PD Research Report for the 2016 year

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Research Theme  Synthetic Study of High-Ordered Iptycene Derivatives Using Isobenzofuran as a Reactive Platform

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Research Results

Isobenzofurans are useful building blocks in synthetic chemistry having 10π-electron systems with quinoid structures. Focusing on the high reactivity toward [4+2] cycloadditions with dienophiles, our group has developed the efficient synthetic methods and applications of highly functionalized isobenzofuran derivatives. For example, a donor–acceptor type isobenzofuran (I), bearing both electron donating and withdrawing groups exist in a molecule, enabling successive cycloaddition to construct polycyclic system. In addition, dual cycloaddition was available to lead polycycles using bis-isobenzofurans (III) as a key intermediate by the sequential generation of isobenzofurans from bis-epoxynaphthalenes (II). Based on these previous results, our interest moved on to the tris-isobenzofuran (V) bearing triptycene skeleton in the core as a three dimensional building block.

Triptycenes (IV) are the simplest member in iptycene family, having [2.2.2]bicyclooctatriene bridgehead system with phenyl rings attached. The bicyclic core derives rigidity and creates prism-like geometry involving void spaces. Supramolecular interactions, opening a substantial potentiality in crystal engineering, host-guest complexes, molecular machines, polymers and liquid crystals.

In order to develop a novel three-dimensional π-extended molecule, our synthetic goal is synthesizing tris-polyacene (VI) utilizing triple [4+2] cycloaddition from tris-isobenzofuran (V).

The key building block, tris-isobenzofuran (4), was synthesized from hexabromotriptycene (I). Upon the treatment of 4.0 equiv. of PhLi in toluene/THF co-solvent (conditions B), triis-epoxynaphthalene (3) was obtained in 41% yield. Mono-isobenzofuran (5) and bis-isobenzofuran (6) was also accessible (conditions A).
Using diphenylfuran (10) instead of 2, isobenzofurans 7, 8, 9 were obtained. In this way, six different kinds of triptycene building blocks bearing isobenzofuran motif were synthesized.

Figure 2. Synthesis of triptycene isobenzofurans

Next, cycloaddition of tris-isobenzofuran (4) and anthraquinone (11) was conducted and following aromatization in acidic conditions gave the tris-pentacenequinone (12) in 14% as a two-step yield. Further transformation toward pentacene derivatives was also performed. TIPS ethynyl group was added to the 12, then upon the treatment of SnCl2 and 10% HCl in THF solution gave the desired tris-pentacene (13) in 16% yield (2 steps). Further studies toward electronic and photochemical characteristics of 13 will be studied.

Figure 3. Synthesis of tris-pentacenequinone and tris-pentacene

In conclusion, the highly reactive triptycene based isobenzofurans were synthesized and applied to the synthesis of tris-pentacene derivative, a high-ordered iptycene derivative. We will continue our study on supermolecular activity of this three-dimensional π-extended iptycenes as a potential organic material.

Conference Presentations
(1) Sunna Jung and Toshiyuki Hamura, “Synthetic Study of High-Ordered Iptycene Derivatives Using Isobenzofuran as a Reactive Platform”, Spring CSJ meeting, 2F1-19 (Presentation), Kanagawa, Japan, 2017, March. (English)