PD Research Report for the 2017 year

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

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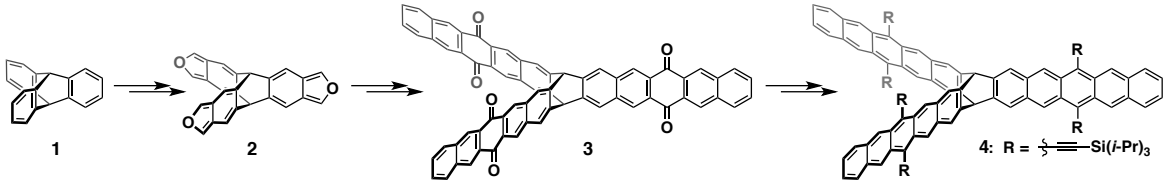
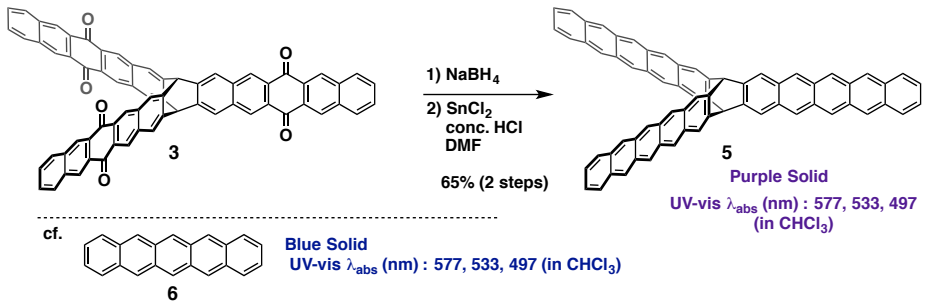
Research Results

Three dimensional π-conjugated molecules have been drawing substantial attentions among organic chemists due to their intriguing structures, physical properties and potential applications as organic materials. Focused on iptycene derivatives, their unique geometrical shapes, derived from the bicyclo[2.2.2]octatriene system with aromatic rings in three blades, bring to the development of the high ordered iptycene derivatives in various area. So far, we have been succeeded in three-directional polycyclic iptycene derivatives by developing iptycene building block, tris-isobenzofuran (**2**). Due to the high reactivity of 10π-electaron systems with quinoid structures, [4+2] cycloadditions with dienophiles following several steps of transformations progressed smoothly to deliver tris-pentacenequinone (**3**) and tris-TIPS-pentacene (**4a**). In this report, further synthesis toward parent pentacene skeleton was examined and physical properties of these novel 3D molecules were studied.



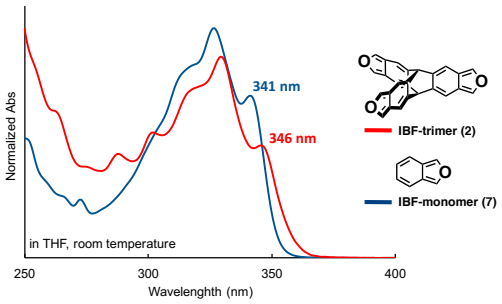
1. Synthesis of tris-pentacene

According to the previous report, tris-pentacenequinone **3** and tris-TIPS-pentacene **4** were prepared starting from triptycene (**1**). Attempts toward pentacene derivatives with no substituent groups were examined, therefore, reduction of ketones in tris-pentacenequinone **3** by sodium borohydride and following reductive aromatization [Tin chloride and concentrated HCl] gave tris-pentacene **5** in 65% yield as purple solid. It is unstable in air and light and can be stored on bench for several days under dark conditions. Comparing to the parent pentacene **6**, which is obtained as blue solid, both pentacene derivatives **5** and **6** shows UV-vis absorption at 577, 533, 497 nm in chloroform solution. Both **5** and **6** are insoluble in various organic solvents, such as chloroform, dichloromethane, ethyl acetate, acetone, toluene, and hexane.

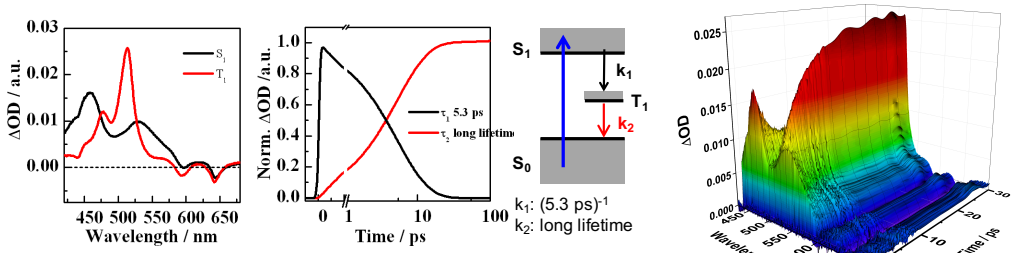


2. Physical properties of tris-isobenzofuran and tris-pentacene

The physical properties of tris-isobenzofuran **2** and tris-TIPS-pentacene **4** was investigated. Since both **2** and **4** have rigid three-dimensional structures, through-space electronic coupling effect between either isobenzofuran or pentacene subunits can be expected. According to the UV-visible spectra, weak homoconjugation effect was observed between isobenzofuran subunits in tris-isobenzofuran **2**. UV-visible absorption spectra of two isobenzofuran derivatives, tris-isobenzofuran **2** and isobenzofuran monomer **7**, were measured in THF solutions right after the purification under the Ar atmosphere. The absorption of **2** at 346 nm showed redshift of 5 nm relative to the absorption of **7** at 341 nm, indicating intramolecular electronic coupling between isobenzofuran moieties. According to the B3LYP-6-31G** level of calculations, the energy gap between HOMO and LUMO of isobenzofuran monomer **7** (4.07 eV) became smaller in tris-isobenzofuran **2** (3.81 eV) due to the electronic coupling. Both HOMO and LUMO of **7** split into two stabilized HOMOs/LUMOs and one destabilized HOMO/LUMO when they exist in iptycene derivative **2**.



In addition to homoconjugation effect, intramolecular singlet fission in tris-pentacene **4** was studied using transient absorption spectroscopy. Singlet fission is a spin allowed process that is a conversion of *one* singlet excited state into *two* triplet excited states. This process makes it possible to develop solar cell devices with better efficiency by generating more high-energy photons. Pentacenes are qualified to show singlet fission, therefore, they are attractive compounds as potential photovoltaic materials. Since there are three pentacene subunits in tris-isobenzofuran **4**, intramolecular singlet fission was observed by measuring transient absorption spectroscopy in dilute chloroform solution. After 5.3 picoseconds, triplet states are increasing which has long life time (~ ns) with ~200 % of triplet yield. This result indicates that intramolecular singlet fission observed in tris-pentacene **4** will bring to a new stage of photovoltaic materials or phosphorescent material.



Intramolecular Singlet Fission (S_1+S_0→$2T_1$)
Triplet yield: ~200%

Conference Presentations

(1) Sunna Jung and Toshiyuki Hamura, "Synthetic Study of High-Ordered Iptycene Derivatives Using Isobenzofuran as a Reactive Platform", 28th Symposium on Physical Organic Chemistry, 1A10 (Presentation), Fukuoka, Japan, **2017**, September. (*Japanese*)

(2) Sunna Jung and Toshiyuki Hamura, "Synthetic Study of High-Ordered Iptycene Derivatives Using Isobenzofuran as a Reactive Platform", 6th JACI/GSC symposium, E-03 (Poster), Tokyo, Japan, **2017**, July. (*Japanese*)