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

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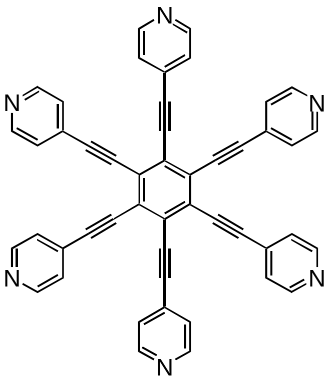
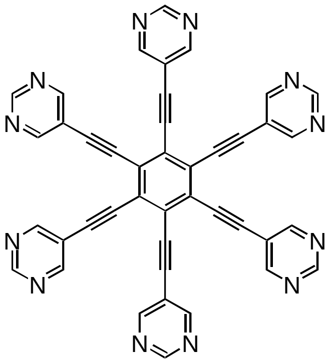
Abstract – Two new members of snowflake-shaped carbon-rich molecules possessing nitrogen-heterocycles as functional end groups, hexakis(4-pyridylethynyl)benzene (**1**) and hexakis(5-pyrimidylethynyl)benzene (**2**), have been prepared by six-fold Sonogashira cross-coupling reaction of hexabromobenzene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



1



2

Six-fold Pd-catalyzed coupling of hexabromobenzene with a large excess (30 equiv.) of 4-ethynylpyridine[10] in benzene/Et_3N (1:1) at 60 °C for 3 days in the presence of $PdCl_2(PPh_3)_2$ (10 mol%) and CuI (10 mol%) afforded **1** in 23% isolated yield, after extensive column chromatography on Al_2O_3 (eluted with $CHCl_3$) followed by preparative GPC. Similar Sonogashira coupling of hexabromobenzene with 5-ethynylpyrimidine[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 $CHCl_3$, CH_2Cl_2, or benzene. FD-MS spectrum clearly showed their molecular ion peaks as base peak (*m/z* 684 for **1** and 690 for **2**). The ^{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 ^{13}C NMR spectrum of **1**, which include resonances for two sp-carbons (δ 89.57 and 97.62) and four sp^2-carbons (δ 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 ^{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 ε 5.58), consistent with an effective π-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 (λ_{max} 340 nm) and emission (λ_{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.[12] To date, we have been unable to obtain their single crystals suitable for X-Ray diffraction studies.

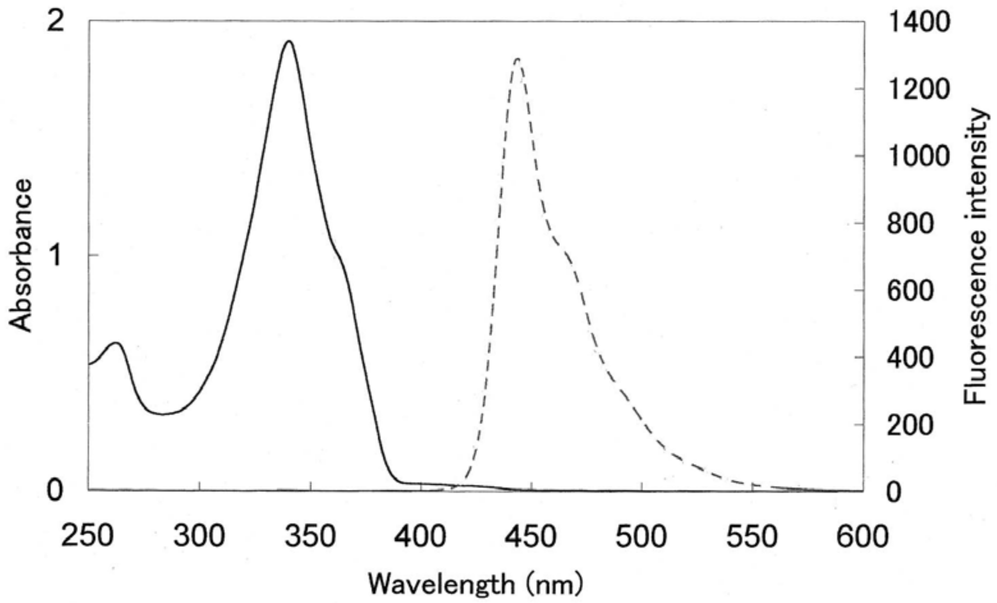


Figure 1. Absorption (solid lines) and emission (dashed lines) spectra of **1** in dichloromethane (5 x 10^{-6} M) at room temperature. Emission spectrum was obtained upon excitation at 340 nm.

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 π-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.[13,14] 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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