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Ni(COD)$_2$ coupling of 3,6-dibromocarbazoles as a route to all-carbazole shape persistent macrocycles

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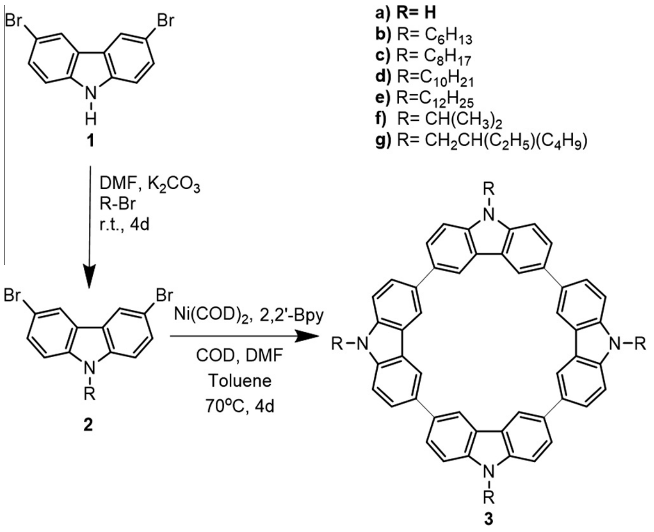
ABSTRACT

The number of applications for carbon-based materials has experienced tremendous growth over the last decade arising from their low toxicity, straight-forward chemical modification, and interesting electronic properties. Among these materials, self-assembled structures based on shape persistent macrocycles are perhaps the most exciting as they offer a means to prepare a wide range of morphologies through reversible assembly of these molecular precursors. In this letter, we report on the preparation of a novel family of all-carbazole shape persistent macrocycles through the simple single-step reaction of the corresponding 3,6-dibromocarbazoles over Ni(COD)$_2$. The resultant macrocycles display optical properties characteristic of the parent *N*-alkyl polycarbazoles, with quantum yields ranging from 11% up to 21% suggesting that certain substituents induce the formation of highly emissive aggregates, which could potentially provide a mechanism for the preparation of functional self-assembled nanomaterials.

In recent years shape persistent macrocycles (SPMs) have been the subject of intense research because of their useful properties, and their propensity to self-assemble into interesting micro and nano-scale structures.[1–5] While molecules based upon a carbazole substructure have found widespread application in electronics,[6] sensing,[7–9] and biological applications,[10,11] relatively few examples of carbazole-based SPMs have been reported.[12–16] Notable success has been achieved with arylene-ethynylene and carbazyl-ethynylene monomers that readily react via precipitation driven alkyne metathesis to produce macrocycles.[2,5,17,18] This methodology allows control over macrocycle size and shape, and has facilitated the development of a new family of compounds with a rigid core conformation that self-assemble into a variety of supramolecular structures.[3,13,19]

A brief report published in 2003 suggested the polymerization of *N*-alkylated 3,6-dibromocarbazole yielded substantial quantities of cyclic oligomers when the reactions were performed under dilute conditions.[15] Given recent interest in shape-persistent macrocycles and the straightforward *N*-alkyl functionalization and C–C coupling of 3,6-dibromocarbazole, we have prepared a family of all-carbazole cyclic tetramers. The tetramers were prepared bearing *N*-alkyl solubilizing side-groups of varied chain length and steric bulk with the intent of investigating their opto-electronic properties.

Alkylated carbazole monomers (**2a–g**, Scheme 1) were prepared by straightforward room temperature deprotonation of 3,6-dibromocarbazole followed by reaction with appropriate alkyl halides to produce *N*-alkylated 3,6-dibromocarbazoles with alkyl groups ranging from 3 to 12 carbons in length (Table 1).[20] The alkylated



Scheme 1. Synthetic scheme used to prepare compounds **2b–g** and **3a–g**.

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Table 1
Preparation of 3,6-dibromo-*N*-alkyl carbazoles and their corresponding tetramers

R	Monomer	Monomer yield %	Tetramer	Tetramer yield %
H	**1**	–	**3a**	67[a]
C_6H_{13}	**2b**	43	**3b**	54
C_8H_{17}	**2c**	41	**3c**	63
$C_{10}H_{21}$	**2d**	19	**3d**	72
$C_{12}H_{25}$	**2e**	30	**3e**	60
$CH(CH_3)_2$	**2f**	52	**3f**	51
$CH_2CH(C_2H_5)C_4H_9$	**2g**	33	**3g**	47

[a] **3a** reacts under the acidic conditions used to isolate the other compounds, as such a different purification method was employed.

products were isolated from unreacted carbazole using column chromatography with the exceptions of compounds **2d** and **2e**, which were readily recrystallized from ethanol.

Compounds **1** and **2b**–**2g** were subsequently coupled using a variation of a literature procedure previously employed to prepare tetramer **3g** (see Table 1).[15] Briefly, the desired 3,6-dibromocarbazole monomer was coupled over Ni(Bpy)(COD) and quenched in methanol to yield crude products as green-gray solids. The target compounds, **3a**–**g**, were extracted and purified using one of two methods depending on the substitution at *N*. The alkyl substituted **3b**–**g** were purified by adding 1 M HCl and acetone to the crude product in methanol in a 1:1:1 ratio followed by extraction into toluene. This process removed the majority of the unreacted catalyst, and Ni byproducts formed during the coupling reaction. The cyclic compounds were then isolated from the crude product mixture by extraction into hot acetone.

The alkyl-free tetramer **3a** readily oxidizes to produce the green, insoluble quinoid form under acidic conditions making the purification procedure described above ineffective.[21] To avoid product decomposition during purification, we turned to soxhlet extraction; first washing the crude product with methanol, then acetone. The product **3a** was then obtained from the crude mixture by extracting the cyclic products from insoluble impurities using cold THF. Following evaporation of the THF, residual Ni impurities were removed from the product by suspending the brown solid in a 3% solution of sodium dimethylglyoximate (NaDMG) in ethanol, followed by filtration to remove the precipitated $Ni(DMG)_2$. The desired product, **3a**, was recovered as a glassy tan solid in 67% yield.

Purified **3a** was evaluated using MALDI-TOF and showed a single high-intensity peak consistent with 4 linked monomers (Fig. 1a). Further analysis using high-resolution MALDI-FTICR (Fig. 1b) showed the fragment of highest intensity occurred at $m/z = 660.231$ with an isotopic distribution pattern corresponding to that predicted for the expected cyclic structure. Of important note, no evidence of an isotopic distribution pattern centered at $m/z = 662.2$, as expected for the linear tetramer, was detected (Fig. 1b). Consistent with the present MS results, and the proposal of a cyclic structure, the ^1H NMR spectrum showed resonances readily assigned to protons in the 4 and 5 positions of the carbazole structural units that are shifted downfield to 8.51 ppm (Fig. 1c).[15] Further discounting the presence of the linear tetramer, no resonances at 8.04 ppm, corresponding to terminal protons on linear oligomers, were detected at the sensitivity of ^1H NMR technique.[22]

MALDI-TOF spectrometry confirmed the solids isolated from the extraction of the crude alkyl substituted products were also primarily cyclic tetramers (**3b**–**3g**, Table 1). The spectra revealed

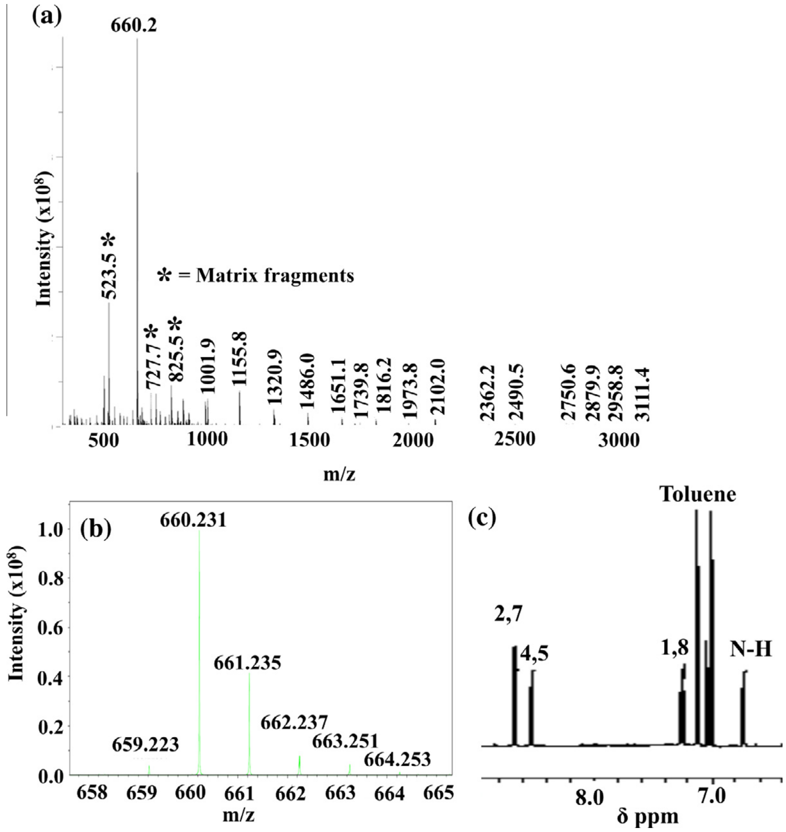

Figure 1. (a) Low resolution MALDI-TOF spectrum and (b) high resolution MALDI-FTICR trace obtained for **3a** showing the mass-to-charge ratio and isotopic distribution of the parent ion. (c) The aromatic region of the ^1H NMR spectrum of **3a** recorded in toluene-d8 including the proton NMR assignment.

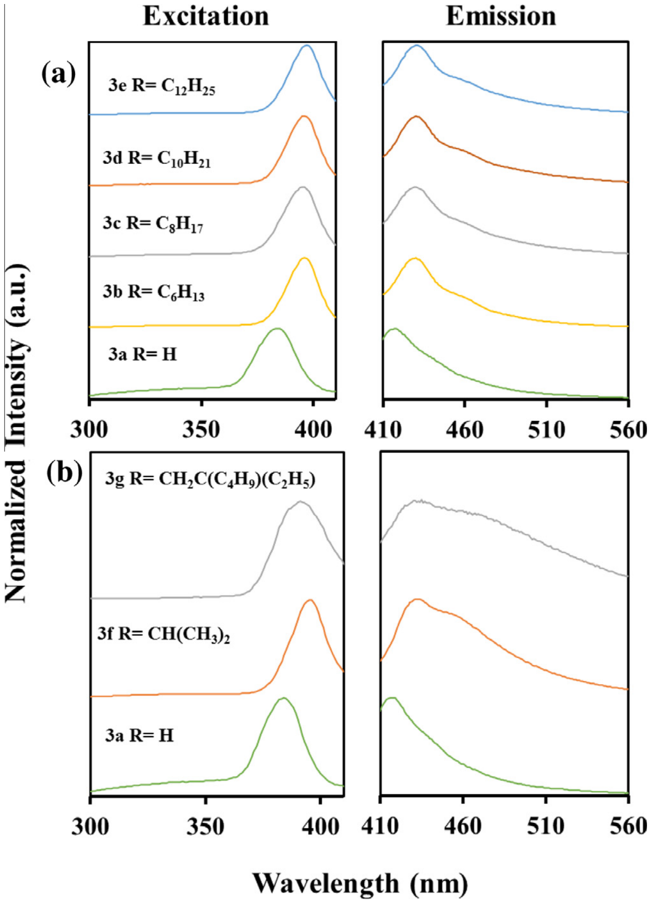

Figure 2. PL and PLE spectra of the tetramers **3a**–**g** recorded in THF solution for tetramers with (a) linear R groups and (b) branched R groups.

peaks of high intensity at *m*/*z* that correspond to the expected molecular ion [M+] of the target cyclic tetramer (spectra are provided in ESI). High resolution MALDI-FTICR further confirmed the *m*/*z* ratio was consistent with the molecular formulas of **3b**–**g**. In addition, inspection of the ^{1}H NMR spectra shows the resonances of protons at the 2,7 and 4,5 positions are shifted downfield relative to the monomers; similar to what was observed in the proton NMR spectrum of **3a** discussed above. Based upon these data we conclude **3b**–**g** are primarily cyclic tetramers.

Given the central role of optical properties in many applications of carbazole-based materials, the excitation (PLE) and emission (PL) spectra of THF solutions of **3a**–**g** were evaluated (Fig. 2). Qualitative inspection of the spectra reveals two trends; one trend relating to the length of alkyl chains in tetramers with linear R groups (Fig. 2a), and a second relating to the length of the pendant group in samples prepared with branched R groups (Fig. 2b).

The PLE and PL spectra of macrocycles bearing linear R groups (i.e., **3b**–**3e**) are very similar, with nearly identical excitation and emission maxima and similar definition of vibronic features. The spectroscopic similarities indicate that **3b**–**3e** are experiencing similar chemical environments. This observation is not unexpected given the optical properties of the tetramers originate from the all-carbazole backbone.

In contrast, PL spectra of **3f** and **3g** are broad with more pronounced vibronic features. It is reasonable these observations are a consequence of fixed molecular conformations in solution,[23] possibly the result of molecular aggregation which induces broadening of spectral signatures.[24–26] This aggregation effect is also observed in the PL spectrum of **3a**, which bears no solubilizing alkyl substituent. In this case, the broad PL is accompanied by a blue-shift of the PLE maximum which is consistent with the presence of H-aggregates (Table 2).[27]

Table 2
Relevant optical properties of the tetramers **3a**–**g** determined in THF. λ_{EM} and λ_{EX} are the maximum PL and PLE wavelengths, respectively

Compound	R	λ_{EX} (nm)	λ_{EM}(nm)	Φ_{fl}
3a	H	384	417	15
3b	C_6H_{13}	396	430	13
3c	C_8H_{17}	395	430	11
3d	$C_{10}H_{21}$	396	430	12
3e	$C_{12}H_{25}$	397	431	12
3f	$CH(CH_3)_2$	395	432	12
3g	$CH_2CH(C_2H_5)C_4H_9$	391	430	21

To further investigate the presence/influence of stable molecular aggregates and the origin of the broad PL spectrum of **3a** and **3g**, PL quantum yields (i.e., Φ_{fl}) were evaluated for all tetramers (Table 2). The Φ_{fl} measured for **3g** is 21%, greater than those noted for the majority of the alkyl-substituted tetramers studied, and of the same magnitude as those observed for macrocycles with short alkyl chains (i.e., Φ_f = 15%, 13%, and 12% for **3a**, **3b**, and **3f**, respectively). It is likely that the influence of the relatively large 2-ethylhexyl group is driving the aggregation process, which in turn restricts twisting motions between carbazole units.[28,29] This effect could be responsible for the large quantum yield of **3g** when dissolved in THF when compared to both the other tetramers prepared, and the literature values measured for linear carbazole oligomers (Table 2).[30–32] The source of these observations, including the influence of solvent polarity on the assembly of the molecules into unique nanostructures, and its impact on optical properties of the macrocycles, is the subject of ongoing investigation.

In conclusion, we have prepared a novel family of carbazole-based SPMs bearing pendant alkyl chains of varied lengths by coupling the corresponding 3,6-dibromocarbazoles using Ni(COD)$_2$. Subsequent evaluation of the optical properties of the tetramers indicates the PL spectra of carbazole macrocycles depends upon the nature of the *N*-alkyl substituent and is consistent with substituent-dependent aggregation. These findings suggest the macrocycles prepared herein could find use as building-blocks in highly emissive assemblies.

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Supplementary data

Supplementary data (details of the synthesis, and quantum yield determination, as well as ^{1}H NMR, ^{13}C NMR, MALDI TOF and MALDI FTICR traces are provided online) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.08.048.

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