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Construction of rod-like diketopyrrolopyrrole oligomers with well-defined length

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Abstract—Oligomers of well-defined length were prepared by a stepwise sequence of Suzuki couplings using brominated 1,4-dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) derivatives and 1,4-dibromo-2,5-di-n-hexylbenzene as the monomers. The resulting oligomers contained three, five and seven DPP units, respectively, and could be characterized by ¹H NMR spectroscopy. These compounds could be of potential use as new electroluminescent materials. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

1,4-Dioxo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) and variously substituted analogues are a relatively new class of red pigments that usually display excellent photostability and a high quantum yield for fluorescence.^{1–6} These properties give them a potential interest for the construction of new luminescent materials. Recently we used this molecule as a core reagent in dendrimers, which could thus be detected by single molecule spectroscopy.7 A few examples of DPP-containing aliphatic copolyesters and copolyurethanes have been reported by other authors.⁸ Beyerlein and coworkers used the Suzuki coupling to synthesize π -conjugated polymers consisting of various ratios of the building blocks 1, 2 and 3 depicted in Fig. 1.9 The π -conjugated polymers were found to be strongly luminescent and more photostable than the corresponding saturated polymers containing isolated DPP units in the backbone. These compounds were anticipated to be suitable for electronic applications such as the construction of organic light emitting devices.

2. Results and discussion

We wished to prepare oligomers of controlled length using a similar approach based on Suzuki coupling. These oligomers might allow even better processability into thin films and display superior electronic properties compared to the analogous polymers. In order to



Figure 1.

obtain highly soluble oligomers, we used building block 4 instead of 1 (Fig. 1). The preparation of 4 (as well as the terminating unit 5), by N-alkylation of the dibromo (or monobromo) DPP¹ with 3,5-bis-t-butylbenzyl bromide instead of *n*-hexyl bromide, was found to be far more efficient than the described alkylation yielding 1. Dibromide 4 could readily be isolated in good yield (72%) by simple precipitation with n-pentane. In order to guarantee an easy separation by column chromatography we esterified boronic acid 3^{10} analogously to a literature procedure using pinacol in dioxane at 60°C,¹¹ to obtain the diester 6. This reduces the polarity of the boron containing intermediates. Moreover, the use of pinacol ester provides a convenient handle to characterize these intermediates by ¹H NMR spectroscopy due to the presence of an intense singlet arising from the methyl protons of the pinacolates.

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The construction of the desired oligomers proceeded readily using a combination of both convergent and divergent coupling strategies. The convergent strategy starts from the peripheral unit **5** which was allowed to react with a 5-fold excess of diboronic ester **6** under standard Suzuki-coupling conditions $(Pd(PPh_3)_4, tolu-ene/Na_2CO_3 1 M, reflux, overnight) giving$ **7**in 91% isolated yield after column chromatography (Scheme 1). This boronic ester**7**could then be coupled to dibromide**4**yielding the DPP trimer**8**.

For the construction of longer oligomers, basically a divergent strategy was used. Thus, we started from dibromide 4, which was allowed to react with a 10-fold excess of diboronic ester 6 giving species 9 in 76% isolated yield (Scheme 2). Successive reactions with a 10-fold excess of 4, a 10-fold excess of 6 and finally again a 10-fold excess of 4 gave rise, via intermediates 10 and 11 (Table 1), to the dibromo oligomer 12, consisting of five DPP units, in acceptable yield. Analogously, pentamer 13 could be prepared by reaction of bisboronate 11 with the terminating unit 5. For the preparation of heptamer 14 we decided to couple monoboronate 7 with bisbromide 12 as we expected the chromatographic purification to be easier because of the more pronounced difference in polarity between the



starting material and the desired product. An overview of the synthesized oligomers can be found in Table 1.

The synthesized DPP oligomers 8–14 turned out, as anticipated, to be highly soluble in common solvents such as dichloromethane, chloroform and toluene. The solubility of dibromide 4 was significantly lower in the latter solvent, allowing us to remove a large part of the excess 4 from the reaction mixtures leading to 10 and 12 by simple precipitation from toluene. The excess of bisboronic ester 6 could be recuperated by column chromatography from the reaction leading to 9 and 11. This is of interest because of the poor yields of the literature procedure to obtain the precursor 3.¹⁰

The oligomers described could be readily characterized by ¹H NMR spectroscopy. For instance, in the ¹H NMR spectrum of bisboronic ester **9**, triplets (each 4H) at δ 2.85 and 2.55 ppm correspond to the benzylic CH₂ of the hexyl group, respectively, *ortho* to the boronic ester or the phenyl substituent on the heterocycle. Singlet resonances at δ 7.69 and 7.00 ppm (each 2H) can be, respectively attributed to the corresponding aryl protons. The intensities of the signals have the expected ratios towards the pinacolate singlet (24H).

The ¹H NMR spectrum of the tris DPP dibromide **10** shows three singlets (each 4H) between δ 4.9 and 5.2 ppm, reflecting the symmetry of the molecule, which has three different 3,5-bis-*t*-butylbenzyl groups. The displacement of the benzylic triplet around 2.85 ppm to a signal of higher field (2.58 ppm) indicates that the boronic ester has reacted. The two doublets at 7.64 and 7.56 ppm can be assigned to the peripheral 4-bromophenyl substituent. Moreover, the integration ratios confirm that there are indeed three DPP residues present. The other ¹H NMR spectra of **11–14** can be assigned in the same way.

Finally we wanted to show that dendritic oligomers could be prepared as functionalization with dendrons might allow changing solubility and crystallization properties. Thus, we prepared the dendritic monobromide **15** by a procedure analogous to the synthesis of **5** namely *N*-alkylation with the second generation dendritic benzyl bromide developed by Fréchet (Scheme 3).¹² Dendron **15** was then reacted with bisboronic ester **6** affording boronic ester **16**. This compound was coupled to bisbromide **4** affording the dendritic trimer **17**, which was also found to be highly soluble in dichloromethane, chloroform and toluene.

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Scheme 2.

Entry	End groups	Isolated yield (%)	Mol. weight (g/mol)	No. of DPP units
8	Н	69	2563	3
9	Boronate	76	1434	1
10	Br	55	2722	3
11	Boronate	69	3304	3
12	Br	51	4592	5
13	Н	46	4434	5
14	Н	58	6305	7

Table 1. Overview of the synthesized rod-like DPP oligomers



Scheme 3.

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