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# Post-Coordination of Multinuclear Transitional Metal Clusters to Azulene-Based Polymers: A Novel Strategy for Tuning Properties in $\pi$-Conjugated Polymers

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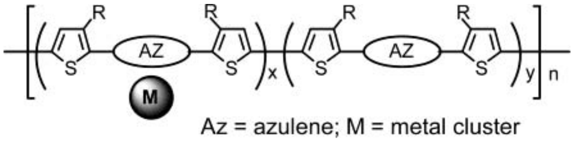
## ABSTRACT



**Direct treatment of azulene–thiophene copolymers with $Ru_3(CO)_{12}$ led to unique examples of coordination of a multinuclear transition metal cluster to conjugated polymers. The polymer–metal cluster formation could be confirmed by $^1H$ NMR spectroscopic studies, and the coordination mode could be deduced from the crystallographic structure of model compounds. The composition of ruthenium carbonyl cluster could be used as a governing factor to tune the electronic, optical, and morphological properties of the organometallic polymers.**

Conjugated polymers such as polyacetylenes, polythiophenes, and polyanilines, as well as oligomers and derivatives of these materials, have been extensively studied.[1] Incorporation of transition-metal complexes into conjugated polymer backbones could result in more interesting and promising advanced materials. The transition metals may impart desired magnetic, electronic, and optical properties, as well as unique catalytic and sensory characteristics.[2] Conventional designs of $\pi$-conjugated organometallic polymers include arrangement of the metal core: tethered to the polymer backbone by a linker, coordinated directly to the conjugated backbone, or located directly in the conjugated backbone. Among these organometallic polymers, ones containing nitrogen atoms or diimine groups have been used extensively as ligands for transition metals.[3] There were, however, few successes in coordinating multinuclear transitional metal clusters into the $\pi$-conjugated polymer backbones as the face-capping ligand.[4] Such a coordination would be desirable because multinuclear transition-metal clusters have many promising properties such as catalytic capacity,[5] the ability to form bulklike metallic properties along the polymer backbone, and the addition of sensitivity to anions and small molecules (e.g., CO, $O_2$, and NO).[2c]

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Herein, we present our initial study of the synthesis and characterization of soluble organometallic azulene-based conjugated polymers with multinuclear ruthenium clusters. The composition of ruthenium carbonyl cluster was found to govern the electronic and optical properties of the resulting organometallic polymers.

1,3-Bis(3-methylthienyl)azulene was prepared by a Ni-catalyzed cross-coupling reaction between 2-bromo-3-methylthiophene and 1,3-dibromo-azulene.[6] Heating a solution of [$Ru_3(CO)_{12}$] and **1** in xylenes for 2 h gave three complexes **1a**−**c** that could be separated by chromatography. Prolonged reaction time resulted in slow decomposition of the reactant. Compounds **1a**−**c** were confirmed to be di-, tri-, and tetraruthenium complexes, respectively, by spectral and elemental analysis. These correspond to three types of coordination mode between the azulene-cored conjugated molecules and ruthenium carbonyl clusters. The major product, **1c**, was isolated as an intensely red crystal, and its single-crystal structure is illustrated in Figure 1.

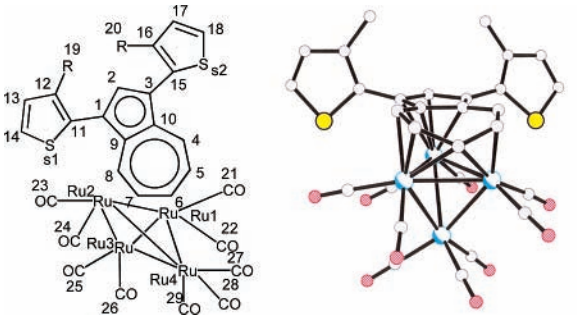

**Figure 1.** An ORTEP diagram of complex **1c**.

The $^1H$ NMR spectrum of the diruthenium complex **1a** suggests an asymmetric conformation. This was evident from the resolution of signals for H13 and H17, and H14 and H18, respectively (Table 1), and their significantly different coupling constants compared to those in **1b** and **1c**. Both complexes **1b** and **1c** showed symmetric $^1H$ NMR spectra with similar chemical shifts and coupling constants for H13, H14, H17, and H18. On the other hand, the protons of **1b** and **1c**, in positions proximal to the cluster-bound carbon framework, show significant differences in chemical shift (Table 1). This was presumably symptomatic of the two different cluster nuclearities involved. FT-IR spectra of the ruthenium cluster complexes **1a**−**c** showed strong, characteristic absorption peaks that corresponded to the CO stretching mode and appeared within the range of 2060−1770 $cm^{-1}$, depending on the position of the terminal carbonyl groups. Complexes **1a** and **1c** displayed only the presence of terminal carbonyls in the solid state, whereas **1b** exhibited absorption in both the terminal and bridging carbonyl regions.

**Table 1.** $^1H$ NMR Data for Compound **1** and Its Ruthenium Complexes

| | chemical shift ($\delta$) | | | |
|---|---|---|---|---|
| proton[a] | **1** | **1a** | **1b** | **1c** |
| H(2) | 7.98 (s) | 6.02 (s) | 6.58 (s) | 6.25 (s) |
| H(4) | 8.38 (d) | 4.79 (d) | 5.04 (d) | 4.31(d) |
| H(8) | 8.38 (d) | 5.23 (d) | 5.04 (d) | 4.31 (d) |
| H(5) | 7.20 (t) | 5.44 (t) | 3.98 (t) | 5.14 (t) |
| H(7) | 7.20 (t) | 5.28 (t) | 3.98 (t) | 5.14 (t) |
| H(6) | 7.63 (t) | 3.70 (t) | 2.28 (t) | 2.08 (t) |
| H(13) | 7.06 (d) | 6.98 (d) | 6.86 (d) | 6.83 (d) |
| H(14) | 7.34 (d) | 7.27 (d) | 7.12 (d) | 7.12 (d) |
| H(17) | 7.06 (d) | 6.87 (d) | 6.86 (d) | 6.83 (d) |
| H(18) | 7.34 (d) | 7.08 (d) | 7.12 (d) | 7.12 (d) |

[a] Refer to numbering system given in Figure 1.

Complex **1c** was crystallized as triclinic system with a *P*-1 space group. Figure 1 shows that the four ruthenium atoms define a distorted tetrahedron in the tetranuclear complex and three of the four ruthenium atoms associated with the azulene ligand are each bonded to two terminal carbonyl ligands, whereas the fourth is linked to three terminal carbonyl groups. In complex **1c**, azulene is arched across the face of the ruthenium cluster. Carbons in the five-membered ring of azulene are bound to one ruthenium atom in the conventional $\pi$-cyclopentadienyl-metal coordination mode. The remaining five carbons in the seven-membered ring are bound to the other two ruthenium atoms in a $\mu_2$-pentadienyl coordination mode, with the central carbon bonded to two ruthenium atoms.

The absorption spectrum of compound **1** features two strong bands with $\lambda_{max} = 297$ and 242 nm that are assigned to the $\pi-\pi^*$ transition of the thiophene and azulene units in the compound, respectively. The coordination of ruthenium carbonyl clusters and azulene introduced a dramatic blue shift of the $\pi-\pi^*$ transition absorption of azulene in the ruthenium complexes. The $\pi-\pi^*$ transition absorption in the **1**-ruthenium cluster (**1a**−**c**) shifted about 50 nm to a shorter wavelength, compared with that of compound **1**. The large blue shift is likely derived from rehybridization of the metal-bonded carbons of azulene, from $sp^2$ to $sp^3$, thus decreasing the extent of delocalization of the $\pi$ electrons.

Copolymers of poly(bithienyl-azulenyl) with different side chains ($C_{10}H_{21}$ or $OC_{12}H_{25}$), namely **2** and **3**, respectively, were prepared by oxidative polymerization in the presence of $FeCl_3$ according to our previously published procedure (Scheme 1).[6] They were obtained with a good yield (ca. 40−60%) and high molecular weights. GPC analysis of **2** and **3**, using polystyene as standards, showed number-average molecular weights ($M_n$) of 25 600 and 31 500, respectively. These polymers were found to be thermally more stable than the monomer, and their corresponding organometallic complexes were prepared by simply refluxing the conjugated polymers and $Ru_3(CO)_{12}$ in xylenes under an argon atmosphere for 6 h. Four polymeric complexes with different ruthenium contents were prepared in this work: **4a** and **5a** were prepared by reacting **2** and **3**, respectively, with $Ru_3$-

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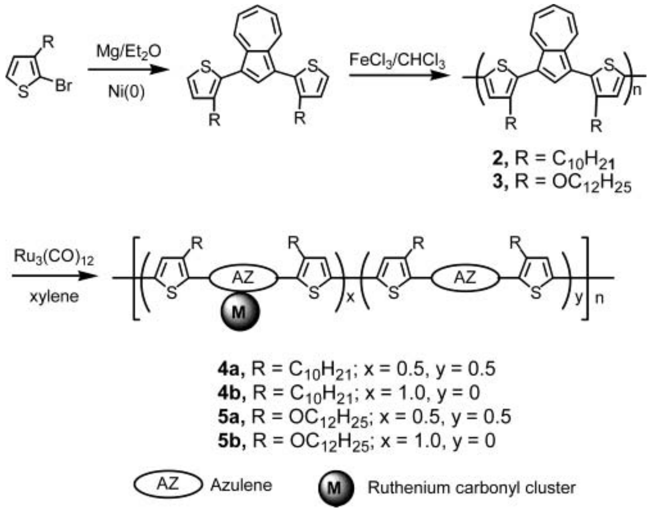
**Scheme 1.** Synthesis of the Four Polymer-Ruthenium Carbonyl Clusters **4a**,**b** and **5a**,**b**



$(CO)_3$ in a 1.0:0.5 ratio; **4b** and **5b** were obtained using a ratio of 1.0:1.1 of the two reactants in each attempt. After each reaction, the dark green solution was cooled to room temperature and then added to hot methanol to precipitate the polymer complex. The polymer complex was then washed with hot methanol several times and dried under reduced pressure for 8 h. All four polymer complexes are soluble in most organic solvents such as chloroform, THF, toluene, and xylenes. In this communication, polymer **3** and its complexes **5a** and **5b** will be used to illustrate the tuning of their properties going from the free polymer to its polymer complexes.

The polymer-ruthenium carbonyl cluster formation was confirmed by $^1$H NMR spectrum (Figure 2). Generally, in the metal-free conjugated polymer, the protons on the azulene ring appear within the normal aromatic region (7.1−8.6 ppm). These protons will be, however, significantly shifted upfield to 2.2−6.0 ppm, as observed in the model complexes **1a**−**c**, after coordination with ruthenium carbonyl clusters. A comparison of the proton chemical shifts of **4** and **5** with those of model compounds **1a**−**c** suggests that di-, tri-, and tetramultinuclear coordination clusters could also be formed in the obtained polymer complexes. Interestingly, the ruthenium cluster content in these complexes could be controlled, as demonstrated by the $^1$H NMR spectral data. For exmple, the $^1$H NMR spectrum of **5a**, obtained by refluxing 1.0 equiv of conjugated polymer **3** with 0.5 equiv of $Ru_3(CO)_{12}$, showed an approximately 1:1 ratio (Figure 2) for the two groups of signals at 8.6, 8.4, and 7.6 ppm (protons on metal-free seven-membered ring of azulene) and those at 6.5, 5.2, and 4.8 ppm (metal-complexed seven-membered ring of azulene), respectively. Going from **3** to **5b** resulted in disappearance of the signals within the region of 8.7−7.2 ppm, indicating that essentially all azulene rings in the polymer backbone of **5a** were coordinated to a ruthenium carbonyl cluster.

The UV−vis absorption spectra (Figure 3) exhibit a blue shift going from the metal free polymer **3** to its metal complexes **5a** and **5b**. The shift in $\lambda_{max}$ depends on the content of ruthenium carbonyl clusters attached to the conjugated polymer backbone. The spectrum of metal-free polymer **3** is dominated by a $\lambda_{max}$ at 458 nm arising from the $\pi-\pi^*$ transition of the conjugated polymer backbone. When coordinated with ruthenium carbonyl clusters, **5a** was blue-shifted about 15 nm and **5b** about 30 nm. This progressive blue shift is clearly associated with an increasing degree of disruption of the diatropicity of the azulene ring resulted from coordination with ruthenium carbonyl clusters, thus increasing the HOMO−LUMO gap of the conjugated polymer backbone.

The effect of ruthenium content on the electrochemical properties of the complexes was examined from their cyclic voltammograms (CV). Comparisons of the redox potentials

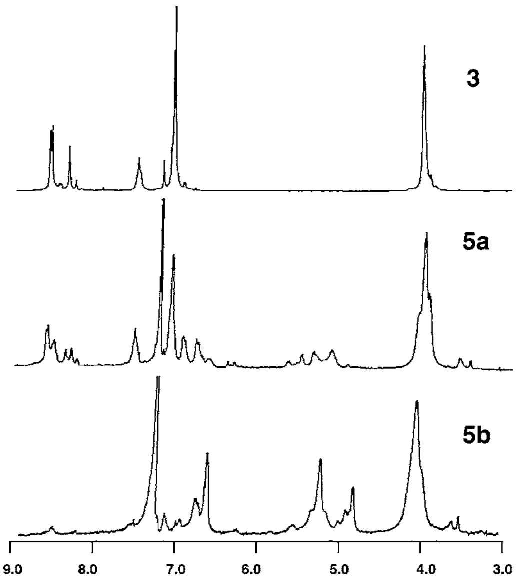


**Figure 2.** A comparison of the $^1$H NMR spectra of polymer **3** and its ruthenium complexes **5a** and **5b**.

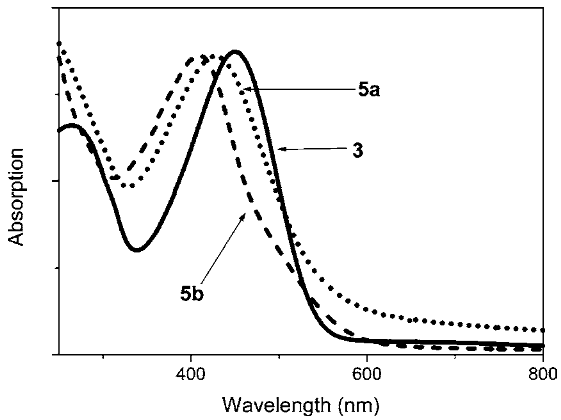


**Figure 3.** UV−vis spectral changes going from polymer **3** to its ruthenium complexes **5a** and **5b**.

of the metal-free polymers **2** and **3** with those of their complexes revealed that the oxidation onsets and oxidation potentials, corresponding to the conjugated polymer backbone, shifted cathodically (i.e., to more negative potentials) after coordination with ruthenium carbonyl clusters. They shifted more negatively for the complexes with higher ruthenium carbonyl cluster content, indicating that the tunable electrical properties of the complexes are affected by the interaction between the ruthenium carbonyl clusters and the $\pi$-conjugated backbone.

The sensitivity of the complexes to small molecules is illustrated by electrochemical quartz crystal microbalance (QCM) measurements of the polymer films during exposure to iodine vapor. Figure 4 displays the frequency variations of metal-complexed or metal-free polymer films upon iodine vapor absorption. As seen in the figure, the metal-free polymer film **3** had a 3 470 Hz change within the first 10 min, whereas **5a** and **5b** showed changes of 2.5 and 4.0 times larger, respectively, within the same period. These changes might have been due to a higher surface area and sensitivity of the multinuclear transitional metal centers.

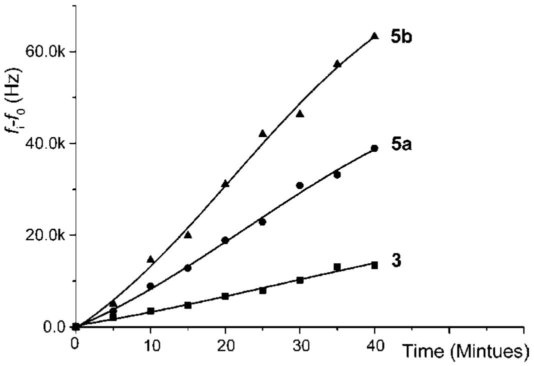


**Figure 4.** QCM measurement of mass increase caused by iodine absorption by polymers film of **3**, **5a**, and **5b**.

The morphology of the polymers and their metal complexes was determined by scanning electron microscopy (SEM). As shown in Figure 5a, **3** has a relatively smooth surface, but the surface structure and morphology of its metal complexes change significantly after their coordination with ruthenium carbonyl clusters. Cauliflower structures growing on this smooth surface were observed for freshly prepared **5a**, whereas freshly prepared **5b** displayed a spongelike structure (Figure 5b). It is also interesting to note that the morphology of the complexes changes further after prolonged annealing at room temperature, where small particles were found to anneal into globular spheres with diameters between 100 nm to 1 $\mu$m. Generally, it was found that the higher the ruthenium carbonyl cluster content, the smaller the average sphere diameter. The enhanced surface-to-volume ratio of these metal-complexed materials is predicted to yield enhanced sensitivity and catalytic ability, compared with the metal-free polymers.

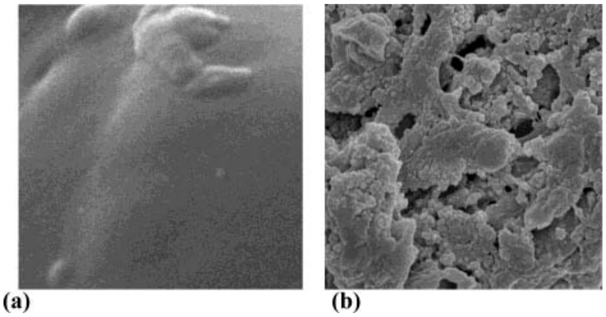


**Figure 5.** SEM micrographs of (a) **3** and (b) freshly prepared **5b**.

In conclusion, to the best of our knowledge **4** and **5** are the first examples of coordinating a multinuclear transitional-metal cluster to a $\pi$-conjugated polymer backbone. The coordination mode was assumed to be similar to that in model compounds. As predicted, the metal-complexed polymers displayed tunable optical and electrical properties with a dependence on the metal cluster content. Importantly, the metal-complexed polymers were highly sensitive to doping with iodine vapor. It was also shown that the annealing processes of these complexes led to formation of spheres with diameters between 100 nm and 1 $\mu$m. The post-coordination process described in our work offers a straightforward but versatile route to prepare organometallic polymers with controllable multiple compositions and thus tunable optical and electronic properties. Further work on the sensitivity and catalytic properties of this class of complexes is ongoing.

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**Supporting Information Available:** Crystallographic data of **1c** in CIF format and experimental and spectroscopic/elemental data of **1a**−**c**, **4a,b**, and **5a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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