

## Synthesis and Characterization of Ferrocene-terminated Ruthenium Phenylacetylide Complexes with Alligator Clips

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**Abstract:** Ferrocene-terminated *trans*-Ru(dppm)<sub>2</sub> (dppm=Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)-containing molecular wires with alligator clips were prepared. They are suitable for self-assembly on gold electrode to investigate the influence of metal incorporation on the electron transportation property of the molecular wires.

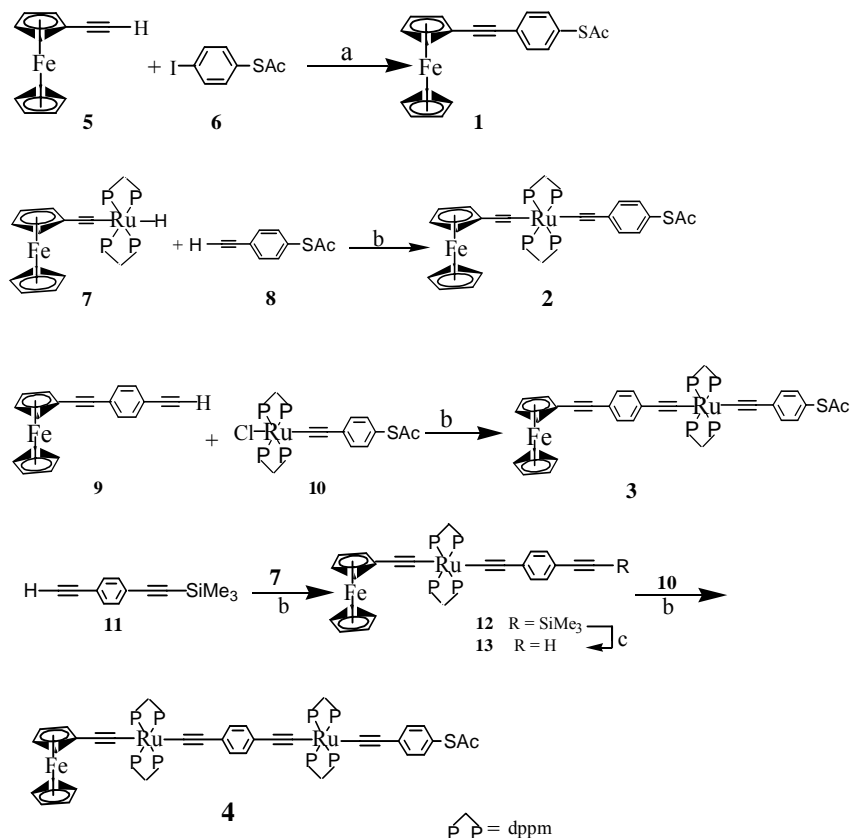
**Keywords:** Molecular wires, ferrocene, ruthenium phenylacetylide complexes.

Molecular wires, a kind of linear conjugated oligomers capable of conducting electrons or photons, play a crucial role in developing molecular electronics<sup>1</sup>. Organometallic complexes possess unique physical, chemical and optical properties, which are inaccessible for pure organic systems. Appropriate selection of the metal species linkage may achieve more electron delocalization along the  $\pi$ -conjugated organic system<sup>2</sup>. Although a number of papers on the synthesis of metal-containing  $\pi$ -conjugated oligomers and polymers have been published<sup>3</sup>, there are very few reports on conductivities of these materials. One reason lies in that most of these oligomers contain no alligator clips essential for self-assembly on metal electrodes. Here we report the synthesis of a series of ferrocene-terminated ruthenium phenylacetylide complexes with alligator clips (*e.g.* thioacetyl groups), which can be self-assembled onto gold electrode.

### Results and Discussion

As shown in **Scheme 1**, **2** was prepared directly from **7** and **8** in 45% yield with a modified method developed by Dixneuf and Long<sup>4-7</sup>. **3** was obtained from **9** and **10** in 40% yield, where **10** was prepared from **8** and *cis*-Ru(dppm)<sub>2</sub>Cl<sub>2</sub> in 45% yield by a modified Dixneuf's method. **4** was synthesized in two steps. First, **12** was prepared from **7** and **11** with the same procedure as that of **2**, and **13** was obtained in 90% yield by treatment of **12** with tetrabutylammonium fluoride (TBAF) to remove trimethylsilyl group<sup>5,8</sup>. Second, **13** was allowed to react with **10** for 48 h to afford target molecular wire **4** in 30% yield. **1** was prepared according to Sita's method<sup>9</sup>.

Scheme 1

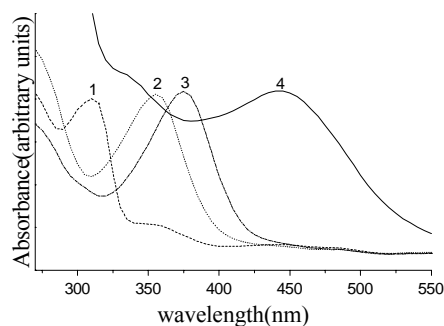


Reagents and conditions: (a) Pd(PPh<sub>3</sub>)<sub>2</sub> (5mol%), CuI (5mol%), *i*-Pr<sub>2</sub>NEt, THF, 50°C, 24 h, N<sub>2</sub> (b) (i) NaPF<sub>6</sub>, *i*-Pr<sub>2</sub>NEt, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 24 h, N<sub>2</sub> (ii) DBU, r.t., 2 h, N<sub>2</sub> (c) TBAF, CH<sub>2</sub>Cl<sub>2</sub>, r.t., 2 h.

The UV-vis spectra of complexes **1-4** are shown in **Figure 1**. Great changes in the UV-vis absorption bands of the complexes are observed. Complex **1** has maximum absorption band centered at 310 nm, insertion of C≡C-Ru(dppm)<sub>2</sub> unit (*e.g.* complex **2**) produces a red shift of 45 nm. Moreover, insertion of two C≡C-Ru(dppm)<sub>2</sub> units in complex **1** (*e.g.* complex **4**) causes a red shift of 125 nm. As a reference, insertion of C≡C-Ph unit in complex **2** can produce complex **3** and cause only 20 nm of red shift in the UV-vis absorption, which is consistent with Wolf's report<sup>2b</sup>.

These complexes may possess two advantages as molecular wires. One is that the *trans*-Ru(dppm)<sub>2</sub> has distorted-octahedral geometry<sup>2b,4,5</sup> where its extended phenyl groups cover the conjugated core, providing an efficient insulating protection among the complexes. The other is that the dppm group could enhance the solubility of the complex by reducing interchain interaction energy among the complex molecules.

Figure 1 UV-vis absorption spectra of **1-4** in CH<sub>2</sub>Cl<sub>2</sub>



## Experimental

### Preparation of **2**

Under N<sub>2</sub> protection, solution of *i*-Pr<sub>2</sub>NEt (0.035 mL, 0.2 mmol) and **8** (0.0176 g, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added to another solution of **7** (0.1134 g, 0.1 mmol) and NaPF<sub>6</sub> (0.0168 g, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was allowed to stir for 24 h at room temperature in the absence of light. After addition of 0.015 mL (0.1 mmol) of DBU, the mixture was stirred for another 2 h. The mixture was filtered and purified by FC (Al<sub>2</sub>O<sub>3</sub>) to provide **2** (56.3 mg, 45%) as yellow solid. Data for **2**: IR (KBr, cm<sup>-1</sup>): 2065 (C≡C), 1706 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): 2.36(s, 3H), 3.53(t, 2H, *J*=1.6Hz), 3.70(s, 5H), 3.80(t, 2H, *J*=1.6Hz), 4.84(m, 4H), 7.58-6.58(m, 44H). ES-MS [M]<sup>+</sup>(*m/z*), 1254.0, calcd., 1254.1. UV-vis (λ<sub>max</sub>, CHCl<sub>3</sub>): 355 nm. Anal.: Calcd. for C<sub>72</sub>H<sub>60</sub>P<sub>4</sub>OSFeRu: C 68.95, H 4.82; found: C 68.63, H 4.96.

### Preparation of **3**

**9** (0.031 g, 0.1 mmol) and **10** (0.1081 g, 0.1 mmol) were treated in the same procedure as above to obtain 54.2 mg (40% yield) of **3** as a yellow solid. Data for **3**: IR (KBr, cm<sup>-1</sup>): 2061 (C≡C), 1702 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): 2.37(s, 3H), 4.22(t, 2H, *J*=1.6Hz), 4.24 (s, 5H), 4.47(t, 2H, *J*=1.6Hz), 4.83 (m, 4H), 7.49-6.18(m, 48H). ES-MS [M]<sup>+</sup>(*m/z*), 1354.4, calcd., 1354.1. UV-vis (λ<sub>max</sub>, CHCl<sub>3</sub>): 375 nm. Anal.: Calcd. for C<sub>80</sub>H<sub>64</sub>P<sub>4</sub>OSFeRu: C 70.95, H 4.76; found: C 70.67, H 4.60.

### Preparation of **4**

The procedure was very similar to the preparation of **2**, except that it needs a longer reaction time (48 h) before adding DBU. The yield of the target complex **4** is 30%. Data for **4**: IR (KBr, cm<sup>-1</sup>): 2063 (C≡C), 1704 (C=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): 2.28(s, 3H), 3.74(m, 9H), 4.85(m, 8H), 7.57-6.98(m, 88H). ES-MS (*m/z*), 2250.8 [M+2H]<sup>+</sup>, calcd., 2248. UV-vis (λ<sub>max</sub>, CHCl<sub>3</sub>): 435 nm. Anal.: Calcd. for C<sub>132</sub>H<sub>108</sub>P<sub>8</sub>OSFeRu<sub>2</sub>: C 70.52, H 4.84;

found: C 70.84, H 5.03.

Data for **10**: IR (KBr,  $\text{cm}^{-1}$ ): 2070( $\text{C}\equiv\text{C}$ ), 1701( $\text{C}=\text{O}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz): 2.36(s, 3H), 4.90(m, 4H), 7.48-6.04(m, 4H). ES-MS  $[\text{M}]^+(m/z)$ , 1078.9, calcd., 1080.0.

Data for **12**: IR (KBr,  $\text{cm}^{-1}$ ): 2060( $\text{C}\equiv\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz): 0.229(s, 9H), 3.54(t, 2H,  $J=1.6\text{Hz}$ ), 3.71(s, 5H), 3.81(t, 2H,  $J=1.6\text{Hz}$ ), 4.84(m, 4H), 7.58-6.06(m, 4H). ES-MS  $[\text{M}]^+(m/z)$ , 1275.8, calcd., 1276.1.

Data for **13**: IR (KBr,  $\text{cm}^{-1}$ ): 3280( $\equiv\text{C}-\text{H}$ ), 2062( $\text{C}\equiv\text{C}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400MHz): 3.04(s, 1H), 3.54(t, 2H,  $J=1.6\text{Hz}$ ), 3.70(s, 5H), 3.81(t, 2H,  $J=1.6\text{Hz}$ ), 4.85(m, 4H), 7.58-6.10(m, 4H). ES-MS  $[\text{M}]^+(m/z)$ , 1203.7, calcd., 1204.0.

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