SYNTHESIS AND CHARACTERIZATION OF
HEXAKIS(4-PYRIDYLETHYNYL)BENZENE AND
HEXAKIS(5-PYRIMIDYLETHYNYL)BENZENE

Masakazu Ohkita,* Chihaya Adachi,† Miki Kawano,†† and Takanori Suzuki††

Department of Applied Chemistry, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso, Nagoya 466-8555, Japan; e-mail: ohkita.masakazu@nitech.ac.jp
† Department of Photonics Materials Science, Chitose Institute of Science and Technology (CIST), 758-65 Bibi, Chitose 066-8655, Japan
†† Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Abstract – Two new members of snowflake-shaped carbon-rich molecules possessing nitrogen-heterocycles as functional end groups, hexakis(4-pyridylethynyl)benzene (1) and hexakis(5-pyrimidylethynyl)benzene (2), have been prepared by six-fold Sonogashira cross-coupling reaction of hexabromobenzene with 4-ethynylpyridine and 5-ethynylpyrimidine, respectively.

Carbon-rich organic materials composed of acetylene units have attracted great deal of recent interest as large conjugated \( \pi \)-systems with unique electronic and optical properties, and an increasing number of carbon-rich materials with various shapes and functional units have been developed.\(^1\) As for snowflake-shaped acetylenic carbon-rich molecules, Vollhardt and co-workers have reported the first preparation of parent hexaethynylbenzene in 1986.\(^2\) After this pioneering work, hexaethynylbenzenes possessing functional end groups such as porphyrin,\(^3\) azulene,\(^4\) or oligothiophene\(^5\) as well as its differentially substituted derivatives\(^6\) have been synthesized. In addition, the hexaethynylbenzene skeleton has been successfully applied as a scaffold for the construction of functional materials including liquid crystals,\(^7\) nonlinear optical materials,\(^8\) and dendrimers.\(^9\) In this study, we introduced two new
members of carbon-rich molecules of this series having nitrogen-heterocycles as functional end groups, i.e. hexakis(4-pyridylethynyl)benzene (1) and hexakis(5-pyrimidylethynyl)benzene (2). Herein we report the synthesis and characterization of 1 and 2.

Six-fold Pd-catalyzed coupling of hexabromobenzene with a large excess (30 equiv.) of 4-ethynlypyridine\textsuperscript{10} in benzene/Et\textsubscript{3}N (1:1) at 60 °C for 3 days in the presence of PdCl\textsubscript{2}(PPh\textsubscript{3})\textsubscript{2} (10 mol%) and CuI (10 mol%) afforded 1 in 23% isolated yield, after extensive column chromatography on Al\textsubscript{2}O\textsubscript{3} (eluted with CHCl\textsubscript{3}) followed by preparative GPC. Similar Sonogashira coupling of hexabromobenzene with 5-ethynlypyrimidine\textsuperscript{11} afforded 2 in 32% yield. Compounds (1) and (2) were obtained as rather photo-sensitive bright yellow solids that are poorly soluble in common organic solvents; quite slightly soluble in CHCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}, or benzene. FD-MS spectrum clearly showed their molecular ion peaks as base peak (\textit{m}/\textit{z} 684 for 1 and 690 for 2). The \textsuperscript{1}H NMR spectrum of 1 exhibits only a single set of AA’XX’ signals due to the pyridyl moieties at 7.42 and 8.70 ppm, reflecting its highly symmetric nature. The simplicity of the \textsuperscript{13}C NMR spectrum of 1, which include resonances for two sp-carbons (\(\delta\) 89.57 and 97.62) and four sp\textsuperscript{2}-carbons (\(\delta\) 125.27, 128.01, 130.12, and 150.27), is again consistent with the hexamer structure. The high symmetry of 2 is also manifested by the single set of singlet signals at 8.90 and 9.26 ppm in the \textsuperscript{1}H NMR spectrum. Figure 1 shows the absorption and emission spectra of 1 in dichloromethane. The lowest energy electronic transition of 1 occurs between 300 and 385 nm with an absorption maximum at 340 nm (log \(\varepsilon\) 5.58), consistent with an effective \(\pi\)-conjugation between the heterocyclic rings and the central benzene core through the triple bonds. Compound (1) exhibits intense fluorescent emission with a maximum at 443 nm (Figure 1). Compound (2) shows absorption (\(\lambda_{\text{max}}\) 340 nm) and emission (\(\lambda_{\text{em}}\) 443 nm) spectra similar to those of 1. The large Stokes shift observed for 1 and 2 (104 nm) may be attributable to their large conformational change between the ground- and excited-states.\textsuperscript{12} To date, we have been unable to obtain their single crystals suitable for X-Ray diffraction studies.
Finally, it is interesting to point out that compounds (1) and (2) may be regarded as potential nitrogen-based multidentate ligands to transition-metals possessing a novel $\pi$-extended carbon-rich backbone with $D_{6h}$ symmetry. These features would make them promising building blocks for metallo-supramolecular architectures with unique structural and optical properties. Further investigations using these ligands for the construction of finite supramolecular assemblies as well as infinite coordination networks are in progress.

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REFERENCES AND NOTES


