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Self-Assembled Arene-Ruthenium-Based Rectangles for the Selective Sensing of Multi-Carboxylate Anions

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Abstract

Novel arene-ruthenium [2+2] metalla-rectangles, **4** and **5**, were synthesized by the self-assembly approach using a dipyrrolyl amide ligand (**3**) and arene-ruthenium acceptors (arene: benzoquinone (**1**); naphthacenedione (**2**)), and characterized by NMR and ESI-MS. The solid-state structure of **5** determined by X-ray diffraction shows the encapsulated diethyl ether molecules in the rectangular cavity of **5**. The luminescent **5** was further utilized for anion sensing where the amidic linkage serves as a hydrogen bond donor site for anions, and the ruthenium moiety serves as a signaling unit. A UV-vis titration study demonstrates that, while **5** interacts very weakly with the common mono anions as well as flexible dicarboxylate anions such as malonate and succinate, it displays significant binding affinity ($K > 10^3$ in MeOH) for the rigid multi-carboxylate anions such as oxalate, citrate, and tartrate in a 1:1 fashion. It is suggested that the 1:1 bidentate hydrogen bonding assisted by the proper geometrical complementarities is mainly responsible for the increased affinity of **5** towards such anions. In particular, a fluorescence titration study reveals a large fluorescence enhancement of **5** upon binding with multi-carboxylate anions. This indicates that the fluorescence enhancement is attributed to the blocking of the photo-induced electron transfer process from the arene-Ru moiety to the amidic donor in **5** as a result of hydrogen bonding between the donor and the anion.

Keywords

Multi-carboxylate; turn-on sensor; anion sensing; amidic donor; metalla-rectangles

Introduction

Interest in the molecular sensing of anions is growing due to their fundamental role in chemical as well as biological processes.^[1] Among the anions, multi-carboxylates^[2] are an important and essential class of oxy anions found in nature. For example, the oxalate anion plays an important role in the functioning of the human body, as quite a number of diseases are associated with the disruption of oxalate exchange.^[3] Citrate and tartrate are key metabolites in cellular intermediary metabolism, such as the Krebs's cycle, and are also

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essential sources of fatty acids and cholesterol, which are important for hormone synthesis and tissue regeneration.^[4] Citrate can also be used as a biomarker in a reliable screening method for prostate cancer.^[5] Determination of these anions is found to be important in clinical conditions and in normal cell metabolism, as diminished anion levels can cause severe disorders.^[6] Therefore, the detection of trace amounts of carboxylate anions is an important task.

For this purpose, chemosensors^[7,8] based on anion-induced fluorescence changes have gained particular attention because of their simplicity and high detection limits. A variety of receptors with complementary sites like amide, urea, amidinium, guanidium or Lewis acids have been synthesized and successfully employed for the detection of carboxylate anions.^[9] Many artificial sensors for multi-carboxylates have also been developed.^[10] However, very few examples of effective fluorescent sensors for citrate and tartrate have been reported to date.^[11] The receptors designed for these carboxylate anions are also important for the recognition of a variety of biomolecules, especially amino acids.^[12] Thus, the design of efficient luminescent receptors remains a continuing challenge.

Among the most appropriate architectures for inclusion of the guest, functional supramolecules^[13] could offer a suitable receptor site to encapsulate various guests.^[14,15] In recent years, supramolecular chemistry based on an organometallic half-sandwich moiety containing Ru, Rh, and Ir metals with multifunctional ligands has received considerable attention because of their versatility in designing various geometries like rectangles, squares and prismatic cages.^[16] In this regard, half-sandwich Ru-based 3-D structures have been extensively explored as the host for various guests and evaluated as anticancer agents.^[16] However, not much attention has been paid to the organometallic rectangles, although they display interesting functional properties and potential applications in various fields including host-guest chemistry, catalysis, redox activities, and anion sensing.^[17]

Herein, we report the synthesis and characterization of a new class of functional rectangles (**4** and **5**) containing an arene-Ru moiety (**1** and **2**) linked by a dipyridyl amide donor (**3**) using a self-assembly approach. The amide linkage provides the propensity for hydrogen bonding and a means for the introduction of the arene-Ru moiety that could serve as a new fluorescent-sensing motif. We have also explored the sensing behavior of the new metalla-rectangle **5** towards a variety of anions and discovered the highly selective and sensitive sensing properties of **5** towards multi-carboxylate anions such as oxalate, citrate, and tartrate.

Results and Discussion

Synthesis and Characterization

The reaction of arene-Ru acceptors, **1** and **2**, with dipyridyl amide ligand, **3**, in nitromethane/methanol (1:1) solution generates molecular rectangles, **4** (86%) and **5** (82%), respectively, in high yields (Scheme 1). The identities of **4** and **5** have been characterized by ¹H NMR spectroscopy, ESI-MS, and finally X-ray diffraction study. The ¹H NMR spectra of rectangles **4** and **5** display two doublets (δ 8.18 and 7.97 for **4**, δ 8.66 and 7.97 for **5**) for the pyridyl protons after self-assembly, along with a sharp singlet at δ 11.55 (**4**) and 11.31 (**5**) for amidic protons of the ligand. The *p*-cymene protons are observed at δ 6.13 and 5.88 for **4** and δ 6.03 and 5.81 for **5**. The benzoquinone protons of **4** are observed as a singlet at δ 5.83 ppm, and the naphthacenedione protons of **5** as two multiplets at δ 8.40 and 7.80 ppm.

The formation of rectangular structures **4** and **5** are also supported by ESI-MS spectra, as shown in Figure 1. Two charged states for **4** at *m/z* = 1000.1 ([*M* – 2OTf]²⁺) and 617.2 ([*M*

– 3OTf]³⁺), and one state for **5** at $m/z = 1150.1$ ($[M - 2OTf]^{2+}$) are clearly seen and isotopically resolved. These peaks also matched well with the theoretical distributions.

For a better understanding of the molecular structures, the crystal structure of **5** was determined by X-ray crystallography (Figure 2). Single crystals of **5** suitable for X-ray analysis using synchrotron radiation were obtained by slow vapor diffusion of diethyl ether into the nitromethane/methanol solution of **5**. X-ray structural analysis provided unequivocal proof of the molecular rectangle **5**, containing a diethyl ether molecule inside of the rectangular molecular cavity of $12.3 \text{ \AA} \times 6.6 \text{ \AA}$. The average Ru-N and Ru-O bond distances are 2.12 and 2.03 Å, respectively. The Ru1 ... Ru2 diagonal length in the rectangular structure is approximately 15.76 Å and the Ru-Ru distance in the dimetallic pillar is 8.43 Å. The centroids of the two amidic donors were separated by a distance of 7.28 Å.

Absorption and Emission Studies

The UV-vis absorption and photoluminescence (PL) emission spectra of metalla-rectangles **4** and **5** along with their corresponding metal acceptors (**1** and **2**) were investigated. The absorption spectra of **4** and **5** in a methanol solution ($1.0 \times 10^{-5} \text{ M}$) exhibit intense bands at $\lambda_{\text{abs}} = 307 \text{ nm}$ and 499 nm for **4**, and $\lambda_{\text{abs}} = 377 \text{ nm}$, 567 nm , 611 nm for **5**, respectively. The intense bands for **5** show similar features with those for **1** and **2**, except for the large red-shift in **5** after complexation with the donor ligand, **3** (Figure 3, top). Because the donor **3** shows no absorption at the lower energy region ($> 300 \text{ nm}$), the electronic transition in **4** and **5** could be ascribed to mixed intra- and intermolecular π - π^* and MLCT transitions associated with the arene-Ru moiety.^[18]

The photo-excitation at 377 nm (Figure 3, bottom) of **4** shows emission at around 425 nm while **5** shows emission bands at a much lower energy region ($\lambda_{\text{em}} = 524 \text{ nm}$ and 558 nm). The fact that the emission wavelengths of **4** and **5** match well with those of the acceptors **1** and **2**, respectively, indicates that the emission also originated from the arene-Ru moiety. Interestingly, the fluorescence intensity of **5** is decreased markedly in comparison with that of the acceptor **2** at the same molar concentration of arene-Ru moiety, while the intensity of **4** is slightly decreased compared with **1**. This result may imply the occurrence of intramolecular photo-induced electron transfer (PET) in **5** from an arene-Ru fluorophore to an amide donor, as also observed in other supramolecular systems.^[19]

Anion Sensing Studies

The presence of hydrogen bonding sites in the amidic donor ligand and the intense fluorescence in the visible region could be the key features of metalla-rectangle **5**, which prompted us to explore the anion sensing properties of **5**. With this in mind, we first carried out anion sensing studies of **5** using absorption and emission titrations against two series of anions in methanol. The first one is a series of mono anions like F^- , Br^- , Cl^- , and CH_3COO^- and the second series includes rigid to flexible dicarboxylate anions such as oxalate, malonate and succinate. The UV-vis titration results indicate that **5** exhibits very weak binding affinity towards the aqueous solution of all the mono anions (Figure 4, top). In contrast, the oxalate anion exhibits strong binding interactions with **5**. This finding may suggest that the metallo-rectangle, **5**, selectively binds with the dicarboxylate anion. Interestingly, the addition of flexible dicarboxylates such as malonate and succinate does not reveal any significant binding, implying that the efficient geometrical complementarities between the dianion and **5** play a crucial role in the strong binding (see also Figures S7 in supporting information). These observations were further supported by the emission studies. The changes in emission intensity were monitored after the addition of an excess amount of anion. Upon excitation at 377 nm , a methanol solution of **5** (see Figure 4, bottom) does not display significant changes in its emission spectrum after the addition of 2.5 equiv of

aqueous solution of the first series (F^- , Br^- , Cl^- , and CH_3COO^-) anions, but an immediate large enrichment in emission intensity is noticed with the addition of an aqueous solution of oxalate anion.

Based on this finding we carried out detailed titration experiments with oxalate anion. As shown in Figure 5 (top), the new absorption bands grow at ~ 447 nm, ~ 480 nm, and ~ 514 nm with a decrease in the band at 384 nm in addition to the appearance of clean isosbestic points at 430 nm and 526 nm. This result indicates the presence of an equilibrium binding process, supporting the hydrogen bonding interaction between the amide donor and the oxalate anion.

In particular, the Job's plot (supporting information) confirms that the binding occurs via a 1:1 stoichiometry between the oxalate and **5**, thus likes indicating simultaneous hydrogen bonding between the two amide donors and two carboxylate groups in the oxalate. Based on the 1:1 binding isotherm, the binding constant (K) of $4 \times 10^3 \text{ M}^{-1}$ was determined. It is interesting to note from the PL titration that the gradual addition of an aqueous oxalate anion solution to a methanolic solution of **5** leads to a 2.5-fold fluorescence enhancement compared with the emission intensity of free rectangle, **5** (Figure 5, bottom). The Stern-Volmer constant for the emission change is calculated to be $5 \times 10^4 \text{ M}^{-1}$. The observed enhancement in emission may be related to the blocking of the PET process from the arene-Ru fluorophore to the amide receptor upon binding of the carboxylate to the amide moiety as a result of hydrogen bonding, which results in the enrichment of the fluorescence. The large enhancement of fluorescence upon oxalate binding could be particularly interesting since it may serve as a basis for a "turn-on" oxalate sensor.

To address the binding interaction in detail, ^1H NMR titration experiments between **5** and oxalate anion were carried out. To avoid the solubility problems associated with sodium oxalate, the ^1H NMR titration studies have been done with tetrabutylammonium salt of oxalate anion. Also the experiments were conducted in acetone- d_6 owing to the absence of -NH proton signal in methanolic medium. According to the results of the ^1H NMR titrations of **5** with oxalate anion (Figure 6), it can be seen that the intensity of the singlet amidic proton of **5** at δ 11.47 decreases with a gradual addition of oxalate anion from 0.5 to 1.0 equivalent, which finally disappeared after addition of more than two equivalents of oxalate anion. This result reveals that hydrogen bonding between the amide -NH proton of pyridyl donor moieties in **5** and the oxalate anion is responsible for the strong binding interactions.

It is also noted from the experiments that all -NH groups bind with oxalate anion in acetone medium when the anion presents in excess (> 2 equiv). This result could be attributed to the fact that acetone is much less competing medium for hydrogen bonding than methanol. In fact, inspection of the proton intensity of **5** in the presence of one equivalent of oxalate anion (Figure 6c) indicated that the intensity is decreased to almost half of that observed in free **5** (Figure 6a), suggesting the involvement of 1:1 bidentate interaction. All these results thus supports that the metalla-rectangle **5** has high selectivity and affinity towards oxalate anion via strong bidentate hydrogen bonding assisted by the proper geometrical complementarities.

From the foregoing oxalate anion binding results using the metalla-rectangle **5**, we moved on to systematically investigate the detection of tartrate and citrate, which are also important anions in various physiological and enzymatic processes.

It can be clearly seen that the addition of incremental amounts of an aqueous solution of citrate and tartrate into the methanol solution of **5** also leads to significant absorption changes, indicating the presence of a strong interaction between **5** and the anions (Figure 7).

The binding constants derived from 1:1 binding isotherms are calculated to be $5 \times 10^3 \text{ M}^{-1}$ and $8 \times 10^3 \text{ M}^{-1}$, respectively, which are slightly higher than that of oxalate. These results may indicate that the metalla-rectangle **5** could be useful in the selective sensing of multi-carboxylate anions.

Further investigation of emission changes upon gradual addition of the aqueous solution of citrate and tartrate into the solution of **5** indicates a 3- and 4.5-fold fluorescence enhancement, respectively, after the addition of 9.0 equiv of anions (see Figure 8). The high Stern-Volmer constants of $1.4 \times 10^5 \text{ M}^{-1}$ for citrate anion and $1.8 \times 10^5 \text{ M}^{-1}$ for tartrate anion are also in parallel with the large enhancement of fluorescence as well as the increase in the binding constant compared to those found in the binding of the oxalate anion.

Conclusion

Here we disclose novel examples of [2+2] metalla-rectangles, **4** and **5**, composed of functional amidic donor, **3**, and arene-ruthenium metalla-acceptors, **1** and **2**, respectively. These new metalla-rectangles were characterized by ^1H NMR, HR-ESI-MS, and the solid-state structure of **5** was further confirmed by X-ray crystallography. The luminescent metalla-rectangle, **5**, with the amidic receptor site has been successfully explored for the selective sensing of biologically important multi-carboxylate anions. The PET-based signaling mechanism was utilized for the sensing of anions where enhanced fluorescence was noticed by blocking the PET upon binding of the anion with the metalla-rectangle, **5**. This system showed selective and strong binding towards oxalate, citrate, and tartrate anions in methanol while the mono anions interacted only weakly with **5**. It is suggested that the 1:1 bidentate hydrogen bonding assisted by the proper geometrical complementarities is mainly responsible for the increased affinity of **5** towards multi-carboxylate anions.

Experimental Section

General Details

Arene-ruthenium acceptors (**1**^[16c] and **2**^[16i]) and donor **3**^[1k] were prepared according to reported methods. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a Bruker 300 MHz spectrometer. ^1H NMR chemical shifts were reported relative to residual solvent signals. HR-ESI-MS spectra for the self-assemblies were recorded on a Micromass QuattroII triple-quadrupole mass spectrometer using electrospray ionization with a Mass Lynx operating system. UV-vis spectra were recorded on Cary 100 Conc. Fluorescence titration studies were carried out on a HORIBA FluoroMax-4 fluorometer.

Single-crystal X-ray Crystallography

The diffraction data from the single crystal of **5** mounted on a loop were collected at 100 K on an ADSC Quantum 210 CCD diffractometer with a synchrotron radiation ($\lambda = 0.90000 \text{ \AA}$) at Macromolecular Crystallography Beamline 6B1, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The raw data were processed and scaled using the program HKL2000. The structure was solved by direct methods, and the refinements were carried out with full-matrix least-squares on F^2 with appropriate softwares implemented in SHELXTL program package. X-ray data for **5**: $\text{C}_{58}\text{H}_{67}\text{F}_6\text{N}_4\text{O}_{16.50}\text{Ru}_2\text{S}_2$, $M = 3280.91$, Orthorhombic, *Pbca* (No. 61), $a = 20.456(4) \text{ \AA}$, $b = 17.225(3) \text{ \AA}$, $c = 36.110(7) \text{ \AA}$, $V = 12724(4) \text{ \AA}^3$, $Z = 8$, $T = 100 \text{ K}$, $\mu(\text{synchrotron}) = 1.170 \text{ mm}^{-1}$, $\rho_{\text{calc}} = 1.529 \text{ g}\cdot\text{cm}^{-3}$, 48786 reflections measured, 7972 unique ($R_{\text{int}} = 0.0890$), $R_I = 0.0756$, $wR_2 = 0.2172$ for 5526 reflections ($I > 2\sigma(I)$), $R_I = 0.1061$, $wR_2 = 0.2410$ (all data), GoF = 1.067, 830 parameters and 89 restraints. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to their

geometrically ideal positions. CCDC 799376 (5) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 4—A CH_3NO_2 solution (0.5 mL) of donor **3** (2.4 mg, 0.01 mmol) was added dropwise to a CH_3OH solution (0.5 mL) of ruthenium triflate acceptor **1** (9.1 mg, 0.01 mmol). The mixture was then stirred for 6 h at room temperature. Upon addition of diethyl ether, a winered, crystalline powder was isolated. Yield: 86%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): δ = 11.55 (s, NH), 8.18 (d, $^3J(\text{H,H})$ = 6.9 Hz, 8H, H α), 7.7.97 (d, $^3J(\text{H,H})$ = 6.9 Hz, 8H, H β), 6.13 (d, $^3J(\text{H,H})$ = 6.3 Hz, 8H, H γ), 5.88(d, $^3J(\text{H,H})$ = 6.3 Hz, 8H, H γ), 5.83 (s, 4H, H η), 2.79 [sept, 4H, $\text{CH}(\text{CH}_3)_2$], 2.04 (s, 12H, CH_3), 1.24 [d, $^3J(\text{H,H})$ = 6.9Hz, 24H, $\text{CH}(\text{CH}_3)_2$] ppm; ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ = 183.3, 158.7, 153.3, 147.4, 132.3, 116.1, 102.7, 98.9, 83.6, 81.0, 30.7, 21.9, 17.5 ppm; HR-ESI-MS for 4 ($\text{C}_{80}\text{H}_{80}\text{F}_{12}\text{N}_8\text{O}_{24}\text{Ru}_4\text{S}_4$): 1000.1 $[\text{M} - 2\text{OTf}]^{2+}$; 617.2 $[\text{M} - 3\text{OTf}]^{3+}$.

Synthesis of 5—A CH_3NO_2 solution (0.5 mL) of donor **3** (2.4 mg, 0.01 mmol) was added dropwise to a CH_3OH solution (0.5 mL) of the acceptor **2** (10.6 mg, 0.01 mmol). The mixture was then stirred for 6 h at room temperature. Upon addition of diethyl ether, a dark green, crystalline solid was formed and collected. Yield: 82%. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$): δ = 11.31 (s, NH), 8.66 (d, $^3J(\text{H,H})$ = 3.6 Hz, 8H, H β), 8.40 (d, $^3J(\text{H,H})$ = 6.0 Hz, 8H, H α), 7.97 (d, $^3J(\text{H,H})$ = 3.6 Hz, 8H, H γ), 7.80 (d, $^3J(\text{H,H})$ = 6.06 Hz, 8H, H β), 6.03 (d, $^3J(\text{H,H})$ = 5.7Hz, 8H, H γ), 5.81 (d, $^3J(\text{H,H})$ = 5.7Hz, 8H, H γ), 2.72 [sept, 4 H, $\text{CH}(\text{CH}_3)_2$], 2.09 (s, 12H, CH_3), 1.24 [d, $^3J(\text{H,H})$ = 6.9Hz, 24H, $\text{CH}(\text{CH}_3)_2$] ppm; ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$): δ = 168.4, 158.2, 152.0, 146.8, 133.1, 127.0, 118.5, 115.8, 106.3, 102.6, 99.2, 83.8, 82.0, 30.0, 22.0, 17.1 ppm; HR-ESI-MS for 5 ($\text{C}_{104}\text{H}_{92}\text{F}_{12}\text{N}_8\text{O}_{24}\text{Ru}_4\text{S}_4$): 1150.1 $[\text{M} - 2\text{OTf}]^{2+}$.

UV-vis Anion Binding Study

A 2 mL (1×10^{-5} M) stock solution of **5** in CH_3OH was prepared and placed in a quartz cell. 1×10^{-3} M stock solutions of the corresponding anions in water were incrementally added to the solution of **5**, and the absorption spectra were recorded at 298 K. The stoichiometry of the receptor-anion interaction was obtained from the plot of changes in the absorption spectra of **5** ($A - A_0$) as a function of increasing oxalate anion concentration (Job's plot). The result indicates that **5** forms 1:1 receptor-anion adduct with oxalate anion. The binding constant, K , of the host-guest complex was determined by fitting the experimental data to a 1:1 binding isotherm.

Fluorescence Sensing Study

A series of aqueous solutions of 1×10^{-3} M of the tetrabutylammonium sodium salts of F^- , Br^- , Cl^- , CH_3COO^- , oxalate, malonate, succinate, tartrate, and citrate were prepared. A 2 mL stock solution of **5** (1.0×10^{-5} M) in CH_3OH was placed in a quartz cell and the anion solutions were added in an incremental fashion. Their corresponding fluorescence spectra were recorded at 298 K. For all measurements, $\lambda_{\text{exc}} = 377$ nm was used and the emission wavelength was monitored at 524 nm and 558 nm. Analysis of the fluorescence intensity (I_0/I) as a function of increasing anion concentration ($[\text{G}]$) was done by following the Stern-Volmer equation: $I_0/I = 1 + K_{\text{SV}} [\text{G}]$. K_{SV} was calculated from the slope of the Stern-Volmer plot.

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Figure 1.
Calculated (top) and experimental (bottom) HR-ESI-mass spectra of metalla-rectangles **4** (a) and **5** (b).

Figure 2.
X-ray crystal structures of the molecular rectangle, **5**. Hydrogen atoms and counter anions are omitted for clarity.

Figure 3. UV-vis absorption (top; 1 – 5) and emission spectra (bottom; 1, 2, 4, and 5) in methanol.

Figure 4.

Changes in the absorption (top) and emission (bottom) spectra of **5** in methanol upon addition of incremental amounts of an aqueous solution of various anions; Cl = tetrabutylammonium chloride, Br = tetrabutylammonium bromide, F = tetrabutylammonium fluoride, AcO = sodium acetate, mal = disodium malonate, suc = disodium succinate, ox = disodium oxalate.

Figure 5. Changes in the absorption (top; the inset shows the 1:1 binding isotherm) and emission spectra (bottom; the inset shows the Stern-Volmer plot) of **5** (in methanol) upon addition of incremental amounts of aqueous solution of oxalate anion.

Figure 6. ^1H NMR spectra of **5** in acetone- d_6 with the addition of $[\text{Bu}_4\text{N}]_2\text{oxalate}$. (a) 0, (b) 0.5, (c) 1.0, and (d) 2.2 equiv of $[\text{Bu}_4\text{N}]_2\text{oxalate}$.

Figure 7. Changes in the absorption spectra of **5** in methanol upon addition of incremental amounts of aqueous solution of citrate anion (top) and tartrate anion (bottom). The insets in both figures show the 1:1 binding curves; tart = disodium tartrate, cit = trisodium citrate.

Figure 8.

Changes in the emission spectra of **5** in methanol upon addition of incremental amounts of aqueous solution of citrate (top) and tartrate anion (bottom). The insets in both figures show the Stern-Volmer plots.

Scheme 1.

Synthetic route to the self-assembled metalla- rectangles, **4** and **5**.