

Experimental

General procedure for preparation of model compounds 1a-c. A mixture of 1,3-bis[2-(3-methylthienyl)]azulene (1.0 mmol) and $[\text{Ru}_3(\text{CO})_{12}]$ (1.0 mmol) was dissolved in freshly distilled xylenes (20 ml) and the mixture was heated at reflux for 2 under argon. The mixture was cooled to room temperature, concentrated, and the residue chromatographed on silica gel. Elution with hexane afforded the unreacted monomer **1** and $[\text{Ru}_3(\text{CO})_{12}]$. Elution with a mixture of hexane and CH_2Cl_2 with a gradual increase in the percentage of CH_2Cl_2 led to the isolation of the three complexes **1a-c**.

Complex 1a: Yield: 8%, yellow oil. TLC: $R_f = 0.67$ (Hexane: $\text{CH}_2\text{Cl}_2 = 1:1$). ^1H -NMR (CDCl_3) δ 7.21 (d, $J = 5.2$ Hz, 1H), 7.02 (d, $J = 5.2$ Hz, 1H), 6.91 (d, $J = 5.2$ Hz, 1H), 6.81 (d, $J = 5.2$ Hz, 1H), 5.95 (s, 1H), 5.36 (q, 1H), 5.25 (d, 1H), 5.18 (q, 1H), 4.73 (d, 1H), 3.62 (t, 1H), 2.34 (s, 3H), 2.33 (s, 3H). ^{13}C -NMR (CDCl_3) δ 198.4, 138.2, 137.8, 131.0, 130.6, 128.7, 127.4, 127.1, 125.6, 125.1, 115.9, 100.4, 92.0, 89.4, 87.9, 85.1, 77.5, 58.2, 50.1, 14.2, 15.0. IR (KBr, cm^{-1}) 3062, 2920, 2060, 2005, 1913, 1448, 716, 550. Anal. Calcd for $\text{C}_{25}\text{H}_{16}\text{O}_5\text{Ru}_2\text{S}_2$: C, 45.31; H, 2.43; S, 9.68%. Found: C, 45.28; H, 2.42; S, 10.01%.

Compound 1b: Yield: 15%, red crystal. TLC: $R_f = 0.12$ (Hexane: $\text{CH}_2\text{Cl}_2 = 1:1$). ^1H -NMR (CDCl_3) δ 7.12 (d, $J = 5.2$ Hz, 2H), 6.83 (d, $J = 4.8$ Hz, 2H), 6.25 (s, 1H), 5.15 (q, $J = 6.2$ Hz, 2H), 4.31 (d, $J = 6.2$ Hz, 2H), 2.40 (s, 6H), 2.17 (t, $J = 6.4$ Hz, 1H). ^{13}C -NMR (CDCl_3) δ 195.9, 130.4, 126.4, 122.9, 99.5, 84.8, 65.9, 65.6, 60.1, 32.2, 15.6. IR (KBr, cm^{-1}) 3060, 2922, 2040, 1998, 1949, 1764, 722, 511. Anal. Calcd for $\text{C}_{27}\text{H}_{16}\text{O}_7\text{Ru}_3\text{S}_2$: C, 39.56; H, 1.97; S, 7.82%. Found: C, 39.56, H, 1.94; S, 7.02%.

Compound 1c: Yield: 36%, red crystal. TLC: $R_f = 0.39$ (Hexane: $\text{CH}_2\text{Cl}_2 = 1:1$). ^1H -NMR (CDCl_3) δ 7.12 (d, $J = 5.2$ Hz, 2H), 6.86 (d, $J = 5.2$ Hz, 2H), 6.58 (s, 1H), 5.04 (d, $J = 6.6$ Hz, 2H), 3.98 (t, $J = 6.8$ Hz, 2H), 2.44 (s, 6H), 2.20 (t, $J = 1.7, 8.5$ Hz, 1H). ^{13}C -NMR (CDCl_3) δ 204.8, 138.5, 130.4, 126.7, 124.1, 98.8, 86.8, 74.5, 68.3, 64.0, 31.9, 14.9. IR (KBr, cm^{-1}) 3071, 2925, 2044, 1997, 1463, 723, 531. Anal. Calcd for $\text{C}_{29}\text{H}_{16}\text{O}_9\text{Ru}_4\text{S}_2$: C, 35.66; H, 1.65; S, 6.57%. Found: C, 35.65, H, 1.73; S, 7.57%.

General procedure for the synthesis of metal-complexed polymers 4 and 5. The polymer **2** or **3** (200 mg) was dissolved in xylenes (15 ml) under argon and $\text{Ru}_3(\text{CO})_{12}$ (200 or 400 mg) was heated. The mixture was heated at solvent refluxing temperature for 6 h. The solution was cooled to room temperature and poured into hot methanol. The powder was filtered and heated in refluxing methanol for 30 min and filtered. The process was repeated 3 times and the product was dried under reduced pressure for 8 h.

Complex 4a: Yield: 92%, dark brown powder. ^1H -NMR (CDCl_3): several broad signals were centred at δ 8.50 (1H), 7.86 (0.5H), 7.62 (0.5H), 7.02 (2H), 6.02 (1H), 5.35 (0.5H), 5.14 (1H), 4.25 (0.5H), 3.61 (1H), 2.56 (s, 4H), 2.17 (s, 4H), 1.55 (s, 12H), 1.23 (s, 16H), 0.85 (s, 6H). FT-IR (KBr, cm^{-1}): 2912, 2841, 2048, 1990, 1924, 1770, 1597, 1519, 1440, 1344, 1089, 806, 522.

Complex 4b: Yield: 96%, brown powder. ^1H NMR (CDCl_3): several broad signals were centred at δ 8.45 (0.5H), 7.12-6.66 (m, 2H), 6.03 (0.5H), 6.00-5.50 (m, 0.5H), 5.10 (2H), 4.25 (1H), 3.50 (s, 1H), 2.52 (4H), 2.20 (1H), 1.58 (s, 16H), 1.26 (s, 16H), 0.88 (s, 6H). FT-IR (KBr, cm^{-1}): 2910, 2841, 2048, 1984, 1921, 1770, 1535, 1441, 1332, 1074, 806, 524.

Complex 5a: Yield: 92%, brown powder ^1H NMR (CDCl_3): several broad signals were centred at δ 8.60 (m, 1H), 8.38 (m, 0.5H), 7.60 (s, 1H), 7.12 (2H), 7.00 (m, 0.5H), 6.80 (m, 0.5H), 5.50-5.00 (m, 2H), 4.06 (m, 4H), 2.60 (br, 0.5H), 1.60 (m, 4H), 1.56 (s, 16H), 1.25 (4H), 1.22 (s, 16H), 0.85 (s, 6H) FT-IR (KBr, cm^{-1}): 2918, 2846, 2048, 2032, 1988, 1926, 1766, 1537, 1462, 1330, 1068, 794, 732, 538.

Complex 5b: Yield: 98%, dark brown powder. ^1H NMR (CDCl_3): several broad signals were centred at δ 7.10-7.00 (m, 1H), 6.70 (2H), 6.62 (2H), 5.22 (m, 2H), 4.72 (m, 1H), 4.04 (4H), 1.84 (m, 4H), 1.56 (s, 16H), 1.23 (s, 20H), 0.87 (s, 6H). FT-IR (KBr, cm^{-1}): 2912, 2841, 2048, 1988, 1919, 1762, 1525, 1454, 1336, 1058, 798, 526.

Crystal of **1c** was grown from a mixture of CH_2Cl_2 and hexane and mounted on glass fibers. X-ray data was collected with a Rigaku AFC 7R diffractometer, equipped with a graphite monochromator. Calculations were carried out using the Unics-III program system. Neutral atomic scattering factors and anomalous dispersion effects were taken from "International Tables for X-Ray Crystallography." All data were corrected for absorption based on empirical azimuthal scans. The positions of the heavy atoms were determined from the patterson map and expanded using Fourier techniques.

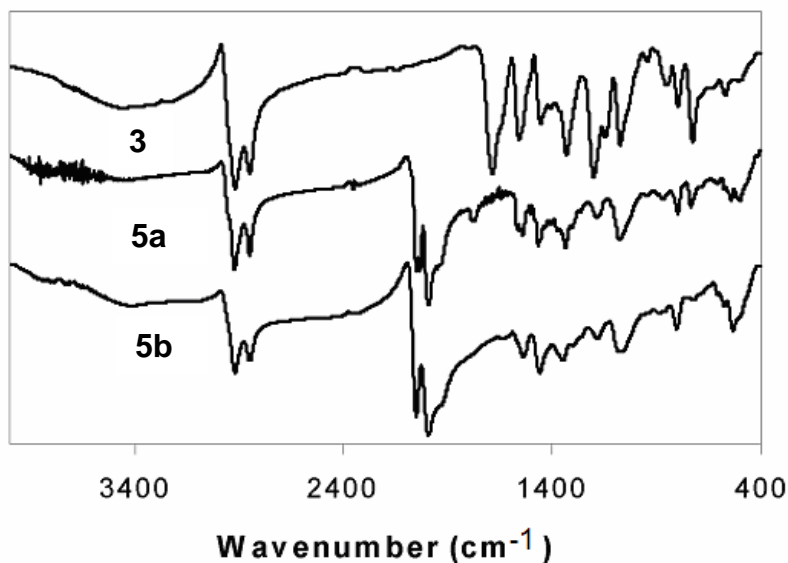


Figure 6. FTIR spectrum of polymer **3**, polymer complexes **5a** and **5b**.

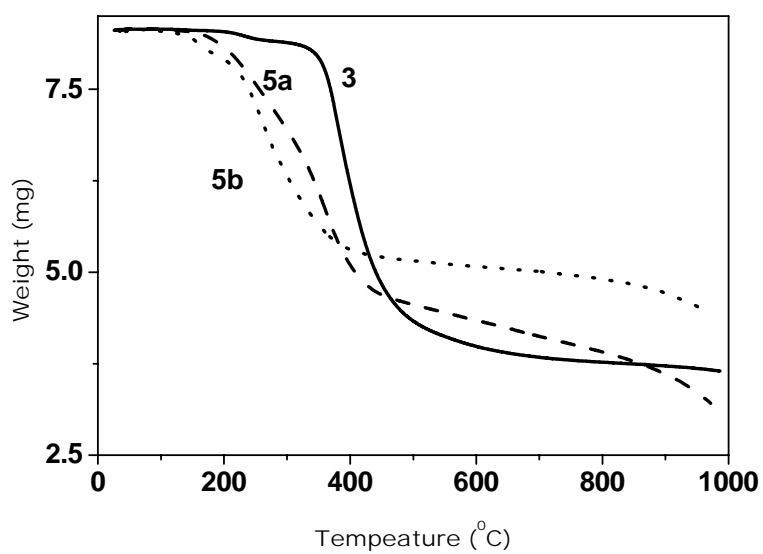


Figure 7. Thermal analysis of polymer **3**, polymer complexes **5a** and **5b**.

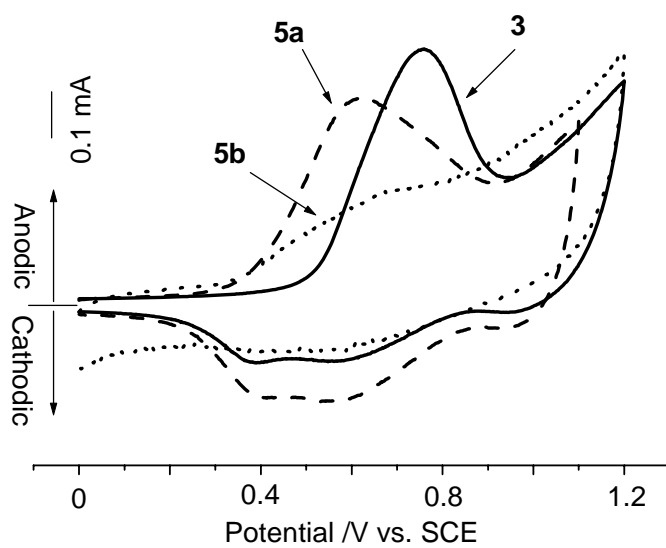


Figure 8. Cyclic voltammogram of polymer **3**, polymer complexes **5a** and **5b**.