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# Amino acid ester salt recognition by ferrocene-based ditopic receptor bearing oligoethylene glycol with pendant bipy subunits: CV, UV-vis and ESR studies

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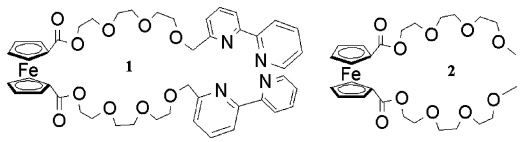
The novel ferrocene-based ditopic receptor **1** was synthesized. This receptor bears two oligoethylene glycol arms with pendant 2,2′-bipyridine unit at the identical cyclopentadienyl rings, $Cu^{I}$ cation binds to **1** to form the 1 : 1 complex (**1**·$Cu^{I}$) with the cavity consisting of polyether, and the resulting complex acts as a receptor for amino acid ester salts to give the ditopic complex (**1**·$Cu^{I}$·AAOMe–HCl). The $^{1}$H NMR spectrum of **1**·$Cu^{I}$·LeuOMe–HCl exhibits strong broadening at the bipyridine region, and the ESR spectrum of the same sample gives the signals assigned as $Cu^{II}$ species. With these data, the binding of **1**·$Cu^{I}$ towards AAOMe·HCl leads to the conformational change, and the $Cu^{I}$ complex is simultaneously oxidized to the $Cu^{II}$ complex.

## Introduction

Ferrocene-based receptors have attracted much attention and extensive researches are being focused on the dynamic control of their structural and spectroscopic features using redox reactions. Such redox switchable receptors are also useful as an electrochemical probe of the binding of metal cations. In most cases, the structure of these receptors includes the redox-active ferrocene unit and the metal cation binding site such as crown ether,[1,2] aza-crown ether[3–5] or cryptand[3,6] moieties, and the cation binding event is directly detected by a change in redox-potential. Beer and co-workers reported the anion selective recognition[7,8] and the simultaneous recognition[4] of both cations and anions using ferrocene-based polyaza macrocycles. Although there are numerous studies on ferrocene derivatives bearing crown ether or related macrocycle units acting as ion selective receptors,[9–12] reports on ferrocene-based receptors having open-chain recognition sites are considerably less frequent and only a few examples have been published.[13–15] Among non-crown ether type ferrocenyl ligands, only the ferrocene–bipyridine conjugate was exceptionally well-examined.[16–18]

In this paper, we describe the synthesis of the novel ferrocene-based ditopic receptor **1** (Scheme 1) bearing two identical oligoethylene glycol arms with pendant 2,2′-bipyridine unit at the independent cyclopentadienyl (cp) rings and the recognition behavior of receptor **1** towards amino acid methyl ester salts. The complexation of 2,2′-bipyridine unit towards $Cu^{I}$ cation is one of the most studied examples of the metal–ligand interaction,[19,20] thus the complexation between the present receptors and $Cu^{I}$ was utilized for pre-organization of receptor cavity. The electrochemical properties of this ditopic receptor are also investigated.

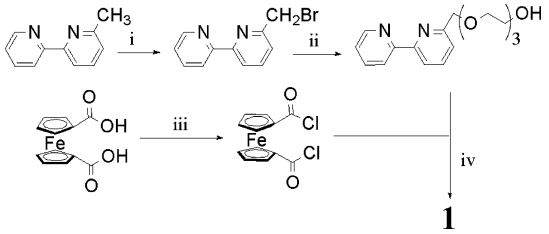



**Scheme 1** Chemical structures of the ferrocene receptor **1** and the reference compound **2**.

## Results and discussion

### Synthesis and characterization of ferrocene receptor 1 and its $Cu^{I}$ complex

The condensation of 1,1′-bis(chlorocarbonyl)ferrocene[21] with two equiv. of 2,2′-bipyridine-pendant oligoethylene glycol resulted in the formation of the desired ferrocene receptor **1** as brown oil in nearly quantitative yield. (Scheme 2) Since the reaction was slow but clean, a similar reaction was effective to prepare the reference compound **2** without 2,2′-bipyridine unit. (Scheme 1) Compound **1** and **2** were characterized by $^{1}$H NMR spectroscopy and electron spray ionization mass spectrometry (ESI-MS).




**Scheme 2** Synthesis of the ditopic ferrocene receptor **1**. Reagents and conditions: (i) *N*-bromosuccinimide, AIBN, $CCl_4$, reflux, 6 h, (ii) triethylene glycol, KOH, 1,4-dioxane, reflux, 13 h, (iii) oxalyl chloride, pyridine, $CH_2Cl_2$, rt, 12 h then reflux, 6 h, (iv) $CH_2Cl_2$, reflux, 39 h.

The corresponding $Cu^{I}$ complex could be obtained by the simple mixing of two separate acetonitrile solutions of **1** and $[(CH_3CN)_4Cu]PF_6$. In order to determine the stoichiometry of the ligand **1**–$Cu^{I}$ salt complex, spectrophotometric titrations were performed. Job's method was employed using 11 different mixtures of the acetonitrile solutions of **1** (50 μM) and $[(CH_3CN)_4Cu]PF_6$ (50 μM). The UV absorption was measured at the absorption maxima appeared at 445 nm which was assigned as the metal to ligand charge transfer absorption band.[22,23] The Job's plot clearly shows the formation of a 1 : 1 complex. (Fig. 1)

In electrospray ionization mass spectrometric studies, no multinuclear complex (**1**$_n$·$Cu_n$) was detected, and the peak corresponding to the 1 : 1 complex was observed at $m/z = 937$

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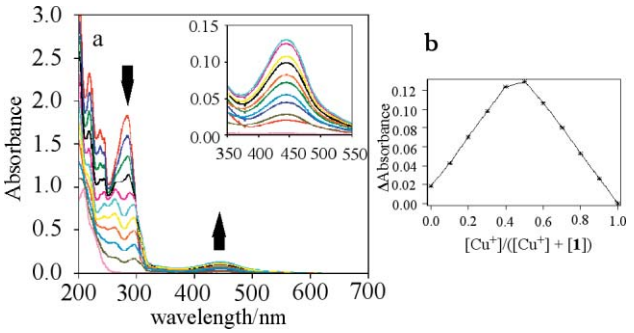


**Fig. 1** (a) Absorption titration profiles recorded during stepwise addition of $Cu^{I}$ cations to a solution of **1** in acetonitrile. (b) Job's plot in the complexation of **1** with $[(CH_3CN)_4Cu]PF_6$. The total concentration of the two components was 50 μM in acetonitrile, with mole fractions varying from 0 to 1. The absorbance at 445 nm was measured at 25 °C.

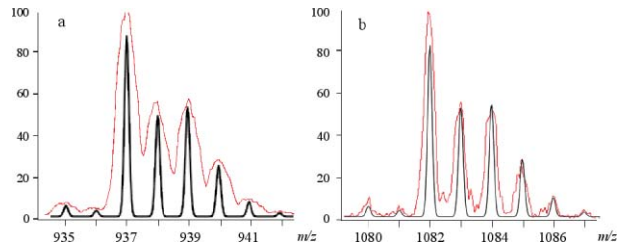


**Fig. 2** Observed electrospray mass spectrum (red line) for (a) complex **1**·$Cu^{I}$ and (b) ditopic complex **1**·$Cu^{I}$·LeuOMe, with the calculated isotopic pattern (black line) for (a) $C_{46}H_{50}N_4O_{10}Fe_1Cu_1$ and (b) $C_{53}H_{65}N_5O_{12}Fe_1Cu_1$.

with the isotopic peaks separated by 1.0 $m/z$ unit. (Fig. 2a) These results also indicate that the mixing of ligand **1** and $Cu^{I}$ cation gave the 1 : 1 complex as a sole coordination product. Moutet and co-workers reported the structure of the complex formed between similar ferrocene-bipyridyl ligand and $Cu^{I}$ cation. Because of the insolubility of binuclear complex, they obtained a 2 : 2 complex in the solid state,[16] while 1 : 1 and 2 : 1 complexes in solution.[17,18f] In the present case, no precipitate was observed when the solution of **1** combined with a solution of $Cu^{I}$ salt at any concentration examined.

### The ditopic nature of ferrocene receptor 1

Several metallo-helicates bearing the oligoethylene glycol unit act as ditopic receptors for metal cations.[24] In contrast to the electrochemical studies of alkali- and alkaline earth-metal cation binding receptors, the examples of redox-active ammonium sensors are very few.[5] Thus, we have investigated the ditopic nature of receptor **1** by way of the evaluation of cation binding behavior at the pendant 2,2′-bipyridine unit and the oligoethylene glycol arms using $Cu^{I}$ and ammonium cations of amino acid methyl ester salts, respectively. The ESI-MS spectrum of the reference compound **2** in the presence of LeuOMe·HCl shows the peak at $m/z$ = 712 assigned as **2**·LeuOMe accompanied by the peak at $m/z$ = 589 (**2**·$Na^+$). This result indicates the effective host–guest recognition between **2** and LeuOMe·HCl. Judging from similar preliminary ESI-MS studies, receptor **1** does not bind to amino acid ester hydrochloride unless complexed by the addition of $Cu^{I}$ cation. However, when the ditopic receptor **1** is pre-organized by the complexation with $Cu^{I}$ cation, the conformation and the cavity size are fixed and binding ability and selectivity are enhanced to recognize the ammonium part of amino acid ester hydrochloride even in the presence of large excess of another onium salt, such as tetrabutylammonium perchlorate. The observed isotopic pattern of **1**·$Cu^{I}$·LeuOMe agreed very closely with that obtained by calculation for $C_{53}H_{65}N_5O_{12}Fe_1Cu_1$. (Fig. 2b)

The UV-vis spectra of **1**·$Cu^{I}$ in acetonitrile binding with LeuOMe·HCl of varying concentrations are shown in Fig. 3a. Absorption titration at 280 nm did not provide a linear Benesi–Hildebrand plot, thus curve fitting was carried out by least square approximation with nonlinear parameters according to eqn (1).

$$\Delta A_{obs} = b\Delta\varepsilon/2K_a[1 + K_a[H]_0 + K_a[G]_0 - \{(1+K_a[H]_0 + K_a[G]_0)^2 - 4K_a^2[H]_0[G]_0\}^{1/2}] \quad (1)$$

where $b$ is the optical path length (constant), $[H]_0$ is the initial concentration of host molecule (constant), $[G]_0$ is the initial concentration of guest molecule, and $K_a$ is the association constant. From the curve fitting, the binding constant was determined as $K_a = 1.726 \times 10^3$ $M^{-1}$. Pratt has reported[25] that the association constant of an oxidized ligand and guest cations ($K_{ox}$) could be calculated according to eqn (2) for cases where the association constant of neutral ligand, $K_{neutral} > 10^4$ $M^{-1}$.

$$E_{1/2}^{receptor} - E_{1/2}^{complex} = (RT/nF)\ln(K_{ox}/K_{neutral}) \quad (2)$$

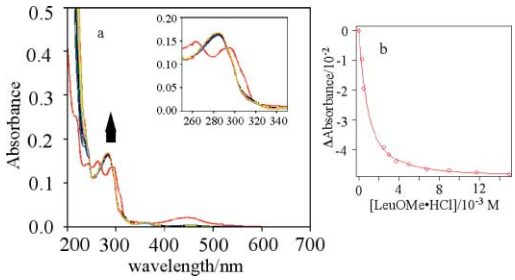


**Fig. 3** (a) Absorption titration profiles recorded during stepwise addition of LeuOMe·HCl to a solution of **1**·$Cu^{I}$ in acetonitrile at 25 °C. (b) The observed $\Delta A$ at 280 nm (red open circles) and the calculated curve (red line), where the curve fitting was carried out by least square approximation with nonlinear parameters according to eqn (1).

When $K_{neutral}$ was very small such as $K_{neutral} < 1$, there is another way to determine $K_{ox}$ value.[25] In the present case, the $K_a$ value is in the range $1 < K_a < 10^4$, there is no straightforward method to determine the binding constant $K_{ox}$ for the interaction between oxidized ligand (**1**$^{+\bullet}$·$Cu^{I}$) and LeuOMe·HCl.[14,25]

### Electrochemical analysis of 1·$Cu^{I}$ and 1·$Cu^{I}$·AAOMe–HCl

Fig. 4 shows the cyclic voltmmograms (CVs) of **1**·$Cu^{I}$ in acetonitrile containing 0.1 M TBAP. The CV curve for ferrocene moiety of **1**·$Cu^{I}$ (Fig. 4a) was characterized by a reversible one electron redox wave corresponding to the ferrocene/ferricinium redox couple with a half wave potential $E_{1/2}$ = 726 mV with peak separation $\Delta E$ = 61 mV and the ratio of peak currents was approximately unity. The irreversible reduction peaks located at 4 and −700 mV corresponded to $Cu^{I}/Cu^{II}$ and $Cu^{0}/Cu^{I}$, respectively. The irreversibility of $Cu^{I}/Cu^{II}$ and $Cu^{0}/Cu^{I}$ redox processes are explained on the assumption that a copper atom is released from the complex by the reduction of $Cu^{I}$ to $Cu^{0}$ (the second irreversible peak at about −700 mV) and as a result, two pendant arms are moving apart from each other to show the 1,3′-substitution of ferrocene group.[26] This hypothesis was

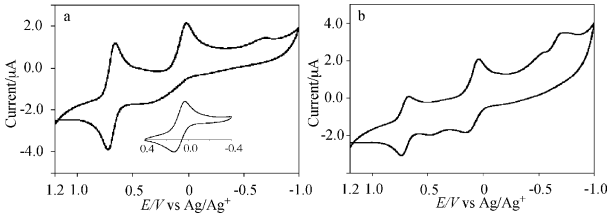


**Fig. 4** Cyclic voltammograms of (a) complex **1**·$Cu^{I}$ and (b) ditopic complex **1**·$Cu^{I}$·LeuOMe (after addition of 1 equiv. of LeuOMe·HCl) in acetonitrile. Scan rate = 100 mV $s^{-1}$.

**Table 1** Cyclic voltammetric data for receptor **1**, complex **1**·$Cu^{I}$ and their amino acid ester salt complexes

| Compounds | $Fc/Fc^{+}$ [a] | $Cu^{I}/Cu^{II}$ [a] |
|---|---|---|
| **1** | 696 (58) | — |
| **1**·$Cu^{I}$ | 726 (61) | 77 (104) |
| **1**·$Cu^{I}$ + Gly-OMe·HCl | 704 (74) | 108 (135) |
| **1**·$Cu^{I}$ + Ala-OMe·HCl | 708 (69) | 101 (129) |
| **1**·$Cu^{I}$ + Val-OMe·HCl | 705 (66) | 112 (152) |
| **1**·$Cu^{I}$ + Leu-OMe·HCl | 700 (68) | 94 (120) |
| **1**·$Cu^{I}$ + Ile-OMe·HCl | 700 (69) | 97 (121) |
| **1**·$Cu^{I}$ + Thr-OMe·TosOH | 703 (67) | 107 (135) |
| **1**·$Cu^{I}$ + Tle-OMe·TosOH | 706 (70) | 107 (145) |
| **1**·$Cu^{I}$ + Nva-OMe·TosOH | 703 (65) | 98 (115) |

[a] $E_{1/2}$, in mV, *vs.* $Ag/Ag^{+}$, 333 μM solutions of **1**, $Cu^{I}$ and AA-OMe salt in acetonitrile 0.1 M TBAP; $v = 100$ $mVs^{-1}$; anodic to cathodic peak separations ($\Delta E$) appear in parentheses, mV. All the experiments were repeated at least 3 times to get reliable values for $E_{1/2}$ and $\Delta E$.

supported by the result that the reversible redox wave (77 mV) was observed when the CV was measured between −400 and +400 mV ($Cu^{I}/Cu^{II}$ region; Fig. 4a, inset).

On the contrary, the CV curve for **1**·$Cu^{I}$·LeuOMe–HCl exhibited two sets of reversible redox waves located at 700 mV ($\Delta E =$ 68 mV) and 94 mV ($\Delta E = 120$ mV) which corresponded to the ferrocene/ferricinium and $Cu^{I}/Cu^{II}$ redox couples, respectively. (Fig. 4b) This means that after the reduction from $Cu^{I}$ to $Cu^{0}$ in **1**·$Cu^{I}$·LeuOMe–HCl, the conformation of two pendant arms are still 1,1′- or 1,2′-substitution[26] owing to the binding of amino acid salt to the oligoethylene glycol cavity, which prevents the two side chains from going apart from each other. When other amino acid ester salts were added to the complex **1**·$Cu^{I}$, similar CV responses were observed. Their electrochemical data are summarized in Table 1.

The complexation between ferrocene-based ligands and cations usually leads to a positive shift of the ferrocene/ferricinium redox couple,[1,27] which is in line with the electrostatic repulsion and makes the removal of electrons more difficult than for ferrocene-based ligand itself. Contrary to these findings, the ferrocene/ferricinium redox couple of present receptor **1**·$Cu^{I}$ exhibited slight negative shifts (18–26 mV) by the complexation with amino acid ester salts as compared with **1**·$Cu^{I}$. These negative shifts indicate the stabilization of ferricinium state by 1.74–2.51 kJ $mol^{-1}$.[28] A similar unexpected negative shift was observed in the complexation between sulfide-linked ferrocene ionophore and potassium cation.[10,29] Beer explained that the origin of this effect may be a redirection of the lone pairs of the sulfur donor atoms towards the ferrocene redox center. In the present case, it is presumed that two carbonyl groups play a similar role, but the detailed mechanism is not clear at present.

### $^{1}$H NMR and ESR studies of the complexation behavior of 1

We tried to examine the complexation behavior of **1** using $^{1}$H NMR spectroscopy. Fig. 5 shows three spectra of free ligand **1**, the complex **1**·$Cu^{I}$ and the ditopic complex **1**·$Cu^{I}$·LeuOMe–HCl. In the spectrum of **1**·$Cu^{I}$, the peaks corresponding to the bipyridine and oligoethylene glycol units shift downfield and upfield, respectively. (Fig. 5b) These observations mean that the complexation between $Cu^{I}$ and the bipyridine units of **1** results in the lowering of the electron density of bipyridine unit and the conformational change. While the spectrum of the ditopic complex, **1**·$Cu^{I}$·LeuOMe–HCl exhibits an extremely broad peak between 7.4 and 9.0 ppm and other peaks are also broadening to some extent. (Fig. 5c) This type of unusual strong broadening is usually observed upon addition of paramagnetic ions. According to the effect of ligands on $Cu^{I}/Cu^{II}$ reduction potential reported,[30] a ligand environment that produces a tetrahedral geometry will stabilize $Cu^{I}$ over $Cu^{II}$ and the presence

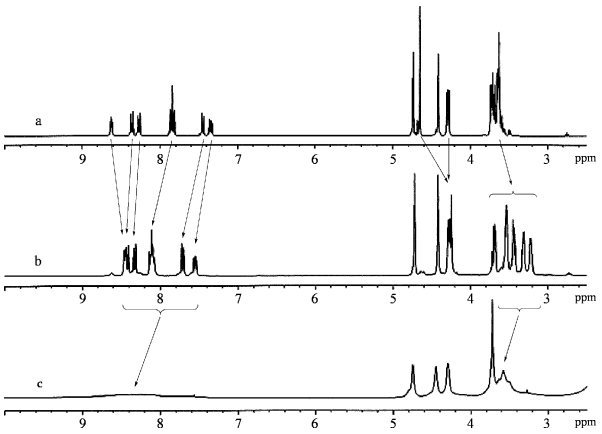


**Fig. 5** $^{1}$H NMR spectra of (a) ligand **1**, (b) complex **1**·$Cu^{I}$ and (c) ditopic complex **1**·$Cu^{I}$·LeuOMe in acetonitrile-$d_3$.

of bulky substituents in the $Cu^{II}$ complex distorts the geometry from planar towards tetrahedral, making it easier to reduce the copper and raising the potential. Thus, we suppose that the addition of LeuOMe·HCl leads to the conformational change of the copper complex from tetrahedral towards planar and this results in the oxidation of $Cu^{I}$ cation to paramagnetic $Cu^{II}$.

In order to confirm this assumption, ESR measurements were carried out. The receptor **1**·$Cu^{I}$ was ESR silent unless LeuOMe·HCl was added. On the other hand, the ESR signal emerged when LeuOMe·HCl was added to the acetonitrile solution of **1**·$Cu^{I}$. (Fig. 6) There is a close relationship between the coordination structure and the ESR parameters of the $Cu^{II}$ complex.[31,32] In the present case, the obtained parameter $g_{//} =$ 2.2607 is estimated for the dihedral angle of approximately 60° between two terminal pyridine rings.[31] With this information, together with the obtained value of $A_{//} = 1.527 \times 10^{-2}$ $cm^{-1}$, the coordination structure was the distorted tetrahedral geometry towards square-planar.

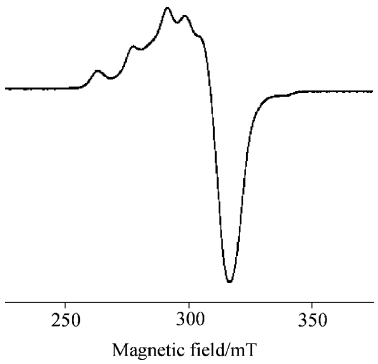


**Fig. 6** ESR spectrum of ditopic complex **1**·$Cu^{I}$·LeuOMe in acetonitrile solution at 77 K.

## Conclusions

The complexation with $Cu^{I}$ cation and the recognition of amino acid ester salts were investigated using novel ferrocene-based ditopic receptor **1** bearing two oligoethylene glycol arms with pendant 2,2′-bipyridine units at the identical cyclopentadienyl rings. The receptor **1** and $Cu^{I}$ cation formed a 1 : 1 complex and an positive shift of the respective ferrocene/ferricinium redox couple was observed in electrochemical analysis. On the other hand, the electrochemical analysis of the ditopic complexes, which were obtained from the mixing of the complex **1**·$Cu^{I}$ and AAOMe·HCl exhibited unexpected negative shifts presumably owing to the conformational change. Besides the negative shift of ferrocene/ferricinium redox couple, the oxidation of $Cu^{I}$ to paramagnetic $Cu^{II}$ occurred simultaneously. This observation

was also explicable in terms of the conformational change from tetrahedral to square planar induced by the addition of AAOMe·HCl. The oxidation was confirmed by the strong broadening of $^1$H NMR signals and the emergence of ESR signals assigned as $Cu^{II}$ species. The demonstration of the detection of ESR active species by the addition of cationic guest molecule may suggest a new tool for sensing of amino acid ester salts and other cationic species.

## Experimental

### General procedures

Most of the reagents and solvents were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Kasei Kogyo Co. and Sigma-Aldrich Co. and used without further purification. 1,1′-Bis(chlorocarbonyl)ferrocene was prepared according to the literature procedure.[21] Products were isolated by column chromatography on silica gel (Wakogel C-300) or preparative TLC on silica gel (Wakkogel B-5F). Melting points were measured on a Yanagimoto hot stage micro melting point apparatus and are uncorrected. $^1$H NMR spectra were recorded on a Varian UNITY 300 spectrometer at 299.94 MHz by using $CDCl_3$ or $CD_3CN$ as a solvent and tetramethylsilane as an internal standard and *J* values are given in Hz. UV-vis spectra were recorded on Shimadzu UV-1600PC spectrophotometer. Mass spectra were measured with a Waters micromassZQ 2000 under the following ionizing conditions: electrospray, cone voltage 60 V; capillary voltage 3.50 kV; extractor voltage 4 V; RF lens voltage 0.3 V; source temperature 150 °C; desolvation temperature 350 °C. All solution electrochemical measurements were performed with a 630A Volammetric Analyzer (ALS) in anhydrous acetonitrile at room temperature. Tetrabutylammonium perchlorate was used as supporting electrolyte (0.1 M in acetonitrile). A Pt disk was used as a working electrode (diameter 3.0 mm) and a Pt wire was used as a counter electrode. The Pt disk working electrode was polished with alumina (0.05 μm) prior to use to remove any surface contaminants. The reference electrode was a Ag/Ag+ electrode. *i*R compensation was applied. Backgrounds of the solvent containing the supporting electrolyte were corrected before each set of experiments and then subtracted from the CVs. The experiments were repeated at least 3 times to get reliable values for $E_{1/2}$. ESR spectra were obtained using a JEOL JES-FA100 ESR spectrometer operating at 100 kHz modulation frequency at room temperature (25 °C) or at liquid nitrogen temperature (77 K). Solutions in Biotech grade acetonitrile (Sigma-Aldrich Co.) were degassed by five freeze/pump/thaw cycles.

### Preparation of 6-bromomethyl-2,2′-dipyridine[33]

To a solution of 6-methyl-2,2′-dipyridine (0.45 g, 2.66 mmol) in carbon tetrachloride (15 $cm^3$) was added 1 equiv. of *N*-bromosuccinimide (0.47 g, 2.66 mmol) and catalytic amount of 2,2′-azobis(isobutyronitrile) (30 mg, 0.18 mmol) at room temperature under nitrogen atmosphere. The mixture was stirred at reflux temperature for 6 h. The solvent was removed under vacuum for recycling use and the residue was dissolved in chloroform (50 $cm^3$). The resulting solution was washed with water (3 × 50 $cm^3$) and brine (3 × 50 $cm^3$), then dried over $Na_2SO_4$. The solvent was removed and the residue was purified by preparative TLC using dichloromethane–acetone = 50 : 1 mixed solvent as an eluent to give the title compound as a pale yellow crystal (0.35 g, 53% yield), mp 65–66 °C; $^1$H NMR ($CDCl_3$, 300 MHz) δ 4.62 (s, 2H, benzyl-C$H_2$), 7.30 (ddd, *J* = 1.2, 4.8, 7.5, 1H, Ar*H*), 7.45 (dd, *J* = 0.9, 7.8, 1H, Ar*H*), 7.80 (t, *J* = 7.8, 2H, Ar*H*), 8.30 (dd, *J* = 0.9, 7.8, 1H, Ar*H*), 8.43 (td, *J* = 1.2, 8.1, 1H, Ar*H*) and 8.65 (ddd, *J* = 0.9, 1.8, 4.8, 1H, Ar*H*); *m*/*z* (ESI) 249 ($M^+$ + H, 100%), 251 ($M^+$ + H, 99), 271 ($M^+$ + Na, 31) and 273 ($M^+$ + Na, 30).

### Preparation of 10-(2′,2″-bipyridin-6′-yl)-3,6,9-trioxadecan-1-ol[24]

The mixture of 6-bromomethyl-2,2′-dipyridine (0.277 g, 1.12 mmol), triethylene glycol (1.5 $cm^3$, 11.2 mmol) and potassium hydroxide (0.088 g, 1.57 mmol) in 1,4-dioxane (distilled over calcium hydride, 8 $cm^3$) was refluxed for 13 h under nitrogen. After the removal of solvent, the residue was purified by silica gel column chromatography (chloroform–methanol–triethylamine = 100 : 5 : 1) to give the title compound as a yellow oil (0.336 g, 95% yield); $^1$H NMR ($CDCl_3$, 300 MHz) δ 3.60–3.63 (m, 2H, C$H_2$), 3.70–3.80 (m, 10H, C$H_2$), 7.29 (ddd, *J* = 1.2, 4.8, 7.2, 1H, Ar*H*), 7.49 (dd, *J* = 1.2, 7.8, 1H, Ar*H*), 7.80 (dt, *J* = 1.8, 7.8, 1H, Ar*H*), 7.81 (t, *J* = 7.8, 1H, Ar*H*), 8.25 (dd, *J* = 0.9, 7.8, 1H, Ar*H*), 8.37 (td, *J* = 1.2, 8.1, 1H, Ar*H*) and 8.65 (ddd, *J* = 0.9, 1.8, 4.8, 1H, Ar*H*); *m*/*z* (ESI) 319 ($M^+$ + H, 100).

### Preparation of bis 10-[2,5,8-trioxa-1-(2′,2″-bipyridin-6′-yl)]decyl ferrocene-1‴,1⁗-dicarboxylate (1)

The solution of 1,1′-(bischlorocarbonyl)ferrocene (0.118 g, 0.38 mmol) and 10-(2′,2″-bipyridin-6′-yl)-3,6,9-trioxadecan-1-ol (0.242 g, 0.78 mmol) in dichloromethane (distilled over Drierite®, 4 $cm^3$) was stirred at reflux temperature for 39 h. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (chloroform–methanol–triethylamine = 100 : 5 : 1) to give the title compound **1** in excellent yield as a brown oil (0.323 g, 97% yield); $^1$H NMR ($CDCl_3$, 300 MHz) δ 3.67–3.81 (m, 20H, C$H_2$), 4.36–4.40 (m, 8H, C$H_2$), 4.75 (s, 4H, benzyl-C$H_2$), 4.83(t, *J* = 2.1, 4H, *cp*) 7.28 (ddd, *J* = 1.2, 4.8, 7.2, 2H, Ar*H*), 7.47 (dd, *J* = 0.6, 7.5, 2H, Ar*H*), 7.75–7.82 (m, 4H, Ar*H*), 8.24 (d, *J* = 8.1, 2H, Ar*H*), 8.36 (td, *J* = 1.2, 7.8, 2H, Ar*H*) and 8.65 (ddd, *J* = 0.9, 1.8, 4.8, 2H, Ar*H*); *m*/*z* (ESI) 875 ($M^+$ + H, 100) and 897 ($M^+$ + Na, 38).

### Preparation of reference compound (2), bis (3,6,9-trioxadecyl)-1,1′-ferrocene dicarboxylate

To a solution of 1,1′-bis(chlorocarbonyl)ferrocene (0.117 g, 0.38 mmol) in dichloromethane (distilled over Drierite®, 4 $cm^3$) was added triethylene glycol monomethyl ether (0.130 $cm^3$, 0.84 mmol). The mixture was stirred at reflux temperature for 38 h. The solvent was removed and the residue was purified by silica gel column chromatography using chloroform–methanol = 13 : 1 as eluent to obtain compound **2** as a brownish-yellow oil (0.206 g, 92% yield); $^1$H NMR ($CDCl_3$, 300 MHz) δ 3.36 (s, 6H, C$H_3$), 3.52–3.55 (m, 4H, C$H_2$), 3.62–3.74 (m, 12H, C$H_2$), 3.77–3.81 (m, 4H, C$H_2$), 4.36–4.39 (m, 4H, C$H_2$), 4.42 (t, *J* = 1.8, 4H, *cp*) and 4.85 (t, *J* = 1.8, 4H, *cp*); *m*/*z* (ESI) 589 ($M^+$ + Na, 100).

### Preparation of the receptor 1·$Cu^I$

For CV and ESR studies, equal volumes of equimolar solutions (1 mM) of **1** and tetrakis(acetonitrile)copper$^I$ hexafluorophosphate in Biotech grade acetonitrile in the presence or absence of supporting electrolyte were mixed at room temperature. For NMR spectroscopy, $CD_3CN$ was used instead. The color of the solution immediately turned yellow. Judging from TLC analysis, yield was quantitative. $^1$H NMR ($CD_3CN$, 300 MHz) δ 3.20–3.23 (m, 4H, C$H_2$), 3.30–3.33 (m, 4H, C$H_2$), 3.41–3.46 (m, 4H, C$H_2$), 3.51–3.54 (m, 4H, C$H_2$), 3.67–3.72 (m, 4H, C$H_2$), 4.21 (s, 4H, benzyl-C$H_2$), 4.26–4.29 (m, 4H, C$H_2$), 4.41 (t, *J* = 1.8, 4H, *cp*), 4.72 (t, *J* = 1.8, 4H, *cp*), 7.55 (dd, *J* = 5.4, 7.2, 2H, Ar*H*), 7.71 (d, *J* = 7.5, 2H, Ar*H*), 8.08–8.14 (m, 4H, Ar*H*), 8.33 (d, *J* = 8.1, 2H, Ar*H*), 8.42 (d, *J* = 7.8, 2H, Ar*H*) and 8.45 (d, *J* = 4.8, 2H, Ar*H*); *m*/*z* (ESI) 937 ($M^+$, 100), 938 (56), 939 (58), 940 (31) and 941 (10).

### Preparation of ditopic complex 1·$Cu^I$·amino acid ester salt

To a solution of **1**·$Cu^I$ in acetonitrile was added the solution of amino acid ester salt in acetonitrile. The mixed solution was

allowed to stand for 14 h prior to measurement of UV, CV, ESI-MS, $^1$H NMR and ESR spectra. $^1$H NMR ($CD_3CN$, 300 MHz) $\delta$ 3.2–3.9 (br, 24H, C$H_2$), 3.70 (brs, 3H, LeuOC$H_3$), 4.27 (brs, 4H, benzyl-C$H_2$), 4.43 (brs, 4H, *cp*), 4.72 (brs, 4H, *cp*) and 7.4–9.2 (br, 14H, Ar*H*); *m*/*z* (ESI) 1082 ($M^+$–HCl, 5, base beak; 937 (**1**·$Cu^I$)).

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