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Synthesis and physical properties of polyfluoro-acridines bearing perfluoroalkyl chains

Antonio Papagni [a,*], Paolo Campiglio [a], Marcello Campione [a], Paola Del Buttero [b], Antonio Mani [a], Luciano Miozzo [a], Enrico Tonelli [a]

[a] *Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, via R. Cozzi 53, I-20125 Milano, Italy*
[b] *Dipartimento di Chimica Organica e Industriale, Università degli Studi di Milano, via Venezian 21, I-20133 Milano, Italy*

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Abstract

Here we describe the synthesis of polyfluoro-acridines functionalised with perfluoro-alkyl and perfluoro-alkoxy chains, obtained by Ullmann coupling reaction or aromatic nucleophilic substitution. Surface wettability of PMMA is changed by doping with tetrafluoro-perfluorodecyl-acridine, as shown by AFM and contact angle measurements.

Keywords: Tetrafluoro-acridine; Perfluoro-alkyl chain; Surface segregation; Phase contrast AFM

1. Introduction

The synthesis of perfluoro-alkyl compounds has attracted a huge interest in recent years because of their peculiar physical properties and for their promising applications in materials science; for instance they can be applied to obtain n-type organic semiconductors or for other applications such as liquid crystals, low-k dielectrics. More recently, they are also employed to improve both hydro- and lipophobicity of plastics and fibres or to reduce their surface friction by exploiting the tendency of perfluoro-alkyl chains to give superficial segregation [1–6]. Within this background 1,2,3,4-tetrafluoro-acridines (Scheme 1) represent an interesting class of fluorinated molecules showing peculiar properties for potential applications in materials science: they are potential n-type semiconductors [7] and their high fluorescence was exploited to develop new electroluminescent devices [8]. This class of compound can be easily synthesised through a one-pot synthesis from pentafluoro-benzaldehyde and substituted anilines, so different kinds of substituents can be easily introduced allowing a fine control of their physical and optical properties [7]. The introduction of perfluoro-alkyl chains on the tetrafluoro-acridine nucleus represents an interesting structural modification, since it is expected to sensibly influence their physical, optical and electronic properties. Moreover the doping of a polymeric matrix with a functionalised polyfluoro-acridine can be a useful way to obtain a multifunctional material; indeed polyfluoro-acridines are fluorescent systems and can have a potential use as antibacterial drugs. These properties together with the possibility to obtain surface segregation can have useful applications in materials science. Here we describe the synthesis and the properties of a series of tetrafluoro-acridines bearing perfluorinated chains and a first experiment aimed to modify the wettability of the surface of a polymer after doping with one of the title compounds.

2. Results and discussion

In principle perfluoro-alkyl-substituted-fluoro-acridines can be prepared following two different strategies:

(1) Starting from perfluoro-alkyl substituted benzaldehyde or aniline precursors.
(2) Introduction of perfluoralkyl chains on the suitable fluoro-acridine nucleus.

* Corresponding author. Tel.: +39 0264485234; fax: +39 0264485400.
E-mail addresses: antonio.papagni@mater.unimib.it (A. Papagni), luciano.miozzo@mater.unimib.it (L. Miozzo).

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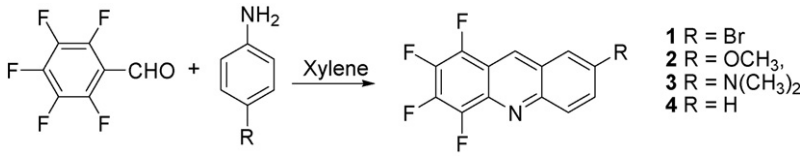


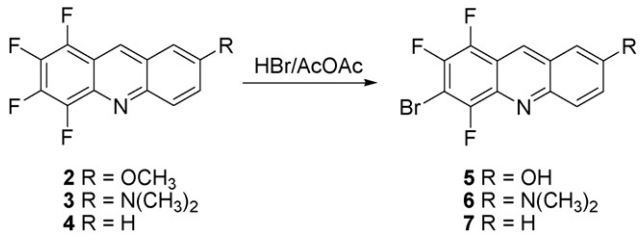
Scheme 1. Structure of 1,2,3,4-tetrafluoro-acridines. (**1**) R = Br, (**2**) R = OCH_3, (**3**) R = $N(CH_3)_2$, (**4**) R = H. At least two equivalent of amine are necessary two obtain the desired tetrafluoro-acridine.

We preferred the second strategy, because the first one presents some drawbacks. Indeed, it is known that anilines bearing electron-withdrawing fluoroalkyls are unreactive with pentafluoro-benzaldehyde in the synthesis of fluoroacridines [7]. Moreover perfluoro-alkylated tetrafluoro-benzaldehydes are not commercially available and their synthesis is not simple and straightforward. In addition, in our hands the octafluoro-acetophenone, which in principle could afford 1,2,3,4-tetra-fluoro-5-perfluorophenyl-acridines, was in this respect found unreactive with anilines. On the other side, the introduction of perfluoro-alkyl chains can be performed by copper mediated cross-coupling reaction between bromo- or iodo-aromatic substrates and perfluoro-alkyl-iodide (Ullmann reaction) or by nucleophilic aromatic reaction between a fluorinated alcohol and a reactive aromatic molecule. We studied the introduction of perfluoro-alkyl chain on tetrafluoro-acridines with both the methods. Halogen substituted tetrafluoro-acridines suitable for copper mediated cross-coupling reaction can, in principle, be synthesised by reacting pentafluoro-benzaldehyde with bromo- or iodo-anilines. Indeed, in our hands, only the 4-bromo-aniline afforded an appreciable amount of 7-bromo-tetrafluoro-acridine (**1**), while the 2-bromo-aniline was found totally unreactive [9] and the 4-iodo-aniline produced a complex reaction mixture arising from the decomposition of the starting aniline. In this latter case no traces of the expected 7-iodo-tetrafluoro-acridine were collected (Scheme 1).

The direct synthesis of bromo- or iodo-trifluoro-acridines, i.e. with the bromine or iodine atom on the fluorinated part of acridine nucleus is even more complicated since bromo- or iodo-tetrafluoro-benzaldehydes are not commercially available or hard to prepare [10]. On the contrary, a bromo- or iodo-fluorine exchange on tetrafluoro-acridines is easily accessible; in particular fluorine atom in position 2 is described in the literature to be more prone to be replaced by oxygen and nitrogen nucleophiles (alcohols and amines) through a classical aromatic nucleophilic substitution reaction [11–13]. More recently, we described a bromo/fluoro exchange during our attempts of ether function hydrolysis performed on the 1,2,3,4,-tetrafluoro-9-methoxy-acridine [14]. Indeed, by refluxing this substrate in HBr 47% aqueous solution the substitution of the fluorine in position 2 by a bromine atom was observed together with the ether hydrolysis. The position of substitution was clarified by X-ray diffraction from a single crystal of the 2-bromo-1,3,4,-trifluoro-9-hydroxy-acridine. Surprisingly, we did not observe a similar bromo/fluoro substitution performing this reaction on 1,2,3,4,-tetrafluoro-7-methoxy-acridine (**2**); only under more forcing conditions, such as those described by Bäuerle et al. [15] (in refluxing hydrobromic acid/acetic anhydride mixture) we observed a complete bromine–fluorine exchange, besides to the hydrolysis of ether function. As shown by ^{19}F NMR (see Section 4) only monosubstitution in position 2 occurs analogously to that observed on the 1,2,3,4,-tetrafluoro-9-methoxy-acridine. The same reaction was carried out on other tetrafluoro-acridines, affording the expected trifluoro-bromo-acridines (Scheme 2).

The reaction proceeds on the corresponding acridinium hydrobromide which makes the fluorine atoms more prone to nucleophilic substitution. The reaction is particularly fast on the acridine **3** where the protonation of the $N(CH_3)_2$ group makes this substrate even more electron-poor than in the other cases. We studied also the introductions of an iodine atom following the same procedure, but all the attempts were unsuccessful. In Table 1 the experimental conditions and yields of the synthesised 1,3,4-trifluoro-2-bromo-acridines are summarised. We performed the insertion of the perfluoro-alkyl chain through the Ullmann reaction starting from the bromo-fluoro-acridines **1**, **6** and **7** with 1-iodo-perfluoro-hexane in the presence of copper bronze as catalyst. In the case of acridine **1** the reaction was also performed with 1-iodo-perfluorodecane (Scheme 3).

Coupling reaction of **1** to give **8** and **9** proceeded as expected, with a good yield. Besides unreacted compound **1**, another by-product was collected. On the basis of ^1H NMR and by comparison with an authentically sample, this latter is the 1,2,3,4-tetrafluoro-acridine **4** produced by the reduction of C–Br bond in **1** promoted by copper bronze. No homo-coupling product of two bromo-tetrafluoro-acridines **1** was observed and isolated. The reaction was less clean when carried out on the acridine **6** and **7**. Indeed, when the compound **7** was reacted with 1-iodo-perfluoro-hexane under the same conditions, a complex mixture of fluorescent products was obtained and it was not possible to isolate any analytically pure product. Also the reaction of **6** with 1-iodo-perfluoro-hexane produced a complicated mixture of fluorescent products, but in this case the desired product was predominant and it was collected in 25% yield after chromatography of the crude reaction mixture. The great difference between the reactivities of compounds **1** and **7**



Scheme 2. Introduction of bromine atom by nucleophilic substitution in acidic medium. R = H, $N(CH_3)_2$. When R = OCH_3 ether hydrolysis occurs together with bromine insertion.

Table 1
Synthesis of 1,3,4-trifluoro-2-bromo-acridine

Product	Reagent	Reaction time (h)	Yield (%)
1,3,4-Trifluoro-2-bromo-7-hydroxy-acridine (**5**)[a]	**2**	18	85
1,3,4-Trifluoro-2-bromo-7-(*N*,*N*)-dimethyl-amino-acridine (**6**)	**3**	1	84
1,3,4-Trifluoro-2-bromo -acridine (**7**)	**4**	14	79

[a] Ether hydrolysis occurs together with bromine insertion.

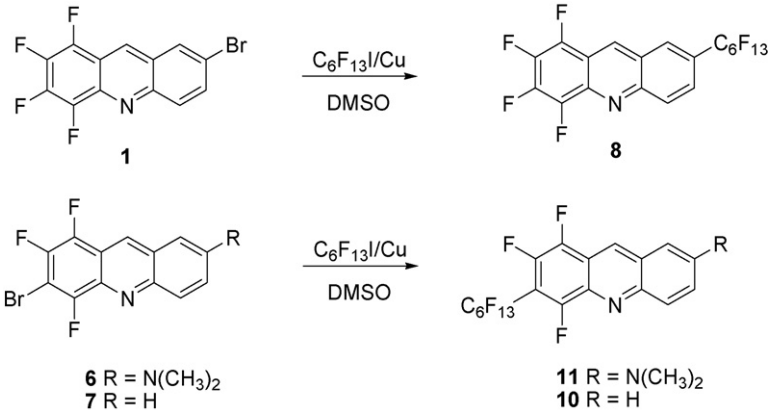
Table 2
Synthesis of perfluoro-alkyl-polyfluoro-acridines

Product	Reagent	Reaction time (h)	Yield (%)
1,2,3,4-Tetrafluoro-7-perfluorohexyl-acridine (**8**)[a]	**1**	18	70
1,2,3,4-Tetrafluoro-7-perfluorodecyl-acridine (**9**)[b]	**1**	18	30
1,3,4-Trifluoro-2-perfluorohexyl-acridine (**10**)[a]	**7**	14	–[c]
1,3,4-Trifluoro-2-perfluorohexyl-7-dimethylamino-acridine (**11**)[a]	**6**	12	26

[a] Prepared by coupling with perfluorohexyl-iodide catalyzed by copper bronze.
[b] Prepared by coupling with perfluorodecyl-iodide catalyzed by copper bronze.
[c] A complicate mixture of products was obtained and we were not able to isolate the desired product.

can be explained assuming that in the compound **7** the bromine atom is more reactive and furthermore, after perfluoro-alkyl chain insertion, the reactivity of fluorine atoms on acridine could be enhanced by the presence of a strong electron-withdrawing group (EWG) and thus they could react with the copper bronze or the organo-metallic reagent present in solution, giving the mixture observed. On the other case, when an electron donor such as a dimethyl-amino is present, the same phenomenon is less pronounced. In Table 2 are summarised experimental conditions, yields and physical properties of the synthesised perfluoro-alkyl-acridines. Exploiting the reactivity of the fluorine atom in position 2 towards the nucleophilic substitution perfluoro-alkyl chains, we introduced also a different perfluoro-alkyl chain by reacting tetrafluoro-acridine **1**–**4** with the sodium salt of perfluoro-(1H,1H)-undecanol (Scheme 4).

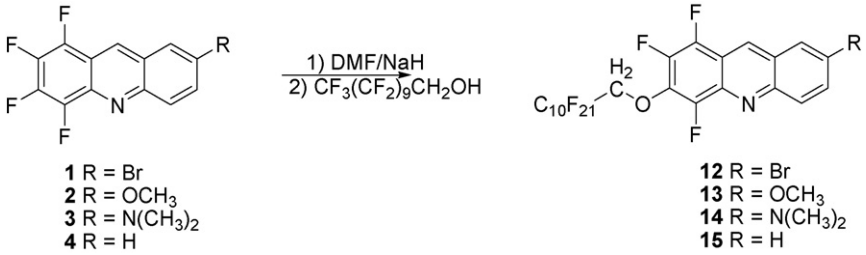
We performed the reaction in dry DMF at room temperature, using a 10% excess of sodium alkoxyde with respect of tetrafluoro-acridine, generated in situ from the alcohol with NaH. The substituted polyfluoro-acridine derivatives have been obtained in good yields (Table 3). The introduction of electron-withdrawing groups on the tetrafluoro-acridine skeleton can shift the position of the electronic levels. We investigated these phenomena by means of absorption and fluorescence measurements on solutions of the compound presented so far. The introduction of perfluoro-alkyls has only a minor effect on the molecular gap (i.e. the energy difference between HOMO and LUMO). In Fig. 1a is reported a comparison between the low energy region of the absorption spectra of compounds **9** and **15** together with the parent compound **4**. Only minor differences are present and the spectra of **4** and **9** are nearly superimposable. The same behaviour was observed for the other molecules. The same trend is present in fluorescence spectra, which show very similar spectra after and before the insertion of perfluorinated chains. A slightly different behaviour is observed with polyfluoro-dimethylamino-acridines (compounds **3**, **11**, **14**, Fig. 1b), where compounds **11** and **14** show a little red shift with respect to the parent compound **3**. We can account for this behaviour formulating the hypothesis that the first excited state of compound **3** has a large electric dipole moment, which causes a pronounced stokes shift in slightly to polar solvents, due to the relaxation of the molecule in the



Scheme 3. Copper catalysed Ullmann reaction between polyfluoro-bromo-acridines and perfluoro-alkyl iodides. R = NMe_2; when R = H the reactions fails.

Table 3
Synthesis of 2-(1H,1H)-perfluoroundeciloxy-trifluoro-acridines

Product	Reagent	Reaction time (h)	Yield (%)
1,3,4-Tetrafluoro-2-$C_{10}F_{21}CH_2O$-7-bromo-acridine (**12**)	**1**	15	68
1,3,4-Tetrafluoro-2-$C_{10}F_{21}CH_2O$-7-methoxy-acridine (**13**)	**2**	60	60
1,3,4-Trifluoro-2-$C_{10}F_{21}CH_2O$-7-(*N*,*N*)-dimethyl-amino-acridine (**14**)	**3**	60	71
1,3,4-Tetrafluoro-2-$C_{10}F_{21}CH_2O$-acridine (**15**)	**4**	20	72



Scheme 4. Reaction between some tetrafluoro-acridines and the sodium salt of 1H,1H-perfluoroundecanol.

excited state [7]; within this frame, the insertion of a electron-withdrawing can enhance the solvent effect, shifting to longer wavelength the emission spectrum. The same hypothesis can account for the strong solvatochromic effect observed in the fluorescence spectra of **11** (Fig. 1c).

Preliminary experiments of surface segregation of per-fluoro-alkyl chains have been performed on film realised by spin coating of polymethylmetacrilate (PMMA) doped with **9**. The surface segregation was monitored by contact angle analysis and atomic force microscopy (AFM) before and after thermal annealing at T_g temperature of PMMA (Fig. 2). Through the analysis with optical microscope we estimated the saturation limit for compound **9** in PMMA; the analysis showed that at concentrations higher than 1% of **9** in PMMA, microcrystals of acridine appeared within the polymers. All the subsequent analyses were carried out by exploring the range of concentration between 0.1% and 0.5%, in order to avoid the occurrence of spontaneous precipitation of aggregates. Before thermal annealing the contact angle of thin film is the same of pure PMMA (57°), but it increases of 10° after 30 min of annealing at T_g of PMMA and no change are observed after longer annealing. When the annealing was extended over 12 h the contact angle recovers the starting value (pure PMMA). This phenomenon is due to a slow sublimation of **9** from the surface and it was also confirmed by optical analysis; indeed, the film before annealing is fluorescent with the typical acridine emission, while after a prolonged annealing the fluorescence completely disappeared. Phase contrast AFM analysis was carried out to study locally the change of chemical–physical properties of the surface, because superficial segregation of fluorinated chains can change the interaction between the tip of the AFM and the surface. Fig. 2 reports the surface topography of a PMMA film doped with 0.5% of 9, after an annealing treatment for 5 h at the T_g of the polymer. The surface is smooth, with a roughness (rms) of ca. 16 nm, as measured on an area of 50 μm × 50 μm. On the same area, the phase contrast image shows the presence of dark regions, covering about 10% of the surface, within a uniform background. These two levels correspond to two regions with different stiffness, which we attribute to the formation of fluorocarbon-rich domains segregated from pure PMMA as a consequence of the annealing treatment; the dark areas in the false colours image should correspond to the fluorinated regions.

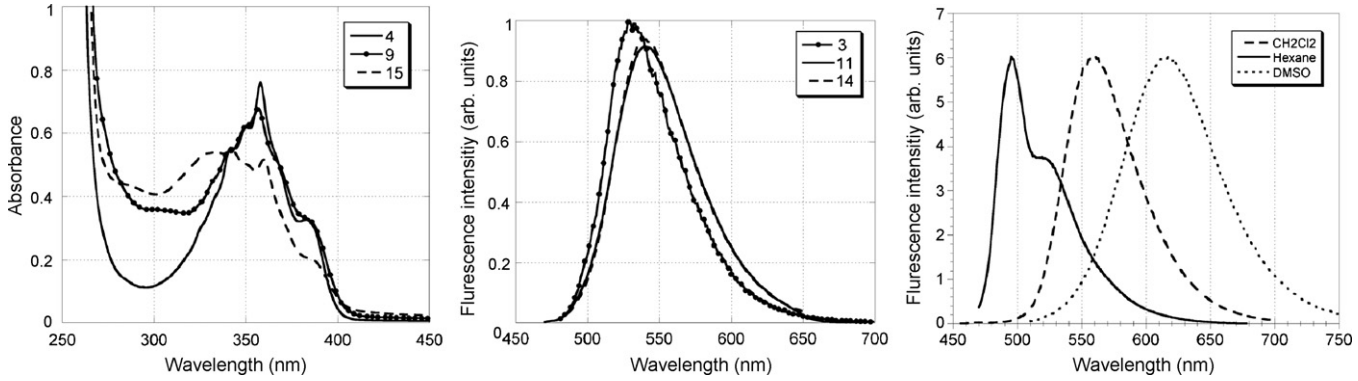


Fig. 1. (a) On the left, absorption spectra of compounds **4**, **9**, **15** in 10^{-5} M solution of CH_2Cl_2; (b) in the centre, fluorescence spectra of compounds **3**, **11**, **14** in 10^{-5} M solution of CH_2Cl_2; (c) on the right, fluorescence spectra of compound **11** in different solvents (hexane, CH_2Cl_2 and DMSO).

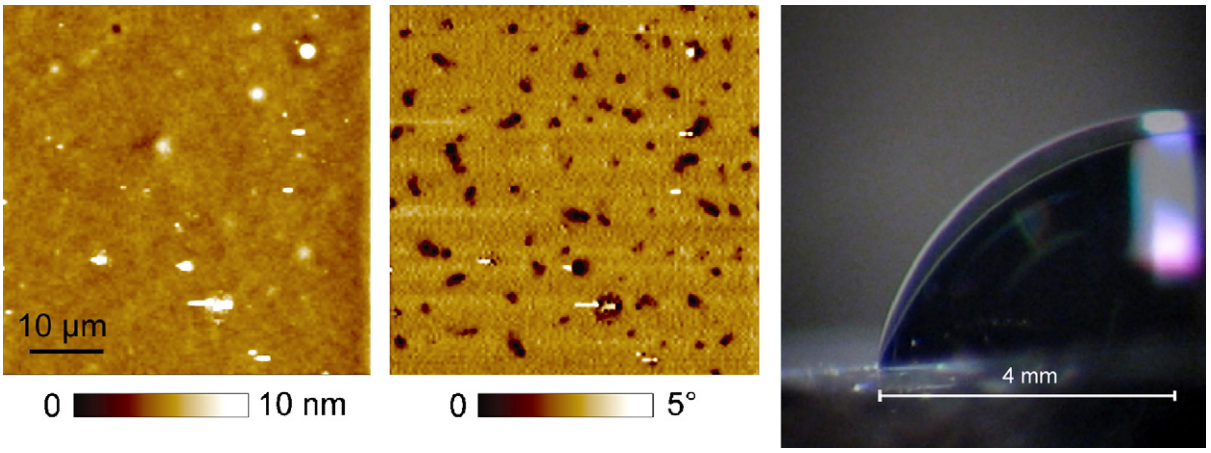


Fig. 2. Topography (left) and phase contrast (center) AFM images of the surface of the PMMA film doped with 0.5% of **9**, after annealing for 5 h at T_g of PPMA. On the right image of a drop of water on the surface of PMMA before and after the thermal annealing. The contact angle goes from 75° to 79°.

3. Concluding remarks

We have studied the introduction of perfluoro-alkyl chains in some polyfluoro-acridines, highlighting how the position of functionalization or the presence of a substituent can modify the reactivity of similar compounds towards the same reagent. The preparation of trifluoro-bromo-acridines gives the possibility to introduce also other substituents with metal-catalyzed or cross-coupling reactions. Preliminary studies about surface segregation carried out by doping PMMA with the compound **9** underline that this compound shows a considerable mobility in the polymeric matrix because all the acridine can easily reach the surface. The nature of the surface changes after the segregation of perfluorinated chains, as demonstrated by angle contact and AFM measurements.

4. Experimental

4.1. General experimental procedures

All starting materials were purchased from commercial sources (Aldrich Chemical Co.; Fluorochem for fluorinated reagents). Solvents were of analytical grade and used as received. ^{1}H and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 400 spectrometer and Bruker 300, using $CFCl_3$ as internal standard for ^{19}F spectra; all chemical shifts δ are reported in ppm and coupling constants (J values) in Hz. AFM images were collected with a Nanoscope IIIa MMAFM (Digital Instruments, Veeco) in tapping™ mode with silicon cantilevers under ambient conditions. The setpoint/free amplitude ratio of the oscillation was set to 0.5 (moderate tapping), in order to be sensitive to surface stiffness variations [16]. Synthesis of 1,2,3,4-tetrafluoro-acridines (compounds **1**–**4**) was carried out as described in the literature. For some compounds bearing fluorinated alkyl chains, elementar analyses gave sometimes disagreements between calculated and found results for C, H, N, due to the non-perfect combustion of fluorinated chains.

4.2. General procedure for the synthesis of 1,3,4-trifluoro-2-bromo-acridines with HBr/Ac_2O

HBr solution (47%, 15 mL) was added dropwise to acetic anhydride (Ac_2O, 14 mL); the reaction was strongly exothermic and the solution must be cooled with brine. 1,2,3,4-Tetrafluoro-acridine (0.4 mmol) was added to the HBr/Ac_2O solution and the reaction was monitored with TLC. The solution was heated under reflux (see Table 1 for the total refluxing time) until the reagent (tetrafluoro-acridine) disappeared, then it was poured into an ammonia solution (25%) to destroy Ac_2O and extracted with CH_2Cl_2 or ethyl acetate. The collected organic phases were dried with Na_2SO_4 and then the solvent removed. If necessary the solid was purified by a quick filtration under vacuum on a bed of silica.

4.2.1. 1,3,4-Trifluoro-2-bromo-7-hydroxy-acridine (**5**)

Yellow solid. ^{1}H NMR (DMSO), δ: 10.65 (s, 1H H_5), 8.98–8.95 (d, 1H, H_9), 8.09–8.05 (d, 1H, H_8), 7.56–7.60 (d, 1H, H_6), 7.36 (s, 1H, OH); ^{19}F NMR ($CDCl_3$), δ: −118.4 (d, 1F, F_3), −134.4 (d, 1F, F_4), −151.1 (t, 1F, F_1). Anal. Calcd for $C_{13}H5BrF_3NO$: C, 47.59; H, 1.54; N, 4.27. Found: C, 46.98; H, 1.40; N, 4.02.

4.2.2. 1,3,4-Trifluoro-2-bromo-7-(N,N)-dimethyl-amino-acridine (**6**)

Dark orange solid. ^{1}H NMR ($CDCl_3$), δ: 8.67 (s, 1H, H_5), 8.42 (d, 1H, J = 9.7, H_9), 8.28–8.24 (dd, 1H, J_1 = 9.7, J_2 = 2.8, H_8), 8.04–8.01 (d, 1H, J = 2.8, H_6), 3.20 (s, 6H, CH_3); ^{19}F NMR ($CDCl_3$), δ: −118.9 (d, 1F, F_3), −135.1 (d, 1F, F_4), −151.7 (t, 1F, F_1). Anal. Calcd for $C_{15}H_{10}BrF_3N_2$: C, 50.73; H, 2.84; N, 7.89. Found: C, 49.98; H, 2.70; N, 7.92.

4.2.3. 1,3,4-Trifluoro-2-bromo-acridine (**7**)

Pale yellow solid. ^{19}F NMR ($CDCl_3$): δ (ppm) −117.8 (d, 1F, F_3), −133.7 (d, 1F, F_4), −150.5 (t, 1F, F_1). Anal. Calcd for $C_{13}H_5BrF_3N$: C, 50.03; H, 1.61; N, 4.49. Found: C, 49.90; H, 1.41; N, 4.56.

4.3. General procedure for the coupling of perfluoro-alkyl-iodide with polyfluoro-bromo-acridines mediated by copper bronze

A suspension of Cu bronze (90 mg, 1.42 mmol) in dry DMSO (24 mL) was heated under vigorous stirring at 125 °C for 15 min under N_2 atmosphere. Perfluoro-alkyl iodide (0.92 mmol) was added and the temperature kept below 135 °C. After 45′ polyfluoro-bromo-acridines was added and the reaction mixture was stirred at 125 °C (see Table 2 for the total reaction time). The reaction was monitored by TLC (CH_2Cl_2, silica gel). After the end of the heating, the reaction was quenched with water and filtered through celite, which was washed with ethyl acetate (AcOEt). The aqueous phase was extracted with AcOEt and the organic phases were combined, washed again with water and dried over Na_2SO_4. After filtration the solvent was evaporated to give a solid, which was purified by chromatography on silica gel (CH_2Cl_2/hexane, 2:1) to afford a pure product.

4.3.1. 1,2,3,4-Tetrafluoro-7-perfluorohexyl-acridine (**8**)

Pale yellow solid. mp 151 °C. ^{1}H NMR ($CDCl_3$), δ: 9.22 (s, 1H, H_5), 8.42 (s, 1H, H_6), 8.50–8.47 (d, 1H, J = 9.2, H_9), 8.04–8.01 (d, 1H, J = 9.2, H_8); ^{19}F NMR ($CDCl_3$): δ: −81.16 (d, 3F), −111.17 (s, 2F), −121.79 (s, 4F), −123.15 (s, 2F), −126.50 (s, 2F), −149.76 (t, 2F, F_2 and F_3), −151.06 (s, 1F, F_4), −156.01 (s, 1F, F_1). Anal. Calcd for $C_{19}H_4F_{17}N$: C, 40.09; H, 0.71; N, 2.46. Found: C, 44.17; H, 1.07; N, 3.02.

4.3.2. 1,2,3,4-Tetrafluoro-7-perfluorodecyl-acridine (**9**)

Pale yellow solid. ^{1}H NMR ($CDCl_3$), δ: 9.23 (s, 1H, H_5), 8.42 (s, 1H, H_6), 8.51–8.48 (d, 1H, J = 9.3, H_9), 8.04–8.01 (d, 1H, J = 9.2, H_8); ^{19}F NMR ($CDCl_3$), δ: −81.16 (d, 3F), −117.17 (s, 2F), −122.07 (m, 12F), −123.06 (s, 2F), −126.47 (s, 2F), −149.73 (t, 2F, F_2 and F_3), −151.07 (s, 1F, F_4), −156.04 (s, 1F, F_1). MS (EI): 769 *m/z*. Anal. Calcd for $C_{23}H_4F_{25}N$: C, 35.91; H, 0.52; N, 1.82. Found: C, 35.36; H, 0.56; N, 2.84.

4.3.3. 1,3,4-Trifluoro-2-perfluorohexyl-7-(N,N)-dimethyl-amino-acridine (**11**)

Dark orange solid. mp 197 °C. ^{1}H NMR ($CDCl_3$), δ: 8.65 (s, 1H, H_5), 8.21–8.18 (d, 1H, J = 9.7, H_9), 7.70–7.66 (dd, 1H, J_1 = 9.7, J_2 = 2.8, H_8), 6.88–6.87 (d, 1H, J = 2.8, H_6), 3.22 (s, 6H, CH_3); ^{19}F NMR ($CDCl_3$), δ: −81.15 (s, 3F), −106.12 (m, 6F), −120.58 (m, 2F), −122.64 (t, 2F), −126.48 (s, 1F, F_1), −144.96 (s, 1F, F_4), −152.29 (s, 1F, F_3). Anal. Calcd for $C_{21}H_{10}F_{16}N_2$: C, 42.44; H, 1.70; N, 4.71. Found C, 51.23; H, 1.90; N, 4.89.

4.4. General procedure for the nucleophilic substitution with (1H,1H)-perfluoro-undecanol

To a stirred mixture of NaH (60% in paraffin) in anhydrous DMF (5 mL), perfluorinated undecanol (5% excess) was added and the mixture allowed to react 10 min at room temperature. Tetrafluoro-acridine (50 mg) was added to the pale red solution and the mixture was allowed to react until no more acridine was detected by thin layer chromatography. The reaction was quenched by adding water (10 mL) and extracted with CH_2Cl_2. The collected organic phases were dried with anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The product was crystallized from CH_2Cl_2 affording analytically pure 2-perfluoro-alkoxy substituted acridine.

4.4.1. 1,3,4-Trifluoro-2-(1H,1H)-perfluoroundeciloxy-7-bromo-acridine (**12**)

Pale yellow solid. ^{1}H NMR ($CDCl_3$), δ: 8.94 (s, 1H, H_5), 8.25–8.22 (d, 1H, J = 9.6, H_9), 7.96–7.93 (d, 1H, J = 9.3, H_8), 7.0 (s, 1H, H_6), 4.97–4.93–4.89 (t, 2H, J = 13, CH_2); ^{19}F NMR ($CDCl_3$), δ: −81.15 (s, 3F), −120.85 (s, 2F), −122.06 (m, 10F), −123.03 (s, 2F), −123.43 (s, 2F), −126.44 (s, 2F), −146.07 (s, 1F, F4), −150.97 (m, 1F, F_3), −151.95 (s, 1F, F_1); MS (EI): 859 *m/z*. Anal. Calcd for $C_{24}H_6BrF_{24}NO$: C, 33.51; H, 0.70; N, 1.63. Found: C, 33.91; H, 0.89; N, 1.56

4.4.2. 1,3,4-Trifluoro-2-(1H,1H)-perfluoroundeciloxy-7-methoxy-acridine (**13**)

Yellow solid. ^{1}H NMR ($CDCl_3$), δ: 8.74 (s, 1H, H_5), 8.12–8.09 (d, 1H, J = 9, H_9), 7.48–7.45–7.42 (t, 1H, J = 9, H_8), 6.91 (s, 1H, H_6), 4.54 (s, 3H, –CH_3), 4.82–4.79–4.75 (t, 2H, J = 12, –CH_2–); ^{19}F NMR ($CDCl_3$), δ: −81.13 (s, 3F), −120.93 (s, 2F), −122.09 (m, 10F), −123.05 (s, 2F), −123.46 (s, 2F), −126.46 (s, 2F), −146.43(s, 1F, F_1), −151.81 (m, 1F, F_3), −153.53 (s, 1F, F_4); MS (EI): 811 *m/z*. Anal. Calcd for $C_{25}H_9F_{24}NO_2$: C, 37.01; H, 1.12; N, 1.73. Found: C, 40.41; H, 1.23; N, 1.56.

4.4.3. 1,3,4-Trifluoro-2-(1H,1H)-perfluoroundeciloxy-7-dimethyl-amino-acridine (**14**)

Orange solid. ^{1}H NMR ($CDCl_3$), δ: 8.63 (s, 1H, H_5), 8.15–8.19 (d, 1H, J = 9.6, H_9), 7.61–7.62 (d, 1H, H_8), 6.87–6.86 (d, 1H, H_6), 4.87–4.83–4.79 (t, 2H, J = 7.1, –CH_2–), 3.16 (s, 6H, –CH_3); ^{19}F NMR ($CDCl_3$), δ: −81.15 (s, 3F), −120.95 (s, 2F), −122.09 (m, 10F), −123.06 (s, 2F), −123.48 (s, 2F), −126.47 (s, 2F), −146.85 (s, 1F, F_1), −152.93 (d, 1F, F_3), −154.98 (s, 1F, F_4); MS (EI):824 *m/z*. Anal. Calcd for $C_{26}H_{12}F_{24}N_2O$: C, 37.88; H, 1.47; N, 3.40. Found: C, 34.75; H, 1.17; N, 3.27.

4.4.4. 1,3,4-Trifluoro-2-(1H,1H)-perfluoroundeciloxy-acridine (**15**)

Yellow solid. ^{1}H NMR ($CDCl_3$), δ: 9.00 (s, 1H, H_5), 8.32–8.29 (d, 1H, J = 8.8, H_6), 8.06–8.01 (d, 1H, J = 8.37, H_9), 7.90–7.88–7.85 (t, 1H, J = 9, H_7), 7.67–7.64–7.62 (t, 1H, J = 9, H_8), 4.94–4.90–4.86 (t, 2H, J = 12, –CH_2–); ^{19}F NMR ($CDCl_3$), δ: −81.15 (s, 3F), −120.86 (s, 2F), −122.05 (m, 10F), −123.03 (s, 2F), −123.44 (s, 2F), −126.44 (s, 2F), −146.52(s, 1F, F_1), −151.49 (m, 1F, F_3), −153.53 (s, 1F, F_4); MS (EI): 781 *m/z*. Anal. Calcd for $C_{24}H_7F_{24}NO$: C, 36.90; H, 0.90; N, 1.79. Found: C, 34.58; H, 1.12; N, 1.56.

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