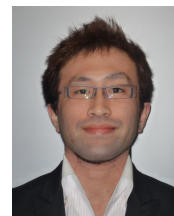# Selective Bromine-Lithium Exchange on the Hexaphenylbenzene Framework

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Abstract: Hexaphenylbenzene (HPB) is a versatile scaffold for various materials and a useful precursor of graphene fragments such as hexabenzocoronene. While derivatized HPB compounds have been prepared through metal-catalyzed cyclotrimerization of diarylacetylenes or through Diels-Alder reaction of tetraphenylcyclopentadienone derivatives and diarylacetylenes, both of the methods can selectively achieve the limited substitution patterns.

We developed the selective alternate trilithiation protocol of the HPB framework, which can selectively and efficiently afford C_3- or C_{2v}-symmetric HPB derivatives (Scheme).[1,2] Through the monitor of the lithiation process, this selectivity was found to derive from the two-stage mechanism. At first, the solubility-controlled lithiation affords the mixture of the completely lithiated species and the starting HPB derivative based on the low solubility of the starting HPB derivative, and then the reversible ArBr/ArLi exchange, halogen dance, affords the alternately trilithiated species selectively under thermodynamic control. In some cases, the addition of mesityl bromide (MesBr) or *p*-(dimethylamino)phenyl bromide (MapBr) was crucial for the reaction because *in situ* generated MesLi or MapLi can achieve the lithiation of the HPB derivatives at high temperature in THF instead of unstable *t*-BuLi. We experimentally confirmed that the thermodynamic preference of the alternate lithiation pattern results from the strong electronic repulsion between the adjacent lithiophenyl groups.
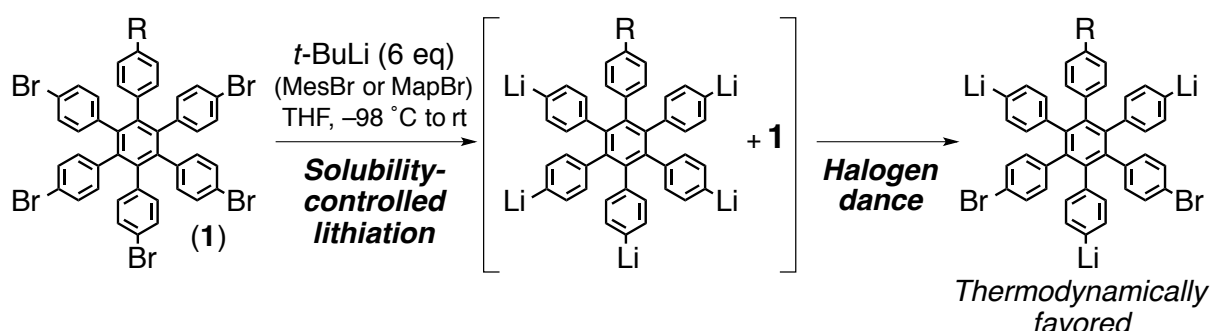
Scheme. Selective alternate trilithiation of the HPB derivatives.

References:
1) T. Kojima; S. Hiraoka, *Org. Lett.* **2014**, *16*, 1024-1027.
2) T. Kojima; S. Hiraoka, *Chem. Commun.* **2014**, *50*, 10420-10423.