Novel base-dopable poly(2,7-fluorenylene) derivatives

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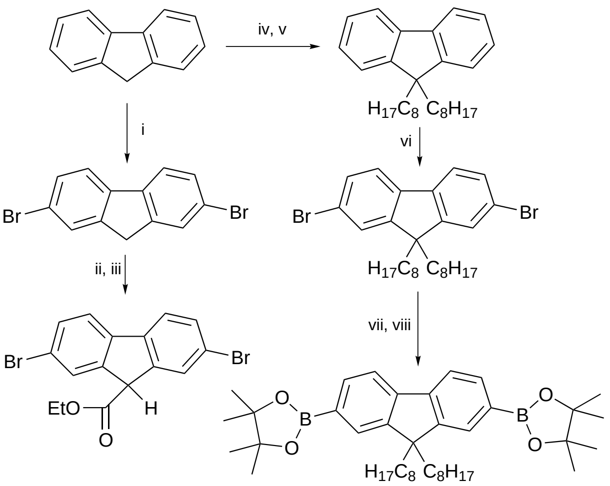
A novel acidic poly(fluorenylene) derivative has been synthesized which, upon base-doping, shows electrical conductivities of 10^{-6}–10^{-5} S cm^{-1}; this new doping method for conjugated polymers opens the way to the preparation of air-stable n-type conducting polymers.

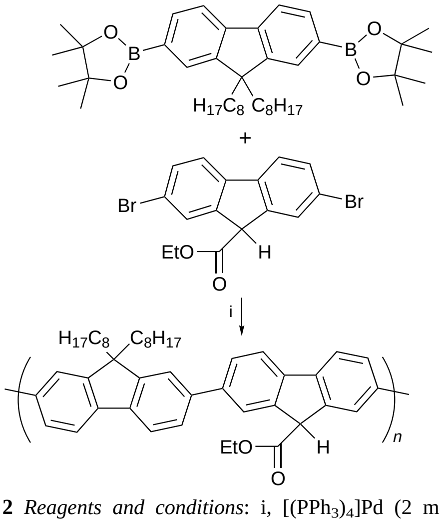
Conjugated polymers, such as poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, *etc.*, can undergo redox processes (partial oxidation or reduction) which create mobile charge carriers (radical cations, dications or their negative analogs) and lead to high electrical conductivities.[1] These reversible redox reactions (also called doping reactions) modify the electronic structure of the conjugated polymers and are also accompanied by colour changes (electrochromism). Another major development in the field of conducting polymers appeared with the possibility of creating positive charge carriers through the protonation of basic conjugated polymers. For instance, poly(aniline)s can exhibit an insulating-to-conducting transition through a simple protonation of the imine moieties (without any external redox process).[2] Once again, this doping reaction induces colour changes which are related to the formation of the charge carriers. Conversely, acidic conjugated polymers could be base-dopable and this approach should lead to negative charge carriers which could be particularly interesting for the development of electron-injecting electrodes in light-emitting or electrochemical devices. Along these lines, interesting work on poly(2-hydroxy-1,4-phenylene) was recently published by Pei *et al.*,[3] where delocalization of negative charges on the side chains onto the conjugated main chain led to conductivities of 5×10^{-9} S cm^{-1}. However, it could be more interesting to create charge carriers directly on the backbone and for this purpose, 9-monosubstituted poly(2,7-fluorenylene)s are certainly promising candidates. Indeed, fluorenes bearing a cyano or an ester group at the 9-position exhibit relatively low pK_a (8–10) values in organic solvents, which can be rationalized by the fact that the deprotonation reaction induces the aromatization of the inner ring.[4] Therefore, we report here the first synthesis of a well-defined acidic poly(2,7-fluorenylene) derivative and the characterization of its electrical and optical properties upon base-doping.

As shown in Scheme 1, ethyl 2,7-dibromofluorene-9-carboxylate was easily synthesized in two steps from fluorene. Recently, Pei and Yang[5] reported the nickel-catalysed reduction with metallic zinc of 2,7-dibromo 9,9-disubstituted fluorenes to yield well-defined 9,9-disubstituted poly(2,7-fluorenylene)s, but first attempts with this method were found to be inefficient in the case of acidic 2,7-dibromofluorene-9-carboxylates. The oxidative synthesis of fluorene-9-carboxylates, following the method reported by Yoshino and co-workers,[6] gave only highly cross-linked polymers. Finally, as reported for the synthesis of well-defined processable poly(*p*-phenylene)s,[7] it has been found that palladium-catalysed Suzuki couplings between 2,7-dibromofluorene-9-carboxylates and fluorene derivatives bearing diboronic moieties lead to well-defined poly(2,7-fluorenylene) derivatives. For this purpose, as also described in Scheme 1, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene was synthesized, in good yield, in three steps from fluorene. This synthetic procedure could not be applied to 2,7-dibromofluorene-9-carboxylate because of the use of organolithium compounds in the preparation of the boron derivatives. All monomers were characterized by NMR spectroscopy and mass spectrometry and complete details of their synthesis will be published in a forthcoming publication. As shown in Scheme 2, this method yields a well-defined alternating copolymer where 50% of the repeat units can be base-doped. Nevertheless, this alternating structure can indeed be useful since it has been shown that fully protonated polyanilines are less conducting than 50% acid-doped polyanilines.[8]



Scheme 1 *Reagents and conditions*: i, $CuBr_2$, Al_2O_3, CCl_4, reflux, 5 h, 97%; ii, LDA (2.1 equiv.), THF, −78 °C; iii, $ClCO_2Et$ (1 equiv.), 92% over two steps; iv, Bu^{n}Li (2 equiv.), THF, −78 °C; v, $C_8H_{17}Br$ (3 equiv.), 99% over two steps; vi, Br_2 (2 equiv.), $FeCl_3$ (2 mol%), $CHCl_3$, $0 \rightarrow 25$ °C, 24 h, 99%; vii, Bu^{n}Li (2.1 equiv.), THF, −78 °C; viii, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.5 equiv.), 65% over two steps

The synthesis of this alternated poly(2,7-fluorenylene) derivative gives a pale yellow polymer, completely soluble in THF



Scheme 2 *Reagents and conditions*: i, $[(PPh_3)_4]Pd$ (2 mol%), PhMe–Na_2CO_3 (2 M aq.), Ar, reflux, 48 h, 65%

and $CHCl_3$. On the basis of size exclusion chromatography measurements performed in THF, and using a calibration curve obtained with monodispersed polystyrene standards, this polymer has a weight-average molecular weight of 8000 and a polydispersity index of 1.4. This class of materials should show some acidic properties. Indeed, fluorene-9-carboxylate has a pK_a of around 10 in a mixture of DMSO–H_2O (90 : 10 v/v), the deprotonated form giving an absorption maximum around 400 nm.[4] Accordingly, the corresponding neutral polymer exhibits an absorption maximum at 376 nm in THF while a new broad absorption band appears around 430 nm in the presence of potassium *tert*-butoxide. Consequently, this base-doping of the polymer induces a yellow-to-orange colour change. This phenomenon is reversible and, upon protonation, the polymer recovers its initial colour.

Four-probe electrical measurements on dried pressed pellets of the base-doped polymer revealed conductivities of 10^{-6}–10^{-5} S cm^{-1}. This electrical conductivity is excellent for an n-doped polymer considering that the conducting state has been obtained from a simple deprotonation reaction and that all measurements have been carried out in air. Moreover, it is worth noting that poly(fluorenylene)s are not particularly good conducting materials (probably due to weak interchain interactions); for instance, oxidized poly(fluorenylene) derivatives show electrical conductivities of 10^{-3} S cm^{-1}[6,9] whereas neutral poly(fluorenylene) derivatives show conductivities lower than 10^{-9} S cm^{-1}. However, these promising results obtained with a base-dopable poly(fluorenylene) derivative opens a new route for the preparation of n-doped conducting polymers. It is believed that the synthesis of cyano-monosubstituted poly(fluorenylene)s could lead to more conducting materials since, as reported for the monomers, the deprotonated form of fluorene-9-carboxylate may involve a partial localisation of the negative charge on the enolate form of the ester group, which is impossible with a cyano substituent.[4] Moreover, 9-cyanofluorene is more acidic than the carboxylate derivatives. Finally, the preparation of double-stranded, fully soluble poly(fluoreneacene)s, as developed by Scherf and Müllen,[10] bearing strong electron-withdrawing substituents could also lead to conducting, base-doped polymers.

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Footnote and References

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