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A Versatile Copper-Induced Synthesis of Fluorinated Oligo(*para*-phenylenes)

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Abstract

Ullmann-like reductive coupling of 1,4-diiodo-2,3,5,6-tetrafluorobenzene, promoted by copper(I) thiophene-2-carboxylate in *N*-methylpyrrolidinone at room temperature, followed by treatment with lithium aluminum hydride in THF, allowed us to obtain fluorinated poly(*para*-phenylene) oligomers containing up to five aromatic rings with hydrogen atoms as terminal groups.

Keywords: Aryl halides; Coupling reactions; Oligomers; Polyaryls.

Introduction

In recent years poly(*para*-phenylene) (PPP) polymers have attracted considerable attention in relation to their particular properties such as high thermal and chemical resilience, semiconducting properties upon doping, and mechanical behaviour of a true rigid-rod polymer

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[1]. Unsubstituted PPP is an insoluble and not processable material. Therefore, much interest has been devoted to PPPs substituted with suitable alkyl, aryl or alkoxy groups as flexible side chains which may increase to a large extent the solubility of these rigid-rod molecules [2,3]. On the other hand, PPP oligomers have been considered as models for understanding spectroscopic and redox properties of polyaromatic compounds [4,5] and as rod-like liquid crystal molecules [6,7].

The most promising applications of PPPs and their derivatives are nowadays represented by electroluminescent devices such as light organic emitting diodes (LED)s. The presence of substituents on the polyaromatic framework of these polymers may influence, by steric and electronic effects, the HOMO-LUMO band gap and hence the electroluminescence properties [8]. From this point of view, the effect of fluorine atoms as substituents in these conjugated materials has been rarely tested. Recently, a PPP with perfluoroalkyl chains has been prepared [9], and some other reports deal with fluorinated poly(*para*-phenylenevinylene) polymers [10,11]. The electron withdrawing effect of the fluorine atoms should increase the HOMO-LUMO bandgap [10], making these polymers very appropriate for the fabrication of blue-emitting devices. Moreover, increased chemical stability of the material is expected to result from replacing the C-H bonds with stronger and less reactive C-F bonds [10].

Various synthetic methods developed for both polymers and oligomers are based upon cationic polymerization [12], or dehalogenation reactions of di- or polyhalogenated aromatic compounds with copper [13], alkali metals [14], or magnesium in the presence of transition metal complexes [15,16]. Suzuki-Miyaura cross-coupling reactions with appropriate boron derivatives have been reported recently [17-23]. Synthetic methodologies based upon the preparation of an intermediate precursor polymer [24], or polymerization by cycloaromatization of enediynes [25] have been also performed. Quinquephenyl and sexiphenyl were obtained from Wittig reaction coupled with [4+2] cycloaddition reaction [26].

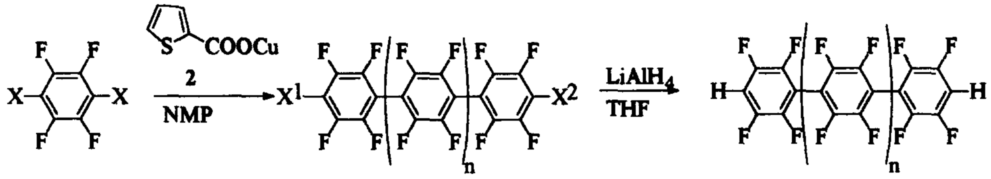
The aryl-aryl coupling can be performed with various synthetic procedures [27]. Recently, an Ullmann-like reductive coupling of aryl halides promoted by copper(I) thiophene-2-carboxylate (CuTC) in *N*-methylpyrrolidinone (NMP) in very mild experimental conditions has been reported [28].

As a further contribution resulting from our recent efforts dealing with the synthesis and properties of conjugated materials [29-31], we report now the results of an investigation on the synthetic potential of this reaction for the preparation of PPP oligomers and/or polymers.

Results and discussion

The starting material used in our investigation is represented by 1,4-diiodo-2,3,5,6-tetrafluorobenzene **1a**. This compound was found to undergo a homocoupling process as shown in Scheme 1.

Scheme 1



1a X = I

1b X = Br

3a-c, 4a-c, 5a-c, 6a-c

3a-6a

3a $X^1= X^2= H$	n = 0	**5a** $X^1= X^2= H$	n = 2
3b $X^1= I\ X^2= H$	n = 0	**5b** $X^1= I\ X^2= H$	n = 2
3c $X^1= X^2= I$	n = 0	**5c** $X^1= X^2= I$	n = 2
4a $X^1= X^2= H$	n = 1	**6a** $X^1= X^2= H$	n = 3
4b $X^1= I\ X^2= H$	n = 1	**6b** $X^1= I\ X^2= H$	n = 3
4c $X^1= X^2= I$	n = 1	**6c** $X^1= X^2= I$	n = 3

Even after long reaction times, a complex mixture of oligomers was obtained and, by flash chromatography, four fractions could be isolated corresponding to a mixture of compounds **3a-c** (fraction 1), **4a-c** (fraction 2), **5a-c** (fraction 3), and **6a-b** (fraction 4). All these compounds were identified by GC/MS analysis. Single components of each fraction could not be separated by flash chromatography.

A nearly quantitative dehalogenation reaction of compounds **3b,c**; **4b,c**; **5b,c** and **6b** was possible by treating each fraction with lithium aluminum hydride in tetrahydrofuran. The whole procedure led to the fluorinated PPP oligomers **3a-6a**, with hydrogen atoms as terminal groups onto the external aromatic rings. A typical composition of the four chromatographic fractions, determined by GC analysis, is reported in Table 1.

Table 1

Cu(I) thiophene-2-carboxylate-induced reductive coupling of **1a** in NMP. GC analysis of the isolated chromatographic fractions from the oligomers mixture.

Chromatographic fraction	Components (%)		
1	**3a** (13)	**3b** (64)	**3c** (23)
2	**4a** (44)	**4b** (45)	**4c** (11)
3	**5a** (46)	**5b** (44)	**5c** (10)
4	**6a** (53)	**6b** (47)	**6c** (–)

Yields of compounds **3a**-**6a** after the dehalogenation step are reported in Table 2.

Table 2

Cu(I) thiophene-2-carboxylate-induced reductive coupling of **1a** in NMP, followed by dehalogenation reaction with $LiAlH_4$ in THF.

Entry	Reaction time (h)	Compounds			
		3a (yield %)	**4a** (yield %)	**5a** (yield %)	**6a** (yield %)
1[a,b]	6	14	21	19	9
2[a,b]	16	17	21	16	10
3[a,b]	24	9	16	18	9
4[a,b]	96	18	18	12	9
5[c,d]	24	13	18	16	8
6[e,f]	44	22	11	6	-

[a] Dehalogenation step performed separately on each chromatographic fraction of the oligomers mixture (see text). [b] Reaction performed with CuTC/**1a** = 6/1 molar ratio. [c] CuTC/**1a** = 3/1 molar ratio. [d] Dehalogenation step performed directly on the mixture of oligomers from reductive coupling. [e] CuTC/**1a** = 2/1 molar ratio. [f] Conversion of **1a** was 62%.

Treatment with $LiAlH_4$ can be performed also on the crude mixture derived from the reductive coupling reaction (entry 5, Table 2) without significant variations in the yields of oligomers **3a**-**6a**. Various experiments have been performed in order to ascertain the influence of experimental parameters such as solvent, Cu(I) salt, and the nature of the substrate. Both CuTC and NMP are essential in this coupling reaction. In fact, other Cu(I) compounds such as CuI or Cu_2O in NMP are ineffective. Moreover, the same CuTC was unable to promote the coupling reaction in other polar solvents such as HMPA or DMF. As far as the ratio CuTC/substrate is concerned, 3 equivalents of CuTC are reported to be necessary for the coupling reaction with monohalogenobenzene derivatives [28]. In our case, almost the same results have been obtained with molar ratios CuTC/**1a** of 6/1 and 3/1 (entries 3 and 5, Table 2) but a lower ratio (2/1) reduced the conversion of the substrate (entry 6, Table 2). The conversion of **1a** is complete after 6 hours and the longer reaction times tested with the aim of increasing the length of oligomers have only the effect of slightly reducing the yields of PPP oligomers.

The nature of the halogen atoms and of the substituents on the aromatic ring have a marked influence upon the reactivity of the dihalide. Indeed, the dibromoderivative **1b** did not react in our experimental conditions. Furthermore, we have found also that 1,4-diiodo-2,5-pentyloxybenzene was unreactive, although this homocoupling reaction is reported to be very efficient with halogenobenzenes substituted either with coordinating electron-donating or with electron-withdrawing *ortho* substituents [28]. On the other hand, compound **1a**, in spite of having only fluorine atoms in *ortho* position, is able to undergo the homocoupling process, thus confirming a rather complex structure-reactivity relationship.

Conclusion

The procedure described here discloses a simple way to a new class of fluorinated PPP oligomers, which may have potential applications as semiconductors in light emitting electronic devices or as rigid-rod liquid crystals. The air-stable easily prepared CuTC allows the performance of the reductive coupling reaction under very mild conditions starting from the readily available diiododerivative **1a**. Further studies are in progress for tuning this useful process to the synthesis of PPP oligomers with a higher number of aromatic rings.

Experimental

Macherey-Nagel silica gel (60, particle size 0.040-0.063 mm) for flash chromatography and Macherey-Nagel aluminum sheets with silica gel 60 F_{254} for TLC were used. GC/massspectrometry analysis was performed on a Hewlett-Packard 5890 gas-chromatograph equipped with a HP-1 capillary column and HP MSD 5970B mass selective detector. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker AM 500 spectrometer at 500 MHz and 125.7 MHz respectively. ^{19}F NMR spectra were recorded at 188.2 MHz on a Varian XL 200 spectrometer ($CFCl_3$ internal reference, δ negative upfield). $LiAlH_4$ (0.04 M solution in diethyl ether), 2-thiophenecarboxylic acid, and 1,4-diiodo-2,3,5,6-tetrafluorobenzene were purchased from Aldrich. Copper(I) thiophene-2-carboxylate was prepared according to a known procedure [32]. THF and *N*-methylpyrrolidinone were distilled over sodium-benzophenone ketyl or 4 Å molecular sieves, respectively. Reactions sensitive to oxygen and moisture were conducted under a nitrogen atmosphere.

Reductive coupling of (1a); typical procedure (entry 4, Table 1). The diiododerivative **1a** (2.000 g, 4.98 mmol) was dissolved in NMP (80 mL) under a nitrogen atmosphere. CuTC (5.700 g, 29.90 mmol) was then added in one portion and the resulting suspension was stirred at room temperature (96 h reaction time). A saturated aqueous solution of $NaHCO_3$ (100 ml) was then added and the resulting mixture was extracted with CH_2Cl_2 (3 x 50 mL). The organic phase was washed with aqueous $NaHCO_3$ (saturated solution 100 mL) and water (3 x 100 mL). The organic phase was dried over anhydrous sodium sulphate and the solvent evaporated at reduced pressure. Residual NMP was removed *in vacuo* overnight at room temperature. By flash chromatography of the residue (0.750 g) with petroleum ether (40-70° C fraction) the following fractions were collected: fraction 1 (0.195 g, containing the products **3a-c**), fraction 2 (0.160 g, containing the products **4a-c**), fraction 3 (0.102 g, containing the products **5a-c**), and fraction 4 (0.065 g, containing the products **6a-b**). Further elution with ethyl acetate afforded another fraction (0.160 g) of unidentified products which, however, do not contain fluorine atoms, as verified by ^{19}F NMR spectroscopy.

2, 3, 5, 6, 2', 3', 5', 6'-octafluoro-[1, 1']-biphenyl (3a). Fraction 1 (0.195 g) deriving from the chromatographic separation of the precedent reaction was treated at 0° C with an excess of $LiAlH_4$ (0.04 M in diethyl ether solution, 4 mL, 0.16 mmol) [33] in THF (12 mL). After one hour, the GC analysis showed the disappearance of compounds **3b,c**. The reaction was quenched with water and the resulting mixture extracted with ethyl acetate (3 x 15 mL). The organic phase was dried over anhydrous sodium sulphate and the solvent evaporated at reduced pressure. The residue was purified by eluting through a short column of silica gel (petroleum ether as eluent). A white solid was obtained (0.134 g, 18% yield calculated upon **1a**) which exhibited IR spectroscopic data consistent with those in the literature [34]. m.p.80-82° C (lit. [34] 79-80° C).

2, 3, 5, 6, 2', 3', 5', 6', 2", 3", 5", 6"-dodecafluoro-[1, 1'; 4', 1"]-terphenyl (4a). This product was obtained from fraction 2 (0.160 g), by treatment with $LiAlH_4$ (0.04 M in diethyl ether, 5.8 mL, 0.23 mmol). A white solid was isolated (0.133 g, 18% yield). Upon heating the product undergoes a phase transition at about 145° C and melts at 210 °C. FTIR (KBr) ν=1509, 1475, 1230, 1180, 999, 929, 706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=7.28 (tt, $J^3_{C\text{-}F}$ = 9.5 Hz, $J^4_{C\text{-}F}$ = 7.3 Hz) ppm; ^{13}C NMR (125.7 MHz, $CDCl_3$) δ=107.43 (t $J^2_{C\text{-}F}$ = 17.5 Hz), 108.31 (t $J^2_{C\text{-}F}$ = 22.4 Hz), 109.23 (m), 144.10 (m $J^1_{C\text{-}F}$ = 263,4 Hz), 146.12 (m, $J^1_{C\text{-}F}$ = 246,2 Hz) ppm; ^{19}F NMR (188.2 MHz, $CDCl_3$) δ = -137.37 (m, 4F), -137.48 ÷ -137.78 (m, 4F), -137.94 ÷ -138.30 (bm, 4F) ppm; UV-Vis ($CHCl_3$) λ_{max} 248 nm; GC/MS *m/z* 446 (M^+, 100), 427 (3), 377 (17), 346 (5), 223 (7), 188 (2). Anal. calcd for $C_{18}H_2F_{12}$: C 48.45, H 0.45, F 51.10; found: C 48.37, H 0.41.

2, 3, 5, 6, 2', 3', 5', 6', 2", 3", 5", 6", 2''', 3''', 5''',6'''-hexadecafluoro-[1, 1'; 4', 1"; 4", 1''']-quaterphenyl (5a). This product was obtained from fraction 3 (0.102 g), by treatment with $LiAlH_4$ (0.04 M in diethyl ether, 3.0 mL, 0.12 mmol). A white solid was isolated (0.089 g, 12% yield). m.p. 232-235° C. FTIR (KBr) ν=1505, 1462, 1231, 1182, 1008, 929, 706 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=7.29 (tt, $J^3_{C\text{-}F}$ = 9.5 Hz, $J^4_{C\text{-}F}$ = 7.4 Hz) ppm; ^{19}F NMR (188.2 MHz, $CDCl_3$) δ=-137.10 (s, 8F), -137.54 ÷ -137.90 (m, 4F), -138.04 ÷ -138.42 (bm, 4F) ppm; UV-Vis ($CHCl_3$) λ_{max} 251 nm; GC/MS *m/z* 594 (M^+, 100) 525 (11), 487 (7), 456 (9), 297 (39), 278 (7), 262 (10), 247 (4), 228 (4). Anal. calcd for $C_{24}H_2F_{16}$: C 48.51, H 0.34, F 51.16; found: C 48.40, H 0.34. The low solubility of this compound did not allow us to obtain a ^{13}C NMR spectrum.

2, 3, 5, 6, 2', 3', 5', 6', 2", 3", 5", 6", 2''', 3''', 5''',6''', 2'''', 3'''', 5'''', 6''''-eicosafluoro-[1, 1'; 4', 1"; 4", 1'''; 4''', 1'''']-quinquephenyl (6a). This product was obtained from fraction 4 (0.065 g), by treatment with $LiAlH_4$ (0.04 M in diethyl ether, 2.0 mL, 0.08 mmol). A white solid was isolated (0.059 g, 8% yield). m.p. 290-293. FTIR (KBr) ν=1506, 1486, 1461, 1231, 1011, 973, 931, 706 cm^{-1}; UV-Vis ($CHCl_3$) λ_{max} 255 nm; ^{19}F NMR (188.2 MHz, $CDCl_3$) δ=-136.21 (s, 4F), -136.56 (s, 8F), -137.05 ÷ -137.42 (m, 4F), -137.58 ÷ -137.92 (m, 4F) ppm; GC/MS *m/z* 742 (M^+, 5), 371 (100), 352 (9), 336 (27), 302 (15), 278 (4), 247 (4). Anal. calcd for $C_{30}H_2F_{20}$:

C 48.54, H 0.27, F 51.19; found: C 48.42, H 0.22. The low solubility of this compound did not allow us to obtain ^{1}H- and ^{13}C NMR spectra.

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