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# Convergent synthesis of hexameric naphthylene macrocycles with dicarboxylic imide appendages



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# ABSTRACT

A series of macrocyclic compounds, [6]cyclo-2,7-naphthylenes ([6]CNAP), composed of six naphthylene units are synthesized through a [3+3] convergent route in good to moderate yields. The synthesis method allowed for the introduction of dicarboxylic imide moieties to the naphthylene units. Crystallographic analysis of a derivative possessing four imide groups showed a trimeric columnar assembly with an alignment of nanometer-sized macrocyclic pores.

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Conjugated macrocycles are an interesting class of compounds, not only because of the growing interest as organic materials but also because of their discrete and  $\pi$ -electron rich structures that tolerate chemical modifications.<sup>1,2</sup> The advent of powerful biaryl coupling methods further facilitated the recent growth in the repertoires of arylene macrocyclic skeletons with direct aryl-aryl connections, which provided interesting cyclic arrays of aromatic units with sp<sup>2</sup>-networks. Unlike phenylene components for the arylene macrocycles,<sup>3</sup> however, naphthylene components have not been exploited until recently, and only two types of cyclonaphthylenes are so far available in the macrocycle repertoires. The first example was planar cyclo-2,7-naphthylenes (CNAP),<sup>4</sup> and the second example was pseudo-tubular cyclo-1,4-naphthylene.<sup>5</sup> The former cyclonaphthylenes, especially hexameric [6]CNAP with  $60\pi$ -electrons, revealed unique properties of naphthylene macrocycles such as bipolar charge transporting ability in organic light emitting devices (OLED) and thermal stability reaching over 600 °C. Along with these unique properties, the availability of various naphthalene bases prompted us to explore the structural variations of [6]CNAP, and we herein report the convergent synthesis of [6]CNAP bearing dicarboxylic imide appendages (hereafter denoted as  $i_n$ -[6]CNAP where *n* represents the numbers of the imide groups). Convergent [3+3] assembly with ternaphthyl units allowed us to synthesize the representative congeners of new i<sub>n</sub>-

[6]CNAP derivatives. An interesting access to unique molecular assembly has been observed to align 30-membered nanosized rings in stacking macrocycles.

Departing from the one-pot,  $[1 \times 6]$  synthesis of unsubstituted i<sub>0</sub>-[6]CNAP with a monomeric 2,7-dibromonaphthalene unit,<sup>4</sup> we developed a new convergent synthesis method with trimeric ternaphthyl units. The new method allowed us to synthesize a series of i<sub>n</sub>-[6]CNAP in good to moderate yields. We first synthesized the fully functionalized naphthylene macrocyle. The coupling reaction of dibrominated ternaphtyl 1 proceeded effectively with Ni complex to afford 1,2,3,4,5,6-i<sub>6</sub>-[6]CNAP in 75% yield (Scheme 1). The reaction was concise enough to be executed on a gram scale with slightly lowered yield (62%).<sup>6</sup>

The efficacy of the Ni-promoted convergent strategy depended on the structures of the trimer, and we only detected a trace amount of 1,2,4,5-i<sub>4</sub>-[6]CNAP from the Ni-promoted coupling of the corresponding dibrominated ternaphthyl. We found, however, that another stepwise coupling method using borylated ternaphthyl and PtCl<sub>2</sub>(cod) was applicable to this congener<sup>7,8</sup> and obtained 1,2,4,5-i<sub>4</sub>-[6]CNAP in 33% yield from diborylated ternaphthyl **2** via Pt-complex formation and subsequent reductive elimination. A possible tetrameric intermediate comprising four Pt atoms and twelve naphthyl units was not detected from this reaction, and the absence is interesting in comparison with the Pt-mediated production of tetramers with rigid arylenes.<sup>7</sup> The Ni-promoted method was applicable to the synthesis of 1,4-i<sub>2</sub>-[6]CNAP, and we obtained the compound in 24% yield from the [3+3] macrocyclization of dibromide **3**. The notable efficiency of i<sub>6</sub>-[6]CNAP macrocyclization is of mechanistic interest and should be further examined in detail in due course.





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Scheme 1. [3+3] Convergent synthesis of in-[6]CNAP.

Table 1	
Solubilities of $i_n$ -[6]CNAP in CHCl <sub>3</sub> at 25 °C	

	i <sub>6</sub> -[6]CNAP	i <sub>4</sub> -[6]CNAP	i <sub>2</sub> -[6]CNAP	i <sub>0</sub> -[6]CNAP
In M In mg/L	$\begin{array}{c} 7.6\times10^{-2}\\ 1.6\times10^5\end{array}$	$\begin{array}{c} 2.0\times10^{-3}\\ 3.3\times10^3 \end{array}$	$1.5  imes 10^{-5}$ 19	$\begin{array}{c} 2.5\times10^{-6}\\ 2.0\end{array}$

We found that the convergent synthesis was also beneficial for the isolation of the macrocycles. When we synthesized unsubstituted congener, i<sub>0</sub>-[6]CNAP, through the convergent route, the compound was isolated in 19% yield. Although the yield was slightly lower than that of the previous one-pot  $[1 \times 6]$  assembly route (24%), the isolation of the compound was more cost-effective for the convergent route. Thus, although the one-pot  $[1 \times 6]$ assembly route required a large amount of expensive solvents for the isolation, the convergent [3+3] route afforded the desired compound simply through a single set of extraction of [9]CNAP with DMF and a single recrystallization step from nitrobenzene.<sup>9</sup>

The introduction of imide groups with diisopropylphenyl (DIP) moieties dramatically improved the solubility of the macrocycles. Thus, the solubilities of  $i_n$ -[6]CNAP increased with the increase in the numbers of the imide substituents to record  $7.6 \times 10^{-2}$ ,  $2.0 \times 10^{-3}$ ,  $1.5 \times 10^{-5}$ , and  $2.5 \times 10^{-6}$  M for n = 6, 4, 2, and 0 in chloroform, respectively (Table 1). The improvement of the solubility is beneficial for the future development of the macrocycles that severely suffered from the low solubility in the absence of the imide appendages.<sup>4</sup>

Among the new macrocycles, we obtained a single crystal of 1,2,4,5-i<sub>4</sub>-[6]CNAP suitable for X-ray diffraction analysis and found few structural features different from the unsubstituted congener.<sup>10</sup> The recrystallization of this compound also reaped a benefit from the improved solubility and did not require a peculiar anthracene melt as the recrystallization solvent.<sup>4</sup> The molecules formed a unique trimeric assembly, and the structures are shown in Figure 1 with mean planes for the central 30-membered ring colored in



**Figure 1.** Structures of  $i_0$ - and 1,2,4,5- $i_4$ -[6]CNAP from X-ray diffraction analysis. Transparent orange planes represent the mean plane of the central 30-membered ring. Color of atoms are as follows: Carbon = gray, hydrogen = white, nitrogen = blue, oxygen = red. (a) Molecular structure of  $i_0$ -[6]CNAP. Angles show the dihedral angles at the single-bond linkages. (b) Molecular structures of 1,2,4,5- $i_4$ -[6]CNAP from Ref.4. Angles show the dihedral angles at the single-bond linkages. (c) Packing structure of tacking trimer of 1,2,4,5- $i_4$ -[6]CNAP in space-filling models. (d) Packing structure of 1,2,4,5- $i_4$ -[6]CNAP in space-filling models showing the positions of neighboring trimers.

orange.<sup>11</sup> As shown in Figure 1a, the original i<sub>0</sub>-[6]CNAP possessed an alternate arrangement of the dihedral angles at the single-bond linkages, which resulted in the alternate orientations of the naphthylene units.<sup>4</sup> The alternate orientation was maintained in the molecules of i<sub>4</sub>-[6]CNAP at the top and the bottom of the trimeric assembly, but the average dihedral angle was shrunk to ~20° from ~30° of i<sub>0</sub>-[6]CNAP (Fig. 1b). The planarization was more profound for the molecule in the middle of the trimer: The average dihedral angle was 7°, and the alternate twist diminished.

Along with the deformation in the molecular structures, we noted a stark difference in the packing structures of i<sub>4</sub>-[6]CNAP and  $i_0$ -[6]CNAP. The packing motif of the unsubstituted congener was a ubiquitous herringbone type despite the unique macrocyclic structure.<sup>4</sup> On the other hand, the basic packing motif was a stacking type for  $i_4$ -[6]CNAP. Thus, the three molecules were assembled in a stacking manner, and, as shown in Figure 1c, the mean planes of the 30-membered rings were aligned parallel to each other. The distance of the mean planes at the top and the bottom measured 6.82 Å, which showed the intimate van der Waals contact of the macrocyclic molecules. The electrostatic complementarity between unsubstituted naphthylene units and imide-appended naphthylene units may have played a key role for the stacking assembly,<sup>12</sup> and the central 30-membered rings of 0.9-nm diameter were aligned to form a nanopore in the trimeric assembly. The stacking, however, ended at the three layers, and the nanopore was capped by the DIP groups of the neighboring trimers (Fig. 1d).<sup>13</sup> The stacking is terminated, most likely because of the steric congestions of the bulky groups at the peripheral of the macrocycle: Twelve DIP groups in the stack left no space available for another four DIP groups to intrude. Designing the multi-layered nanoporous materials from the present macrocycles is of great interest, for instance, through devising peripheral functional groups<sup>14</sup> and will be explored in due course. Preliminary investigations with  $i_2$ -[6]CNAP afforded needle-like crystals, which may indicate the anisotropic crystal growth with  $i_2$ -congeners with higher structural complementarity for stacking.

In summary, we have developed a convergent method for the synthesis of a series of naphthylene macrocycles. As the convergent method is versatile enough to accept cross-coupling reactions for the final [3+3] assembly, further extensions will be reported in due course. The possibility of columnar assembly of the macrocycles with a nanosized ring and  $60\pi$ -electrons is an interesting subject to be explored by devising rational molecular designs in near future.

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# Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.07. 025.

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