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Organic Materials

[*n*]Cyclo-2,7-naphthylenes: Synthesis and Isolation of Macrocyclic Aromatic Hydrocarbons having Bipolar Carrier Transport Ability**

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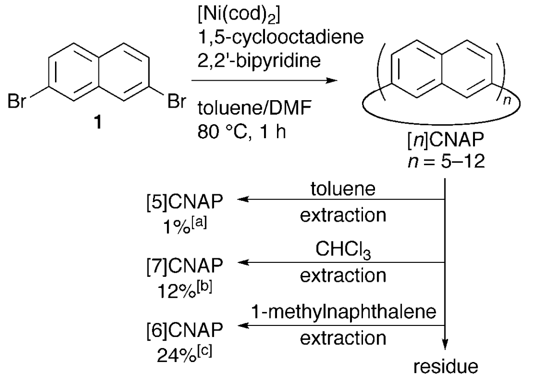
Owing to their potential application as organic semiconductors, acenes that are larger than anthracene have been attractive in providing promising motifs for the design and synthesis of organic materials.[1] In contrast, the smaller acenes, especially the smallest acene naphthalene, have been relatively unexplored, despite their superior chemical stability and intrinsic charge carrier transport ability. Unlike the larger acenes, naphthalene is an air-stable compound, and was among the first organic materials for which bipolar charge carrier mobility was revealed by the time-of-flight method.[2] The subsequent early studies on the conductance of naphthalene led to the fundamental development of organic electronic materials.[3] However, naphthalene has been a material of little practical merit, largely because the solid is thermally labile; as can be seen through its use as the volatile ingredient of mothballs. We envisaged that the macrocyclization of naphthalene molecules through single-bond linkages would be attractive for the design of organic electronic materials without perturbing transparency, chemical stability, or intrinsic mobility.[4] Herein, we report the concise synthesis of the cyclic aromatic hydrocarbons, [*n*]cyclo-2,7-naphthylenes ([*n*]CNAP), and their performance as bipolar carrier transport materials in organic light-emitting diode (OLED) devices. Pure hydrocarbon macrocycles without appended functionalities such as heteroatoms and side chains have been found to enhance thermal stability and bipolar carrier transport ability.

A series of [*n*]CNAPs was synthesized by a nickel-promoted coupling reaction of 2,7-dibromonaphthalene **1**,[5] and three major congeners ($n = 5$, 6, and 7) were isolated by utilizing their stark differences in solubility. A solution of **1** was added dropwise to a solution of [Ni(cod)$_2$], 1,5-cyclooctadiene, and 2,2′-bipyridine in a mixture of toluene and DMF to give a mixture of [*n*]CNAP (Scheme 1). After washing with hydrochloric acid, the toluene extracts from the crude material were separated from the insoluble materials. As shown in Figure S1 in the Supporting Information, analysis with matrix-assisted laser desorption/ionization (MALDI) mass spectra showed that the toluene extracts contained [5]CNAP as a predominant compound, and the insoluble materials contained a mixture of [*n*]CNAP ($n = 6$–12).[6] Isolation of relatively soluble [5]CNAP was accomplished by gel permeation chromatography to afford [5]CNAP in 1% yield from **1** (Figure S1c). After screening various solvents, we found that extraction of the insoluble materials with chloroform afforded [7]CNAP in 12% yield after subsequent recrystallization from *o*-dichlorobenzene (Figure S1e). Finally, [6]CNAP was isolated in 24% yield after extraction of the residue with 1-methylnaphthalene and subsequent recrystallization from nitrobenzene (Figure S1d). Purity of the isolated compounds was confirmed by HPLC, and residual solvents were quantified by elemental analysis. Considering the results of X-ray crystal structure analysis (see below), we think that the persistent solvent molecules may be captured in the macrocyclic opening of CNAP. The



Scheme 1. Synthesis and isolation of [*n*]CNAP. [a] Yield of isolated product after subsequent purification by GPC. [b] Yield of isolated product after subsequent purification by recrystallization from *o*-dichlorobenzene. [c] Yield of isolated product after subsequent purification by recrystallization from nitrobenzene. cod = 1,5-cyclooctadiene, DMF = *N*,*N*-dimethylformamide.

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synthesis and isolation procedure was concise enough to allow the gram-scale preparation of [6]CNAP. Other reactions, such as Ullmann-type coupling,[7] also gave [*n*]CNAP as the product; however the isolation of each compound was hampered by severe contamination of linear oligomeric naphthylenes.

The structures of all the isolated CNAP were established by single-crystal X-ray analysis.[8] Suitable crystals were obtained by crystallization induced by vapor diffusion of acetonitrile or benzene into a solution of [5]- or [7]CNAP in chloroform, respectively. X-ray quality crystals of [6]CNAP were obtained from an anthracene melt.[9] However, we defer any detailed discussion on the structure of [6]CNAP, because of the insufficient quality of data from the crystals. As shown in Figure 1, the cyclic arrays of naphthalene rings are large enough to accommodate small molecules. Thus, the longest distance between hydrogen atoms at the opening periphery measures 0.7 nm for [5]CNAP, 0.9 nm for [6]CNAP, and 1.1 nm for [7]CNAP. A molecule of acetonitrile or benzene was indeed located in the opening of [5]- and [7]CNAP, respectively. Although the macrocycles are not perfectly planar resulting from axial twists between the naphthyl units (Figure 1 a and S3), the overall structures retain a large diameter-to-thickness ratio by adopting mostly alternate twists to form macrocycles. We also noticed that the naphthyl rings are deformed in the planar structure. The average bend angles of the rings are 16° for [5]CNAP and 5° for [7]CNAP (Figure S3).[6,10] Calculations by the DFT method at the B3LYP/6-31G(d,p) level qualitatively reproduced the average bend angles (13° for [5]CNAP, 4° for [6]CNAP, and 3° for [7]CNAP), and the theoretical analysis of strain energy through hypothetical homodesmotic reactions indicated that a larger strain of 19 kcal mol^{-1} is forced on [5]CNAP (2 kcal mol^{-1} and 3 kcal mol^{-1} for [6]- and [7]CNAP, respectively). Such a strain on [5]CNAP may have resulted in the low yield of the compound and may have also affected the thermal stability (see below). Note, however, that the strain energy is much smaller than that of tubular aromatic hydrocarbons, [*n*]cycloparaphenylenes (ca. >30 kcal mol^{-1}).[11,12]

In the crystal packing, CNAP maintains ubiquitous contact motifs of acenes such as the π-stack and CH-π contacts. As shown in Figure 1 b, the intermolecular contacts result in unique columnar arrays of molecules. Having a bowl-like structure, [5]CNAP molecules form dimeric pairs in the column and are oriented nearly orthogonal with respect to the stacking axis. The larger macrocycles, on the other hand, have chair-like structures and are uniformly tilt-aligned in the columns. The largest [7]CNAP shows more frequent contacts between the molecules in the different columns.

Optical and thermal analysis of CNAP revealed properties that are favorable for optoelectronic applications. The UV/Vis spectra of CNAP in chloroform show the maximum absorption band in the UV region (271, 277, and 279 nm for [5]-, [6]-, and [7]CNAP, respectively), with broad tails reaching up to 350 nm. Thus, preserving the characteristic absorption of naphthalene (Figure S4),[6] CNAPs are transparent in the visible light region. Thermal analysis of CNAP solids by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed their highly resistant characters. An endothermic peak of phase transition was detected by DSC for [5]CNAP at 380 °C but none were detected for [6]- and [7]CNAP up to 400 °C. Analysis by TGA under nitrogen showed that the persistent solvent molecules evaporate far above their boiling points (ca. 350 °C) and that CNAP

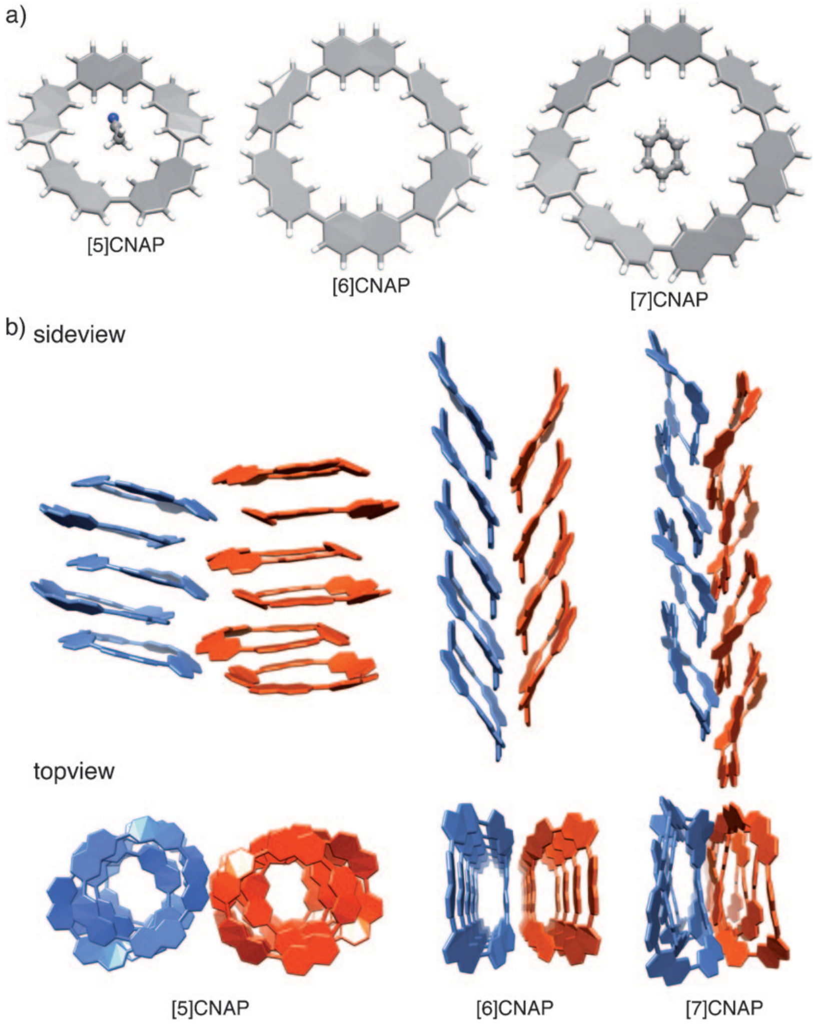

Figure 1. Structures of [*n*]CNAP ($n = 5, 6, 7$) determined by X-ray crystallographic analysis. a) Molecular structures with a representative geometry. To clarify the relative orientation of the naphthyl rings, structures of CNAP are shown in the tube models with filled rings. The solvent molecules in the opening are shown in ball-and-stick models (acetonitrile in [5]CNAP and benzene in [7]CNAP). C gray, H white, N blue. b) Packing structures. Molecules in neighboring columns are different colors. Solvent molecules and hydrogen atoms are omitted for clarity.

decomposes at 539, 638, and 603 °C for [5]-, [6]-, and [7]CNAP, respectively (T_d of $<5\%$ weight loss). Although [5]CNAP decomposes at a relatively lower temperature, most likely as a result of the larger strain energy, their decomposition temperatures are much higher than large acenes such as pentacene (339 °C) and rival those of fullerenes bearing the same numbers of carbon atoms and π-electrons (ca. 600 °C).[13,14] Furthermore, [6]- and [7]CNAP were also oxidatively stable and decomposed at 522 °C, even in air.

Theoretical calculations showed that the large rigid macrocyclic structures, albeit nonplanar, allow effective distribution of charge and spin of radical ions.[4,15] The reorganization energies through the carrier transport for [5]-, [6]-, and [7]CNAP were thus estimated as 88, 66, and 53 meV, respectively, for the hole transport and 132, 134, and 113 meV, respectively, for the electron transport (Table S5). The results show that the CNAPs have a reorganization energy that is much smaller than that of the parent naphthalene (186 meV for hole and 261 meV for electron) and an even smaller energy for the hole transport than that of pentacene (100 meV for hole and 125 meV for electron).[16] The analysis of the charge and spin distribution in radical ions indicated that they are well-delocalized over the macrocyclic structures (Figure S5 and S6). In addition, the calculations revealed the pseudodegenerate frontier molecular orbitals (Figure S7), which may allow effective overlapping of the orbitals between neighboring molecules with various intermolecular contacts.

Finally, the carrier transport performance of CNAP was evaluated with the abundant compounds, [6]- and [7]CNAP, in standard phosphorescent OLED devices with the following configurations:[4,17] ITO (indium tin oxide; 100 nm)/PEDOT:PSS (poly(ethylenedioxy)thiophene:polystyrene sulfonate; 20 nm)/HTL (hole transport layer, 20 nm)/CBP:[Ir(ppy)$_3$, 6 %] (4,4′-*N*,*N*′-dicarbazole biphenyl:tris(2-phenylpyridine)iridium; 40 nm)/BCP (bathocuproine, 10 nm)]/ETL (electron transport layer, 30 nm)/LiF (0.5 nm)/Al (110 nm; see also Figure S8 and S9). The macrocycles are both thermally stable and discrete molecular entity; thus they can be deposited in HTL and/or ETL by vacuum deposition. The performance of these macrocycles as carrier transport materials were compared with devices with *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD) for HTL and with tris(8-hydroxyquinoline)aluminum (Alq$_3$) for ETL. The representative characteristics of the driving voltage (DV) and the external quantum efficiency (EQE) were compared as typical measures of injection efficiency and transport ability of carriers (Table 1 and Figure S10). The green phosphorescence from the guest iridium-emitter was observed in all the devices, and the carrier transport by CNAP was confirmed. The performance of CNAP devices B–E in EQE was comparable or higher than the reference devices with standard materials such as α-NPD or Alq$_3$, and the device E with [7]CNAP in ETL afforded the highest value of 13.2 %. The increase in DV of CNAP devices is most likely a result of the modest efficiency of the carrier injection to CNAP layers, which may have resulted in the lower performance of devices F and G. Importantly, this study adds a very rare example of macrocyclic organic semiconductors to the literature,[18,19] and further studies including both experimental and theoretical investigations would be interesting to fully understand the detailed electronic behavior of these unique cyclic systems.

Table 1: Device performance of OLED at a constant current density of 2.5 mA cm^{-2}.

Device	HTL	ETL	DV[a] [V]	EQE[b] [%]
A	α-NPD	Alq$_3$	6.6	10.7
B	[6]CNAP	Alq$_3$	7.5	12.6
C	[7]CNAP	Alq$_3$	8.0	12.7
D	α-NPD	[6]CNAP	6.4	10.5
E	α-NPD	[7]CNAP	8.5	13.2
F	[6]CNAP	[6]CNAP	11.6	7.9
G	[7]CNAP	[7]CNAP	12.1	9.5

[a] Driving voltage. [b] External quantum efficiency.

In summary, we have developed a concise method of the synthesis for new macrocyclic aromatic hydrocarbons, [*n*]CNAP, by a one-pot procedure from readily available small acenes. The isolation of two abundant CNAPs was successfully achieved without recourse to formidable chromatographic methods, which allowed the gram-scale preparation of [6]CNAP. The finding of bipolar electronic materials from pure hydrocarbon macrocycles composed solely of sp^2-hybridized carbon atoms and hydrogen atoms shows the viability of molecular design without introduction of profound extension of π-conjugation or electronic tunings with heteroatoms. The macrocyclic electronic materials that bear oligomeric π-systems without any termini lie between small molecules and polymers and may stimulate the experimental and theoretical exploration of this series in materials. Development of this series should be further facilitated by an ever-increasing variety of aryl–aryl coupling reactions. The nanoscale opening of the macrocycles composed of sp^2-hybridized carbon atoms in 25-, 30-, and 35-membered rings may also serve as a structural model for porous graphenes,[20] and unique properties such as permeability would be an important subject for future studies. The fine electronic tunings of CNAP through encapsulation of active components in the opening or covalent modifications with substituents, for example, is of great interest for the development of organic semiconductors with specific properties and is currently under investigations.

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