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Synthesis and Properties of Highly-Rigid Conjugation System Based on Bi(benzo[*b*]thiophene)-Fused *o*-Carborane

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ABSTRACT

To demonstrate the validity of *o*-carborane as an electronic anchoring unit for constructing robust conjugation system, bi(benzo[*b*]thiophene)-fused *o*-carborane was designed and synthesized. From the optical measurements, clear vibrational bands not only in the absorption but also in the emission spectra were observed. These data mean that the electronic delocalization should occur on the rigid template. In the cyclic voltammograms, the reversible reduction waves at –1.72 eV and –2.37 eV were detected originated from the electron-accepting ability of *o*-carborane. It is suggested that *o*-carborane should be the versatile unit for constructing robust conjugation with electron-accepting ability.

Conjugated compounds have attracted much attention as a platform for fabricating organic opto-electronic devices. In order to obtain highly-functional materials, the construction of the robust and expanded conjugation system is of significance in the molecular design because the rigid and planar structures are favorable not only for facilitating the electronic interaction through the extended conjugation but also for suppressing structural distortions or perturbations by the reinforced rigidity. The introduction of the fused-aromatic rings is one of feasible strategies for constructing robust conjugated systems. For example, various types of heteroatom-bridged bithiophenes have been synthesized,[1] and their unique optical properties have been reported.[2] In particular, by utilizing an "element-block" which is defined as functional nano-building blocks composed of heteroatoms or inorganic elements, multiple functions originated from the intrinsic properties of each element as well as the electronic conjugation can be expected.[3]

Carborane is the class of cluster compounds composed of boron and carbon atoms, and *o*-carborane which is composed of two carbon atoms and ten boron atoms (1,2-dicarba-*closo*-dodecaborane)[4] has been paid much attention as a versatile optically-functional "element-block" according to the recent reports.[5] *o*-Carborane works as an electron-withdrawing group because of the electron-deficient characteristics of skeletal electrons delocalized via the 3-center-2-electron bonds. Therefore, by the combination with the electron-donating groups, strong emissions were obtained from the intramolecular charge transfer (CT) transition. Furthermore, it was found that *o*-carborane-containing main-chain-type conjugated polymers were aggregation-induced emission (AIE)-active compounds which can show the strong emission only in the solid state.[6] The vibration at the carbon−carbon bond in *o*-carborane can critically consume the excitation energy in the CT state, leading to the annihilation. On the other hand, in the aggregation state, the emission can be recovered by suppressing the decay process. These solid-state emissions are advantageous for fabricating an efficient organic emissive devices.[7]

Recently, the series of biaryl-fused *o*-carboranes were synthesized, and the roles of *o*-carborane in the conjugation as an effective electron-acceptor were investigated.[8] Highly-planar structures were obtained, and it was observed that the energy levels of both highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) were lowered compared to those of the corresponded biaryl compounds such as 2,2'-bithiophene (Figure 1). These data represent that *o*-carborane works as the anchor and the electron-accepting unit. Herein, to show the applicability of the *o*-carborane anchor to the further expanded conjugated system, benzo[*b*]thiophene-fused o-carborane was prepared. From the series of optical and electrochemical measurements, the electronic structures were evaluated. The influence of *o*-carborane on the properties was investigated.

The synthesis of bi(benzo[*b*]thiophene)-fused *o*-carborane (**CB**) was performed according to Scheme 1.[8a] The precursor **3** for constructing *o*-carborane was prepared from 3-trimethylsilylethynylbenzo[*b*]thiophene **2** via the Sonogashira–Hagihara coupling in the presence of $Pd(PPh_3)_2Cl_2$ as a catalyst. The di-substituted *o*-carborane **4** was obtained in the insertion reaction between decaborane and **3** in the presence of Lewis base (*N*,*N*-dimethylaniline) in a good yield (52%). 2-

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