

論文内容の要旨

論文題目 Construction of Unique p-Electron Conjugated Systems by Multi-functionalization of Fullerenes
 〔フラーレンの多重官能基化による特異なパイ電子共役系の構築〕

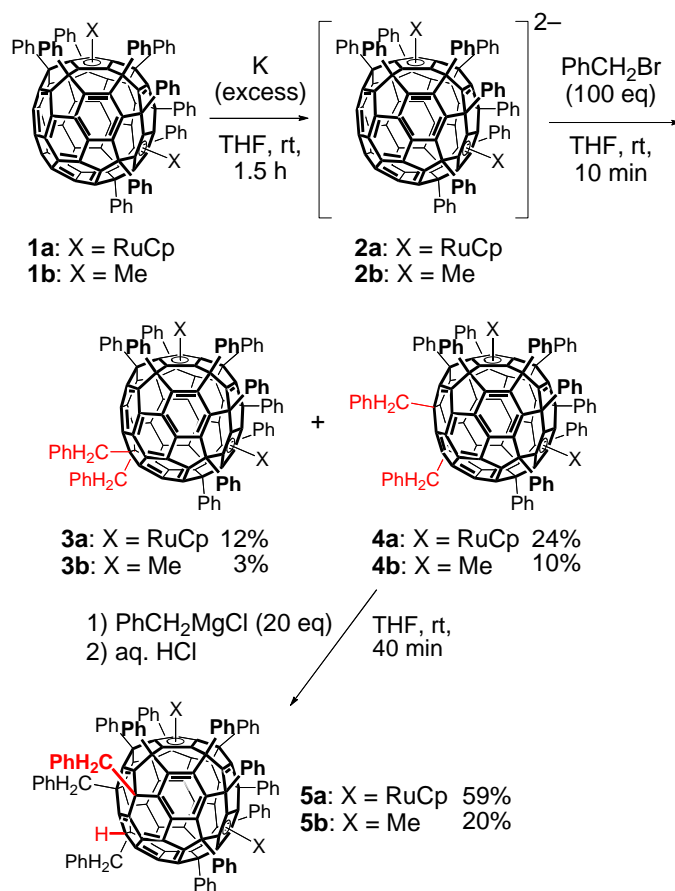
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The present thesis provides topics on construction of new curved π -electron conjugated systems through the detracting of spherical π -systems [60]fullerene and [70]fullerene.

Chapter 1 describes the utility of the methodology for creating new non-planar π -systems through chemical functionalization of fullerenes.

Chapter 2 describes construction of curved bi- and triaryl structures on [60]fullerene by synthesis of dodeca- and trideca(organo)[60]fullerenes. Two regioisomers of dodeca-adducts were obtained with application of reductive functionalization reaction to dibenzo-fused-corannulene-type dodeca-adducts. One isomer of dodeca-adducts underwent further nucleophilic addition reaction with a Grignard reagent to afford a trideca-adduct regioselectively. Dodeca- and trideca-adducts exhibited colorful luminescence based on their structures.

Scheme 1.



Chapter 3 describes control of metal–metal interaction on the fullerene framework of hepta(organo)[70]fullerene diruthenium complexes by redox-active functional groups as the seventh addend. Hepta-adducts obtained with stepwise organocopper addition reactions possess bowl-shaped π -system which not only assist electronic communication between two metal atoms on the fullerene core but also change its electronic structure through the perturbation by external functional groups.

Scheme 2.

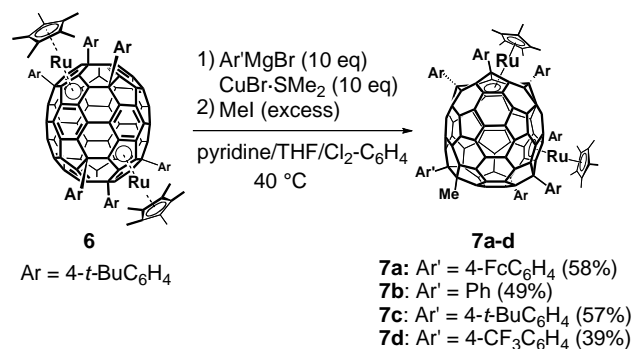


Table 1. Electrochemical Oxidation of Hepta-adducts

| Compounds | $E(\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}) / \text{V}$ | $E_1(\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}) / \text{V}$ | $E_2(\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}) / \text{V}$ | $\Delta E(\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}) / \text{V}$ |
|-----------|--|--|--|---|
| 7a | -0.02 | 0.287 | 0.555 | 0.268 |
| 7b | - | 0.264 | 0.569 | 0.305 |
| 7c | - | 0.257 | 0.551 | 0.294 |
| 7d | - | 0.280 | 0.577 | 0.297 |

Chapter 4 describes construction of another type of bowl-shaped π -system through the synthesis of octa(organo)[70]fullerene dimetal complexes with chemical reduction as the key step. Chemical functionalization reaction of hexa(organo)[70]fullerenes split their original π -systems on the highly unreactive equator part.

Scheme 3. Synthesis of octa-adducts of [70]fullerene.

