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Synthesis and optical behaviour of monodispersed oligo(fluorenylidene)s

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Abstract

The synthesis of the first series of monodispersed oligo(fluorenylidene)s is reported. The synthetic sequence envisages as key steps the obtainment (a) of a bis-pinacolboronate fluorenylidene dimer by a $Ni(cod)_2$ promoted homocoupling of the suitable 7-bromo-fluorenylidene boronic ester and (b) of the bis-pinacolboronate fluorenylidene trimer and tetramer by a $Ni(cod)_2$ promoted coupling of a 7-bromo-fluorenylidene boronic ester with 0.5 equiv of the corresponding 2,7-dibromofluorenylidene derivative. The optical properties of the obtained oligomers were studied. In the case of **OF3** the optical behaviour was compared to that of a suitably synthesized fluorenone-containing model compound.

Keywords: Fluorenylidene; Monodispersed oligomers; $Ni(cod)_2$-promoted coupling; Fluorenone

The tuning of selective synthetic methods aimed at obtaining well-defined oligomers is considered a valuable aid for the organic chemist working on extensively conjugated materials. In this framework, the *p*-phenylene *motif* is ubiquitous and has been investigated in an uncountable number of variants. The introduction of a carbon atom bridging two linked *p*-phenylene rings (to obtain a fluorene structure) offered the possibility of decorating the biphenyl building block with solubilizing alkyl chains.[1] The sp^3 hybridization of this carbon atom, however, forces the substituents to adopt an orthogonal disposition with respect to the aromatic system.[2] A completely different behaviour is to be expected if the two phenyl rings are connected by an sp^2 hybridized C-9, a situation occurring in fluorenylidene systems. In these molecules the C-9 carbon atom forces the whole building block to assume a planar geometry, so that the flattened structure should favour strong intermolecular interactions in the solid state. The chemistry of fluorenylidene-based materials is rather young. The first proposed fluorenylidene-based materials have been polymers conceived for applications in field effect transistors (FET). Poly(fluorenylidene)s showed a good hole transporting ability deriving from the close packing exhibited in the solid state.[3]

The obtainment of monodispersed oligo(fluorenylidene)s through a step-by-step convergent approach would be an intriguing synthetic challenge owing to the reactivity of the fluorenylidene double bond towards nucleophiles and electrophiles, posing constrains on the preparation sequence. Consequently, the strategies for the obtainment of monodispersed oligomers envisaging halogenation and/or metallation of the building blocks, commonly used to obtain monodispersed oligofluorenes,[4] should be excluded in the case of a fluorenylidene-based material, in

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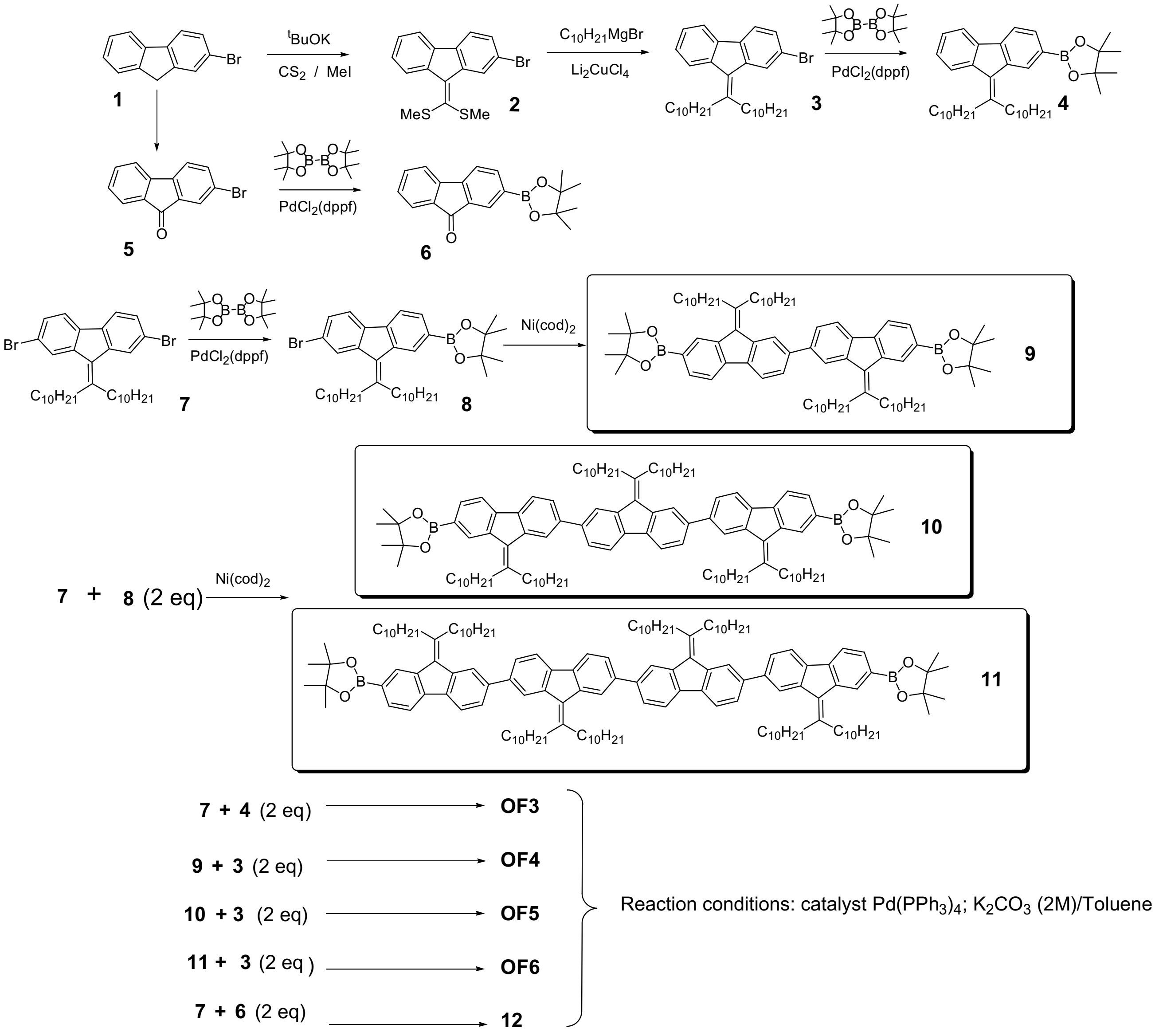
order to avoid unsatisfactory yields and difficult purifications of the obtained products. To date, no reports exist on the synthesis and optical behaviour of monodispersed oligo(fluorenylidene)s.

Following our interest in sharpening the tools of organometallic chemistry to obtain convenient synthetic methods for the selective synthesis of π-conjugated building blocks, we have recently proposed a Ni(cod)$_2$ promoted homocoupling of bromofluorenes functionalized with boronic esters as an efficient method for the preparation of reactive bifluorene building blocks to employ for the obtainment of quaterfluorenes.[5,6] This synthetic approach allows to bypass halogenation and metallation of a bifluorene substrate, and selectively yields the 7,7′-functionalized bifluorene building block.

In this study we decided to tag the synthesis of well-defined oligo(fluorenylidene)s by extending the above-mentioned synthetic protocol to the preparation of reactive bis-functionalized dimers, trimers and tetramers. To test the width of its scope, we applied it to the preparation of monodispersed fluorenylidene trimer, tetramer, pentamer and hexamer. The synthesis of the four oligomers was completed with a study of their optical properties both in solution and in the solid state.

The target molecules were prepared through a convergent synthetic approach (Scheme 1). Starting from 2-bromofluorene (**1**), the initial step was its condensation with carbon disulfide in the presence of potassium *tert*-butylate, followed by a reaction with methyl iodide, yielding the ketene dimethyl dithioacetal **2**. In the subsequent reaction step, **2** was treated with 2 equiv of decylmagnesium bromide to achieve the fluorenylidene derivative **3**. Decyl alkyl chains were chosen to ensure sufficient solubility to the target molecules. An attempt to prepare the boronic



Scheme 1. Synthesis of **OF3–6** and **12**.

ester **4** carried out by the metallation of **3** with *n*-BuLi and subsequent reaction with 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane proved to be unsuccessful due to the reactivity of the fluorenylidene moiety towards *n*-BuLi: a strong red coloration of the solution was in fact observed, indicating the formation of fluoren-9-yl anions due to the attack of *n*-BuLi onto the double bond of fluorenylidene. Compound **4** was obtained in a very modest yield (27%). On the other hand, the synthesis of **4** was accomplished in a good (67%) yield by a $PdCl_2$(dppf) catalyzed reaction between **3** and bis-pinacoldiboron in the presence of potassium acetate as base in DMF at 60 °C. The synthesis of **8** was carried out analogously by a $PdCl_2$(dppf) catalyzed reaction between **7** and 1 equiv of bis-pinacoldiboron.

The key step of the synthetic procedure is the preparation of the fluorenylidene cores **9**, **10** and **11**. For the synthesis of **9** we applied the conditions reported for the preparation of reactive bifluorene building blocks,[5] namely the $Ni(cod)_2$ promoted dimerization of **8** yielding the bifluorene bis-boronic ester **9** in 69% yield.

We were pleased to find that the preparation of the superior homologues (trimer **10** and tetramer **11**) could be achieved by a similar reaction: the $Ni(cod)_2$ promoted coupling of **7** with 2 equiv of **8**. The reaction permitted the obtainment of **10** (41%) and **11** (23%) from the same reaction mixture. The building blocks **10** and **11** could be separated by column chromatography and eventually purified by size exclusion chromatography with BioBeads® stationary phase. The building blocks **9**, **10** and **11** were used in the final reaction step consisting in the cross-coupling reaction with 2 equiv of **3** catalyzed by $Pd(PPh_3)_4$ (Scheme 1). The reactions yielded oligomers **OF4**, **OF5** and **OF6**, respectively, in satisfactory to good yields (54–81%).

Trimer **OF3**, on the other hand, could be obtained by a straightforward Suzuki reaction of **7** with 2 equiv of the boronic ester **4**. The reaction yielded **OF3** with a 70% yield. An analogous Suzuki cross-coupling of **7** with 2 equiv of the fluorenone boronic ester **6** afforded the target molecule **12** in 74% yield. This compound has been used as a model to mimic the oxidative degradation product of trimer **OF3**. The **OF3–6** oligomers have been eventually purified by size exclusion chromatography with BioBeads® stationary phase. The target oligo(fluorenylidene)s are viscous solids that had to be kept under inert atmosphere and in the dark, due to slow decomposition, probably ascribable to the tendency of the fluorenylidene double bond to undergo light promoted [2+2] cyclization (see Fig. 1).

The purity of **9–12** as well as that of **OF3–6** has been checked by size exclusion chromatography, coupled with a UV detector operating at 340, 350 and 360 nm (Fig. 2). ESI-MS provided further confirmation of the obtainment of the molecular structures of **OF3–5**. No mass spectrum could be obtained for **OF6** under the conditions used for the detection of the other monodispersed oligomers.

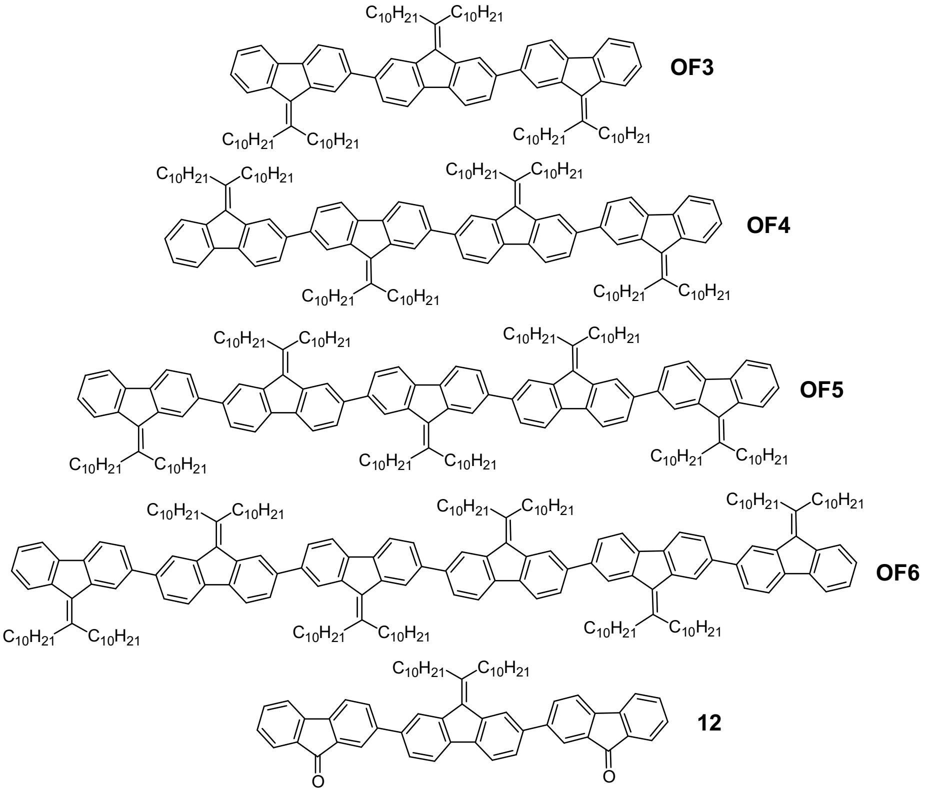


Fig. 1. Chemical structure of **OF3–6** and **12**.

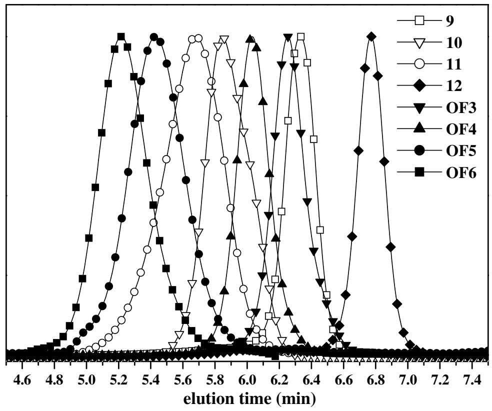


Fig. 2. GPC traces of **9**–**12** and **OF3**–**6**.

The target molecules **OF3**–**6** have been characterized by ^{1}H and ^{13}C{^{1}H} NMR. The very peculiar behaviour of these materials, imparted by the sp^2 hybridization of the C-9 carbon was also apparent from their ^{1}H NMR spectra: the broadening of the signals of **OF5** and **OF6**, with a consequent misfit of the proton integral, can likely be ascribed to the formation of aggregates even in a good solvent such as chloroform. The absorption spectra of **OF3**–**6** were recorded in chloroform solutions ($\sim 10^{-5}$ M) and are reported in Figure 3A. The absorption profile of the oligomers are characterized by a peculiar shoulder, the intensity of which increases passing from **OF3** to **OF6**. This absorption profile is independent of the concentration of the sample and was observed also in extremely diluted solutions of **OF3**–**6**. Therefore this feature cannot be ascribed to aggregation phenomena. The analysis of the absorption behaviour of the fluorenone-containing **12** (Fig. 3C) provided some insight in this aspect. In this molecule the π–π* charge transfer transition band is located at a $\lambda_{\max}$ of 440 nm and the main absorption ($\lambda_{\max} = 344$ nm) related to the π–π* transition of the π-conjugated backbone did not show any transition ascribable to aggregation in solution, notwithstanding the similarity of the structural architecture of **12** and **OF3**.

This absorption shoulder is also present in the absorbance spectrum of the correspondenting poly[9-(1-decylundecylidene)-2,7-fluorene] obtained by Ni(cod)$_2$ promoted homocoupling of **7**, both in solution and as thin film. In solution, its absorption profile is independent of the concentration and is very similar to that obtained in the solid state (see Supplementary data). On these basis we tentatively attribute the shoulder in the absorption profile of **OF3**–**6** to a charge transfer from the π-conjugated backbone to the double bonds.

In the solid state, the absorption spectra of **OF3**–**6** are quite broad (Fig. 3B). The increase of the shoulder at longer wavelengths can be interpreted as the generation of strong intermolecular interaction in the solid state. The optical band gap of the four oligomers was estimated by the onset of the absorption spectra in solution as 2.92 eV (**OF3**), 2.86 eV (**OF4**) and 2.79 eV (**OF5** and **OF6**). Evidently the band gap saturation occurs for the pentamer and higher oligomers.

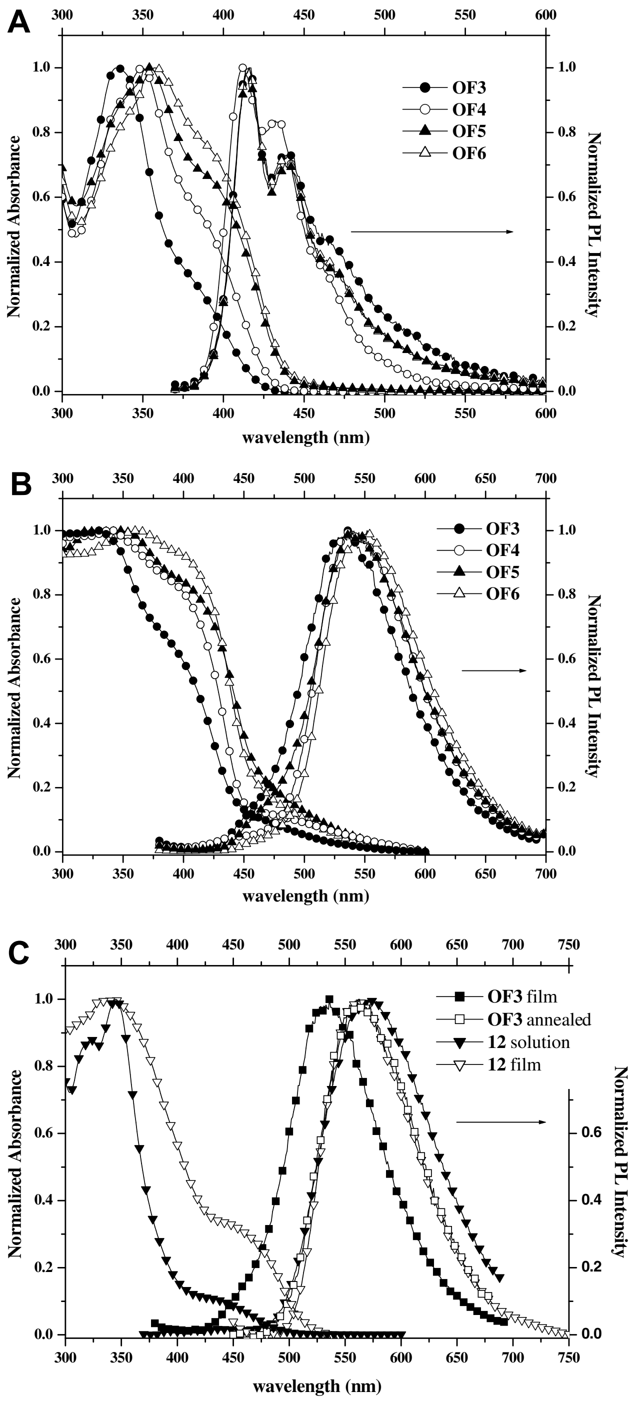


Fig. 3. Optical features of **OF3**–**6** and **12** in CHCl$_3$ solution and in the solid state.

In chloroform solution, **OF3**–**6** shows a structured blue-emission ($\lambda_{\max} = 414$–415 nm). The emission spectra shown in Figure 3A had to be obtained from solutions of ~0.05 absorbance. For more concentrated solutions, a lowering of the intensity of the first vibronic replica was observed for all compounds, due to self-absorption phenomena caused by the small Stokes shift of the compounds in solution. The emission of **OF3–6** in the solid state (Fig. 3B) is strongly red-shifted and shows very close maxima ($\lambda_{\text{max}} = 536\text{–}548$ nm) together with the loss of the vibronic structure. This behaviour can be attributed to the formation of aggregates and/or excimers in the solid state. A similar emission behaviour was observed for the poly[9-(1-decylundecylidene)-2,7-fluorene], showing an emission centred in the blue region in solution ($\lambda_{\text{em}} = 445$ nm) and a low energy emission at 529 nm dominating the solid state emission (see Supplementary data).

Since the emission profiles of **OF3–6** and of the polymer in the solid state resemble that of fluorenone-containing polyfluorenes,[7] a further experiment was carried out to rule out the influence of the possible formation of the fluorenone acceptors in the fluorescence of **OF3–6**. These defects, which can form by oxidative degradation processes, can affect the emission of a fluorene-based material even in amounts undetectable by the common analytical techniques.

By carrying out, however, a photostability test[8] on the spectral stability of **OF3** exposing a film of the molecule to an UV-irradiation under air for 30 min it was observed that the fluorescence of pristine **OF3** was red-shifted of 20 nm and its emission wavelength matched that of the fluorenone-containing model molecule **12**, thus suggesting (a) that a fluorenone moiety is incorporated into **OF3** only after the degradation process, and (b) that the solid state emission recorded for **OF3–6** (Fig. 3B) definitely derives from non-oxidatively degraded molecular structures.

In conclusion, the preparation of the first series of monodispersed oligo(fluorenylidene)s (trimer, tetramer, pentamer and hexamer) was achieved by a convergent synthetic approach founded on the facile obtainment of 2,7′-, 2,7″- and 2,7‴-bis-boronic ester derivatives of bi-, ter- and quater-fluorenylidene, respectively. Their optical properties in the solid state are consistent with a strongly aggregating behaviour.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.01.126.

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