Construction of Conjugated Cyclic Molecules through Multiple Single Bond Formations

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Acenes that are larger than anthracene have been attractive and used as organic semiconductors. On the other hand, the smaller acenes such as naphthalene have been relatively unexplored. Herein, we report concise synthesis of [*n*]cyclo-2,7-naphthylenes ([*n*]CNAP), and their performance as bipolar carrier transport materials in organic light-emitting diode (OLED) devices.[1] Unique assembly of the large cyclic structures will be also discussed.

A series of [*n*]CNAP was synthesized by a nickel promoted coupling reaction of 2,7-dibromonaphthalene **1**, and three major congeners (*n* = 5, 6, and 7) were isolated in 1, 24, and 12% yield, respectively (Scheme 1). The reaction was readily scalable and isolation of abundant [6]-, and [7]CNAP was successfully achieved without recourse to chromatographic methods, which allowed the gram-scale preparation of [6]CNAP. The structures of all the isolated CNAP were established by single-crystal X-ray analysis and columnar alignments were found for all CNAP (Figure 1). Thermogravimetric analysis under nitrogen showed that CNAP decomposes at 539, 638, and 603˚C for [5]-, [6]-, and [7]CNAP, respectively, which showed the highly resistant characters of CNAP.

Scheme 1. Synthesis of [*n*]CNAP

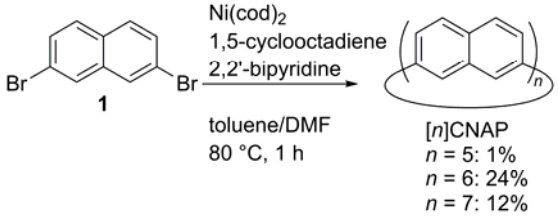
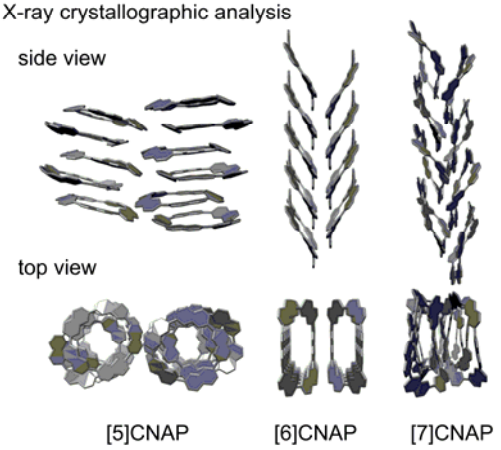


Figure1. Packing structures of [*n*]CNAP determined by X-ray crystallographic analysis



The carrier transport performance of [6]- and [7]CNAP was evaluated in phosphorescent OLED devices. The performance in the external quantum efficiency (EQE) was compared with the device with standard materials, α-NPD for hole transport layer (HTL) and Alq_3 for electron transport layer (ETL). The EQE of the devices with [6]- or [7]CNAP for either HTL or ETL were comparable or higher (10.5 to 13.2%) than the reference device with standard materials (10.7%). The EQE of devices with [6]- or [7]CNAP for both HTL and ETL was 7.9%, and 9.5%, respectively, which showed bipolar carrier transport ability of CNAP.

[1] Nakanishi, W.; Yoshioka, T.; Taka, H.; Xue, J. Y.; Kita, H.; Isobe, H. *Angew. Chem. Int. Ed.* **2011**, published online. (doi: 10.1002/anie.201101314.)