only complex and complex+HSA hybrids for (a) Mn-diphenyl; (b) Co-diphenyl; (c) Mn-cyclo; and (d) Co-cyclo systems.

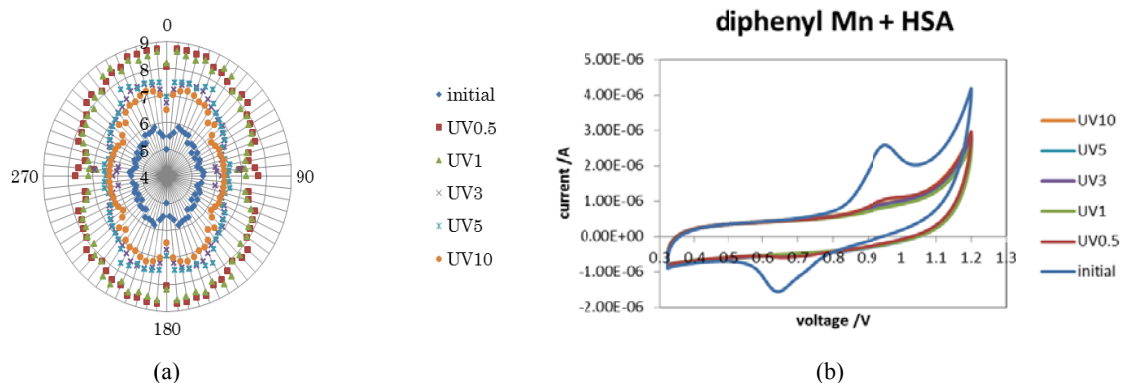


Fig. 5 (a) Angular dependence of intensity of polarized IR spectra for Mn-diphenyl complex + HSA after polarized UV light irradiation. (b) Changes of CV for Mn-diphenyl + HSA after polarized UV light irradiation.

induced molecular orientation associated with perturbation of hydrogen bonding electron transfer paths only for Mn-diphenyl + HSA for the first time. After establishment of reaction conditions, the concept will be potentially applied for artificial metalloproteins [20] as biofuel cell materials [21].

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