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The stepped reaction of decafluorobiphenyl with thiophenol studied by in situ ^{19}F NMR spectroscopy

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ABSTRACT

Kinetic studies on the reaction of decafluorobiphenyl and di- and tetra(phenylthio)-substituted perfluorobiphenyl with thiophenol in the presence of triethylamine were performed by in situ ^{19}F NMR spectroscopy to determine rate constants. In well-defined consecutive reactions, the even-numbered phenylthio derivatives are main products whereas the odd-numbered derivatives are much more reactive and were observed only in low concentrations. Very pronounced differences in rate constants and reactivity were obtained.

1. Introduction

Nucleophilic substitution with thiolates on perfluorinated aromatics offers routes to tailored molecules, networks and polymers [1–4]. The reaction is promoted by electron withdrawing substituents, such as fluorine substituents. Aromatics bearing only one electron withdrawing moiety show only a moderate reactivity with thiolates due to weak activation for nucleophilic substitution under base-mediated conditions [5]. There is noticeable effort to develop transition metal catalysts that enable the formation of sulfur-aryl bonds from single-activated aromatics under mild conditions [6–11]. However, also additional halides or –M substituents in *ortho*-/*para*-position further polarize the carbon-halide bond making highly or perfluorinated compounds interesting starting materials. Brooke [12] reviewed the broad field of reactions on perfluorinated aromatic and heteroaromatic compounds. Thus, perfluorinated aromatic compounds are intrinsically activated and highly reactive toward nucleophilic substitution and should hence lead to higher sulfurated aromatic compounds. Adams et al. [13] as well as Robota and Malichenko [14] reported first on persulfurated arenes. Beck et al. showed that persulfurated arenes could be obtained also without a catalyst by using a polar solvent [15]. In the search for materials with tailored properties, persulfurated aromatic compounds came into focus recently. Gingras et al. [16] reviewed the development of persulfurated compounds showing the versatility of their application based on interesting properties like liquid crystallinity, charge capacity, magnetism, conductivity and complexation capability.

Perfluorinated arenes are for example used to synthesize partially fluorinated polymers as well as persulfurated compounds. Several groups reported on polymers derived from oxygen-nucleophiles [17–20]. Kellmann et al. [1] and Masaki et al. [2] were the first to present partially fluorinated poly(aryl thioether)s. This is surprising because in terms of polymer chemistry perhalogenated arenes are multifunctional monomers and should lead also to branched and/or cross-linked products. Besides application in polymerization reactions, the nucleophilic fluorine substitution by thiolates plays also an important role in the concept of thiol click chemistry since for perfluorinated arenes the reactions result in high yields under benign conditions [21].

Basic studies on the reaction of thiolate anions as nucleophiles with fluorinated arenes were reported in the pioneering works of Peach et al. in the seventies [22] after first studies of Robson et al. who also reported the formation of perfluoropoly(phenylene sulfide) as by-product [23]. For the reaction of hexafluorobenzene or decafluorobiphenyl with an excess of thiolate anion (e.g. methylthiolate, ethylthiolate or thiophenolate) tetra-substituted (hexafluorobenzene) or hexa-substituted products (decafluorobiphenyl) were isolated as highest substituted reaction products beside mono- and di-substituted compound [22a]. Interestingly

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the substitution pattern of the tetra-substituted benzene is not symmetric (1,2,4,5 position) but asymmetric (1,2,3,5 position). In the case of sixfold substitution of decafluorobiphenyl, again an asymmetric substitution (2,2′,4,4′,5,5′ position) on each ring was proposed. Contrary to the reaction of hexafluorobenzene with the aliphatic thiolates, the reaction with a large excess of thiophenolate gave presumably the fully substituted benzene. In all reactions reported in [22] only the major products were isolated and characterized. However, in order to allow better control in reactions involving thiophenols and perfluorinated arenes a deeper understanding of the course of reaction is necessary, which includes the evaluation and characterization of occurring products and their reactivity in a multistep reaction. Such detailed information is of general interest for applying this reaction in polymer synthesis because side reactions can result in irreversible structural defects on the polymer backbone, e.g. in grafting or crosslinking reactions.

In this study, the conversion of decafluorobiphenyl (DFBP) with thiophenol is investigated by in situ ^{19}F NMR spectroscopy using N-methyl-2-pyrrolidone (NMP) as solvent and triethylamine (TEA) as base. Time-conversion plots were evaluated in order to obtain rate constants. The application of ^{19}F NMR as in situ technique here has several advantages. Besides the high NMR sensitivity of the fluorine nucleus, the chemical shifts of fluorine signals possess high sensitivity toward local magnetic fields allowing to distinguish also very similar compounds by individual signals.

Di-, tetra-, hexa- and octa(phenylthio)-substituted perfluorobiphenyls were synthesized and fully characterized as reference compounds in order to assign the signals observed in the in situ NMR spectroscopic investigations.

2. Results and discussion

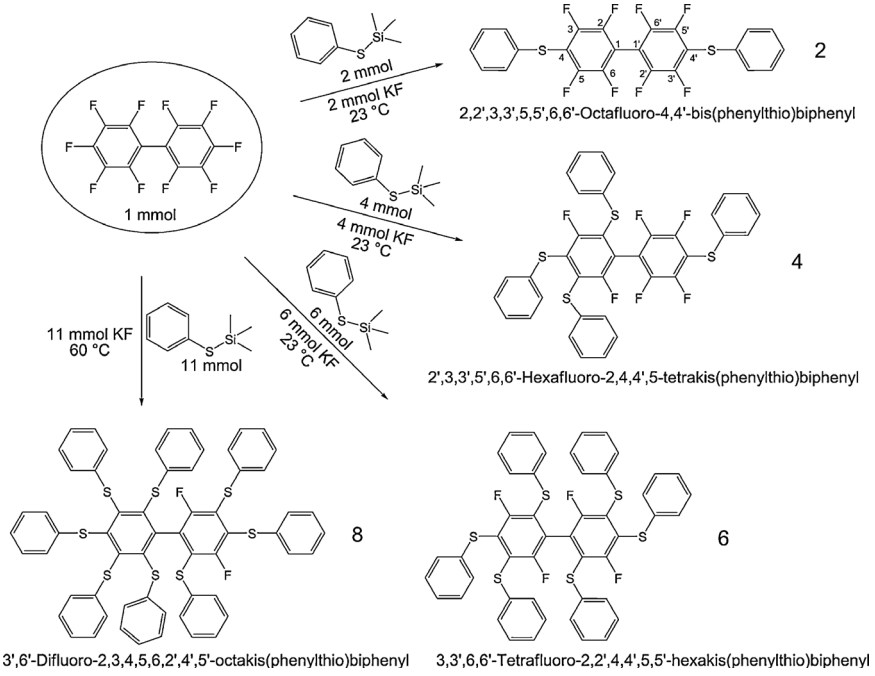
2.1. Synthesis of phenylthio-derivatives of decafluorobiphenyl

In order to assign the ^{19}F NMR signals observed in the course of reaction, model compounds with different degree of substitution were prepared but not with focus on optimized yields. DFBP is reacted with trimethyl(phenylthio)silane (TMPTS) in the presence of equimolar amounts of potassium fluoride (Scheme 1). The use of trimethylsilyl derivatives of nucleophiles has several advantages over the use of free nucleophiles as for example reported by Kricheldorf [24].

Compounds **2**, **4**, **6** and **8** were successfully isolated as main products from the respective reaction mixture (see Section 4) by column chromatography. Products with an odd number of substituents (**3**, **5**) were formed only in small amounts. For example, the crude reaction product from the synthesis of **4** was a mixture of 30 mol% **2**, 0.5 mol% **3**, 62.5 mol% **4**, 3.5 mol% **5** and 3.5 mol% **6** as determined by ^{19}F NMR spectroscopy. The synthesis of the octa-substituted **8** required a higher reaction temperature. Besides **8**, also small amounts of **9** with only one fluorine atom could be identified in the ^{19}F NMR spectrum. However, its position could not be determined unambiguously. The ^{19}F NMR spectra of the even-numbered thiophenyl-substituted fluorobiphenyls **2**, **4**, **6** and **8** are depicted in Fig. 1. All NMR data including ^{1}H and ^{13}C are summarized in Supporting information.

The low-content compounds **3** and **5** were not isolated but the ^{19}F chemical shifts and the coupling pattern of the three remaining fluorine atoms are in accordance with a 3,4-disubstitution of the disubstituted moiety (see Supporting information). Scheme 2 depicts possible products of the nucleophilic substitution of the threefold substituted compound **3** based on preferred *ortho*-/*para*-substitution to –SPh. Reaction of the thiophenolate with the higher fluorinated ring of **3** resulting in **4a** seems to be at first glance most likely due to the expected lower electron density of this benzene ring. However, only compound **4d** (=**4**) could be identified by NMR spectroscopy. Although traces of the other compounds cannot be ruled out, the 2,4,5-substitution pattern is found in all isolated derivatives with three phenylthio substituents on one ring.

This course of reaction may be explained by a strong activation of the position *para* to the phenylthio moiety as proposed by Peach et al. [22]. This strong activation was confirmed by relative rates of the nucleophilic aromatic substitution of non-activated aryl halides by thiolate ions as reported by Tiecco et al. [5]. A low activation was also observed for the *ortho* and *meta* position. Here,



Scheme 1. Main products in the preparation of phenylthio derivatives of decafluorobiphenyl. The reactions were carried out in NMP.

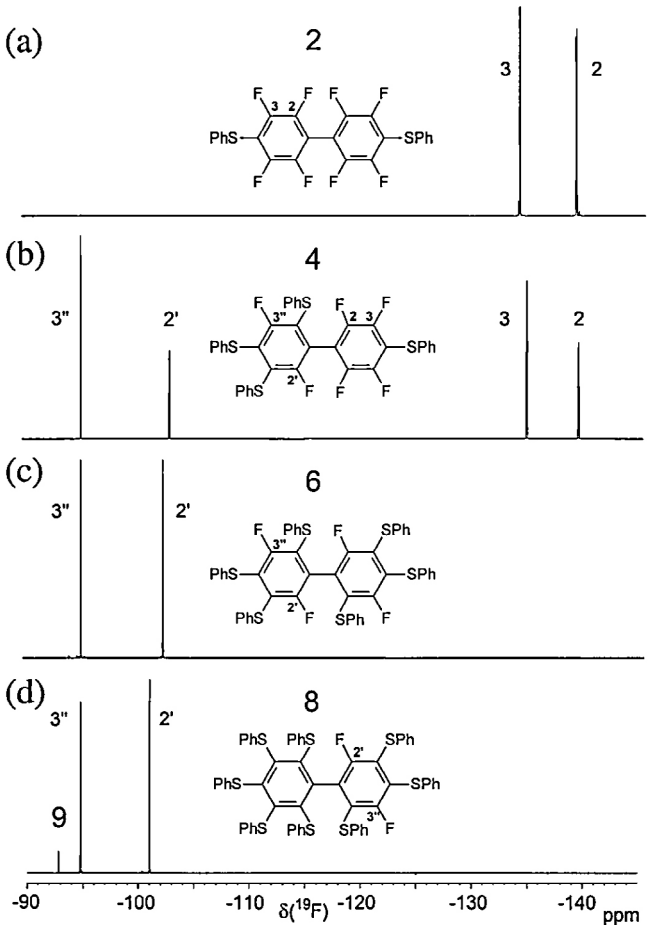


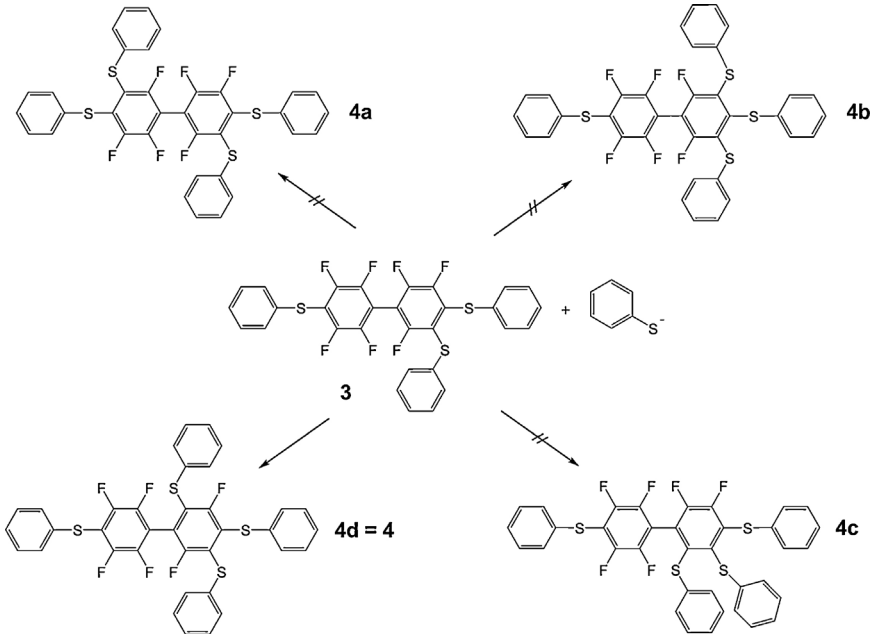
Fig. 1. ^{19}F NMR spectra of model compounds (a) **2**, (b) **4**, (c) **6** and (d) **8** containing 8 mol% **9** (solvent CD_2Cl_2).

the detection of **3** with *ortho*-disubstitution proofs for **2** a higher activation for the *ortho* position than for the *meta* position. The third phenylthio substituent has now a strong activation effect of its *para* fluorine promoting nucleophilic attack and resulting in **4d** (=**4**). This rationalizes the absence (or very low concentration) of **4a**–**4c** as products of an *ortho* substitution. Probably, the sterical shielding of reactive sites *ortho* to phenylthio-substituents as it occurs in **4b** and **4c** additionally prefers the formation of **4d**. The need for a higher reaction temperature to obtain **8** points to a high sterical shielding if six or more phenylthio substituents are attached to the biphenyl. However, with our experiments we cannot distinguish the contribution of each effect leading to this specific substitution pattern.

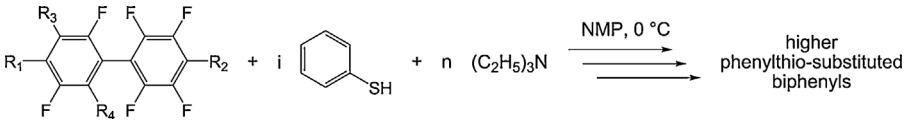
2.2. Kinetic investigations

For the ^{19}F NMR kinetic investigations thiophenol and TEA as base were used because the in situ experiments require a homogenous reaction system and the use of thiophenols is a more realistic scenario for aimed-for polymerizations. N-methyl-2-pyrrolidone as solvent meets all requirements for nucleophilic substitutions (high permittivity, aprotic) and is often applied in polymerization reactions. An excess of thiol and a 1:2 ratio of thiol to TEA should ensure that over a broad range of fluorine substitution the thiolate concentration can be considered as quasi-stationary. Preliminary studies indicated that the reaction rates are rather high at 30 °C, and thus the changes of the substance amounts could barely be followed by ^{19}F NMR spectroscopy. For that reason, the kinetic investigations had been conducted at 0 °C. In the first experiment, R1 (Scheme 3), DFBP was reacted with thiophenol and the kinetics was followed for 60 min. Under these experimental conditions, DFBP was very quickly converted and could not be detected anymore after 2 min, as it became evident from the first spectrum recorded. Therefore, reaction 2 (R2, Scheme 3) was started with **2** to achieve more defined starting conditions. R2 was followed for 406 min. Then reaction 3 (R3) was conducted with a doubled amount of TEA as compared to R2 in order to evaluate the influence of excess base. Finally, reaction 4 (R4) started from **4** to enable a direct kinetic evaluation of the conversion of **4** to **6**.

Fig. 2 depicts selected ^{19}F NMR spectra of R2 in order to illustrate the development of the characteristic signals. The kinetic behavior of R1 and R2 for the first 60 min is compared in Fig. 3. Astonishingly, even at 0 °C no DFBP and no **1** are detectable in the



Scheme 2. Possible tetra(phenylthio)-substituted perfluorobiphenyls as products of the reaction of **3** with thiophenolate.



Scheme 3. General scheme for kinetic studies. Reaction 1 (R1): R_1–R_4 = F (DFBP), i = 11, n = 22; reaction 2 (R2): R_1 and R_2 = SPh, R_3 and R_4 = F (**2**), i = 9, n = 18; reaction 3 (R3): R_1 and R_2 = SPh, R_3 and R_4 = F (**2**), i = 9, n = 36; reaction 4 (R4): R_1–R_4 = SPh (**4**), i = 7, n = 14.

first spectrum representing the first 2 min of reaction time. This means that both, the reaction of DFBP to **1** and its conversion to **2** are very fast. Although R1 seems to have only slight differences in the time-conversion curve compared to R2 the fast DFBP conversion to **2** influences the overall kinetics. Thus, it is not justified to analyze R1 as a reaction starting with **2**.

In all reactions, only the compounds with an even number of phenylthio-substituents (**2**, **4**, **6**) were formed in significant amounts. Despite **3** and **5** could be identified, their total content did not exceed 2 mol% at any reaction time. Thus, the conversion of DFBP and **2**, respectively, with an excess of thiophenol appears as pronounced step-wise reaction in which **2**, **4** and **6** are less reactive compounds compared to the reactive intermediates **1**, **3** and **5**. There was no evidence in the NMR spectra, e.g. by signals with unexpected ^{19}F chemical shifts, that a stable Meisenheimer-like complex was formed in the course of reaction.

Fig. 4 displays the development of the molar fractions with time for R2 and R3. In R2 already after 60 min **2** is completely converted and after 406 min the molar fraction of **6** reaches a value of 59%. However, even after 5 days of reaction time at room temperature no higher substitution patterns than **6** could be identified in the ^{19}F NMR spectrum. Reaction 3, which was conducted under the same conditions as R2 but with increased amount of base, runs almost exactly the same way as R2 up to 100 min. Obviously, increasing the thiophenol/TEA ratio from 1:2 to 1:4 did not lead to a faster conversion of **2** and most likely of DFBP under the applied conditions. The deviation found for longer reaction times might be caused by small differences in concentrations and hence cannot be distinguished from experimental errors (dosing, mixing).

Generally, each step in the reaction sequence starting from DFBP and **2**, respectively, to **6** (and higher degrees of substitution) is an aromatic nucleophilic substitution (S_NAr) under base-mediated conditions [5]. The reaction can occur as a two-step process involving addition of the thiolate to the aromatic ring to form an anionic species followed by elimination of the fluoride anion or as a one-step process with nucleophilic attack and nucleofuge elimination occurring simultaneously.

The reaction sequences **2** → **3** → **4** and **4** → **5** → **6** involve a slow reaction (k_{23}, k_{45}; formation of **3** and **5** due to weak *ortho* activation) and a fast reaction (k_{34}, k_{56}; formation of **4** and **6** due to strong *para* activation). With $k_{23(45)} \ll k_{34(56)}$, the concentrations of **3** and **5** remain very low as observed and their formation is the rate-determining step in the reaction sequences. Under the assumptions that (i) all reactions are irreversible and (ii) the intermediate steps involving **3** (and **5**) are very fast so that their concentrations are quasi-stationary at almost zero and the steady state approximation can be applied, the reaction of **2** toward **4** (and **6**) can be simplified as outlined in Eqs. (1a) and (1b).

$$\mathbf{2} + 2\mathrm{PhS}^- \rightarrow \mathbf{4} + 2\mathrm{F}^- \quad (1a)$$

$$\mathbf{4} + 2\mathrm{PhS}^- \rightarrow \mathbf{6} + 2\mathrm{F}^- \quad (1b)$$

$$r = k_2[\mathbf{2}][\mathrm{PhS}^-]^2 \quad (2)$$

[**2**] and [PhS^-] are the concentrations of the educts and k_2 the rate constant of the rate-determining *ortho* substitution. Further assuming, (iii) that the equilibrium concentration [PhS^-] of the thiolate remains constant because an excess of thiol and base was applied, the rate equation (Eq. (2)) simplifies and an integrated rate law of first order is obtained (Eq. (3)).

$$[\mathbf{2}]_t = [\mathbf{2}]_0 \cdot e^{-k_2' \cdot t} \quad (3)$$

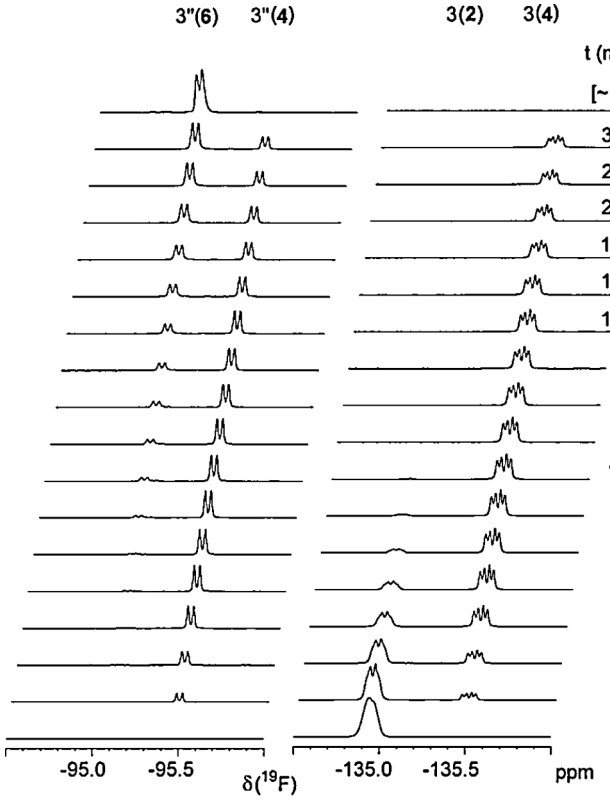


Fig. 2. Selected ^{19}F NMR spectra taken during reaction 2 showing two signal regions with characteristic signals of **2**, **4**, and **6**. Assignment of signals is given in Section 4.

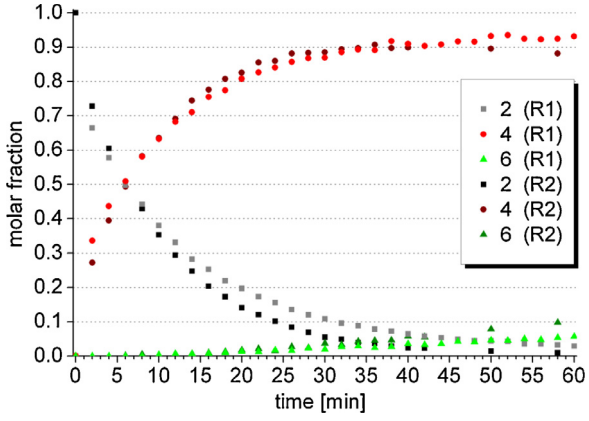


Fig. 3. Comparison of molar fractions of **2**, **4**, and **6** for reactions 1 (R1) and 2 (R2) determined for the first 60 min reaction time.

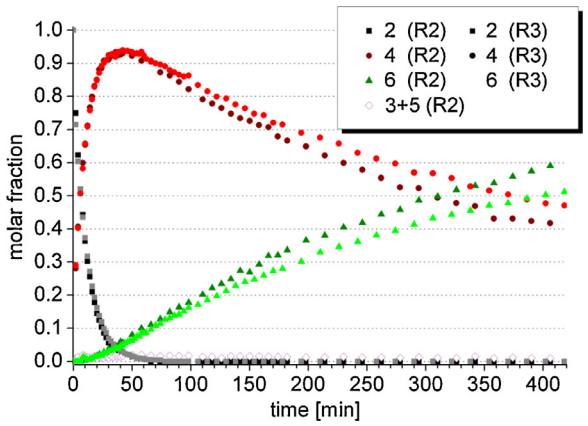


Fig. 4. The development of the molar fractions of educt and reaction products in R2 and R3 as obtained from ^{19}F NMR spectroscopy. The total content of **3** and **5** does not exceed 2 mol% at any reaction time.

Eq. (3) contains an apparent rate constant $k_2' = k_2 \cdot [PhS^-]^2$. $[\mathbf{2}]_t$ was calculated from the signal intensity of **2** at time t related to the signal intensities of all detected species **2**–**6** (=$[\mathbf{2}]_0$). All integrals were corrected by the number of fluorine atoms causing these signals.

Thus, the consumption of **2** in both R2 and R3 was evaluated with a rate law for a first-order reaction. The characteristic kinetic plot $\ln(c_t/c_0)$ vs time (Fig. 5) gives straight lines with very good coefficients of determination, R^2, confirming the first-order kinetics for consumption of **2**. The k_2' values at 0 °C were determined from the slope to $1.59 \times 10^{-3}\ s^{-1}$ (R2) and $1.47 \times 10^{-3}\ s^{-1}$ (R3) in good agreement. However, it should be kept in mind that k_2' depends on the thiolate concentration in the preceding thiol/thiolate equilibrium with TEA as base, i.e. it is an apparent rate constant. In the same way, the conversion of **4** to **6** (R4) was followed. The experimental data can be interpreted as described for R2 and R3 but based on the reaction given in Eq. (1b). The development of the molar fractions is shown in Fig. 6 and the first order kinetic plot in Fig. 7. The consumption of **4** is in good agreement with a pseudo first order kinetics whereby the apparent reaction rate k_4' is $8.17 \times 10^{-5}\ s^{-1}$. Compound **5** was observed only in traces as intermediate, i.e, assumption (ii) (concentration is quasi-stationary at almost zero) is valid. Because **6** was not further converted, this reaction rate can be applied for calculation of [6].

Both, the apparent rate constants k_2' and k_4' describe rate-determining *ortho* (2−) substitution in the 2,5-phenylthio substitution of a 4-thiophenyl-substituted moiety. However, the values obtained under similar conditions with respect to temperature, thiol and base concentration differ by a factor of about 20. Obviously, a 2,4,5-phenylthio substitution (**4**) compared to a 4-phenylthio substitution (**2**) drastically reduces the reactivity of the second 4-thiophenyl substituted ring with respect to further thiolate attack. This applies for the first *ortho* substitution (formation of **5**) but not for the consecutive reaction in 2-position resulting in **6**. This reaction is still fast as can be concluded from the negligible concentration of **5**. In the 2,4,5-triphenylthio substituted moieties the positions of remaining fluorine atoms are hardly activated or sterically shielded as can be concluded from absence of **7** or **8** under experimental conditions.

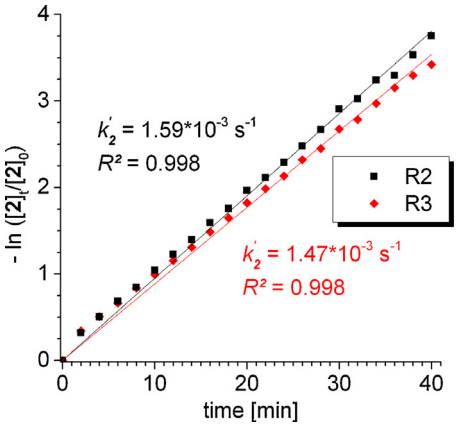


Fig. 5. Ln(c) vs time plots for the consumption of **2** in reactions 2 (R2) and 3 (R3). $[\mathbf{2}]_t/[\mathbf{2}]_0$ corresponds to the molar fraction of **2** as given in Fig. 4.

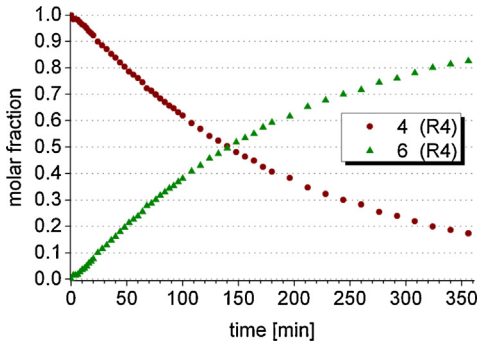


Fig. 6. Development of the molar fractions of **4** and **6** in reaction 4 (R4) as obtained from ^{19}F NMR spectroscopy.

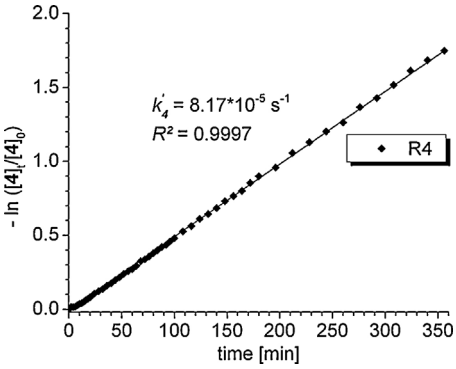


Fig. 7. Ln(c) vs time plot for the consumption of **4** in reaction 4 (R4). $[\mathbf{4}]_t/[\mathbf{4}]_0$ corresponds to the molar fraction of **4** as given in Fig. 6.

3. Conclusion

We have shown that in the reaction of DFBP with phenylthiolate the formation of even-numbered sulfuryl derivatives is strongly favored over the formation of odd-numbered ones, which were observed only in traces. The almost exclusively observed even-numbered substitution pattern are 4,4′ (**2**), 2,4,4′,5 (**4**) and 2,2′,4,4′,5,5′ (**6**). The reactions of DFBP, **2** and **4** with thiophenol and TEA as base could be kinetically studied at 0 °C in NMP using in situ ^{19}F NMR spectroscopy. Whereas DFBP was converted very fast, the consumption of **2** and **4** followed a pseudo-first order kinetics with formation of **3** and **5**, respectively, as rate-determining step. Assuming that the concentrations of **3** and **5** are quasi-stationary at almost zero, pseudo-first order rate constant of the reaction of **2** to **4** ($1.59 \times 10^{-3}\ s^{-1}$ for R2) is about 20 times larger than that for the reaction of **4** to **6** ($8.17 \times 10^{-5}\ s^{-1}$) under applied experimental conditions. Further substitution of the 2,4,5-triphenylthiolted moieties of **6** was not observed. Thus, the efficient reaction also

at ambient temperature and the very pronounced differences in reactivity in combination with a precise balance of monomers are very promising for the synthesis of high molecular or defined molecular weight poly(aryl thioether)s.

4. Experimental

4.1. General remarks

Decafluorobiphenyl (DFBP; 99%, ABCR GmbH) was recrystallized from ethanol/isopropanol (1/1, v/v) and dried in vacuum at 30 °C for 16 h. Dichloromethane (DCM), ethyl acetate, thiophenol (all Acros), diethyl ether, 1,1,1,3,3,3-hexamethyldisilazane (HMDS), *n*-hexane, silical gel (0.063–0.2 mm, all Merck) were used as received. Potassium fluoride (Fluka) was dried in vacuum at 150 °C for 7 h and stored in a desiccator prior use. N-methyl-2-pyrrolidone (NMP; Merck) and triethylamine (TEA; Sigma–Aldrich) were dried by distillation from CaH_2. TMTPS was prepared following a previously reported procedure [7].

The NMR measurements were carried out on a Bruker Avance III spectrometer (Bruker Biospin, Germany) at 500.13 MHz (^{1}H), 125.76 MHz (^{13}C) and 470.59 MHz (^{19}F). Solvent signals served as internal chemical shift reference for ^{1}H ($CDCl_3$: 7.26 ppm; CD_2Cl_2: 5.31 ppm) and ^{13}C ($CDCl_3$: 77.0 ppm; CD_2Cl_2: 53.7 ppm). For ^{19}F NMR spectra, C_6F_6 (−163.0 ppm) was used as external chemical shift reference. ATR-FTIR-spectra were recorded on a Bruker Tensor 27 (aperture 6 mm). Mass spectra were recorded on an Agilent Technologies 6890N GC/5973N MSD device with electron impact (**2**) or on a Bruker Esquire with Ion Trap detector and ESI source (**4**, **6**, **8**).

4.2. Synthesis of thiophenyl-substituted fluorobiphenyls

Exemplary, the synthesis of 2,2′,3,3′,5,5′,6,6′-octafluoro-4,4′-bis(phenylthio)biphenyl (**2**) is described. 1 mmol (0.3341 g) of DFBP and 1 mmol (0.0581 g) of potassium fluoride are weighed in a three-neck flask, equipped with a gas-inlet, gas-outlet and a septum. Under argon atmosphere DFBP is dissolved in 5 ml NMP at 23 °C. The reaction is started by injection of 2 mmol (0.1824 g) TMPTS to the stirred solution. The reaction is stopped by precipitating the reaction product in 75 ml of 0.01 M HCl. The solid raw product is isolated by filtration, washed with water and methanol and finally dried at 50 °C in vacuum for 16 h. The parameters for the preparation of the other compounds are given in Table 1.

The pure products were obtained by column chromatography on silica gel using the following eluents: **2**, **4**: ethyl acetate/*n*-hexane (1/9, v/v); **6**: ethyl acetate/*n*-hexane (2/8, v/v) and **8**: ethyl acetate/*n*-hexane (3/7, v/v).

4.2.1. 2,2′,3,3′,5,5′,6,6′-Octafluoro-4,4′-bis(phenylthio)biphenyl (*2*)

White solid, mp 105–106 °C (lit: 93–94 [22a]); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.45 (m, 4H, H-6), 7.38–7.30 (m, 6H, H-7, H-8). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 147.37 (dd, $^1J_{CF}$ = 248 Hz, J_{CF} = 13 Hz, C-3), 144.60 (dd, $^1J_{CF}$ = 255 Hz, J_{CF} = 16.7 Hz, C-2), 132.55 (C-5), 131.43 (C-6), 129.83 (C-7), 128.64 (C-8), 117.43 (t, $^2J_{CF}$ = 20.1 Hz, C-4), 107.83 (m, C-1). ^{19}F NMR (470 MHz, CD_2Cl_2) δ −134.9 (m, 4F, F-3), −139.7 (m, 4F, F-2). GC–MS (70 eV, *m*/*z*): 516.1 (12), 515.1 (28), 514.1 (100) $[M]^+$, 474.1 (13), 77.1 (25), 51.1 (11). Anal. calcd for $C_{24}H_{10}F_8S_2$: C, 56.03; H, 1.96; S, 12.47; found: C, 56.05; H, 2.16; S, 12.81.

Table 1
Parameters for the synthesis of compounds **2**, **4**, **6** and **8**.

Compound	KF (g)/(mmol)	TMPTS (g)/(mmol)	*T* (°C)	*t* (h)
2	0.0581/2	0.1824/2	23	1
4	0.1162/4	0.3648/4	23	2
6	0.1743/6	0.5472/6	23	6
8	0.2905/11	0.9120/11	80	8

4.2.2. 2,2′,3′,5,5′,6,6′-Heptafluoro-3,4,4′-tris(phenylthio)biphenyl (*3*)

^{19}F NMR (470 MHz, CD_2Cl_2) δ −129.7 (dd, $^3J_{FF}$ = 23.1 Hz, $^5J_{FF}$ = 13.9 Hz, 1F, F-3′), −130.6 (m, 1F, F-2′). Other signals are overlapped by main compound. Signals of the compound were observed as traces in a chromatographic fraction. Numbering corresponds to **4** in Fig. 8.

4.2.3. 2′,3,3′,5′,6,6′-Hexafluoro-2,4,4′,5-tetrakis(phenylthio)biphenyl (*4*)

Light yellow solid, mp 140–141 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 (m, 2H, H-6 at C_6F_4), 7.35–7.30 (3H, H-7 and H-8 at C_6F_4), 7.30–7.20 (10H, H-6, H-6′, H-7, H-7′, H-8, H-8′), 7.19–7.11 (3H, H-7″, H-8″), 7.02 (m, 2H, H-6″). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 159.68 (dd, $^1J_{CF}$ = 248 Hz, $^4J_{CF2'}$ = 3.2 Hz, C-3″), 156.79 (dd, $^1J_{CF}$ = 250 Hz, $^4J_{CF3''}$ = 3.2 Hz, C-2′), 147.16 (m, $^1J_{CF}$ = 247 Hz, C-2), 144.36 (m, $^1J_{CF}$ = 250 Hz, C-3), 134.86 and 134.69 (two d, $^4J_{CF}$ = 2.3, C-5, C-5′), 134.03 (d, $^4J_{CF}$ = 1.6 Hz, C-5″), 132.91 (C-5 at C_6F_4), 131.44 (C-6 at C_6F_4), 130.96 (d, J_{CF} = 20.7 Hz, C-4′), 129.93, 129.76, 129.67, 129.65, 129.60, 129.58, and 129.49 (C-6, C-6′, C-6″, C-7, C-7 at C_6F_4, C-7′, C-7″), 129.39 (d, J_{CF} = 19.8 Hz, C-3′), 128.43 (C-8 at C_6F_4), 127.72, 127.65, and 127.58 (C-8, C-8′, C-8″), 126.08 (dd, J_{CF} = 23.0 Hz, J_{CF} = 1.6 Hz, C-2″), 120.89 (d, J = 21.4 Hz, C-1′), 115.76 (t, $^2J_{CF}$ = 20.0 Hz, C-4), 113.59 (t, $^2J_{CF}$ = 18.6 Hz, C-1). ^{19}F NMR (470 MHz, CD_2Cl_2) δ −95.5 (d, $^5J_{FF2'}$ = 15.3 Hz, 1F, F-3″), −103.6 (dt, $^5J_{FF3''}$ = 15.3 Hz (d), $^5J_{FF2}$ = 4.3 Hz (t), 1F, F-2′), −135.5 (m, 2F, F-3), −139.9 (m, 2F, F-2). MS (25 V, *m*/*z*): 859.7 (9), 802.3 (7), 733.1 (9) $[M+K]^+$, 717.1 (13) $[M+Na]^+$, 712.2 (86) $[M+NH_4]^+$, 695.2 (100) $[M+H]^+$, 419.3 (14). Anal. calcd for $C_{36}H_{20}F_6S_4$: C, 62.23; H, 2.90; S, 18.46; found: C, 62.54; H, 3.14; S, 18.86.

4.2.4. 2′,3,5′,6,6′-Pentafluoro-2,3′,4,4′,5-pentakis (phenylthio)biphenyl (*5*)

^{19}F NMR (470 MHz, CD_2Cl_2) δ −95.0 (d, $^5J_{FF2''}$ = 15.5 Hz, 1F, F-3′ of difluoro ring), −103.0 (dt, $^5J_{FF3'}$ = 15.5 Hz (d), $^5J_{FF2'} \sim {}^5J_{FF2''} \sim 4$ Hz (t), 1F, F-2″ of difluoro ring), −103.1 (dt, $^5J_{FF3''}$ = 13.5 Hz (d), $^4J_{FF} \sim {}^5J_{FF2''} \sim 4$ Hz (t), 1F, F-2″ of trifluoro ring), −130.1 (dd, $^2J_{FF}$ = 24.0 Hz, $^5J_{FF}$ = 13.5 Hz, 1F, F-3′ of trifluoro ring), −131.0 (dt, $^3J_{FF}$ = 24.0 Hz (d), $^4J_{FF} \sim {}^5J_{FF} \sim 4$ Hz (t), 1F, F-2′ of trifluoro ring). Signals of the compound were observed as traces in a chromatographic fraction. Numbering adopted from **6** in Fig. 8.

4.2.5. 3,3′,6,6′-Tetrafluoro-,2,2′,4,4′,5,5′-hexakis(phenylthio)biphenyl (*6*)

Yellow solid, mp 45–46 °C; ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.23–7.10 (24H, H-6, H-6′, H-7, H-7′, H-7″, H-8, H-8′, H-8″), 7.01 (m, 2H, H-6″). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 159.63 (dd, $^1J_{CF}$ = 249 Hz, $^4J_{CF2'}$ = 2.8 Hz, C-3″), 156.44 (dd, $^1J_{CF}$ = 248 Hz, $^4J_{CF3''}$ = 3.5 Hz, C-2′), 135.02 (d, $^4J_{CF}$ = 1.9 Hz, C-5, C-5′), 134.25 (d, $^4J_{CF}$ = 1.8 Hz, C-5″), 129.55 (d, J_{CF} = 20 Hz, C-4′), 129.47, 129.45 (2C), 129.44, 129.24, and 129.22 (C-6, C-6′, C-6″, C-7, C-7′, C-7″), 128.90 (d, $^2J_{CF}$ = 20.2 Hz, C-3′), 127.43, 127.34, and 127.25 (C-8, C-8′, C-8″), 126.93 (d, $^2J_{CF}$ = 21.3 Hz, C-1′), 125.56 (dd, $^2J_{CF}$ = 22.9 Hz, $^3J_{CF}$ = 1.5 Hz, C-2″). ^{19}F NMR (470 MHz, CD_2Cl_2) δ −95.15 (d, $^5J_{FF2'}$ = 15.4 Hz, 2F, F-3″), −102.43 (d, $^5J_{FF3''}$ = 15.4 Hz, 2F, F-2′). MS (10 V, *m*/*z*): 897.2 (19) $[M+Na]^+$, 892.3 (100) $[M+NH_4]^+$, 875.2 (10) $[M+H]^+$. Anal. calcd for $C_{48}H_{30}F_4S_6$: C, 65.88; H, 3.46; S, 21.98; found: C, 65.90; H, 3.43; S, 23.52.

4.2.6. 3′,6′-Difluoro-2,2′,3,4,4′,5,5′,6-octakis(phenylthio)biphenyl (*8*)

Yellow solid (contains 8 mol%/8.6 wt% **9**); ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.2–6.8. ^{13}C NMR (125 MHz, CD_2Cl_2) δ 159.60 (dd,

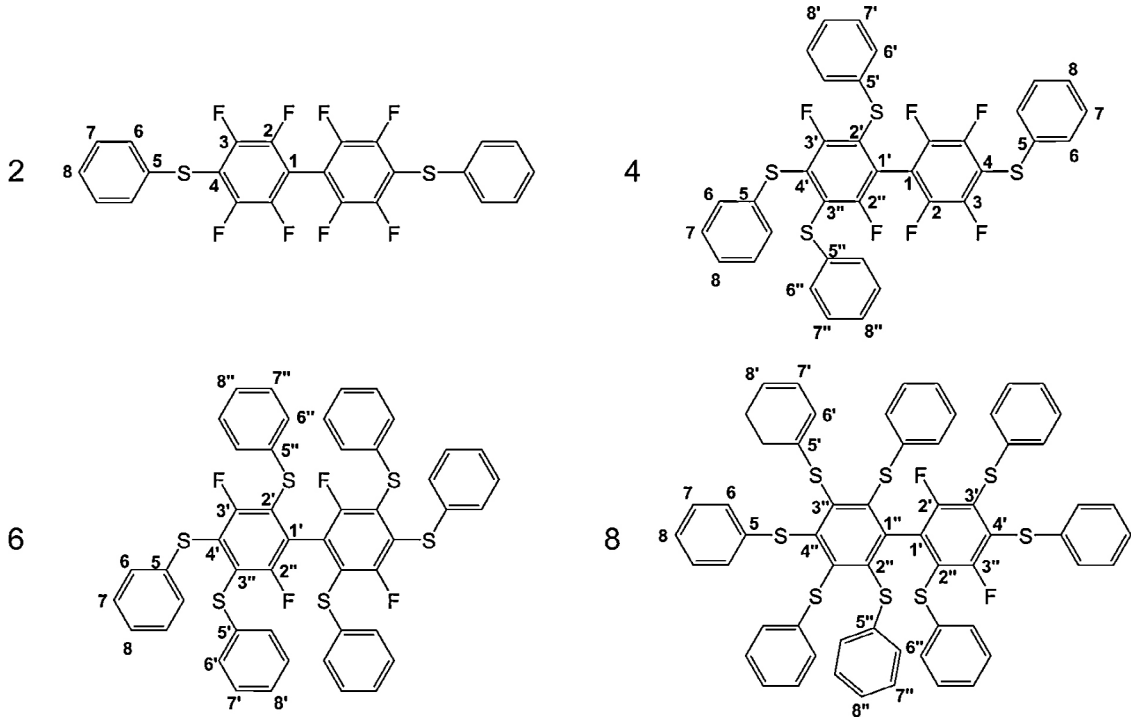


Fig. 8. Chemical formulas of the di- (**2**), tetra- (**4**), hexa- (**6**) and octa-phenylthio-substituted (**8**) fluorobiphenyls with atom numbering used for NMR signal assignment.

$^{1}J_{CF}$ = 249 Hz, $^{4}J_{CF2'}$ = 2.7 Hz, C-3″), 156.44 (dd, $^{1}J_{CF}$ = 246 Hz, $^{4}J_{CF3''}$ = 3.0 Hz, C-2′), 149.96 (C-4‴), 148.00 (C-3‴), 145.11 (br, $J_{CF} < 1$ Hz, C-1″), 143.16 (C-2‴), 138.17 (C-5 of PhS at 4‴), 138.00 and 136.87 (C-5′, C-5″ of PhS at 3‴, 2‴), 135.31 (d, $^{4}J_{CF}$ = 1.8 Hz, C-5, C-5′ of PhS at 4′, 3′), 134.50 (d, $^{4}J_{CF}$ = 2.5 Hz, C-5″ of PhS at C-2″), 133.89 (dd, $^{2}J_{CF}$ = 21.6 Hz, $^{3}J_{CF}$ = 1.6 Hz, C-1′), 129.38, 129.36, 129.33, 129.28, 129.24, 128.73, 128.56, 128.46, 128.17, and 128.09 (C-6, C-6′, C-6″, C-7, C-7′, C-7″), 128.53 (d, $^{2}J_{CF}$ = 20.5 Hz, C-3′), 127.39 (d, $^{2}J_{CF}$ = 20.5 Hz, C-4′), 127.18, 127.08, 126.63 (2 C), 126.74, 126.48, and 126.44 (2 C) (C-8, C-8′, C-8″), 124.96 (dd, $^{2}J_{CF}$ = 22.5 Hz, $^{3}J_{CF}$ = 3.0 Hz, 2″). ^{19}F NMR (470 MHz, CD_2Cl_2) δ −94.79 ppm (d, $^{5}J_{FF}$ = 15.8 Hz, 1F, F-3″), −101.04 ppm (d, $^{5}J_{FF}$ = 15.8 Hz, 1F, F-2′). MS (10 V, *m/z*): 1163.1 (5) $[\mathbf{9}_{13C}+NH_4]^+$, 1072.2 (43) $[M+NH_4]^+$, 1055.2 (100) $[M+H]^+$. Anal. calcd for 92% $C_{60}H_{42}F_2S_8$ and 8% $C_{66}H_{47}F_1S_9$: C, 68.34; H, 3.84; S, 24.37; found: C, 68.37; H, 3.78; S, 25.93.

Characteristic signals of the impurity **9**: ^{13}C NMR (125 MHz, CD_2Cl_2) δ 160.29 (d, $^{1}J_{CF}$ = 252 Hz, CF), ^{19}F NMR (470 MHz, CD_2Cl_2): δ −92.93 ppm (s).

4.3. *In situ* ^{19}F NMR kinetic investigations

In the in situ measurements, 24 scans were accumulated for each data point of the conversion-time curve applying 90° ^{19}F pulses. ^{1}H broadband decoupling and a pulse delay of 4 s were applied. The acquisition time was 1.04 s. Thus, the measuring time for each spectrum adds up to 2 min. The composition of the reaction mixture at different reaction times was determined from signal integrals.

For the in situ experiments, the educt (DFBP, **2** or **4**) is weighted in the NMR tube and dissolved in 0.3 ml NMP. Then triethylamine was added and filled up with NMP to a total volume of 0.5 ml. The NMR tube was thermostated in the NMR spectrometer to 0 °C and the reaction is started by injection of the thiophenol solution in NMP (total volume 0.2 ml) pre-cooled to −5 °C to compensate the warming during the addition. Subsequently, the tube was retransferred to the NMR spectrometer and the measurement was started after 1 min.

Reaction 1 (R1): 20 mg (5.986×10^{-5} mol) DFBP, 72.5 mg (6.585×10^{-4} mol) thiophenol, 0.185 ml (1.317×10^{-3} mol) TEA. Stoichiometry: 1:11:22.
Reaction 2 (R2): 20 mg (3.889×10^{-5} mol) **2**, 38.6 mg (3.5×10^{-4} mol) thiophenol, 0.1 ml (7.175×10^{-4} mol) TEA. Stoichiometry: 1:9:18.
Reaction 3 (R3): 20 mg (3.889×10^{-5} mol) **2**, 38.6 mg (3.5×10^{-4} mol) thiophenol, 0.194 ml (1.4×10^{-3} mol) TEA. Stoichiometry: 1:9:36.
Reaction 4 (R4): 25 mg (3.60×10^{-5} mol) **4**, 27.8 mg (2.52×10^{-4} mol) thiophenol, 0.07 ml (5.04×10^{-4} mol) TEA. Stoichiometry: 1:7:14.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013.07.013.

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