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Electronic Coupling between Two Cyclometalated Ruthenium Centers Bridged by 1,3,6,8-Tetra(2-pyridyl)pyrene (tppyr)

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A new cyclometalating bridging ligand 1,3,6,8-tetra(2-pyridyl)pyrene was designed and synthesized through 4-fold Suzuki couplings between 1,3,6,8-tetrabromopyrene and 2-pyridylboronate. A bis-cyclometalated bisruthenium complex bridged by this ligand showed the presence of an electronic coupling between individual metal centers, as indicated by electrochemical and spectroscopic studies.

Introduction

Since the invention of the Cruetz−Taube ion, $\{[Ru(NH_3)_5]\text{-}(pyrazine)[Ru(NH_3)_5]^{5+}\}$,[1] di- or multimetallic mixed-valence complexes have received a great deal of interest.[2] The electronic couplings between individual metals have been found to greatly depend on the distance between the metal centers, the ability of the bridging ligand to delocalize the electronic charge, and the coordination environments of the metal components.[3] These studies are of significant importance in understanding many naturally occurring photoinduced electron/energy transfer processes and relevance to molecular electronics and switches. According to Robin and Day,[4] three categories of mixed-valences systems are distinguished on the basis of the extent of electronic communications between individual metals. Class I systems are composed of noninteracting centers. Species in Class II systems exhibit weak coupling between individual metal components. Class III systems consist of strongly coupled centers, in which electrons fully delocalize across the whole molecule and electron transfer between redox sites take places without activation barrier. Most of the mixed-valence complexes reported to date could be classified as the Class II system.

Recently, much attention has been drawn to the synthesis and application of cyclometalated polypyridine ruthenium complexes[5] because of their distinguished electrochemical and photophysical properties. We are particularly interested in mixed-valence systems containing these species, since cyclometalated complexes have been reported to greatly enhance electronic coupling between metal centers and have high potential to be used as molecular wires.[6] In this contribution, we report a new bridging ligand, 1,3,6,8-tetra(2-pyridyl)pyrene (**1**, tppyr, Scheme 1), which could efficiently mediate metal−metal communication between two cyclometalated ruthenium centers, benefiting from the presence of the highly conjugated and planar pyrene backbone.

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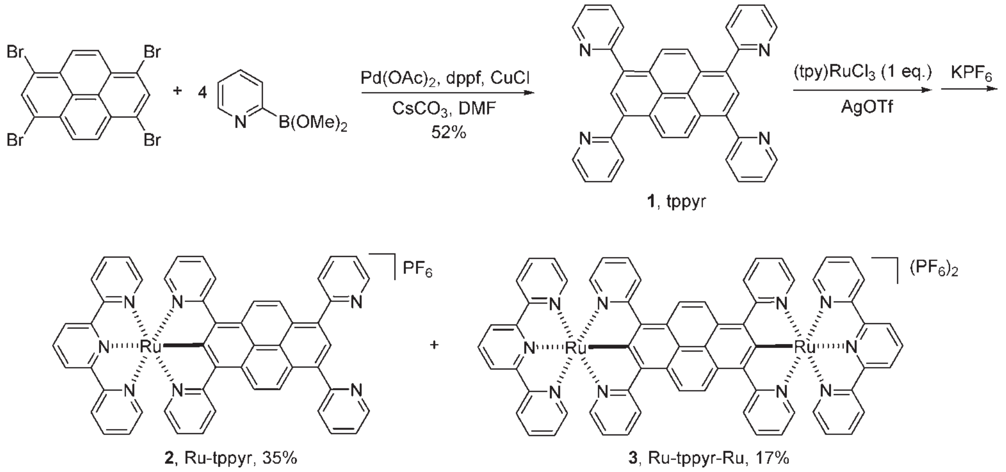
Scheme 1. Synthesis of **1**−**3**



Results and Discussion

As outlined in Scheme 1, tppyr **1** was prepared through 4-fold Suzuki couplings between 1,3,6,8-tetrabromopyrene[7] and dimethyl 2-pyridylboronate, which was generated in situ from 2-bromopyridine and *n*-butyllithium followed by treatment with trimethyl borate.[8] The Suzuki reaction proved problematic in the beginning when conventional coupling conditions were used. For example, when $Pd(PPh_3)_4$ or $Pd(OAc)_2$ coupled with PPh_3 was used as the catalyst, no desired product was isolated.[9] The electron-deficient nature and lability of 2-pyridylboronate or boronic acid make them challenging substrates in Suzuki coupling. To our delight, we succeeded in synthesizing tppyr in 52% yield using copper-facilitated reaction conditions, referencing to recent reports from a couple of groups.[10] The presence of CuCl was found to be crucial for the success of this reaction. Subsequent reaction of 1 equiv of $Ru(tpy)Cl_3$ (tpy = 2,2′;6′,2″-terpyridine) and tppyr in the presence of silver triflate, followed by anion exchange with KPF_6, afforded cyclometalated monoruthenium complex **2** in 35% yield and biscyclometalated bisruthenium complex **3** in 17% yield. Alternatively, bisruthenium complex **3** could be prepared from the reaction of 2 equiv of $Ru(tpy)Cl_3$ and tppyr in 38% yield. These new compounds are fully characterized by ^1H NMR, mass spectra, and microanalysis, as shown in the Experimental Section.

Electrochemistry is frequently employed to study the electronic coupling between metal centers of symmetric dimetallic systems. If there is no electronic coupling between two metals, the voltammetric profile exhibits a single metal-based redox wave. On the other hand, two separated sequential redox waves indicate the presence of an electronic coupling between two metals. However, this principle should be taken with great care because the electrochemical data are largely dependent on the measurement conditions, such as the solvent and supporting electrolyte used. Nevertheless, the separation difference between two redox waves ($\Delta E°$) may serve as a parameter for qualitatively estimating the extent of electronic coupling between two metal centers, if under the same conditions of measurement. The cyclic voltammetric (CV) profile of monoruthenium complex **2** is shown in Figure 1a, which displays one reversible redox couple at +0.58 V versus Ag/AgCl. This is a typical value for a cyclometalated $Ru^{II/III}$ redox process.[5,6] On the other hand, two sequential redox couples at +0.445 and +0.655 V are evident on the CV of bisruthenium complex **3** (Figure 1b), with a potential difference ($\Delta E°$) of 210 mV between two half-wave potentials. Differential pulse voltammetry (DPV) of bisruthenium complex **3** (red line in Figure 1b) also confirms the large splitting between two metal-based oxidation peaks ($\Delta E° = 220$ mV). This suggests the presence an electronic coupling between two ruthenium centers through the tppyr bridging ligand. In contrast, a noncyclometalated bisruthenium polypyridine complex connected by 6,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quaterpyridine displays a single ruthenium-based redox wave. In addition, a biscyclometalated bisruthenium complex bridged by 3,3′,5,5′-tetra(2-pyridyl)-biphenyl exhibits two sequential metal-based redox waves with a potential splitting of 165 mV.[6] The first reduction wave of **2** and **3** occurs at −1.36 and −1.14 V, respectively (Figure S1 in the Supporting Information). The comproportionation constant K_c for the equilibrium $Ru^{II}{-}Ru^{II} + Ru^{III}{-}Ru^{III} \leftrightarrow 2\ Ru^{II}{-}Ru^{III}$, is 3630 in the case of complex **3**,[11] which indicates the high stability of the in situ electrochemically generated intervalence complex.

The UV/vis absorption spectra of the above compounds were recorded (Figure 2). Tppyr **1** shows two peaks at 302 and 390 nm, which are assigned to the $\pi-\pi^*$ transitions of the ligand. Monoruthenium complex **2** displays multiple intraligand $\pi-\pi^*$ excitations at 318, 345, 418, and 442 nm, and the latter two peaks likely originate from the tppyr ligand part. The intense and broad band centered at 561 nm in the visible region is ascribed to metal-to-ligand-charge-transfer (MLCT) transitions. In comparison, both the intraligand and the MLCT transitions of bisruthenium complex **3** exhibit approximately doubled molar absorption coefficients and large red shifts, with low energy features extending down to 850 nm. The red shift of MLCT bands of **3** compared to **2** is a joint result of the stabilization of lowest unoccupied molecular orbital (LUMO) level and destabilization of the highest occupied

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[11] $K_c = 10^{\Delta E\ (\mathrm{mV})/59}$ for a room temperature case. See ref 2.

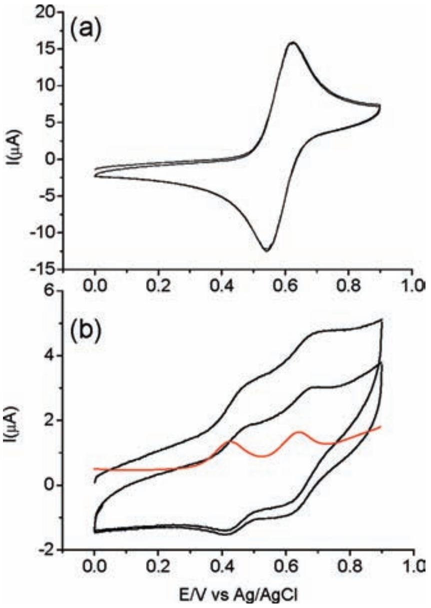

Figure 1. Cyclic voltammetry of (a) **2** and (b) **3** in acetonitrile containing 0.1 M of Bu_4NClO_4 as the supporting electrolyte at a scan rate of 100 mV/s. The red line in (b) is the DPV of **3**, with a step potential of 5 mV and amplitude of 50 mV. The working electrode is a glassy carbon; the counter electrode is a platinum wire.

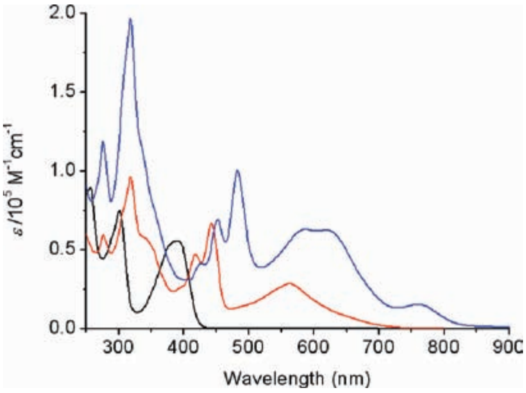

Figure 2. UV/vis absorption spectra of ligand tppyr **1** (black line), monoruthenium complex **2** (red line), and bisruthenium complex **3** (blue line) in dichloromethane (for **1**) or acetonitrile (for **2** and **3**).

molecular orbital (HOMO) level, as observed from the electrochemical analysis.

To further probe the electronic coupling between metal centers of bisruthenium complex **3**, proper amounts of bromine were gradually added to this complex in acetonitrile, and the solution was monitored by UV/vis/NIR spectrophotometry (Figure 3). The in situ generated mixed valence species gave rise to a huge intervalence charge transfer (IVCT) transition centered at 2080 nm (4808 cm^{-1}), with an extinction coefficient of 34000 M^{-1} cm^{-1}. However, we were unable to observe the full band of the IVCT transition because of the tremendous noise of the solvent beyond 2200 nm and the limitation of the spectrophotometer. Nevertheless, the observation of the huge IVCT transition indicates an electronic coupling between two ruthenium centers of a mixed valence complex. When an excess of bromine was added, the IVCT band disappeared completely. The intense peak centered at 734 nm could be assigned to the ligand-to-metal-charge-transfer (LMCT) transition of the two-electron oxidized species. A similar IVCT band could also be observed from the mixed-valent complex of **3** generated by treatment of 1 equiv of cerium(IV) ammonium nitrate (CAN) in acetonitrile (Figure S2 in the Supporting Information). The wide and intense IVCT band is also supported by the spectroelectrochemical measurements. A solution of complex **3** in CD_3CN was subject to electrolysis at +0.52 V versus Ag/AgCl on a platinum mesh electrode. The emergence of a wide transition in the NIR region is evident, which confirms the presence of the IVCT band of the mixed-valent complex of **3** (Figure S3 in the Supporting Information).

According to Hush's expression,[12] the theoretical full width at half-height ($\Delta\nu_{1/2}$) of IVCT of the mixed-valence compound of **3** equals $(2310\nu_{max})^{1/2} = (2310*4808)^{1/2} = 3332\ cm^{-1}$. Assuming a Gaussian band shape and using the high-energy side of the transition, the experimental value of $\Delta\nu_{1/2}$ is around 3070 cm^{-1} determined from the IVCT band of the mixed valence compound generated by treatment with bromine. It is clear that the experimental value of $\Delta\nu_{1/2}$ is close to, albeit slightly narrower than the theoretical value. The Γ parameter, introduced by Brunschwig, Creutz, and Sutin[13] of mixed-valence compound of **3** is 0.08, as determined from the equation $\Gamma = 1 - \Delta\nu_{1/2\text{exp}}/\Delta\nu_{1/2\text{theo}}$. Because of the lack of crystal structure, the distance between two ruthenium atoms of complex **3** is calculated to be 11.041 Å using an Avogadro program (Figure S5 in the Supporting Information).[14] The electronic coupling parameter H_{ab} is calculated to be 1322 cm^{-1}, according to the Hush formula:[2,12,15] $H_{ab} = 2.06 \times 10^{-2}(\varepsilon_{max}\nu_{max}\Delta\nu_{1/2})^{1/2}/(r_{ab})$. On the basis of these facts, we assign the mixed-valence compound of **3** to a Robin and Day class II system.

In summary, a new polypyridine bridging ligand, 1,3,6,8-tetra(2-pyridyl)pyrene (tppyr), was synthesized through 4-fold Suzuki couplings. Reactions of tppyr with 1 or 2 equiv of $Ru(tpy)Cl_3$ afforded corresponding cyclometalated monoruthenium and bisruthenium complexes in moderate yields. Electrochemical studies (CV and DPV) demonstrated a stepwise oxidation of the two ruthenium centers of the dimetallic complex and a splitting of 210 mV between these two redox bands. This suggests that ligand tppyr could efficiently mediate an electronic communication between two cyclometalated rutheniums, which was also supported by the observation of a IVCT band in the NIR region of the corresponding mixed valence complex generated by chemical or electrochemical method. This kind of complex would be of interest for application in molecular electronics. Future work will focus on the preparation and studies of other transition metal complexes based on tppyr.

Experimental Section

Spectroscopic Measurements. All optical ultraviolet−visible (UV/vis) absorption spectra were obtained using a TU-1810DSPC spectrometer of Beijing Purkinje General Instrument Co. Ltd. at room temperature in denoted solvents, with a conventional 1.0 cm quartz cell. UV/vis/NIR spectra were recorded using a JASCO V-570 UV/vis/NIR spectrophotometer.

Electrochemical Measurements. All cyclic voltammetry (CV) were taken using a CHI620D potentiostat. All measurements

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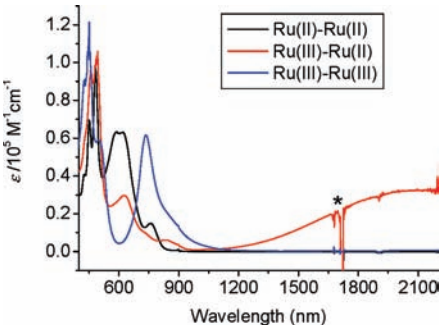

Figure 3. Intervalence charge transfer transition of bisruthenium complex **3** in acetonitrile. Black line: initial spectrum. Red line: at one-electron oxidation. Blue line: at two electrons oxidation. *: Artifacts due to a nonperfect compensation of solvent absorption.

were carried out in 0.1 M of Bu_4NClO_4/acetonitrile at a scan rate of 100 mV/s with a Ag/AgCl reference electrode. The working electrode is a glassy carbon, and a platinum coil is used as the counter electrode.

Synthesis. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Dry ether was distilled from sodium/benzophenone and other solvents (analytical grade) were used without further purification. NMR spectra were recorded in the designated solvent on Bruker Avance 400 M spectrometer. Spectra are reported in ppm values from residual protons of the deuterated solvent for ^{1}H NMR (δ 7.26 ppm for $CDCl_3$ and 1.92 ppm for CD_3CN). Mass spectrometry data were obtained with a Bruker Daltonics Inc. ApexII FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement is 2,5-dihydroxybenzoic acid (DHB) or α-cyano-4-hydroxycinnamic acid (CCA). Microanalysis was carried out using Flash EA 1112 or Carlo Erba 1106 in the Institute of Chemistry, CAS. Compounds 1,3,6,8-tetrabromopyrene[7] and Ru(tpy)Cl_3[16] were prepared according to known procedures.

1,3,6,8-Tetra(2-pyridyl)pyrene (tppyr, 1). To a solution of 2-bromopyridine (2.0 mmol, 0.19 mL) in dry Et_2O (10 mL) at −78 °C was added 0.8 mL of 2.5 M solution of *n*-BuLi (2.0 mmol) in hexane under a N_2 atmosphere. After 30 min, a solution of $B(OMe)_3$ (4.0 mmol, 0.45 mL) in 5 mL of Et_2O was added dropwise over 20 min, and the temperature was raised to room temperature naturally overnight. The solvent was evaporated under reduced pressure in situ, followed by the addition of 5 mL of dry MeOH to remove the light impurity via azeotrope. The resulting reddish orange solid 2-pyridyl boronate ester was used for next transformation without further purification.

Another oven-dried vial was charged with 1,3,6,8-tetrabromopyrene (0.2 mmol, 104 mg), Cs_2CO_3 (4 mmol, 1.3 g), CuCl (1.0 mmol, 99 mg), $Pd(OAc)_2$ (0.08 mmol, 18 mg), dppf (0.16 mmol, 88 mg), and a solution of the above-prepared 2-pyridyl boronate ester in DMF (10 mL). The mixture was purged with nitrogen for 5 min before the vial was capped and heated at 130 °C for 40 h. The reaction was cooled to room temperature and diluted with 150 mL of CH_2Cl_2. After washing with 20 mL ×3 of water, the organic solution was concentrated and purified by silica gel chromatography (eluent: CH_2Cl_2/ethyl acetate/NH_4OH 50/50/0.05) to afford 38 mg of yellow solid **1** in a yield of 52%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J* = 6.0 Hz, 4H), 7.81 (d, *J* = 8.0 Hz, 4H), 7.88 (t, *J* = 7.6 Hz, 4H), 8.39 (s, 2H), 8.43 (s, 4H), 8.87 (d, *J* = 4.4 Hz, 4H). MALDI-TOF (CCA) *m*/*z*: 511.3 $[M + H]^+$. Anal. Calcd. for $C_{36}H_{22}N_4 \cdot H_2O$: C, 81.80; H, 4.58; N, 10.60. Found: C 82.25, H 4.37, N 10.42. ^{13}C NMR spectrum has not been recorded because of low solubility of the sample.

[(tpy)Ru(tppyr)](PF_6) (2) and [(tpy)Ru(tppyr)Ru(tpy)](PF_6)$_2$ (3). To 50 mL of dry acetone were added Ru(tpy)Cl_3 (47 mg, 0.107 mmol) and AgOTf (97 mg, 0.37 mmol), and the mixture was refluxed for 3 h. One hour later, the mixture was filtered to afford a purple-black solution, and the filtrate was concentrated to dryness. To the residue were added 1,3,6,8-tetrapyridylpyrene **1** (55 mg, 0.107 mmol), DMF (15 mL), and *t*-BuOH (15 mL), and the mixture was heated under microwave irradiation (50 W) for 30 min. After cooling to room temperature, the solvent was removed under reduced pressure, and the residue was dissolved in 3 mL of methanol. After addition of an excess of KPF_6, the resulting precipitate was collected by filtering and washing with water and Et_2O. The crude solid was purified by silica gel chromatography to give 42 mg monoruthenium complex **2** (eluent: CH_3CN/H_2O/aq. KNO_3 100/5/0.03 black solid, 35%) and 25 mg bisruthenium complex **3** (eluent: CH_3CN/H_2O/aq. KNO_3 100/10/0.1 black solid, 17%). Alternatively, complex **3** could be prepared from 1,3,6,8-tetrapyridylpyrene **1** and 2 equiv of Ru(tpy)Cl_3 as well as 6 equiv of AgOTf in a yield of 38%.

2: ^{1}H NMR (400 MHz, CD_3CN): δ 6.71 (t, *J* = 6.0 Hz, 4H), 6.99 (m, 2H), 7.22 (d, *J* = 5.0 Hz, 2H), 7.53 (m, 2H), 7.60 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 2H), 7.93 (m, 2H), 8.03 (m, 2H), 8.28 (m, 2H), 8.39 (m, 2H), 8.63 (m, 2H), 8.77 (d, *J* = 7.9 Hz, 4H), 8.90 (m, 2H), 9.04 (m, 2H). ESI-MS *m*/*z*: 844.3 $[M - PF_6]^+$. Anal. Calcd. for $C_{51}H_{32}F_6N_7PRu$: C, 61.94; H, 3.26; N, 9.91. Found: C 61.47, H 3.55, N 9.77.

3: ^{1}H NMR (400 MHz, CD_3CN): ^{1}H NMR (400 MHz, CD_3CN): 6.79 (t, *J* = 6.4 Hz, 4H), 6.89 (t, *J* = 5.9 Hz, 4H), 7.16 (d, *J* = 5.3 Hz, 4H), 7.30 (d, *J* = 5.0 Hz, 4H), 7.71(t, *J* = 7.2 Hz, 4H), 7.82 (t, *J* = 7.1 Hz, 4H), 8.33 (t, *J* = 8.0 Hz, 2H), 8.48 (d, *J* = 8.1 Hz, 4H), 8.81 (d, *J* = 8.0 Hz, 4H), 8.95 (d, *J* = 8.3 Hz, 4H), 9.34 (s, 4H). MALDI-TOF (DHB) *m*/*z*: 1321.7 $[M - PF_6]^+$, 1176.8 $[M - 2PF_6]^{2+}$. Anal. Calcd. for $C_{66}H_{42}F_{12}N_{10}P_2Ru_2 \cdot 4H_2O$: C, 51.50; H, 3.27; N, 9.10. Found: C 51.53, H 3.17, N 8.85.

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Supporting Information Available: Additional electrochemical and spectroscopic data, NMR, and MS spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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