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A General Strategy for the Facile Synthesis of 2,7-Dibromo-9-heterofluorenes

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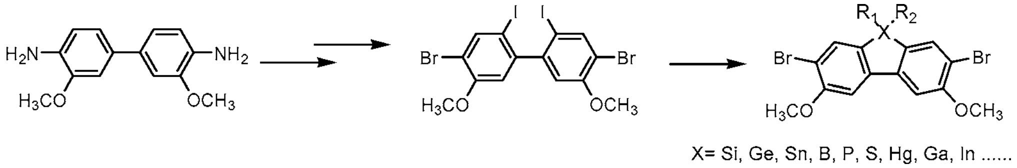
ABSTRACT



A facile, highly efficient, and economical procedure for the preparation of 6,6′-diiodo-4,4′-dibromo-3,3′-dimethoxylbiphenyl has been found. From this compound, a general synthetic strategy for the preparation of 2,7-dibromo-9-heterofluorenes has been developed. Five 2,7-dibromo-9-heterofluorenes have been easily synthesized for the first time according to the procedure presented, opening the door to new classes of inorganic and organometallic conjugated polymeric materials of polyheterofluorenes.

Polyfluorenes (PFs) have been the most intensively investigated conjugated polymers for optical and electronic devices.[1] Polyheterofluorenes, in which the sp^3 hybridized carbons at position 9 of fluorene in PFs are substituted by other atoms, are receiving increasing attention[2] because of their unique electronic structures that result from the particular interactions between the heteroatom and the π-conjugated polyphenylene-like framework.[3] However, the synthesis of dibromo (or diiodo) substituted heterofluorene monomers required by most of the polymerization methods for conjugated polymers[4] is still a challenge for chemists, hindering the development of polyheterofluorenes.

Dibromocarbazole and dibromofluorene are usually prepared by brominating carbazole and fluorene, respectively, but most dibromoheterofluorenes cannot be synthesized accordingly because 9-heterofluorenes are generally sensitive to the common bromination (or iodination) methods, which will lead to their breakage. A fundamental solution is to brominate the diphenyl before the formation of the heterofluorenes. Since a series of 9-heterofluorenes was synthesized by the reaction of 2,2′-dilithiodiphenyl with the suitably disubstituted heteroatoms, the dibromoheterofluorene can be prepared if the 2,2′-dilithio-4,4′-dibromodiphenyl intermediate can be formed. Fortunately, due to the reactivity difference of iodo and bromo substituents toward BuLi, the 2,2′-dilithio-4,4′-dibromodiphenyl intermediate can be formed from 2,2′-diiodo-4,4′-dibromodiphenyl after selective halogen/metal exchange between diiodo substituents and BuLi. Using this method, dibromoborafluorene and dibromosilafluorene have been successfully prepared very recently by Yamaguchi et al.[5] and Holmes et al.,[6] respectively. However, the reported synthesis of the key compound that contains the 2,2′-diiodo-4,4′-dibromobiphenyl substructure is quite complicated with a low yield, making this synthetic route very difficult and expensive in the dibromoheterofluorene preparation, and no other dibromoheterofluorenes have been reported yet.[1]

In this paper, we developed a facile, highly efficient, and economical route to prepare 6,6′-diiodo- 4,4′-dibromo-3,3′-

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(1) Wu, W. S.; Inbasekaran, M.; Hudack, M.; Welsh, D.; Yu, W. L.; Cheng, Y.; Wang, C.; Kram, S.; Tacey, M.; Bernius, M.; Fletcher, R.; Kiszka, K.; Munger, S.; O'Brien, J. *Microelectron. J.* **2004**, *35* (4), 343−348.

(2) Briere, J. F.; Cote, M. *J. Phys. Chem. B* **2004**, *108* (10), 3123−3129.

(3) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34* (1), 2−7.

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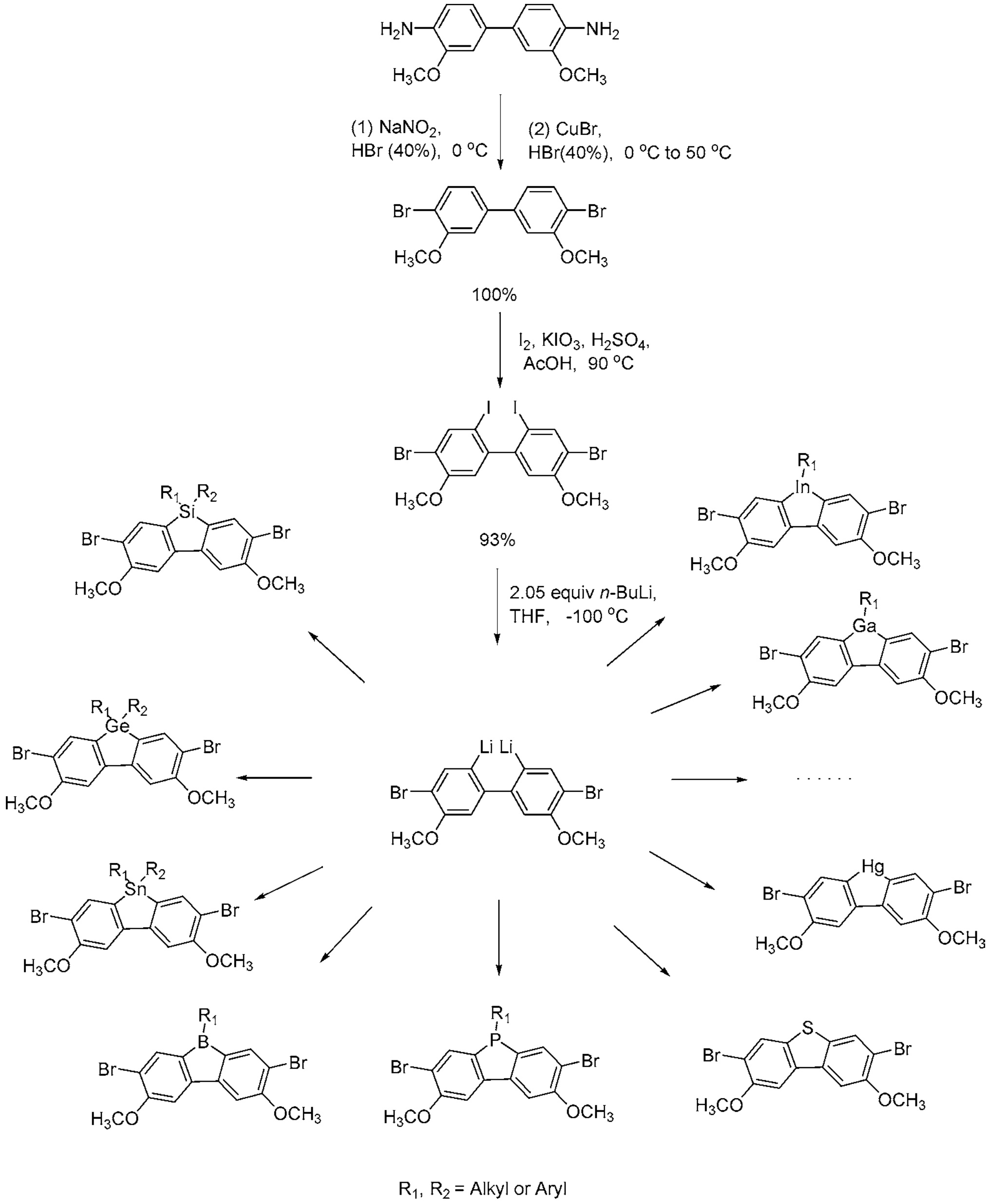
10.1021/ol0524499 CCC: $33.50

Scheme 1. General Synthetic Route for the Preparation of 2,7-Dibromo-9-heterofluorenes



dimethoxylbiphenyl in two steps with very high yield, and a general synthetic strategy was outlined for the preparation of a series of 2,7-dibromo-9-heterofluorenes (see Scheme 1). On the basis of the synthetic strategy, five 2,7-dibromo-9-heterofluorenes were synthesized for the first time (see Table 1). The successful preparation of 2,7-dibromo-9-heterofluorenes will open the door to the synthesis of many novel and interesting organic−inorganic hybrid conjugated polymers of polyheterofluorenes with unique structural features and optical properties. The facile and economical synthesis of the very important intermediate, that is, 6,6′-diiodo-4,4′-dibromo-3,3′-dimethoxylbiphenyl, makes the preparation of polyheterofluorenes feasible in both current scientific research and future commercial manufacturing.

The starting material is *o*-dianisidine, which is a widely used commercial compound in the dye industry. *o*-Dianisidine was easily changed to 4,4′-dibromo-3,3′-dimethoxylbiphenyl by the modified Sandmeyer reaction quantitatively with a yield of almost 100%, compared to the reported low yield of 27%.[7] 4,4′-Dibromo-3,3′-dimethoxylbiphenyl was then iodinated by the I$_2$/KIO$_3$ system to smoothly give rise to 6,6′-diiodo-4,4′-dibromo-3,3′-dimethoxylbiphenyl with a high yield of 93%. The overall yield of 93% is much higher than the 19% of Holmes.[6] In addition, 1.0 g of *o*-dianisidine can finally produce 2.4 g of 4,4′-dibromo-3,3′-dimethoxy-2,2′-diiodobiphenyl according to our synthetic procedure, while 1.0 g of 2,5-dibromonitrobenzene, which is very expensive, can only produce 0.19 g of 4,4′-dibromo-2,2′-diiodobiphenyl, as reported by Holmes.[6] The methoxy groups

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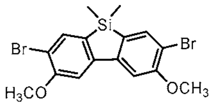
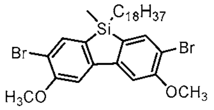
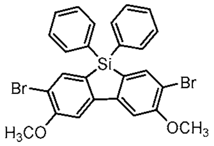
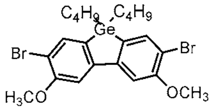
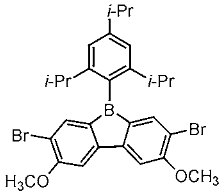
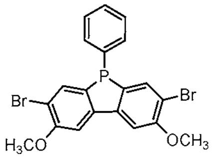
(7) Campbell, N.; Scott, A. H. *J. Chem. Soc., Chem. Commun.* **1966**, 1050−1051.

Table 1. As-Prepared 2,7-Dibromo-9-heterofluorenes

reagent	product	yield %
$(CH_3)_2SiCl_2$		63
$(C_{18}H_{37})_2SiCl_2$		23
Ph_2SiCl_2		12
$(C_4H_9)_2GeCl_2$		36
$PhB(OCH_3)_2$		38[5]
$PhPCl_2$		54*

[a] 17% of the compound has been oxidized to 2,7-dibromo-3,6-dimethoxy-9-phosphafluorene oxide as its ^1H NMR revealed.

in the silafluorene can not only act as an orientation group in the monomer synthesis but also serve as a structural probe in the polymer characterization.

At the heterofluorene formation stage, 2.05 equiv of *n*-BuLi was added to selectively substitute two iodo substituents in 6,6′-diiodo-4,4′-dibromo-3,3′-dimethoxylbiphenyl at −100 °C, and after the dilithiation for about 30 min, suitably disubstituted heteroatom reactant was added, resulting in corresponding 2,7-dibromo-9-heterofluorenes. The formation of the 6,6′-dilithio-3,3′-dimethoxy-4,4′-dibromodiphenyl intermediate is the key step for the preparation of various 2,7-dibromo-9-heterofluorenes. Theoretically, the dilithiated intermediate can react with dichlorosilane,[8] dichlorogermane,[9] or dichlorostannane,[10] resulting in 2,7-dibromo-9-silafluorenes, 2,7-dibromo-9-germafluorenes, or 2,7-dibromo-9-stannafluorenes, respectively; with dimethoxyboron,[5] resulting in 2,7-dibromo-9-borafluorene; with dichlorophosphine,[11] resulting in 2,7-dibromo-9-phosphafluorenes; with sulfur dichloride or $(PhSO_2)_2S$,[12] resulting in 2,7-dibromo-9-sulfafluorenes; and even with dihalogenometals, such as $HgCl_2$,[13] $ArGaCl_2$,[14] and $ArInBr_2$,[14] resulting in 2,7-dibromo-9-mercurafluorene, 2,7-dibromo-9-galliumafluorene, and 2,7-dibromo-9-indiumafluorene, respectively. Those 2,7-dibromo-9-heterofluorenes enable us to prepare inorganic and organometallic conjugated polymers, which have emerged as an important area of research in the field of materials chemistry.[2]

Using this synthetic strategy, we successfully prepared five 2,7-dibromo-9-heterofluorenes for the first time as listed in Table 1. Except for 2,7-dibromo-3,6-dimethoxy-9-phosphafluorene, which will be oxidized by air to its oxide during the post-treatment,[15] those 2,7-dibromo-9-heterofluorenes are stable and can be purified via column chromatography and recrystallization methods. Detailed studies on their polymers prepared by Suzuki coupling polymerization will be reported in the future.

In conclusion, we have outlined a facile and highly efficient procedure for the preparation of 6,6′-diiodo- 4,4′-dibromo-3,3′-dimethoxylbiphenyl, which is a key compound for the preparation of 2,7-dibromo-9-heterofluorenes from the cheap and readily available *o*-dianisidine. A general synthetic strategy for the preparation of 2,7-dibromo-9-heterofluorenes has been developed. Five 2,7-dibromo-9-heterofluorenes were easily synthesized for the first time, and their polymers will be reported elsewhere. The successful preparations of 2,7-dibromo-9-heterofluorenes have opened the door to new classes of functional conjugated polymeric materials based on polyheterofluorenes. In addition, the facile, highly efficient, and economical synthesis of 6,6′-diiodo-4,4′-dibromo-3,3′-dimethoxylbiphenyl makes the preparation of polyheterofluorenes feasible both in scientific research and in commercial manufacturing. The work will greatly promote the research and applications of the inorganic and organometallic conjugated polymers.

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Supporting Information Available: Experimental procedures and characterization of the five 2,7-dibromo-9-heterofluorenes. This material is available free of charge via the Internet at http://pubs.acs.org.

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