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Synthesis of Novel Ruthenium Dyes with Thiophene or Thienothiophene Substituted Terpyridyl Ligands and Their Characterization

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Synthesis of Novel Ruthenium Dyes with Thiophene or Thienothiophene Substituted Terpyridyl Ligands and Their Characterization

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We synthesized new materials for dye-sensitized solar cell (DSSC) which is incorporating highly conjugated π-electron-donating groups, such as thiophene or thieno[3,2-b]thiophene. The synthesized dyes showed similar molar extinction coefficient compared to that of N749. All compounds are analyzed by ^{1}H- and ^{13}C-NMR, and FT-IR spectroscopic measurements. The physical properties of dyes are characterized by UV-vis absorption spectroscopy, cyclic voltamogram and DFT calculation. The power conversion efficiencies (η_{eff}) of two synthesized dyes were 4.0 and 3.4%, respectively, under AM1.5G light source. The reference cell (N749) was evaluated the η_{eff} of 6.0% at the same conditions.

Keywords DFT calculation; dye-sensitized solar cell; Ru-complex; solar conversion efficiency; thionothiophene; thiophene

Introduction

Ruthenium complexes have received great deal of attraction in the field of dye-based dye-sensitized solar cells (DSSCs) because of the photon to current conversion efficiency over 10% [1]. The synthesis of new dyes is very important for increasing the energy conversion efficiency of the solar cell. This is required that dyes have large absorption coefficient in long wavelength up to near IR. Therefore, many researchers have tried to synthesis new Ruthenium dyes. Black dye (N749) absorbs longer wavelength light than other Ruthenium dyes such as N3 and N719. In this study, we synthesized new ruthenium dyes to expand the π-conjugation, which have thiophene or thienothiophene moiety based on N749 dye. The detail synthesis methods as shown in Scheme 1 for new dyes were investigated and

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the photovoltaic performances for new dyes were also characterized compare to those of reference N749 DSSC.

Experimental

1-[2-(4-Methoxycarbonylpyridin-2-yl)-2-oxo-ethyl]–pyridinium-iodide (**1**), ***Krohnke Reagent*** [2]: Methyl 2-acetylisonicotinate (0.24 g, 1.34 mmol) was added to a warmed a solution of I_2 (0.35 g, 1.38 mmol, 1.03 eq) in anhydrous pyridine (10 ml). The reaction mixture was refluxed for 3 hr under Ar condition. After cooling to room temperature, a precipitate was collected by filtration and wash with chloroform and diethyl ether to give 3 as powder (yield: 34%). ^{1}H NMR (400 MHz, DMSO-d6), δppm: 9.10 (1H, d, J = 4.8 Hz), 9.09 (2H, d, J = 5.6 Hz), 9.00 (1H, t, J = 8 Hz), 8.36 (1 H, s), 8.30 (2H, t, J = 6.8 Hz), 8.28 (1H, dd, J = 1.6 Hz, 4.8 Hz), 6.52 (2H, s), 3.95 (3H, s); ^{13}C NMR (100 MHz, DMSO-d6), δ ppm: 191.20, 164.70, 152.07, 151.49, 146.92, 146.84, 139.21, 128.26, 127.88, 120.77, 67.71, 53.69.

Methyl-2-(3-Thiophen-2-yl-acryloyl)-isonicotinate (2)**:** Piperidine (0.6 mL, 6.19 mmol) and acetic acid (0.35 mL, 6.19 mmol) were dissolved in methanol (10 mL) and stirred for 5 min at room temperature. At room temperature, methyl-2-acetylisonicotinate (1 g, 5.58 mmol) were added to solution and stirred for further 5 min. 2-Thiophenecarboxaldehyde (0.62 g (0.52 mL), 5.58 mmol) were added to solution and reflux for 5 h. When yellow precipitate was found on the solution, cool to room temperature. Precipiate was washed with small amount of methanol and no further purification is needed. ^{1}H NMR (400 MHz, DMSO-d6), δ ppm: 8.90 (1H, dd, J = 0.8 Hz, 4.8 Hz), 8.69 (1H, dd, J = 0.8 Hz, 1.6 Hz), 8.13 (1H, s), 8.09 (2H, m), 7.47 (2H, dd, J = 5.2 Hz, 10.8 Hz), 7.12 (1H, t, J = 3.6 Hz), 4.0 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$), δ ppm: 188.28, 165.16, 155.15, 149.75, 140.77, 138.69, 137.74, 132. 52, 129.50, 128.37, 125.88, 122.13, 119.47, 52.93.

Methyl-2-(3-thieno[3,2-b]thiophen-2-yl-acryloyl)-isonicotinate (**2′**): Piperidine (4.69 mL, 47.99 mmol, 1.1 eq) and acetic acid (2.73 mL, 47.99 mmol, 1.1eq) were added to a stirred solution of thieno[3,2-b]thiophene-2-carbaldehyde (7.29 g, 43.33 mmol) and methyl-2-acetylisonicotinate (8.6 g, 47.99 mmol, 1.1 eq) in methanol (50 mL). The mixture was refluxed for 5 h and turned red with precipitation of orange crystals. After cooling to room temperature, the crystals was filtered and washed with methanol. The crude product was chromatographed on silica gel, eluting with hexane: Ethyl acetate (5 : 1) and then it was recrystallized with methanol to give 4 as orange crystals (yield: 58%). ^{1}H NMR (400 MHz, DMSO-d6), δ ppm: 9.03 (1H, d, J = 5.2 Hz), 8.44 (1H, s), 8.18 (1H, d, J = 16 Hz), 8.13 (1H, d, J = 5.2 Hz), 8.05 (1H, d, J = 35.6 Hz), 7.93 (1H, d, J = 5.6 Hz), 7.53 (1H, d, J = 5.2 Hz), 3.95 (1H, s); ^{13}C NMR (100 MHz, DMSO-d6), δ ppm: 187.48, 165.07, 154.72, 151.10, 142.27, 141.83, 140.10, 139.14, 138.91, 133.18, 127.61, 126.56, 121.35, 120.94, 118.71, 53.52.

4,4′′-Dimethoxycarbonyl-4′-thieno[3,2-b]thiophenyl-2,2′:6′2′′-terpyridine (**3**): Enone reagent (**2**) (0.188 g, 0.69 mmol) and Krohnke's reagent (**1**) (0.327 g, 0.85 mmol) were added to a solution of excess ammonium acetate (2 g, 26 mmol) in methanol (3 mL) and the resulting solution was heated to reflux for 4 h. After cooling to room temperature, a precipitate was collected by filtration and triturated successively with methanol (2 × 2 mL) and then with chloroform (2 × 2 mL). The chloroform extract was freed of solvent, and then the crude was washed with methanol and then it was recrystallized with chloroform to give 5 as a brown powder (yield: 27%). ^{1}H NMR (400 MHz, DMSO-d6), δ ppm: 9.16 (2H, s), 8.90 (2H, d, J = 4 Hz), 8.75 (2H, s), 8.00 (1H, s), 7.94 (2H, d, J = 4 Hz), 7.49 (1H, d, J

= 8 Hz), 7.33 (1H, d, J = 4 Hz); ^{13}C NMR (100 MHz, DMSO-d6), δ ppm: 165.97, 157.14, 155.83, 150.08, 144.28, 143.34, 140.36, 140.28, 139.69, 129.01, 123.24, 120.96, 119.88, 118.43, 117.66, 52.94.

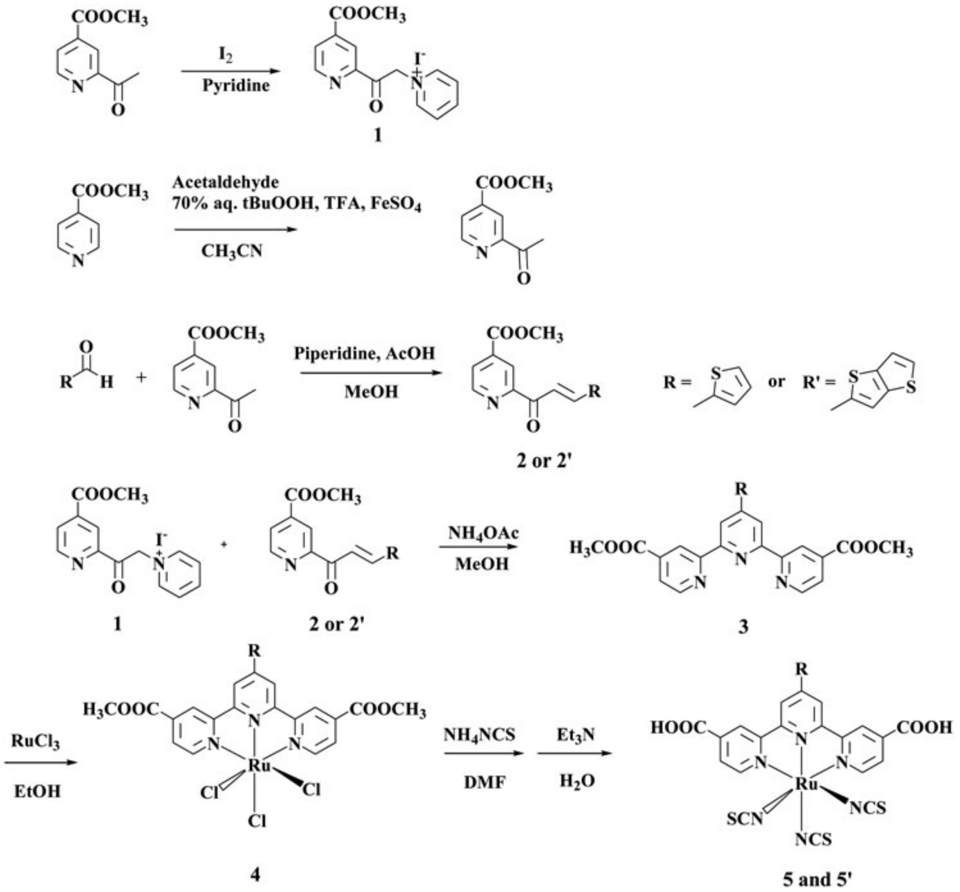
Ruthenium(4,4″-dimethoxycarbonyl-4′-thieno[3,2-b]thiophenyl-2,2′:6′,2″-terpyridine)trichloride **(4)**: Ethyl alcohol (80 mL) and ruthenium trichloride (0.60 g) were reacted under argon. After the mixture stirred for 40 min, a solution of the ligand 4,4″-dimethoxycarbonyl-4′-thieno[3,2-b]thiophenyl-2,2′:6′,2″terpyridine(5), 1.10 g, in 80 mL of dichloromethane, was then added. The reaction mixture was refluxed for 3 h. The solution was concentrated to 10 mL, and the reaction mixture was cooled to room temperature. The precipitated complex was collected on a sintered glass crucible and was washed with ethanol to remove unreacted ruthenium trichloride. The product was air-dried (yield: 75%). ^{1}H NMR (400 MHz, DMSO-d6), δ ppm: 9.16 (2H, s), 8.90 (2H, d, J = 4 Hz), 8.75 (2H, s), 8.00 (1H, s), 7.94 (2H, d, J = 4 Hz), 7.49 (1H, d, J = 8 Hz), 7.33 (1H, d, J = 4 Hz).

Ruthenium (4,4″-Dimethoxycarbonyl-4′-thiophenyl-2,2′:6′2″-terpyridine)trithiocyanate (5): Ru(DMTT)Cl_3 complex (1.47 g, 2.31 mmol) was dissolved in DMF (150 mL) and $[H_4N]NCS$ (5.6 g, 7.39 mmol) was dissolved in H_2O (29mL) and both were stirred for 20 min at room temperature. Two solutions were mixed together in dark under argon atmosphere by refluxing at 130°C. Triethylamine (56 mL) and H_2O (28 mL) were added, and solution was refluxed for a further 24 hr to hydrolyze the ester groups on the terpyridine ligand. The solvent volume was reduced on a rotary evaporator to about 10 mL, and then the solution was added to H_2O (200 mL). The resulting precipitate was filtered and dried. The isolated solid was recrystallized from methanol - diethyl ether. After which it was further purified on a 3 × 100 cm Sephadex LH-20 column, using methanol as eluent. ^{1}H NMR (400 MHz, DMSO-d6), δ ppm: 9.254 (6H, m), 8.353 (1H, s), 8.242 (2H, dd, J = 6 Hz, 13.2 Hz), 7.841 (1H, s), 7.341 (1H, s).

Ruthenium(4,4″-dimethoxy-4′-thieno[3,2-b]thiophenyl-2,2′:6′,2″terpyridine)-trithiocyanate **(5′)**: The compond (**5′**) was synthesized in dark under an argon atmosphere by refluxing at 130°C, a solution of $[NH_4]NCS$ (5.6 g, in 29 mL of H_2O) and Ru(trimethoxycarbonylterpy)Cl_3 complex (1.47 g, in 150 mL of DMF) for 4 h [3]. Then, 56 mL of triethylamine and 28 mL of H_2O were added, and the solution was refluxed for a further 24 h to hydrolyze the ester groups on the terpyridine ligand. The solvent volume was reduced on a rotary evaporator to about 10 mL, and then the solution was added to 70 mL of H_2O. The resulting precipitate was filtered and dried. The isolated solid was recrystallized from methanol-diethyl ether, after which it was further purified on a 100 cm (ϕ = 3 cm) Sephadex LH-20 column, using methanol as eluent to give 7 as a brown powder (yield: 5%). ^{1}H NMR (400 MHz, DMSO-*d*6), δppm: 9.04 (2H, 4 Hz, d), 8.86 (4H, m) 8.76 (1H, s), 8.11 (2H, 2 Hz, d), 7.84 (1H, 4 Hz, s), 7.341(1H, 4 Hz, d).

All Ru-compexes are triply purified using Sephadex LH-20 column to separate isomers and impurity.

The detailed preparation of DSSC has been described earlier [4]. The current–voltage (J–V) curves were measured using a source-measure unit under white-light irradiation from a 1000 W Xe lamp (Thermo Oriel Instruments Co.). The incident light intensity and the active cell area were 100 mW cm^{-2} and 0.25 cm^{2}, respectively. The J–V curves were used to calculate the short-circuit current (J_{sc}), open-circuit voltage (V_{oc}) and fill factor (*FF*) of the DSSC. The incident photon to current efficiency (IPCE) was measured as a function of wavelength from 300 to 900 nm using the IPCE measurement (DEX7, PV Measurements Co.). The absorption spectra were measured using an UV-vis absorption spectrometer (Sinco, Neosys-2000).



Scheme 1. Synthesis route for novel ruthenium dyes.

Results and Discussion

Figure 1 shows the absorption spectra of **5**, **5**′ and N749, which are normalized at 600 nm. The absorption bands around 600 nm of dyes studied here is dominated by metal-to-ligand charge-transfer transitions (^{3}MLCT). The ^{3}MLCT band of **5** and **5**′ at around 600 nm were slightly broader than that of N749. This is attributed to the extent of π-conjugation. At 600 nm, the extinction coefficients ($\varepsilon_{600\text{nm}}$) of **5, 5**′ were 7600 and 7000 M^{-1} cm^{-1}, which are smaller than that (8400 M^{-1} cm^{-1}) of N749. The absorption bands at around 410 nm can be assigned to ^{1}MLCT band. The $\varepsilon_{410\text{nm}}$ of **5**, **5**′ and N749 are 9800, 10400 and 11400 M^{-1} cm^{-1}, respectively. The ε values are reduced ~15% in whole ranges and the absorption maxima for ^{3}MLCT band of **5** and **5**′ at 600 nm observed no shift to longer wavelength.

Figure 2 shows the energy diagram for HOMO (oxidation potential *vs.* NHE) and LUMO of **5** and **5**′. The HOMO levels are determined based on the measurement of cyclic voltammetry. The LUMO energies of dyes are calculated from the oxidation potentials and the $E_{0\text{–}0}$ determined from the intersection of absorption and emission spectra. The HOMO and LUMO levels of **5** and **5**′ are lied lower compare to that of N749. The LUMO levels of **5** and **5**′ are higher than conduction band of TiO_2. Therefore, the electron injection from dyes to TiO_2 can be occurred through the exothermic process.

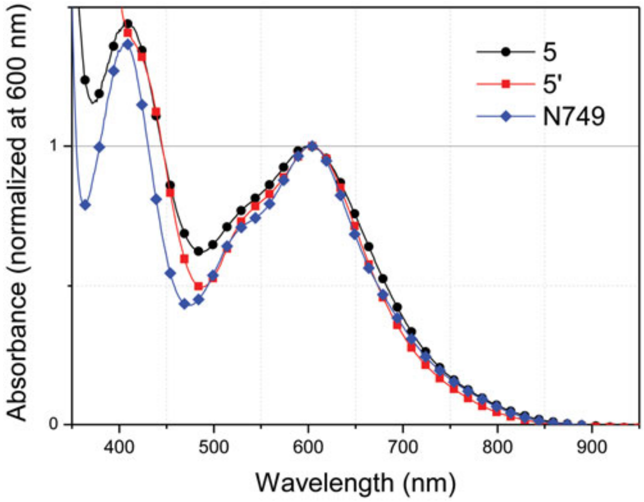


Figure 1. The normalized absorption spectra of **5, 5′** and N749 in ethanol.

Figure 3(a) shows the J–V curves of the **5, 5′** and N749 DSSCs performed under same conditions (TiO_2 thickness, dipping time, concentration of electrolyte, and etc). The reference N749 DSSC showed a high short-circuit current density (J_{sc}) compared with those of **5** and **5′** DSSCs, as listed in Table 1. When compared to that of N749, the power conversion efficiencies (η_{eff}) of **5** and **5′** decreased by about 55 and 65%, respectively. Although the fill factor (FF) value was not much changed the lower efficiency was due to a drop in the J_{sc} and the open-circuit voltage (V_{oc}) values. The small J_{sc} values of **5** and **5′** could be attributed to that the extinction coefficients of **5** and **5′** dyes were about 15%

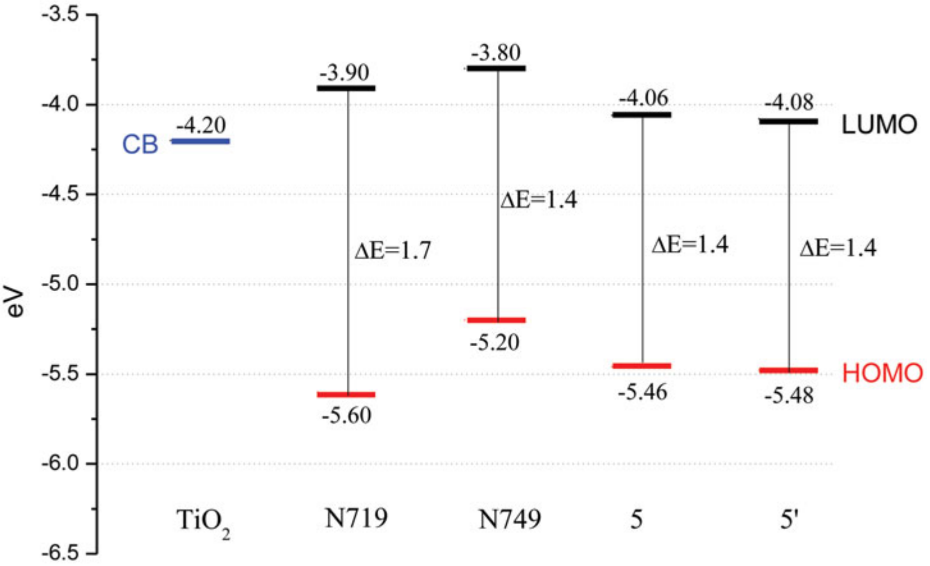


Figure 2. Schematic diagram for HOMO and LUMO energy levels of **5**, **5′**, N719 and N749 dyes.

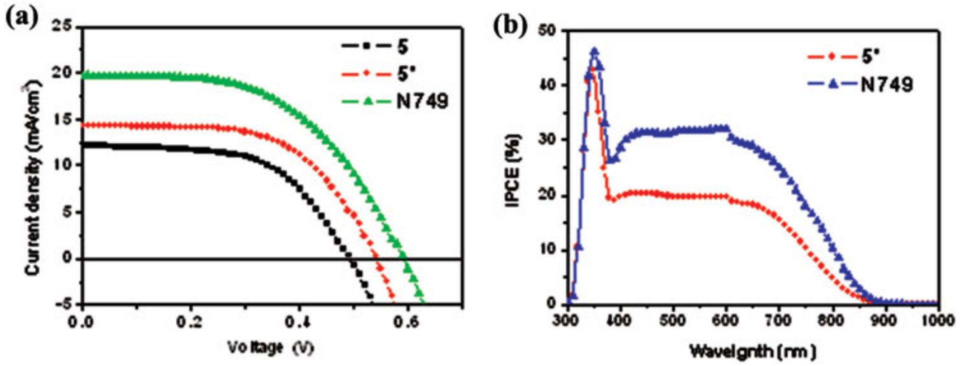


Figure 3. (a) Current-density–voltage (J–V) curves of the DSSC prepared with **5, 5′** and N749 dyes. (b) Incident photon to current conversion efficiency (IPCE) action spectra of DSSC prepared with **5′** and N749 dyes.

smaller than that of N749. The adsorption ability of **5**, and **5′** dyes onto TiO_2 electrode may be low, because of bulky thiophene moieties instead of hydrogen of N749.

As shown in Fig. 4, the electron of HOMO orbital is localized at NCS ligands and metal ion. On the other hand, the electron of LUMO orbital is delocalized terphyridine ligand including thiophene moieties. The electron in L+1 orbital is more populated at carboxyl groups of terphyridine ligand, which is similar with the LUMO orbital of N749. The L+1 orbital is proper for the electron injection into TiO_2, because the electron is mostly populated at the anchoring carboxyl group. The electron of LUMO orbital extended to thiophene moieties. This indicates the π-conjugation is increased, but the electron density is decreases at the anchoring group. We suggest this is also one reason for low efficiency of **5** and **5′** DSSCs.

Generally, the V_{oc} values have close relation to recombination between photoinjected electrons and the oxidized redox species in the electrolyte. In order to explain about lower the V_{oc} of **5** and **5′** DSSCs, we suggest that the high rate of recombination results a decreasing of the V_{oc} values. Further experimentation, therefore, is necessary to prove our expectation about the shorter electron lifetime of **5** and **5′** compared to that of N749.

In conclusion, two thiophene-based N749 dyes have been synthesized to investigate the π-conjugation effect on efficiency of DSSCs. Under same condition, the photovoltaic performance for new dyes was lower than N749 DSSC. In order to optimize the cell performance, we are carrying out further studies such as the increasing concentration of the adsorbed dyes, the control of the size of TiO_2 particle and the increasing of dipping time.

Table 1. Photovoltaic performances of DSSCs

Dyes	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	η_{eff} (%)
5	0.49	12.1	57.4	3.4
5′	0.54	14.2	51.7	4.0
N749	0.59	19.7	53.0	6.2

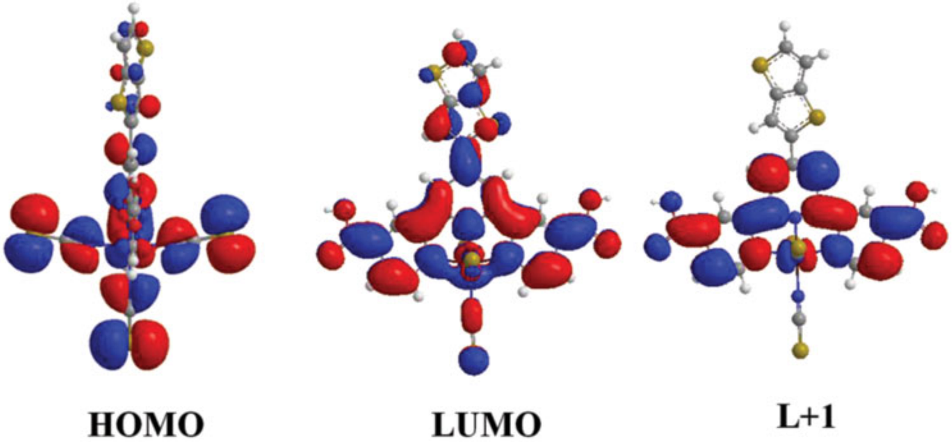


Figure 4. The orbital diagrams of **5′** calculated by density-functional theory (DFT) at the B3LYP/6-31G(d) level, and applied LANL2DZ methods for Ru ion (Gaussian 03 program).

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