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Arsole-Containing π-Conjugated Polymer by the Post-Element-Transformation Technique

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***Abstract:** A synthetic method to obtain an arsole-containing π-conjugated polymer by the post-transformation of the organotitanium polymer titanacyclopentadiene-2,5-diyl unit with an arsenic-containing building block is described. The UV/Vis absorption maximum and onset of the polymer were observed at 517 nm and 612 nm, respectively. The polymer exhibits orange photoluminescence with an emission maximum (E_{max}) of 600 nm and the quantum yield (Φ) of 0.05. The polymer proved to exhibit a quasi-reversible redox behavior in its cyclic voltammetric (CV) analysis. The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were estimated to be −5.43 and −3.24 eV, respectively, from the onsets for oxidation and reduction signals in the CV analysis. Further chemical modification of the arsole unit in the π-conjugated polymer by complexation of gold(I) chloride occurred smoothly resulting in the bathochromic shift of the UV/Vis absorption and lowering of the LUMO energy level.*

The heavier Group 15 elements are attractive components for construction of functional organic molecules. For example, phosphines and arsines possessing trivalent Group 15 elements (PR_3 and AsR_3, respectively) are known to serve as ligands of transition metals which play very important roles to exhibit excellent catalytic activity and optoelectronic features. Although both phosphines and arsines are known to have similar trigonal pyramidal structures with very close steric parameters, such as bond angles and bond length of the element–carbon (As−C and P−C) moieties,[1] their transition metal complexes often exhibit totally different catalytic activities and functions, which are ascribable to the different ability of both the σ-donation of the lone pair in the pnictogen atoms to the metals and the back-donation from the metals to the unoccupied d-orbitals of the pnictogens.[2] That is, the weaker σ-donation of arsines compared to that of phosphines accelerates various transition-metal-catalyzed cross-coupling reactions.[3] Also, some arsenic–metal complexes exhibit interesting optical features that cannot be attained by use of the corresponding phosphines.[4]

In recent years, element-block-containing polymers have attracted increasing attentions as advanced functional materials.[5] Especially, π-conjugated polymers having element-blocks are expected to reveal advanced optoelectronic features suitable for solar cell applications, light-emitting diodes, and chemosensors. Although the optoelectronic features of the π-conjugated polymers are most probably affected largely by the element-blocks, the synthesis of π-conjugated polymers possessing diverse element-blocks have scarcely been attained by the established polycondensation processes owing to the high reactivity of the carbon-element bonds under the polymerization conditions.

Previously, we have reported the synthesis of π-conjugated polymers having phosphole units by the reaction of regioregular titanacyclopentadiene-containing polymers,[6] generated in situ from aromatic diynes and a low-valent titanium complex through the regiospecific metallacyclization,[7] with dichlorophosphine derivatives. The resulting phosphole-containing polymers exhibit attractive electronic features of low LUMO energy levels owing to the σ^*–π^* orbital interaction that cannot be observed in the corresponding pyrrole-containing polymers.[8]

Based on the fact that arsines are attractive Group 15 element-containing building blocks which often reveal superior functions compared to phosphines as mentioned above, the incorporation of arsole units, the arsenic analogue of phospholes, into π-conjugated polymers is an attractive approach to create advanced functional materials. Very recently, Heeney and co-workers reported the synthesis of a π-conjugated polymer possessing dithienoarsole unit.[9] It was also described that the field effect transistor device fabricated from the dithienoarsole-containing polymer exhibits its excellent stability in air. This report encouraged the authors to carry out the synthetic study of arsole-containing π-conjugated polymers.

Concerning the synthesis of arsole derivatives, the reaction of dichlorophenylarsine with dicarboanion equivalents of butadienes such as zirconacyclopentadiene[10] and 1,4-dilithiobutadiene[11] derivatives was reported by Fagan et al. and Ashe III et al., respectively, in the 1980s. However, most probably due to the highly toxic and volatile nature of dichlorophenylarsine, which was in fact misused in the First World War as the chemical weapons, no further progress of

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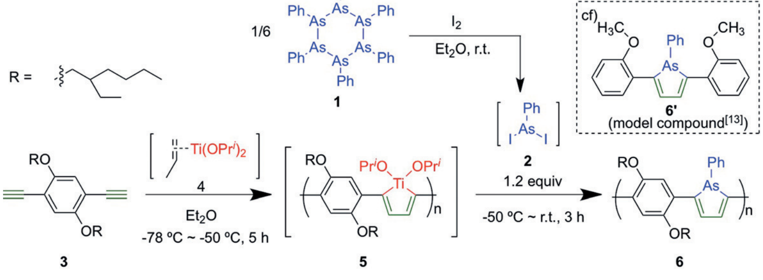
the related chemistry was achieved after these synthetic studies.

Recently, Naka et al. reported a safer way to generate diiodoarsines in situ from less volatile cyclo-oligoarsines with iodine, which were successfully employed in the synthesis of phosphorescence-active dibenzoarsoles by the reaction with 2,2′-dilithiobiphenyl.[12]

We have also described the transformation of the titanacyclopentadiene derivative into 2,5-diaryl-1-phenylarsoles in high yields by use of diiodophenylarsine.[13] Because the attempt to functionalize the 2,5-bis(*p*-bromoaryl)-1-phenylarsoles by the transition-metal-catalyzed cross-coupling reactions resulted in the lower yields of the objective products, probably due to the suppression of the catalytic activity by the arsoles,[13b] it would be difficult to approach the arsole-containing polymers by the transition-metal-catalyzed polycondensation of arsole-containing monomers. On the basis of the fact that the reactivity of the titanacyclopentadiene units is high enough for the smooth transformation into arsole derivatives and that the obtained arsole derivatives are much more stable towards oxidation than the phosphole analogues,[13] we describe the synthesis of unprecedented arsole-containing π-conjugated polymers by the reaction of the organometallic polymer possessing titanacyclopentadiene with diiodoarsine. The unique optical and electronic properties of the arsole-containing π-conjugated polymers are also discussed.

The reaction of the organotitanium polymer (**5**), which was prepared from 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (**3**) and the titanium(II) complex (**4**) generated in situ from titanium(IV) isopropoxide and isopropylmagnesium chloride from −78 °C to −50 °C, with diiodophenylarsine (**2**) was carried out under the conditions for the transformation of titanacyclopentadiene derivatives into arsoles (Scheme 1). By this polymer reaction, the polymer (**6**) was isolated in 88 % yield as a dark red solid after precipitation into methanol. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of **6** were estimated to be 5500 and 2.5, respectively, by SEC (chloroform as eluent, polystyrene standards). The polymer (**6**) is stable enough under ambient conditions. It is soluble in common organic solvents such as chloroform, dichloromethane, tetrahydrofuran, and toluene. The structure of **6** was supported by its ^{1}H NMR and ^{13}C NMR spectra (Supporting Information, Figures S1, S2, and S5). The efficiency of this transformation was found to be quantitative judging from the peak intensity ratio of the aromatic protons and the lateral alkoxy protons in the ^{1}H-NMR spectrum of **6** (Figure S1, observed: 4.00:8.98, expected: 4:9).



Scheme 1. Synthesis of arsole-containing polymer (**6**).

The absorption maximum (λ_{max}) and absorption onset (λ_{onset}) of **6** were observed at 517 nm and 612 nm (Figure 1, respectively, in the UV/Vis absorption spectra taken in CHCl$_3$ which were bathochromically shifted by more than 120 nm compared to those of **6′** ($\lambda_{max} = 395$ nm, $\lambda_{onset} = 446$ nm;[13] Figure 2, Table S1). The extension of the effective π-conjugation was supported by the observed clear bathochromic shifts. In the case of film, the λ_{onset} of **6** was bathochromically shifted approximately by 10 nm compared to that measured in CHCl$_3$. The polymer (**6**) exhibited an orange photoluminescence (PL) in CHCl$_3$ with an emission maximum (E_{max}) and the quantum yield (Φ) of 600 nm and 0.05, respectively. The optical properties of **6** are very close to those of a phosphole-containing polymer ($\lambda_{max} = 522$ nm, $\lambda_{onset} = 620$ nm, $E_{max} = 594$ nm, $\Phi = 0.10$), which was prepared by reaction of the same organotitanium polymer (**5**).[6a] This result indicates that the electronic character of the arsole ring is almost comparable to that of the phosphole ring.

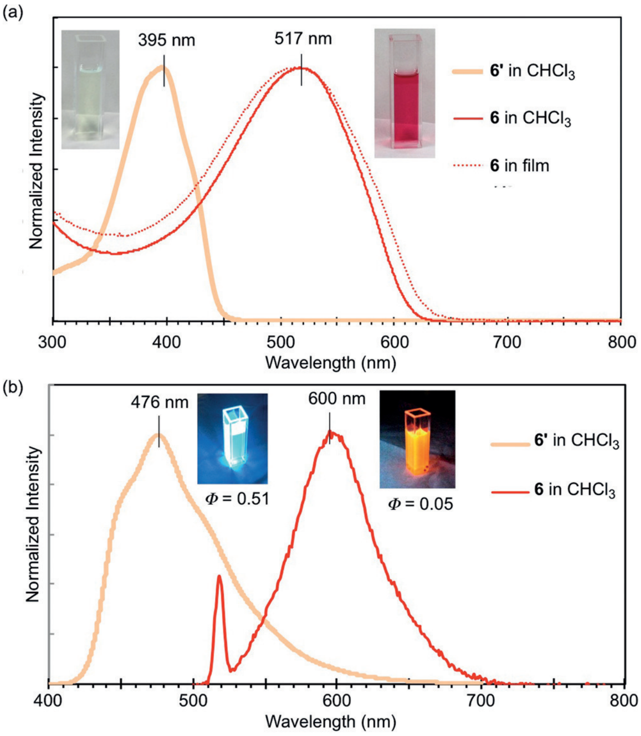


Figure 1. UV/Vis absorption spectra (a) and photoluminescence spectra (b) of **6** and **6′** in CHCl$_3$ solution or film.

In the CV analysis of **6**, the quasi-reversible oxidation and reduction peaks were observed at 0.53 eV and −1.66 eV, respectively (Figure S8). The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were estimated to be −5.43 and −3.24 eV, respectively, from the onsets

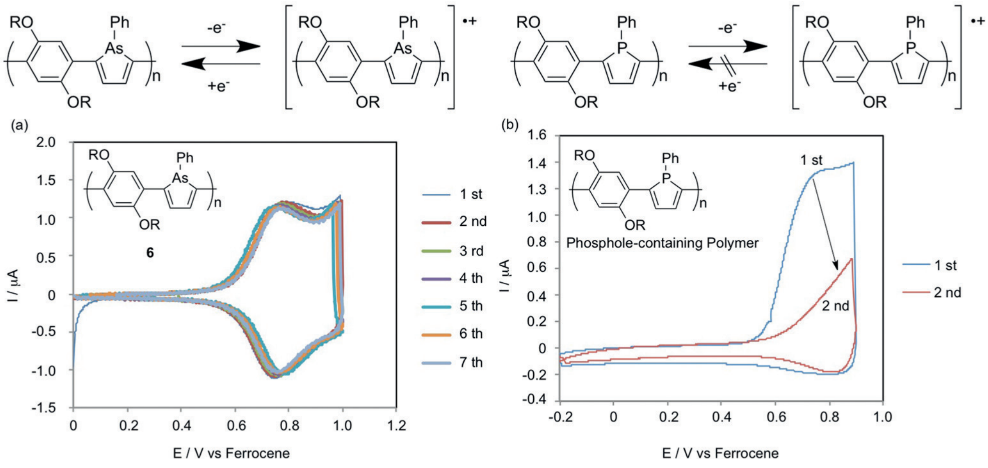
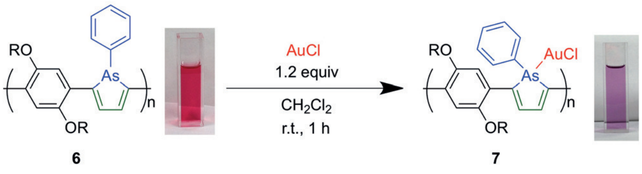


Figure 2. Cyclic voltammograms of **6** (a) and a phosphole-containing polymer (b) in film on a Pt wire immersed in the acetonitrile solution of tetra-*n*-butylammonium hexafluorophosphate (0.10 м), at a sweep rate of 100 mV s^{-1}.

for oxidation and reduction signals in the CV analysis. The HOMO and LUMO energy levels of **6** were very close to those of the phosphole-containing polymer (HOMO = −5.35 eV, LUMO = −3.28 eV).[6a] Namely, the arsole-containing polymer (**6**) also exhibits both electron-donating and -accepting-properties. Especially, the remarkably low LUMO energy level of **6** would be due to the σ*–π* orbital interaction (see below). The polymer (**6**) was found to exhibit the quasi-reversible oxidation under the CV measurement conditions, where the oxidation peak was constantly observed throughout several sweeps (Figure 3 a). To the contrary, the corresponding phosphole-containing polymer undergoes the irreversible structural change under the analogous measurement conditions, resulting in a significant decrease in the oxidation peak after the first sweep (Figure 3 b). The higher reversibility of oxidation of **6** is most probably due to the high stability of the doped form of **6**. The good reversibility and durability of **6** for electronic oxidation would be attractive for the electronic applications of this unique material.

The chemical modification of **6** was further performed to tune up the optoelectronic properties of the polymer. Because the trivalent arsenic atom can coordinate with transition metals such as gold(I) chloride,[13] **6** was subjected to the reaction with gold(I) chloride (1.2 equiv) in CH_2Cl_2 at ambient temperature for 1 h (Scheme 2). A polymer possessing the coordinated structure (**7**) was isolated in 87 % yield as a purple solid after precipitation into hexane. From the SEC analysis, M_n and M_w/M_n of **7** were estimated to be 6100 and 2.3, respectively. Similar to the case of **6**, the polymer (**7**) was stable enough under ambient conditions.



Scheme 2. Chemical modification of **6** with gold(I) chloride.

The structure of the polymer was supported by its ^{1}H NMR and ^{13}C NMR spectra (Figure S6). Especially, in ^{1}H NMR spectrum of **7**, the entire lower magnetic field shift of the peaks of the aromatic protons in comparison with those of **6** strongly supported the quantitative nature of the chemical modification. The UV/Vis absorption spectrum of **7** was taken in $CHCl_3$ (Figure S7 and Table S1), where λ_{max} and λ_{onset} of **7** were observed at 549 nm and 647 nm, respectively, which were bathochromically shifted by about 30 nm compared to those of the polymer (**6**). This bathochromic shift, namely, narrowing of the band gap of the polymer (**7**) by the coordination with gold(I) chloride, was found to be due to the lowering of the LUMO energy level of

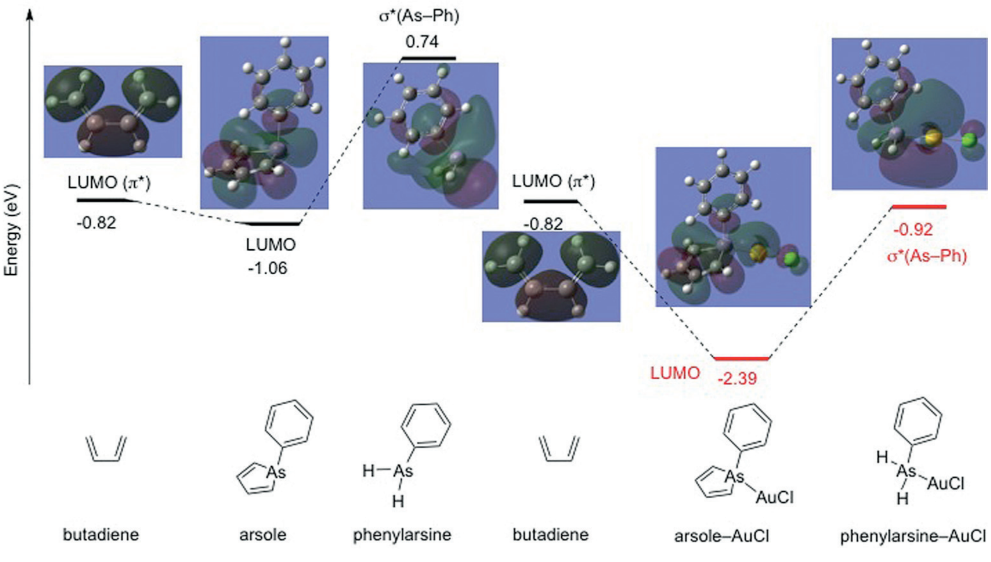


Figure 3. Orbital correlation diagrams for arsole derivatives based on the DFT calculations.

7. The LUMO energy level of **7** (−3.56 eV, estimated from its CV analysis; Figure S9 and Table S2) was significantly lower than that of **6** (LUMO = −3.24 eV), indicating that the arsole-gold complex exhibits a stronger electron-accepting property compared to the uncoordinated arsole unit.

The density functional theory (DFT) calculation at the B3LYP/6-31G(d) and LanL2DZ ECP set combination (ECP for the Au atom only) using the Gaussian09 program package[14] suggested that the low-lying LUMO energy level of the arsole unit comes from the σ*–π* orbital interaction between the π* molecular orbital (MO) of the butadiene moiety and the σ* MO of the As–Ph bond, as proposed in the silole, germole, stannole,[15] and phosphole[8] units. In the case of the gold complex (arsole–AuCl), the energy level of the σ* MO of As–Ph (phenylarsine–AuCl) is lower than that of As–Ph (free phenylarsine), which could bring about the stronger σ*–π* orbital interaction with the energetically similar π* MO of the butadiene moiety. The result obtained in the present study indicates that the LUMO energy level of arsole unit could be tunable by the facile complexation and/or chemical reactions on the arsenic atom.

In summary, an arsole-containing π-conjugated polymer was prepared by the reaction of a regioregular organotitanium polymer with a derivative of diiodoarsine as an arsinating reagent, which was generated in situ from less volatile hexaphenylcyclohexaarsine. The arsole-containing polymer was found to have both high HOMO and low LUMO energy levels. This polymer also exhibited quasi-reversible oxidation peak in CV measurements. The chemical modification of the arsole-containing polymer with gold(I) chloride proceeded smoothly, resulting in remarkable changes in the optical and electronic properties of the polymer. To our knowledge, this is the first example of the synthesis of arsole-containing polymers. On the basis of the unique features of the arsole-containing polymers, further macromolecular design would provide interesting materials that exhibit advanced functions. Thus, the designed synthesis of a series of the polymers and their applications, such as sensor, recovery, storage, and optoelectronic devices, are currently being investigated.

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