# Synthesis and Properties of Polyfluorohydroxyacridines and Their $Zn^{2+}$ Complexes: New Materials for Solid State Emitting Systems

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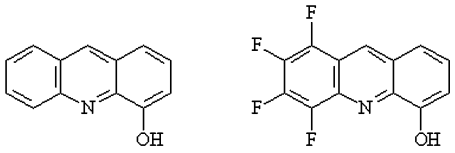
1,2,3,4-tetrafluoroacridines are easily accessible by refluxing electron-rich aromatic amines with pentafluorobenzaldehyde. This procedure, however, fails when 4-hydroxyaniline is employed for the preparation of the corresponding tetrafluorohydroxyacridine. The synthesis of this substrate, here described, has been accomplished by an indirect methodology: the synthesis of the corresponding tetrafluoromethoxyacridine was followed by the ether function cleavage by refluxing them in 47% aqueous HBr. In the case of 1,2,3,4-tetrafluoro-9-methoxyacridine a peculiar reactivity has been observed, indeed the substitution of a fluorine by a bromine atom occurs contemporaneously with the ether hydrolysis. The position of bromine on acridine moiety has been ascertained by X-ray analysis on a single crystal of this compound. The fluorine substitution did not occur when the hydrolysis was carried out employing the ionic liquid triethylammonium eptachloro alluminate. The synthesized polifluorohydroxyacridines have been fully optically and spectroscopically characterized. 1,2,3,4-Tetrafluoro-9-hydroxyacridine and 2-bromo-1,3,4-trifluoro-9-hydroxyacridine were employed to prepare complexes with $Zn^{2+}$. These complexes were optically characterized by optical absorption and photoluminescence both in solution and in the solid state, and a preliminary discussion about the photophysics of these complexes is presented.

## Introduction

1-Hydroxyacridines, prepared for the first time by Matsumura in 1927,[1] have been synthesized so far by different ways involving, in almost all cases, the preparation of alkoxyacridones, their reduction to acridines, and the hydrolytic cleavage of the ether function. 1-Hydroxyacridine (**1**)[2] (Chart 1) has been initially studied for its pharmacological properties[1a] and, more recently, has been extensively studied and employed in analytical chemistry, exploiting the fluorescence properties of its complexes for the determination of metal cations by spectrofluorimetry.[3] In materials science the fluorescence properties of its complexes with divalent cations have also found applications as the emitting component in developing new organic light-emitting devices (OLEDs).[4] From these points of view 1,2,3,4-tetrafluoro-9-hydroxyacridine (**2**) (Chart 1) should be an interesting substrate, since the fluorination modifies both physical and electrochemical properties of the acridine nucleus. Indeed, as recently reported, tetrafluoroacridine shows a reduction potential lowered by 0.2 V with respect to acridine and a peculiar molecular packing in the solid state.[5]

**Chart 1. 1-Hydroxyacridine (1) and 1,2,3,4-Tetrafluoro-9-hydroxyacridine (2).**




**1** **2**

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(1) (a) Matsumura, K. *J. Am. Chem. Soc.* **1927**, *49*, 810. (b) Jensen, H.; Rethwisch, F. *J. Am. Chem. Soc.* **1928**, *50*, 1144.

(2) Various ways of numbering the acridine nucleus have been adopted over time. The system used here was proposed by M. Richter in *Lexicon der Kohlenstoff Verbindungen*; Verlag von Leopold Voss: Hamburg/Leipzig, 1900.

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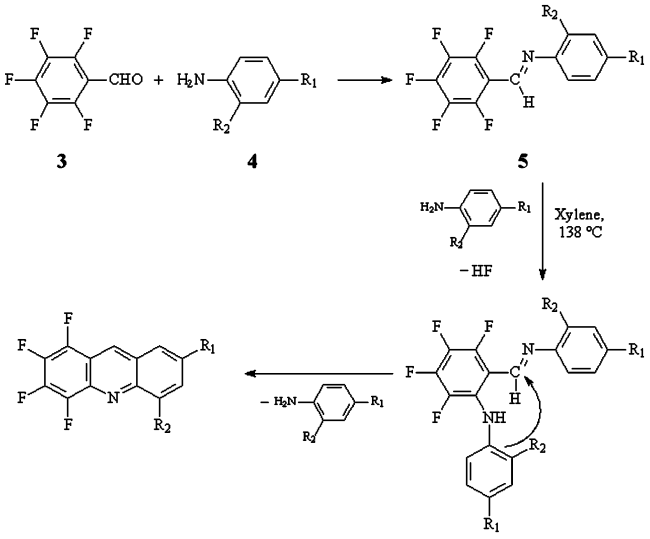
1,2,3,4-Tetrafluoroacridines can be prepared by a simple one-step procedure starting from pentafluorobenzaldehyde (**3**) and electron-rich aromatic amines (**4**), allowing us to preparing several tetrafluoroacridine substrates where the position of the substituent(s) on the acridine moiety is fully determined by its position on the starting aniline[5,6] (Scheme 1). The reaction occurs through the formation of the imine intermediate (**5**) followed by the nucleophilic substitution of the *ortho*-fluorine atom by a second aniline molecule and final acridine ring closure.

**Scheme 1. Synthesis of 1,2,3,4-Tetrafluoroacridines**




This work is aimed to describe the synthesis of polyfluorohydroxyacridines and of their complexes with $Zn^{2+}$, along with the study of their optical properties by means of optical absorption and photoluminescence. The potential use of these complexes should be as electron-poor, light-emitting systems in organic LEDs; this application is beyond the purpose of this article and will be not discussed here.

## Results and Discussion

**a. Synthesis of Fluorinated Hydroxyacridines.** The previously described synthesis of tetrafluoroacridines fails when 2-hydroxyaniline is employed, thus the corresponding 1,2,3,4-tetrafluoro-9-hydroxyacridine is not accessible by this route. Indeed, with this amine the reaction stops at imine level in equilibrium with the emi-aminal form of the aldehyde function or the substitution of more fluorine atoms occurs leading to benzoxazine derivatives as reported in the literature.[7] Here the alternative synthesis of 7- and 9-hydroxytetrafluoroacridines, based on the hydrolysis of the ether function in the corresponding methoxytetrafluoroacridine derivatives is described together with a comparison of their reactivity and properties. Following the synthetic procedure reported in the literature,[5,6] we have synthesized the 1,2,3,4-tetrafluoro-7-methoxyacridine (**6**) and the 1,2,3,4-tetrafluoro-9-methoxyacridine (**7**), by reacting 2-methoxy or 4-methoxyaniline with pentafluorobenzaldehyde in refluxing xylene. As expected[8] the reactivity of the amino function is sterically hindered by the presence of the methoxy group in the ortho position and the final acridine (**7**) has been collected in a lower yield than **6**[9] (see Table 1).

The methyl ether cleavage has been performed with HBr following the classical aromatic ethers hydrolysis. The hydrolysis requires prolonged refluxing in 47% HBr water and proceeds on the corresponding acridinium hydrobromide salt. From the methoxyacridine **6** the corresponding 1,2,3,4-tetrafluoro-7-hydroxyacridine (**8**) was recovered in 85% yield, while from **7** a hydroxyacridine derivative was recovered in 56% yield. On the basis of spectroscopic ($^{19}$F NMR) and mass (MALDI-TTOF) analyses, this latter resulted to be a trifluorobromohydroxyacridine. The structure of 2-bromo-1,3,4-trifluoro-9-hydroxyacridine (**9**) has been assigned by X-ray diffraction analysis on a single crystal grown from solution (see Section b). The incorporation of a bromine atom was unexpected and occurs by fluorine atom nucleophilic substitution by the bromide anion present in the hydrolytic reaction medium and the substitution reaction is highly region-specific. Fluorine substitution has been already observed on similar substrates but with different nucleophiles[10] and also in the case the substitution reaction is highly region-specific. The investigation about the reasons of such region-specificity is obviously beyond the purpose of this article and this reaction was not investigated further. Small amounts of a trifluoroacridine, probably the bromotrifluoro-derivative, was detected with $^{19}$F NMR within the crude hydrolysis mixture of **8**, however the amount of this impurity does not increase sensitively by prolonged refluxing of **8** in HBr, thus the high level of fluorine substitution observed during the hydrolysis of **7** seems to be peculiar of this isomer (see Scheme 2).

Looking for milder hydrolysis conditions avoiding the presence of nucleophilic species, we have tried the liquid ionic trimethylammonium eptachloro dialluminate (TMAH $Al_2Cl_7$), recently proposed as a highly efficient cleavage reagent for a wide range of methoxy aromatic and heteroaromatic derivatives under very mild conditions.[11] The use of this reagent effectively affords the expected 1,2,3,4-tetrafluoro-9-hydroxyacridine **2** in excellent yield[12] (Scheme 3).

In Table 1 are summarized experimental conditions, yields, and physical properties of the synthesized fluoroacridines.

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(9) This effect is enhanced with the thiomethylaniline. Whereas the *para* isomer gave the usual ring-closure product,[5] when using the *ortho* isomer the ring closure is even more hindered and no ring-closure product was detected even using forced reaction conditions.
(10) Orlova, N. A.; Burov, D. M.; Gerasimova, T. N.; Fokin, E. P. *Ser. Khim. Nauk* **1984**, *2* 115.
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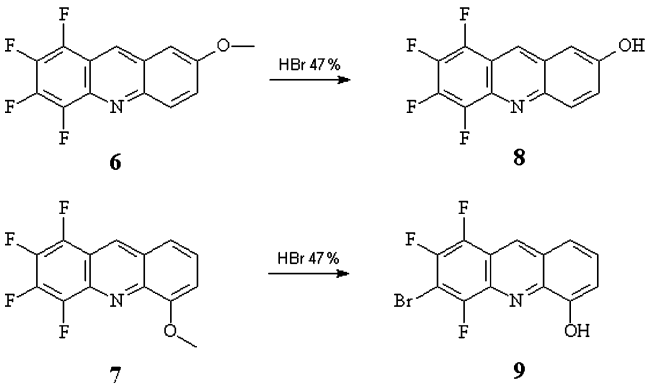
(12) Nevertheless, the related isomer **6** does not react using the same reaction conditions and it was collected unreacted after the usual reaction time.

**Table 1. Synthesized Fluoromethoxy- and Fluorohydroxyacridines and Their Physical Properties**

| compound | reaction time (h) | yield (%) | mp (°C) | sublimation temp. (°C) |
|---|---|---|---|---|
| 1,2,3,4-tetrafluoro-7-methoxyacridine (**6**)[a] | 62 | 74 | 211 | 140 (0.1 mbar) |
| 1,2,3,4-tetrafluoro-9-methoxyacridine (**7**) | 86 | 45 | 219 | 140 (0.1 mbar) |
| 1,2,3,4-tetrafluoro-9-hydroxyacridine (**2**)[b] | 10 | 85 | 202 | 110 (0.1 mbar) |
| 1,2,3,4-tetrafluoro-7-hydroxyacridine (**8**)[c] | 4 | 84 | 206 | 170 (0.1 mbar) |
| 2-bromo-1,3,4-trifluoro-9-hydroxyacridine (**9**)[c] | 14 | 52 | 207 | 140 (0.5 mbar) |

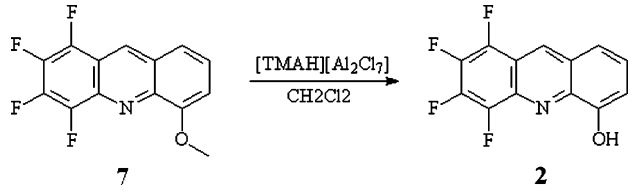
[a] The synthesis of **6** was already described elsewhere.[5,6] [b] Reaction with ionic liquid (chloroaluminate). [c] Reaction with HBr solution.

**Scheme 2. Cleavage of Methylethers with HBr Solution (47%)**




**6** **8** **7** **9**

**Scheme 3. Synthesis of 2 with the Ionic Liquid $[(CH_3)_3NH^+][Al_2Cl_7-]$**




**7** **2**

**b. X-ray Crystallographic Analysis of 2-Bromo-1,3,4-trifluoro-9-hydroxyacridine (9).** Because of the peculiar type and importance of the interactions observed between molecules of **9** in the solid state, the X-ray crystallographic analysis deserves to be discussed in detail. Experimental and refinement data are collected in the Experimental Section and Table 2 (See Supporting Information for a table with selected intra- and intermolecular distances and angles). 2-bromo-1,3,4-trifluoro-9-hydroxyacridine crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with two independent molecules in the asymmetric unit (Figure 1) sitting in general position and giving four molecules in the unit cell. Apart from temperature-induced shrinking of the unit cell parameters on moving from 298 K (indicated as **9**a in Table 2) to 123 K (indicated as **9**b in Table 2), no significant differences were found for the crystal packing at the two temperatures. Therefore, in the subsequent discussion, the geometrical parameters are extracted from the RT data set to better compare them with other systems which were mainly studied around RT. Intramolecular parameters for molecule **9** conform to values already reported for other 1,2,3,4-tetrafluoroacridines bearing a substituent in position 7,[5,13] and they are not discussed in the present paper (see ref 5).

**Table 2. Summary of Crystallographic Data for 2-Bromo-1,3,4-trifluoro-9-hydroxyacridine (9)**

| | **9a** | **9b** |
|---|---|---|
| formula | $C_{13}H_5BrF_3NO$ | |
| FW, g/mol | 328.08 | |
| crystal system | triclinic | |
| space group | $P\bar{1}$ (No. 2) | |
| $T$, K | 298 | 123 |
| $a$, Å | 7.2258(8) | 7.1417(6) |
| $b$, Å | 12.2109(12) | 12.2055(10) |
| $c$, Å | 13.9069(14) | 13.7337(12) |
| α, deg | 110.412(3) | 110.432(2) |
| $\beta$, deg | 96.886(3) | 95.879(2) |
| $\gamma$, deg | 92.829(3) | 92.918(2) |
| $V$, Å$^3$ | 1136.2(2) | 1111.1(2) |
| $Z$ | 4 | 4 |
| $Z'$ | 2 | 2 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.918 | 1.961 |
| $\mu$, mm$^{-1}$ | 3.647 | 3.729 |
| min. rel transmission | 0.76 | 0.66 |
| crystal decay, % | 0 | 0 |
| $\theta$ range, deg | 2.78−25.01 | 1.93−30.02 |
| index ranges, $h$ $k$ $l$ | -8/8 −14/14 −16/16 | -9/10 −17/17 −19/19 |
| reflns collected | 9841 | 13404 |
| indep reflns $R$(int) | 4007, 0.0432 | 6378, 0.0192 |
| data/restraints/params | 4007/0/345 | 6378/0/345 |
| GOF on $F_o^2$ | 0.999 | 0.899 |
| R1, wR2 [$F_o > 4\sigma(F_o)$] | 0.0363, 0.0833 | 0.0272, 0.0725 |
| R1, wR2 [all data] | 0.0694, 0.0978 | 0.0313, 0.0747 |
| max diff. peak/hole, $e$ Å$^{-3}$ | 0.469/−0.381 | 1.166/−0.380 |
| weighting scheme[a], $a/b$ | 0.0458/0.0000 | 0.0487/0.8125 |

[a] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

The more relevant structural features of compound **9** pertain to different kinds of intermolecular contacts (Figure 2) that are responsible for interesting supramolecular motifs involved in the crystal packing of compound **9**. The discussion about the large number of classical and nonclassical interaction is summarized in the Supporting Information.[14−23]

Another relevant feature observed in the crystal structure of **9** is the head-to-tail stacking of the perfluoroarene moiety of one molecule and the arene region of a second molecule embedded within an adjacent 2D sheet (Figure 3). This long known[24] type of interaction (whose intimate nature is still not completely understood[25]), has been already exploited as a steering factor for predefined supramolecular organization.[26] In **9** distances between the stacked planes are in the range 3.27−3.59 Å depending on geometrical details of the molecular overlap. These stacking motifs basically comprise an arrangement of inversion center related molecules resembling hexagonal graphite layers, in a

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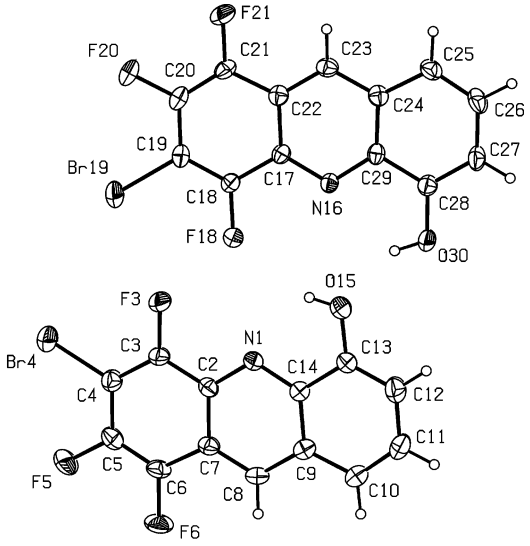


**Figure 1.** ORTEP drawing (ellipsoids at 30% probability level) and numbering scheme for the two crystallographically independent molecules of 2-bromo-1,3,4-trifluoro-9-hydroxyacridine (**9a**, i.e., diffraction data collected at 298 K). Molecules A and B used in subsequent discussion are at the bottom and top of the figure, respectively. Hydrogen atoms were given arbitrary radii.

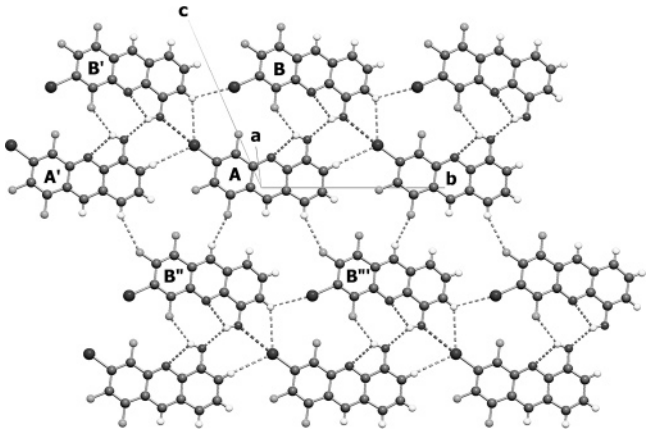


**Figure 2.** View of some of the intermolecular contacts found in crystals of **9** and comprising O−H···O, C−F···H−C, and C−Br···O interactions. Ribbons generated by O−H···O and C−Br···O interactions run parallel to [010]; further attractive C−F···H contacts join the ribbons together side by side to build a two-dimensional network lying parallel to the ($\bar{1}$01) plane. Symmetry operations are defined as follows: molecules A′/B′, A″/B″, and A‴/B‴ are generated with the ($x$, $y - 1$, $z$), ($x - 1$, $y - 1$, $z - 1$), and ($x - 1$, $y$, $z - 1$) operators starting from molecules A and B, respectively.

way like that found in naphthalene/octafluoronaphthalene,[27] 1,2,3,4-tetrafluoro-7-methoxyacridine[13], and 1,2,3,4-tetrafluoro-7-dimethylaminoacridine[5] crystals. At variance with this prototypical stacking motif, owing to the presence of two crystallographically independent molecules, here we observe four stacking modes differing on the degree of the graphite-like overlap due to lateral shifts of the molecules and inner or outer positioning of the bromine atoms with respect to the stacked pairs (Figure 3).

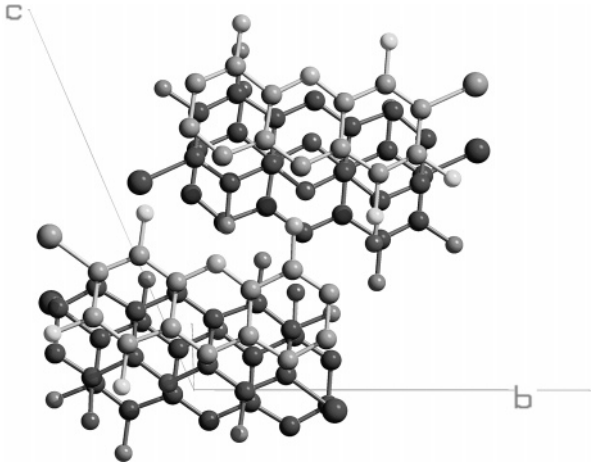


**Figure 3.** SCHAKAL drawing showing the overlap between adjacent layers of 2-bromo-1,3,4-trifluoro-9-hydroxyacridine molecules viewed orthogonal to the average plane of molecule A. Stacking of molecules B is slightly tilted. Hydrogen atoms were omitted for the sake of clarity.

**c. Photophysical Properties of Fluorinated Hydroxyacridines in Solution.** Different behaviors between the tetrafluoromethoxyacridine isomers **6** and **7** and between the polifluorohydroxyacridine isomers **2**, **8**, and **9** have been also observed analyzing their optical properties (absorption and fluorescence) in solution. While compounds **6** and **8** in dichloromethane have absorption spectra (Figure 4) similar to those of other tetrafluoroacridines,[5] compounds **2**, **7**, and **9** present a second absorption band at longer wavelengths. In the derivatives **2**, **7**, and **9** this second band falls between 370 and 450 nm and it is clearly distinguishable from the other bands, with a negligible effect due to the

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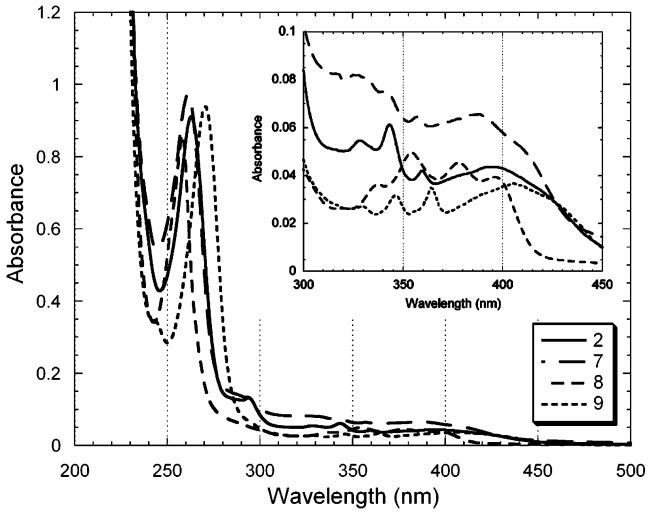


**Figure 4.** Absorption spectra of compounds **2**, **7**, **8**, and **9** in anhydrous $CH_2Cl_2$ ($10^{-5}$ M).

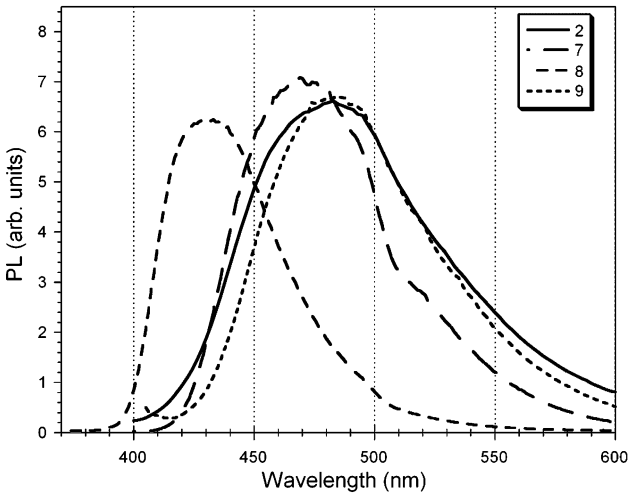


**Figure 5.** Fluorescence spectra of compounds **2**, **7**, **8**, and **9** in anhydrous $CH_2Cl_2$ ($10^{-5}$ M).

substitution of a fluorine atom by bromine. The absorptions of **2**, **7**, and **9** are very similar to those reported for 1-acridinol (**1**).[28] The low energy band in **1** is the $^1L_a$ band (Platt notation) likely to that observed in anthracene,[29] acridine, and tetrafluoroacridine. The band at higher energy is the $^1L_b$ band, hidden by the $^1L_a$ band in anthracene and acridine, but present in **1** because of the red shift of the $^1L_a$ band. Starting from the comparison between the spectra of neutral, cationic, and anionic forms of **1**, it was stated that the $^1L_a$ transition is polarized along the short molecular axis while the structured $^1L_b$ band and the high energy band (between 250 and 290 nm, indicated as $^1B_b$ band) are both polarized along the long molecular axis[28]. Finally, it is known that the position of the $^1L_a$ band has a bathochromic shift in the cationic and anionic form, while $^1L_b$ and $^1B_b$ bands are less sensitive[28]. The same interpretation can be proposed for compounds **2**, **7**, and **9**; if this is correct, a strong bathochromic shift should be observed for the $^1L_a$ band in the absorption spectrum of their complexes with zinc.

The fluorescence spectra of these compounds are affected by various phenomena. The difference between the fluorescence spectra of compounds **6** and **8** (Figure 5) is small, compared with the fluorescence spectrum of compound **7**; this comparison confirms the bathochromic effect of methoxy group in position 9 and agrees with the lowering of the HOMO−LUMO gap observed in the absorption spectra. For compounds **2** and **9** the presence of water in the dichloromethane solution originates a new emitting species (probably the hydrated form); only by using anhydrous $CH_2Cl_2$ is it possible to see the fluorescence of the free molecule (see Supporting Information for the fluorescence spectra in nonanhydrous solvents). Moreover, while all the tetrafluoroacridines synthesized up to now[5] are strongly fluorescent both in solution and in the solid state, the fluorescence efficiency of compounds **2** and **9** in aprotic solvents and in the solid state is very low (as already reported for **1**[30]). This is due to a well-known phenomenon already reported in the literature because the interaction between an alcoholic (or phenolic) hydrogen and a pyridic-like nitrogen causes a strong quenching of the fluorescence.[31]

**Table 3. Cyclic Voltammetry Results[a] for Tetrafluoroacridines**

| compound | $E_p^{red}$ (V) | $E_p^{ox}$ (V) |
|---|---|---|
| **6** | −1.45 | 1.61 |
| **7** | −1.65 | 1.51 |
| **2** | −1.35 | 2.00 |
| **9** | −1.25 | 1.91 |
| **8** | −1.20 | 1.60 |

[a] Oxidation ($E_p^{ox}$) and reduction ($E_p^{red}$) potentials vs SCE from the oxidation and reduction peaks of CV's on Pt microelectrode. Scan rate: 0.1 $Vs^{-1}$ in AN + TBAP 0.1 M.

**d. Electrochemical Analysis.** The electrochemical properties of the tetrafluoroacridine **7** are analyzed by cyclic voltammetry and the results are collected in Table 3 and compared with those of compound **6**.[5]

As expected, the oxidation and reduction potentials are slightly different for the two molecules, reflecting the effects exerted by the methoxy group in positions 7 and 9 (Table 2). Compound **7** shows a lower oxidation potential (lower ionization potential) and a lower reduction potential (lower electron affinity) than compound **6**. Although both the anodic and the cathodic peaks of compound **7** are nonreversible and reasonably affected by subsequent kinetics, the electrochemical band-gap estimated by the voltammetric measurements (3.16 eV peak to peak) is in accordance with the result obtained from the absorption spectrum in solution. The reduction peak of compound **7** shows a pre-peak already observed in previous reports for similar substrates[5,32] and ascribed to the formation of a complex between acridine and oxygen. This pre-peak vanishes by bubbling argon through the solution for about 1 h before performing the voltammetry.

In Table 2 the voltammetric data for the corresponding hydroxyacridines **2**, **8**, and **9** are also reported. The

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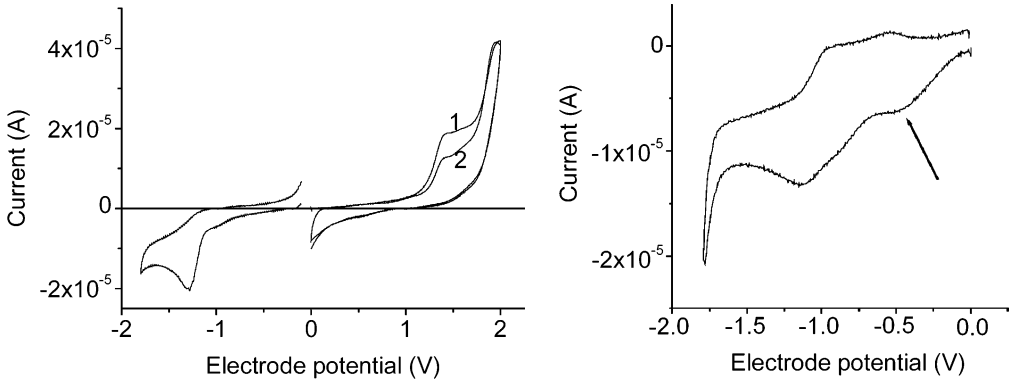


**Figure 6.** Cyclic voltammetry (anodic and cathodic sweeps) of **2**, $1.5 \times 10^{-3}$ in AN + TBAP 0.1 M on Pt, scan rate 0.1 $Vs^{-1}$ M. Left: in the anodic sweep, 1, first cycle; 2, second cycle. Right: cathodic sweep before deaeration (30 min).

oxidation potentials of phenols usually occur at potentials higher than 1.5 V (vs SCE) and shifts toward 2 V depending on the substituents in the aromatic molecule.[33] Owing to the complexity of the electrochemistry of phenols, the observed peak potentials must only give an approximate indication of the ionization potential and the electron affinity of the compounds. Indeed, both the oxidation and the reduction peaks are totally irreversible, at least till 200 mV $s^{-1}$. The anodic peaks of compounds **2**, **8**, and **9** show a pre-peak that meaningfully decreases in the subsequent cycles (Figure 6), probably due to adsorbed material on the electrode, not evident in the case of the corresponding alkoxy compounds. The anodic peaks of compounds **2** and **8** can be reasonably attributed to a two-electron process, in accordance with previous literature on the electrochemistry of phenol compounds.[33] The comparison of the height of the anodic with that of the cathodic peak supports this hypothesis (Figure 6). Two separated one-electron processes can be observed in the anodic voltammetry of compound **9**. The cathodic voltammetries of **2**, **8**, and **9**, as those of the alkoxy parents, show a pre-peak due to a complex with the oxygen which quite completely disappears by bubbling argon for 20−30 min (Figure 6).

**e. Synthesis and Properties of Complexes of $Zn^{2+}$ with Polyfluoro-9-hydroxyacridine.** Complexes of 8-hydroxyquinoline and 1-hydroxyacridine with divalent cations are well-known and they have been prepared and studied in analytical chemistry for the determination of cations and for their possible application as emitters in electroluminescent devices.[4] Our attention was focused on complexes with $Zn^{2+}$; indeed it is known that among the huge number of 8-hydroxyquinoline complexes with different metals, the complex with zinc shows the highest quantum yield in solution.[34] Moreover a complex of 4-acridinol with $Zn^{2+}$ was recently used as emitter in an OLED.[4]

Polyfluorohydroxyacridines are easily deprotonated by weak organic bases, thus for the synthesis of complexes of $Zn^{2+}$ we have used zinc acetate, using a standard technique already exploited for the synthesis of similar complexes.[35] The optical properties of the complexes of

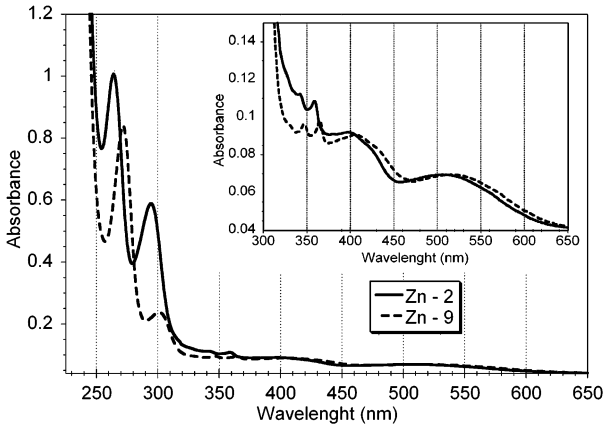


**Figure 7.** Absorption spectra of Zn-**2** and Zn-**9** in chloroform.

polyfluorohydroxyacridine with $Zn^{2+}$ were studied by absorption and photoluminescence both in solution and in the solid state. When the complexes of polifluorohydroxyacridine with $Zn^{2+}$ are dissolved in organic solvents, a partial hydrolysis of the complex to give back the free ligand is observed. This hydrolysis reaction was investigated further and it seems that an equilibrium between the free ligand and the ligand bond to $Zn^{2+}$ is established; indeed, the resulting absorption spectrum is the superposition of two spectra: in the region between 370 and 600 nm are detectable the $^1L_a$ bands of the free ligands (peak around 400 nm) and the corresponding $^1L_a$ band of the ligands bond to $Zn^{2+}$ (peak around 500 nm), strongly red shifted with respect to the neutral ligand, as expected. (Figure 7). The whole absorption spectrum of zinc-bis(2-bromo-1,3,4-tetrafluoroacridin-9-olate) (Zn-**9**) is slightly red-shifted with respect to Zinc-bis(1,2,3,4-tetrafluoroacridin-9-olate) (Zn-**2**); this is clearly the effect of the substitution of a fluorine atom with a more electron-donating halogen atom.

The instability of complexes toward hydrolysis can be ignored in fluorescence spectra, since the excitation is fixed on the $^1L_a$ band of the complex where the free ligand is completely transparent and only the fluorescence of the complex is detectable. As already reported in the literature, the absorption spectra of metal-8-hydroxyquinolinates are related to those of the ligand and, qualitatively, they strongly resemble the spectra of protonated form of the free ligand, showing a strong bathochromic shift of the $^1L_a$ band.[36] Fluorescence of metal-quinolinate and metal-acridinolate also is ligand centered and the cation modifies the energy and the

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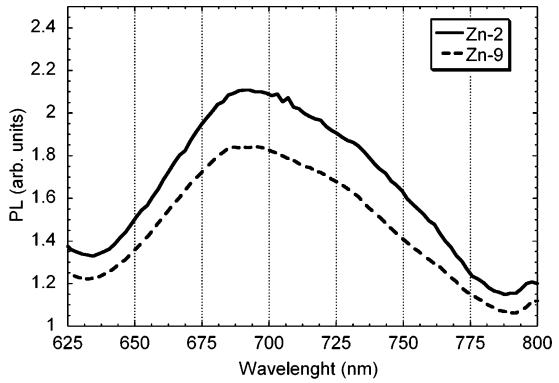


**Figure 8.** Fluorescence spectra of Zn-**2** and Zn-**9** in chloroform.

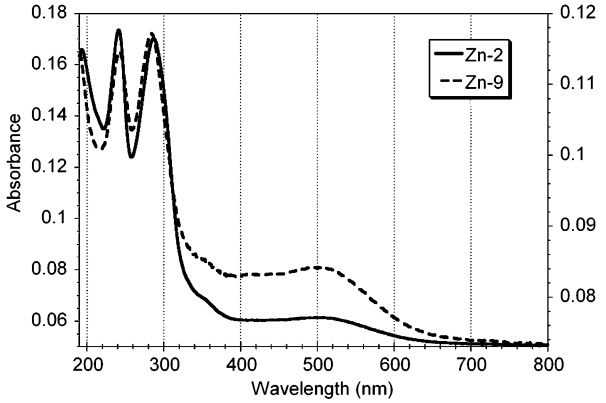


**Figure 9.** Absorption spectra of film of Zn-**2** and Zn-**9**.

quantum yield of emission, as well-known for metal-8-hydroxyquinolinates.[34] Moreover, the strong Stokes shift observed in the fluorescence spectra of metal-8-hydroxyquinolinates indicates that the state responsible for the emission is not that directly excited during absorption. For metal-8-hydroxyquinolinates it was suggested that the emitting state is qualitatively related to the zwitterionic form of the ligand, where a positive and a negative charge are respectively centered on nitrogen and oxygen,[36] a form unstable in solution at any pH. This cannot be observed in absorption, anyway in the excited state it should have the lowest energy and then the emission originates from this state. Also for Zn-**2** and Zn-**9** a strong Stokes shift is observed in the fluorescence spectra in solution (Figure 8) and then, on the basis of the structural similarity between hydroxyquinoline and hydroxyacridine, we apply here the same model.

The problem of the instability of the complexes observed in solution is not present in the solid state. Cast films of both the complexes (Z-**2** and Zn-**9**) were prepared from a chloroform solution on substrates of fused silica. In the absorption spectra of both compounds (Figure 9), the main feature is the strong bathochromic shift of the low energy band ($^1L^a$), likely that observed in solution. The difference with the absorption spectrum of the solutions is quite low for both the complexes, indeed because of the weak molecular interactions, only small changes in photophysical properties between isolated or solvated molecules and amorphous thin films are present in this class of compounds.

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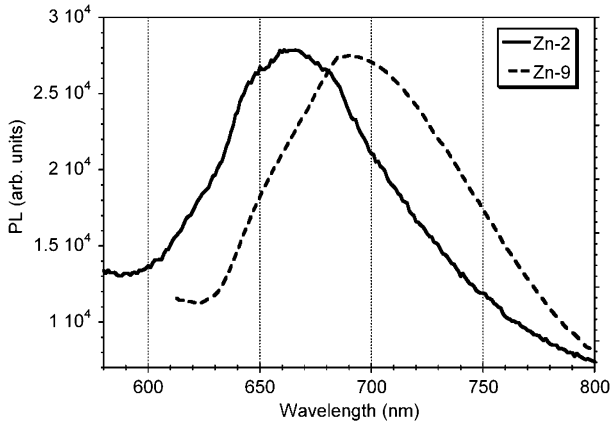


**Figure 10.** Photoluminescence spectra of film of Zn-**2** and Zn-**9**.

Photophysical properties of Zn-**2** and Zn-**9** are strictly related in solution, indicating that the electronic structure of complexes is only slightly perturbed by substitution of a fluorine with a bromine on acridine nucleus. This result is partially confirmed in the solid state, because, while the absorption spectra of films of Zn-**2** and Zn-**9** are very similar, their photoluminescence (PL) spectra are significantly different (Figure 10). While the PL spectrum of Zn-**9** in the solid state is very close to that of the fluorescence spectrum in solution, the related complex Zn-**2** showed an unexpected blue shift of its PL spectrum in the solid state with respect to the fluorescence spectrum in solution. While for the Zn-**9** the emitting state in the solid state could be closely related to the aforementioned zwitterionic state observed in solution (the same is observed for $AlQ_3$), perhaps for Zn-**2** the intermolecular interactions in the solid state modify the nature of this emitting state, raising its energy and enlarging the molecular gap. This phenomenon for Zn-**9** could be hindered because of the presence of a bulky atom on the acridine nucleus, able to space out near fluoroacridine units to influence the intermolecular interactions. Anyway the determination of the crystalline structure of the complexes is necessary to evaluate, from the analyses of the interatomic distances, interactions present between neighbor molecules in the solid state (for instance, the role of areneperfluoroarene interactions and intermolecular interactions involving the bromine atom) and to evaluate their effect on the electronic state and then on the PL spectra of the complexes.

In the electroluminescence spectra of the complex of $Zn^{2+}$ with nonfluorinated hydroxyacridine the maximum lies around 600−610 nm,[4] while in this case the introduction of fluorine atoms in the ligand causes a red shift in the PL spectrum of about 50−100 nm. The origin of this effect is not clear and we need to improve our knowledge about the photophysics of these complexes. A detailed comparison between the absorption and PL spectra of fluorinated and nonfluorinated complexes is the first step; this effect could be used to shift fluorescence of similar complexes to lower energies, in the low-energy side of the UV−visible region of the electromagnetic spectrum.

## Conclusions

In summary, we have applied a versatile one-pot method to synthesize partially fluorinated hydroxy-

acridines. The intermediates and the products were fully characterized, highlighting the effects of the same substituent in different positions on their reactivity and physical properties. In principle, the synthesis presented here is applicable also to slightly different anilines, and with partially fluorinated benzaldehydes as an example the reaction could be extended to 2-fluorobenzaldehyde giving a new entry to 1-hydroxyacridine. The presence of a bromine atom strongly affects the crystal packing; indeed, a peculiar supramolecular motif is observed in the single crystal of **9**, originating from weak halogen, hydrogen, and oxygen bond interactions. Electrochemical studies have shown a common behavior with respect to the already known tetrafluoroacridines, in particular the presence of oxygen complexes. The photophysics of free ligands was explained within the frame of well-established theories for similar substrates. The comparison with known systems, such as metal-hydroxyquinolinates, has allowed us to interpret the results about the optical properties of the complexes, indicating the presence of similar emitting species.

Our studies to apply the prepared ligands to the synthesis of complexes with divalent and trivalent cations are still underway. To improve our knowledge about the photophysics of these systems we will compare the results presented here with those from complexes with different cations and complexes with nonfluorinated hydroxyacridine. Possible applications of these systems are in OLEDs as emitting systems, and moreover we are investigating their use as electron-poor photoconductors in blends with semiconducting polymers.

## Experimental Section

**General Experimental Procedures.** All starting materials were purchased from commercial sources (Aldrich Chemical Co.); pentafluorobenzaldehyde was purchased from Fluorochem and used without further purification. Column chromatography was performed on Merck Silica gel 60 (0.063−0.200 mm). 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 a Bruker 300, using $CF_3CH_3$ as internal standard for $^{19}$F spectra. Mass spectra were recorded with the MALDI-TOF method on a Kratos Maldi II (linear flight). The UV−vis absorption spectra of the solutions were measured with a Perkin-Elmer Lambda 900 spectrophotometer. The fluorescence spectra were recorded on an Aminco-Bowman spectrofluorometer at room temperature. An AMEL 5000 multifunction apparatus was used for the electrochemical characterization. The working electrode consisted of a platinum hemisphere. A platinum wire was used as counter-electrode and a saturated calomel electrode (SCE, to which all the potentials are referred in this work) was used as reference. Both electrodes were separated from the solution by a glass septum. Cyclic voltammetries of 2 mM solutions were carried out at room temperature in acetonitrile (AN) and 0.1 M tetrabuthylammonium perchlorate (TBAP). AN (UVASOL Merck product) was stored and manipulated under argon atmosphere. TBAP (Fluka AG purum) was crystallized from methanol.

**General Procedure for the Synthesis of 1,2,3,4-Tetrafluoromethoxyacridine (6 [5] and 7).** A solution of pentafluorobenzaldehyde (3.5 mmol) and aniline (7 mmol) in xylene (25 mL) was gently refluxed under nitrogen atmosphere. After 20 h of reflux another 3.5 mmol of aniline was added (see Table 1 for the total refluxing time). At the end of reflux, xylene was removed and the crude was purified by column chromatography (silica gel, $CH_2Cl_2$) and by sublimation.

**1,2,3,4-Tetrafluoro-9-methoxyacridine (7).** Yield: 45%. Pale yellow solid; mp 219 °C (sublimation at 140 °C, 0.1 mbar). $^1$H NMR (300.15 MHz, $CDCl_3$): $\delta$ 8.98 (s, 1H), 7.63−7.60 (d, 1H, $J$ = 8.6 Hz), 7.59−7.53 (t, 1H, $J_1$ = 7.1 Hz, $J_2$ = 8.5 Hz), 7.15−7.12 (d, 1H, $J$ = 7.1 Hz); 4.16 (s, 3H). $^{19}$F NMR ($CDCl_3$): $\delta$ −150.5 (t, 1F), −151.2 (t, 1F), −153.4 (t, 1F), −157.7 (t, 1F). Anal. Calcd for $C_{14}H_7F_4NO$: C 59.80%, H 2.51%, F 27.02%, N 4.98%. Found: C 60.1%, H 2.5%, F 26.6%, N 5.1%. MALDI-TOF *m/z*: 281.5 $[M]^+$.

**General Procedure for Cleavage of Aromatic Ethers with HBr Solution (8 and 9).** 1,2,3,4-Tetrafluoromethoxyacridine (0.8 mmol) was dissolved in 30 mL of HBr solution (47%). The orange-red solution was heated under reflux for 4h. pH of the solution was initially increased with NaOH, adjusted to pH 8 with $NaHCO_3$, and then extracted with $CH_2Cl_2$. The organic phase was dried with $Na_2SO_4$ and then the solvent was removed. The yellow solid was purified by sublimation to give the desired product.

**1,2,3,4-Tetrafluoro-7-hydroxyacridine (8).** Yield: 84%. Pale yellow solid; mp 206 °C (sublimation at 170 °C, 0.1 mbar). $^1$H NMR (300.15 MHz, $CDCl_3$): $\delta$ 8.81 (s, 1H), 8.28 (d, 1H, $J$ = 9.4 Hz), 7.58 (dd, 1H, $J_1$ = 9.41 Hz, $J_2$ = 2.6 Hz), 7.31 (d, 1H, $J$ = 2.6 Hz), 5.70 (s, 1H). $^{19}$F NMR ($CDCl_3$): $\delta$ −151.6 (t, 1F), −152.5 (t, 1F), −154.9 (t, 1F), −158.3 (t, 1F). Anal. Calcd for $C_{13}H_5F_4NO$: C 58.44%, H 1.89%, F 28.44%, N 5.24%. Found: C 58.8%, H 1.8%, F 27.8%, N 5.1%. MALDI-TOF *m/z*: 268.5 $[M]^+$.

**2-Bromo-1,3,4-trifluoro-9-hydroxyacridine (9).** Yield: 45%. Pale yellow solid; mp 207 °C (sublimation at 140°, 0.5 mbar). $^1$H NMR (300.15 MHz, $CDCl_3$) $\delta$ 8.95 (s, 1H), 8.29 (s, 1H), 7.55−7.49 (m, 2H), 7.28 (dd, 1H, $J_1$ = 6.3 Hz, $J_2$ = 2.3 Hz). $^{19}$F NMR ($CDCl_3$): $\delta$ −118.1 (d, 1F), −133.3 (d, 1F), −150.1 (t, 1F). Anal. Calcd for $C_{13}H_5BrF_3NO$: C 47.59%, H 1.54%, Br 24.35%, F 17.37%, N 4.27%. Found: C 47.7%, H 1.5%, F 16.8%, N 4.4%. MALDI-TOF *m/z*: 328.2−330.2 $[M]^+$.

**X-ray Analysis of 2-Bromo-1,3,4-trifluoro-9-hydroxyacridine (9).** Crystals of compound **9** were grown from toluene solutions by slow evaporation, giving pale yellow crystals. Two different data collections were performed at 298(2) K (**9**a) and 123(2) K (**9**b), respectively, to check whether the structural features observed at RT were also present at lower temperatures and to exclude phase transitions below RT which could hamper low-temperature physical characterization of **9**. A Bruker SMART CCD area-detector diffractometer was used to collect data using Mo Kα radiation ($\lambda$ 0.71073 Å) and the $\omega$-scan method, within the limits $\theta \leq 25°$ (**9**a) and $\theta \leq 30°$ (**9**b). Data were corrected for Lorentz and polarization effects, and for absorption and decay using the SADABS program. Crystal data for **9**, $C_{13}H_5BrF_3NO$: triclinic, space group $P\bar{1}$ (No. 2), $Z = 4$, $Z' = 2$. **9a**: $T$ = 298 K, $a$ = 7.2258(8) Å, $b$ = 12.2109(12) Å, $c$ = 13.9069(14) Å, $\alpha$ = 110.412(3)°, $\beta$ = 96.886(3)°, $\gamma$ = 92.829(3)°, $V$ = 1136.2(2) Å$^3$, $\rho_{calcd}$ = 1.918 g cm$^{-3}$, final R1 = 0.0363 for 2690 independent reflections with $F_o > 4\sigma(F_o)$. **9b**: $T$ = 123 K, $a$ = 7.1417(6) Å, $b$ = 12.2055(10) Å, $c$ = 13.7337(12) Å, $\alpha$ = 110.432(2)°, $\beta$ = 95.879(2)°, $\gamma$ = 92.918(2)°, $V$ = 1111.1(2) Å$^3$, $\rho_{calcd}$ = 1.961 g cm$^{-3}$, final R1 = 0.0272 for 5701 independent reflections with $F_o > 4\sigma(F_o)$. The structure was solved by direct methods (SIR97)[37] and refined using all reflections by full-matrix least-squares on $F_o^2$ (SHELX-97)[38]). Anisotropic displacement parameters were assigned to all nonhydrogen atoms. Aromatic hydrogen atoms were located in approximate positions by difference Fourier maps and subsequently introduced in the final stages of refinement as isotropic scatterers in idealized positions and riding on their parent carbon atoms. The two independent hydroxyl hydrogens were located in a difference Fourier map and their positions were refined using torsional refinement on the bonded atom with instruction AFIX 147 within thge SHELX97 program. ORTEP and packing figures were generated with PLATON[39] and

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SCHAKAL,[40] respectively. A summary of crystallographic data and refinement parameters is provided in Table 2.

**General Procedure for Cleavage of Aromatic Ethers with Chloroaluminate Ionic Liquid (2).** The ionic liquid was prepared following the procedure described elsewhere.[11] To a solution of 1,2,3,4-tetrafluoromethoxyacridine in anhydrous $CH_2Cl_2$ was added dropwise the ionic liquid dissolved in anhydrous $CH_2Cl_2$; the red solution was refluxed for 10 h. The reaction mixture was poured in water, and the aqueous phase was basified to pH 8 with $NaHCO_3$ and finally extracted with $CH_2Cl_2$. The organic phase was dried with $Na_2SO_4$ then the solvent removed and the solid was purified by sublimation.

**1,2,3,4-Tetrafluoro-9-hydroxyacridine (2).** Yield: 84%. Pale yellow solid; mp 202 °C (sublimation at 110 °C, 0.1 mbar). $^1$H NMR (300.15 MHz, $CDCl_3$) $\delta$ 9.02 (s, 1H), 8.36 (s, 1H), 7.57 (d, 1H, $J$ = 9 Hz), 7.51 (s, 1H), 7.30 (t, 1H, $J$ = 4 Hz). $^{19}$F NMR ($CDCl_3$): $\delta$ −150.3 (t, 1F), −152.2 (t, 1F), −152.7 (t, 1F), −157.7 (t, 1F). Anal. Calcd. for $C_{13}H_5F_4NO$: C 58.44%, H 1.89%, F 28.44%, N 5.24%. Found: C 58.7%, H 1.9%, F 27.9%, N 5.3%. MALDI-TOF *m/z*: 268.0 $[M]^+$.

**General Procedure for the Synthesis of Zinc-polyfluoro-9-acridinolate from Zinc Acetate.** To a solution of 50 mg of polyfluoro-9-acridinol in 50 mL of ethanol is added a half equiv of zinc acetate, and the purple solution is refluxed under nitrogen atmosphere. After 1 h the solution is allowed to cool, a dark purple solid precipitates. The precipitate is collected by filtration and washed with ethanol.

**Zinc-bis(1,2,3,4-tetrafluoroacridin-9-olate) (Zn-2).** Yield: 65%. Dark blue solid; mp > 300 °C. Because of the instability of the complex in solution, in the $^1$H NMR spectrum peaks of both complex and free ligand are present. Peaks are broad and very noisy. $^1$H NMR: (300.15 MHz, $CDCl_3$) $\delta$ 9.27, 7.73, 7.44.

**Zinc-bis(2-bromo-1,3,4-tetrafluoroacridin-9-olate) (Zn-9).** Yield: 62%. Dark blue solid; mp >300 °C. The instability and the poor solubility if this complex do not allow collection of a $^1$H NMR spectrum.

**Acknowledgment.** We thank MIUR-PRIN 2003, 2003034479006 "Composti Fluorurati: Nuovi Materiali per Applicazioni Avanzate" and MIUR-PRIN 2003, 2003030237, "Fluorinated Nanoreactors with designed structures and optimized functions" for financial support. M. Moret gratefully acknowledges Dipartimento di Chimica Strutturale e Stereochimica Inorganica (Università degli Studi di Milano) for the availability of the X-ray diffractometer.

**Supporting Information Available:** Fluorescence spectra of compounds **9** in nonanhydrous solvents (pdf). Complete crystallographic data in CIF format for compound **9**. Selected bond lengths (Å) and angles (deg) for compound **9** at 298(2) K (**9**a) and 123(2) K (**9**b). This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) Keller, E. Kristallographisches Institut der Albert-Ludwigs-Universität, Freiburg i. Br., Germany.