Novel σ-π Alternating Polymers Having 2,2'-Bipyridyl in the Polymer Backbone and Their Ruthenium Complexes

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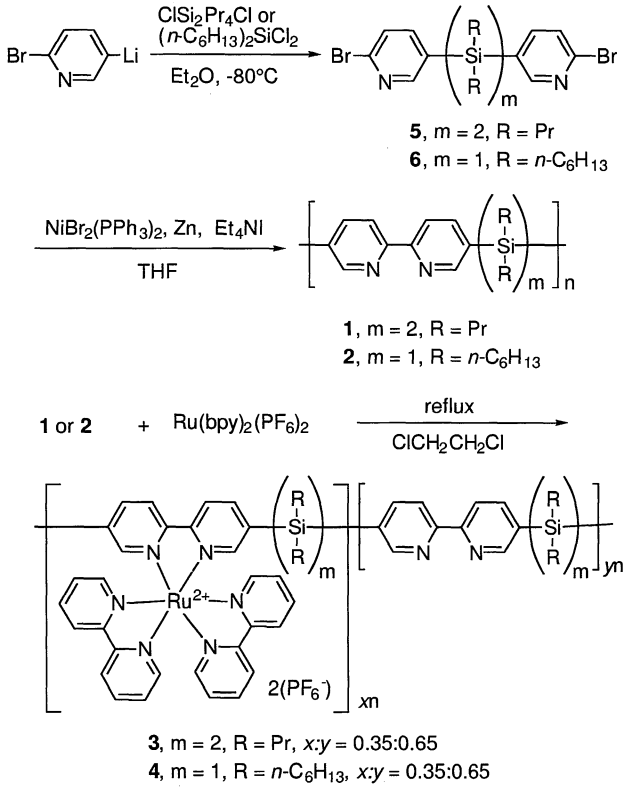
Novel σ-π alternating copolymers, poly(disilanylene-2,2'-bipyridine-5,5'-diyl) and poly(silylene-2,2'-bipyridine-5,5'-diyl) and their ruthenium complexes, were synthesized. The ruthenium complexes showed photoconductivity caused by metal-to-ligand charge-transfer excitation.

There has been considerable interest in the chemistry of polymers having a regular alternating arrangement of a silicon σ unit and a π-system in the backbone.[1-5] 2,2'-Bipyridyl may serve as an interesting π system in the σ–π alternating copolymers because the electron affinity may be tunable by regulating coordination to a Lewis acid or a transition metal. In addition, tris(bipyridine)ruthenium complexes are known to exhibit interesting electron-transfer properties through metal-to-ligand charge transfer (MLCT) process.[6] Although many soluble polymers having 2,2'-bipyridine in the polymer side chain have been known, very few polymers containing 2,2'-bipyridine derivatives in the polymer backbone have been reported so far.[6-11] Yamamoto et al. have investigated synthesis and properties of a number of poly(2,2'-bipyridine-5,5'-diyl) derivatives.[7,8] Yu et al. have recently prepared new conjugated polymers with tris(2,2'-bipyridyl) ruthenium complex in a polymer backbone.[9] In this paper, we report synthesis and optoelectronic properties of new polymers having a regular alternating arrangement of a silicon σ unit and a 2,2'-bipyridyl π system in the backbone and their ruthenium complexes, in which the polymer backbone may act as an electron channel after electron injection via the MLCT excitation. Actually, we have found photoconductivity of the polymer complexes.

Poly(tetrapropyldisilanylene-2,2'-bipyridine-5,5'-diyl) **1**[12] and poly(dihexylsilylene-2,2'-bipyridine-5,5'-diyl) **2**[13] were synthesized by dehalogenative coupling of 1,2-bis(2-bromo-5-pyridyl)tetrapropyldisilane (**5**)[14] and bis(2-bromo-5-pyridyl)-dihexylsilane (**6**),[15] respectively, using nickel (0) catalyst (Scheme 1).[16,17] Compounds **5** and **6** were prepared by reactions of the corresponding dichlorosilanes with 2-bromo-5-lithiopyridine, which was prepared by the mono-lithiation of 2,5-dibromopyridine with *n*-butyllithium. The molecular weights (M_W) of **1** and **2** were determined by GPC to be 11000 and 9000, respectively, relative to polystyrene standard; **1** and **2** are highly soluble in common organic solvents such as dichloromethane, chloroform, benzene, and THF. Polymers **1** and **2** should hold regular repetition of disilanylene-bipyridyl and silylene-bipyridyl units, respectively, as proved by NMR spectroscopy.

The ruthenium complexes of **1** and **2**, polymers **3** and **4**, were prepared as light orange solids by reactions of bis(bipyridine)ruthenium ion $Ru(bpy)_2^{2+}$ with **1** and **2**, respectively.[18] The Ru contents in both **3** and **4** were determined to be about 35 mol% per bipyridine in the polymer backbone by ^1H NMR spectroscopy. The absorption spectra of polymers **1** and **3** in dichloromethane are shown in Figure 1. Absorption maxima of bipyridine π-π* transition of **1** and **3** appear at around 310 and 293 nm, respectively. In addition, **3** shows the MLCT band maximum at 459 nm, which is close to the reported value for $Ru(bpy)_3^{2+}$ (454 nm)[6b]. Similarly, the MLCT band maximum of **4** was found at 462 nm.



Scheme 1.

Irradiation of a thin film of **3** in air with a xenon lamp (500 W) led to facile degradation of the polymer as observed UV-vis spectroscopically,[19] while no serious degradation occurred when the same sample was irradiated with visible light (λ > 400 nm).

Photoconductivity of **3** and **4** was measured in a sandwich type cell with aluminum and indium-tin-oxide (ITO) as top and bottom electrodes, respectively. The monochromatic light from a tungsten lamp was irradiated through the bottom electrode on a quartz plate. Both **3** and **4** were photoconductive. Typically, photocurrent spectrum of **3** measured in an argon atmosphere is shown in Figure 2. A similar film of **4** showed photocurrent with the maximum at ca. 470 nm. Because these spectra are well in accord with the MLCT absorption bands, the electron carriers are suggested to be produced through the MLCT excitation in a tris(bipyridine)ruthenium moiety.

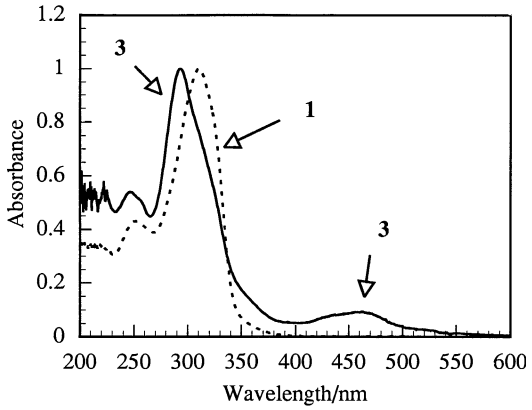


Figure 1. UV-vis spectra of polymers **1** and **3** in CH_2Cl_2.

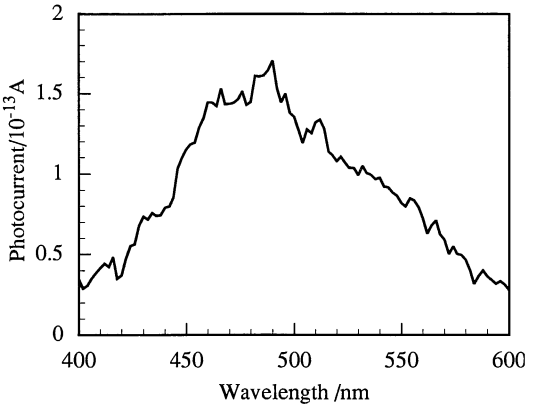


Figure 2. Photocurrent spectrum of polymer **3** in an ITO/**3**/Al sandwich type cell at 6 V.

Further work is in progress to determine the relative efficiency of the photoconductivity between **3** and **4**.

References and Notes

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12 Polymer **1**: Yield, 35%; ^{1}H NMR ($CDCl_3$) δ 0.94-1.02 (m, 20H), 1.30-1.40 (m, 8H), 7.73-7.76 (m, 2H), 8.27-8.32 (m, 2H), 8.53-8.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.4, 18.1, 18.7, 123.3, 132.9, 142.5, 154.2, 155.9; ^{29}Si NMR ($CDCl_3$) δ -20.0; UV (hexane) λ_{max}/nm (ε) 310 (23700), 251 (10200). *Anal.* Found: C, 68.40; H, 8.87; N, 6.98%. Calcd for $C_{22}H_{34}N_2Si_2$: C, 69.05; H, 8.95; N, 7.32%. M_w = 11000, M_n = 7000.

13 Polymer **2**: Yield, 52%; ^{1}H NMR ($CDCl_3$) δ 0.84 - 0.90 (m, 6H), 1.13 - 1.45 (m, 20H), 7.90-7.93 (m, 2H), 8.38 - 8.41 (m, 2H), 8.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 12.2, 14.1, 22.6, 23.5, 31.4, 33.3, 120.5, 131.1, 143.6, 154.3, 156.6; ^{29}Si NMR ($CDCl_3$) δ -7.1; UV (CH_2Cl_2) λmax/nm (ε) 300 (23600), 255 (12900), 249 (12300). *Anal.* Found: C, 74.72; H, 9.67; N, 7.65%. Calcd for $C_{22}H_{32}N_2Si$: C, 74.94; H, 9.15; N, 7.94%. M_w = 9000, M_n = 5900.

14 **5**: Yield, 58%; ^{1}H NMR ($CDCl_3$) δ 0.87-1.01 (m, 20H), 1.23-1.38 (m, 8H), 7.34 (dd, ^{3}J= 8.0, ^{4}J = 2.1 Hz, 2H), 7.40 (dd, ^{3}J = 8.0, ^{5}J = 0.8 Hz, 2H), 8.22 (dd, ^{4}J = 2.1, ^{5}J = 0.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 18.0, 18.4, 127.8, 131.2, 143.0, 144.1, 154.6; ^{29}Si NMR ($CDCl_3$) δ -19.8; MS (70 eV) *m/z* 542 (M^+, 11), 541 (15), 463 (18), 228 (40), 202 (22), 186 (100), 149 (51), 107 (33). *Anal.* Found: C,48.70; H, 6.08; N, 5.21%. Calcd for $C_{22}H_{34}Br_2N_2Si_2$: C, 48.71; H, 6.32; N, 5.16%.

15 **6**: Yield, 57%; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 6.7 Hz, 6H), 1.05 - 1.32 (m, 20H), 7.49 (dd, ^{3}J= 8.0, ^{5}J = 1.0 Hz, 2H), 7.55 (dd, ^{3}J = 8.0, ^{4}J = 2.1 Hz, 2H), 8.37 (dd, ^{4}J = 2.1, ^{5}J = 1.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.2, 18.0, 18.4, 127.8, 131.2, 143.0, 144.1, 154.6; ^{29}Si NMR ($CDCl_3$) δ -19.8; MS (70 eV) *m/z* 512 (M^+, 2), 427 (26), 343 (100), 263 (5), 186 (10), 107 (4).

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18 Typically, a reaction of **1** (1.6 mmol of bipyridyldisilanylene unit) with $Ru(bpy)_2(PF_6)_2$ (0.66 mmol) in 1,2-dichloroethane (16 ml) at reflux for 5 h gave **3** in 39% yield. **3**: ^{1}H NMR (CD_2Cl_2) 0.80–1.43 (m, 28H), 7.30–8.68 (m, 11.6H). From the intensity ratio between aromatic and aliphatic protons in the ^{1}H NMR, the Ru content in **3** was determined as 35%.

19 A number of disilanylene-π alternating polymers have been known photoreactive to give lower molecular weight products via homolytic scission of Si-Si bonds.[1]