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Facile synthesis of novel monodisperse linear 3,9-linked oligocarbazoles

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Abstract—Novel monodisperse linear 3,9-linked oligocarbazoles (OCAs) were prepared stepwise using Ullmann coupling reaction in seal-tubes. The resulting OCAs were soluble in common organic solvents. The UV–vis spectra of OCAs exhibited small red shift and their intensities increased linearly with the increase of the carbazole moieties, suggesting that no intramolecular π -interactions appeared at \leq 8-mer. All the OCAs gave strong fluorescence and it was found that the conjugated degree of linear OCAs would be saturated when the number of carbazole units reaches four. © 2005 Elsevier Ltd. All rights reserved.

Monodisperse, well-defined π -conjugated oligomers have recently attracted much attention due to their potential applications in electronic or photonic devices,¹ such as organic light-emitting diodes (OLEDs),² solar cells,³ field-effect transistors (FETs),⁴ etc. They are especially, ideal models for the evaluation of structure– functionality relationship of macromolecules.^{1b,2c,5–10} Nowadays, many oligomers with special properties have been synthesized such as oligo(benzyl ether)s,⁵ oligofluorenes,⁶ oligo(*p*-phenylene)s,⁷ oligothiophenes,⁸ oligonaphthalenes,⁹ oligo(*m*-aniline)s,¹⁰ etc.

The design and synthesis of carbazole-based oligomers is also attractive because of their applications in photoconductors, charge-transporting and emitting materials in OLEDs. Among them, most carbazole units are coupled via 2,7-positions or 3,6-positions.¹¹ It was well known that the oligocarbazoles (OCAs) may show different conformations if the carbazole units are linked at different positions, leading to their unique photoelectron properties.^{11a,g} Up to now, no monodisperse linear OCAs linked via 3,9-positions have been reported. As it is known that *N*-arylation of carbazole can also be realized by Pd-catalyzed reactions under milder conditions, but it is difficult to handle and the catalyst as well as the ligand are expensive.¹² Herein, we report that the Ullmann coupling reactions take place in seal-tubes in which the solvents with lower boiling point can be selected as reaction medium and the airtight system saturated with N_2 can avoid the oxidative degradation, thereby facilitating the operations. In this letter, we present a repetitive synthetic strategy for preparation of a series of linear OCAs linked through 3,9-positions, in which the formation of C–N bond will be a benefit for the electronic energy transition between carbazole units. It was found that these OCAs showed strong fluorescence emission.

The synthetic routes for the desired OCAs are illustrated in Scheme 1. They were prepared stepwise employing Ullmann coupling reactions. First, 3-iodo-9-tosylcarbazole was prepared according to the literature,^{11d,13} which was coupled with carbazole to yield compound 2 via Ullmann coupling. Dicarbazole 4 was obtained from 3, which was the deprotected product of 2. Compound 5 is key for us to extend the carbazole units of the linear OCAs, which was synthesized from compound 2 through iodination. In the beginning, we would like to couple 3-bromocarbazole¹⁴ with 3-iodo-9-tosylcarbazole using 1,10-phenanthroline, CuCl as catalyst to synthesize compound 5.¹⁵ But the results showed that the selectivity for the coupling reaction between C-Br and C-I bond to carbazole was poor, no pure compound 5 was obtained. Cuprous-catalyzed Ullmann coupling

Keywords: Carbazoles; Oligomers; Ullmann coupling; Iodination; Seal-tube; Fluorescence.

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Scheme 1. Synthesis of OCAs. Reagents and conditions: (a) Cu₂O, DMAc, 170 °C, 24 h; (b) KOH, DMSO, THF, H₂O, reflux, 4 h; (c) KI, KIO₃, AcOH, 80 °C, 4 h; (d) (i) NaH (60%), DMF, 0 °C, 20 min, (ii) benzyl chloride, rt, 1 h.

reactions were then employed to achieve the growth of OCAs due to its convenience to use and high yields. Compound 7 was readily prepared via cross-coupling of 3 and 5, followed by a cleavage with DMSO, THF, and KOH/H₂O.^{11c,d} Repetitive cross-coupling and deprotection reactions finally gave octamer 11, a monodisperse well-defined linear OCAs. It was found that the reactivities of N–H in carbazole moieties would decrease upon the increase of the number of carbazoles in OCAs.¹¹ For example, the Ullmann coupling reaction between carbazole and 3-iodo-9-tosylcarbazole could be carried out by employing Cu₂O, DMAc at 160 °C for 24 h, but the coupling reaction of compounds 6 and 9 did not occur under this condition even after 2 days. When the temperature increased to 200 °C, the reaction did take place within 24 h as we hoped. All compounds (from compounds 2 to 11) were characterized strictly with ¹H NMR spectroscopy and MALDI/ TOF-MS measurements. They have good solubility in common solvents, including THF, dichloromethane, chloroform, toluene, ethyl acetate, etc.

The UV-vis spectra of monomer 1, dimer 4, tetramer 8, hexamer 10, and octamer 11 in THF are shown in Figure 1. We observed that the absorption bands of OCAs exhibited a small red shift and their intensities increased linearly with the increase of the carbazole moieties compared with that of 1. We deduced this phenomenon to the large torsion angle between the cabazoles, just as the structure of binaphthalene derivatives. The molar



Figure 1. UV-vis absorption spectra for OCAs in THF solution.

extinction coefficient at the absorption maximum (243 nm; 1×10^{-5} M) increased linearly depending on the oligomer length from monomer to octamer, while no deviations from the slope were observed at ≤ 8 -mer (Fig. 2). In this concentration, the intermolecular association was negligible because each oligomer obeyed Beer's law, so that if there were any deviations from the slope, we can deduce the presence of intramolecular π -interactions. Therefore, no intramolecular π -interactions occurred for the OCAs at ≤ 8 -mer. Figure 3 shows the photoluminescence (PL) spectra of 9-benzylcarbazole and the linear OCAs in dilute solution $(1 \times 10^{-5} \text{ M})$. We found that all the compounds gave strong fluorescent peaks, and the emission bands for OCAs red-shifted significantly from that of monomer 1. For example, 9-benzylcarbazole showed two isolated emission bands at 347 and 363 nm, while OCAs gave asymmetric single peaks around 380 nm except for dicarbazole 4, whose emission was at ca. 375 nm with a shoulder, suggesting that the conjugated degree of OCAs would be enlarged with the increase of carbazole moieties until the number of carbazoles reached four.¹⁶ The fluorescent quantum yields are listed in Table 1.¹⁷ It shows that the fluorescent efficiency decreases rapidly from monomer, to dimer, and up to tetramer OCAs, where the fluorescent efficiency appears to reach a limit.

We have established a facile synthetic strategy for a series of novel monodisperse well-defined linear oligocarbazoles linked through 3,9-positions. The key to the



Figure 2. Plotting between the molar extinction coefficient (at 243 nm) and the degree of oligomerization for OCAs.



Figure 3. Emission spectra of OCAs in THF solution (excited at 290 nm).

Table 1. Fluorescence quantum yields ($\Phi_{\rm F}$) of OCAs in THF^a

Samples	Monomer	Dimer	Tetramer	Hexamer	Octamer
	1	4	8	10	11
$arPhi_{ m F}$	0.49	0.25	0.24	0.14	0.24

^a The fluorescence quantum yields were determined against quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 0.546$) as the standard.

synthesis of oligocarbazoles was the use of a repeating unit 5, which was prepared from 2 with iodination. In the seal-tube, the Ullmann coupling reaction took place using Cu₂O as a catalyst in DMAc, which can be easily removed afterwards. Besides, seal-tube can also avoid the byproducts from oxidation and make the operations easy to handle. All the OCAs gave strong fluorescence and we found that the conjugated degree would be saturated when the number of carbazole units reaches four and no intramolecular π -interactions occurred for the OCAs at \leq 8-mer. They were soluble in common organic solvents.

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Supplementary data

Experimental procedures, characterizations of the key compounds, and computer generated 3D model of compound **3** are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.08.012.

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