Synthesis and Properties of Some Derivatives of 1,2,3,4-Tetrafluoroacridine for Solid State Emitting Systems

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The resonant energy transfer (RET) between fluorescent organic molecules is a very important phenomenon widely investigated for its potential in developing devices such as light-emitting diodes and lasers. Energy transfer processes take place between two different molecules and they are usually observed when the emission spectrum of the first molecule (called donor) overlaps with the absorption spectrum of the other one (called acceptor). The individuation of this kind of molecule inside a common structural motif represents an interesting approach aimed at simplifying the modeling of their synthetic procedure; indeed the desired couple can be obtained simply acting on the electronic properties of substituents present on the molecule and helps the understanding of the energy transfer processes. The tetrafluoroacridines, readily accessible from aniline and pentafluorobenzaldehyde, have been selected as a structural motif because their absorption and emission properties can be easily tuned by acting on the nature of substituents present on the starting aniline. The synthesis of new terms of these molecules along with a preliminary study on their optical, electrochemical, and structural properties, in solution and in the solid state, is described. We present here a study on the optical properties of a molecular crystal of donor doped with molecules of acceptor, both chosen among the prepared tetrafluoroacridines; the temperature dependence of luminescence spectrum allowed us to take a glance upon the energy transfer and excitation migration phenomena occurring in this system.

Introduction

A lot of effort has been devoted during recent years to understanding the physical phenomena involved with the excited states in organic molecular materials. For example, tracking excitonic processes plays an important role in the comprehension of the behavior of organic semiconductors, while energy transfer processes between similar or dissimilar molecules characterize the excitonic behavior of doped molecular organic thin films.[1] Even if organic crystals and polymers doped with fluorescent[2] (or phosphorescent[3]) molecules are well-known in the literature, there is still a lack of comprehension about the phenomena concerning the energy transfer and migration; the real luminescence spectrum of a doped organic crystal is often unpredictable, and the real nature of its emitting center[4] and the related energy transfer phenomena are still not completely understood.

The processes through which the excitation is transferred from one molecule (called donor) to another (called acceptor) are collected under the name of *energy transfer*. Energy transfer in the solid state can take place via two mechanisms: (1) exciton migration, and (2) resonant energy transfer. Exciton migration is a thermal-activated process, as the excitation moves toward the solid by hopping, whereas resonant energy transfer is a process based on the interaction between the transition dipole moment. It was first described by Foerster[5] as a single-step resonant transfer; Foerster

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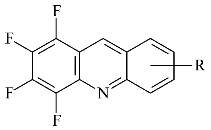
energy transfer involves singlet excitons and it occurs at long intermolecular distances (up to 10 nm). Resonant (i.e., Foerster's) energy transfer is temperature independent and requires a match between the energy levels of donor and acceptor. The rate of the resonant energy transfer is expressed in terms of experimental data: it is proportional to the overlap integral between the absorption spectrum of the acceptor and the normalized fluorescence spectrum of the donor, to the absorption cross section of the acceptor ($\sigma_A \propto \epsilon_A$, molar extinction coefficient) and to $^1/_R$,[6] where R is the distance between donor and acceptor. The rate of the energy transfer strongly depends on the concentration of the acceptor and on the overlap between the absorption spectrum of the acceptor and the emission (fluorescence) spectrum of the donor. Doping an organic crystal with a molecule acting as acceptor can modify the absorption spectrum of the solid, and, even in a stronger way, the emission spectrum.[6] When the excited-state energy levels of the doping molecule are lower than those of the host crystal, the acceptor molecule can act as a trap, and the emission spectrum originating from these trap states (populated by energy transfer) is related to the acceptor molecule and not to the host crystal. The nature and the strength of the interactions between the acceptor molecule and the surrounding crystal modify the position of the energy levels of the trap. When the trap is deep (i.e., far from the excitonic band), its emission is due to a localized state, moving through the solid by hopping, and its emission spectrum may be similar to a solution spectrum. If the trap is close to the excitonic band (shallow trap), its energy levels can participate with the collective excited states of the crystal and the propagation of the excitation takes place under the so-called "*quasi-resonance*" conditions, and the emission spectrum of the acceptor is similar to its emission spectrum in the solid state. This work is aimed to find a couple of molecules (donor/acceptor) with specific characteristics and to study the excitation or energy transfer processes between them in the solid state. Suitable molecules should possess the following: (1) a good spectral overlap between the absorption band of the acceptor and the emission band of the donor; (2) good fluorescence quantum yields in solution and in the solid state; and (3) good thermal, chemical, and photochemical stability. Among the huge number of molecules possessing all or part of the above requisites, acridines have been selected because they are fluorescent with high quantum yields in both solution and solid states (quantum yield of acridine $\Phi_e = 0.83$ in ethanol solution[7]); and their absorption and emission properties can be tuned simply by acting on the nature, number, and position of the substituents connected to the structure. These features make it possible, in principle, to find a couple of molecules belonging to this structural motif and satisfying all the above-mentioned prerequisites for energy transfer. In particular, we have focused our attention on the 1,2,3,4-tetrafluoroacridines[8] (Chart 1). Although they have been known since 1960, their optical properties have been little investigated.

Chart 1. Structure of 1,2,3,4-Tetrafluoroacridine



In addition, the presence of four fluorine atoms on the aromatic ring should improve the thermal and chemical stability of the acridine. Furthermore, the high electronegativity and the small dimension of fluorine atom generally impart interesting chemical and physical properties to molecules.[9]

Results and Discussion

A. Synthesis of Materials. 1,2,3,4-tetrafluoroacridine was synthesized for the first time in the late 1960s, through a multistep reaction from bromobenzene involving a modified Lehmsted−Tananescu rearrangement,[10] with the aim of studying the effect of fluorination on the pharmacological effects of some acridine derivatives. Later on, fluoroacridines were produced by heating fluorinated acetophenones with aniline.[11] The most interesting way to prepare fluoroacridines was reported by Banks et al. in the early 1990s when the synthesis of these substrates was performed by reacting the pentafluorobenzaldehyde with *p*-anisidine.[12] Banks also investigated the mechanism of this reaction. They found that two equivalents of amine for one equivalent of pentafluorobenzaldehyde are necessary for the formation of tetrafluoroacridine. The first equivalent leads to the formation of the pentafluorobenzaldehyde Schiff's base, and the second one, after substitution of the fluorine atom in position ortho to the imine function, is responsible for acridine moiety formation by an intramolecular electrophilic substitution (Scheme 1).

Although the imine formation goes to completeness without heating, the acridine formation requires prolonged refluxing (about 70 h). Banks had also extended the reaction to other anilines preparing a series of acridines. The flexibility and the feasibility of this synthesis, together with the availability of a large number of different anilines, open the possibility of preparing a large pool of these substrates. First, we have repeated some of the synthesis of tetrafluoroacridine in refluxing toluene, as described in the literature,[12] obtaining similar results. However, the use of refluxing xylene (bp 138−140 °C) as solvent and increasing the amount of aniline to 3 equiv allowed us to improve the yields. We have used these new experimental conditions

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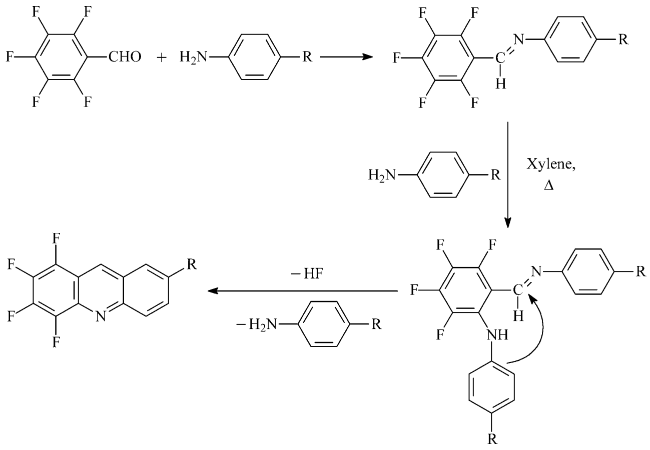
Scheme 1. Mechanism of 1,2,3,4-Tetrafluoroacridines Formation



not only for synthesizing some of the acridines already prepared by Banks but also for preparing new terms. New tetrafluoroacridines bearing a phenyl, a phenoxy, a phenyl-amino, and a thiomethyl group in the position 7 have been synthesized. The nucleophilic character of the amino group is critical for the substitution of the ortho fluorine atom at imine level. Indeed, using an electron-rich aniline (R = OMe, $N(Me)_2$) the ring closure to acridine occurs in fair to good yield (70−80%), whereas with electron-poor aniline such as 3,5-bis-trifluoromethyl or 2,4-di-fluoroaniline, the reaction stops at the stage of Schiff's base without formation of tetrafluoroacridine even when the reaction was performed using the aniline as solvent and heating to 200 °C.[13] Steric effects also are of crucial importance: when using electron-rich and bulky anilines such as *p*-carbazolyl or *p*-diphenylamino group (synthesized by modifying the procedure reported in the literature,[14] see Experimental Section) the reaction does not proceed beyond the imine level. In the case of *p*-9-carbazolylaniline, after heating the reaction mixture without solvent at 200 °C for several hours, we were able to observe the formation of and isolate the corresponding tetrafluoroacridine in moderate yield (26%). All the synthesized molecules were characterized by ^1H and ^{19}F NMR. In Table 1 the synthesized acridines and their properties are listed.

B. Electrochemical Analysis. The substitution of hydrogen with more electronegative fluorine atoms has, as expected, an appreciable influence on oxidation and reduction properties of acridine nucleus. Indeed, as recently reported by Russian researchers,[15] tetrafluoroacridine shows a reduction potential lowered by 0.2 V with respect to acridine; also the oxidation potential is increased in tetrafluoroacridine. In this work the electrochemical properties of the tetrafluoro acridines **a**, **b**, **c**, and **e** are analyzed by cyclic voltammetry and the results are collected in Table 2.

Table 1. Synthesized Tetrafluoroacridines and Their Properties[a]

R	compound	reaction solvent	time (h)	yield (%)	mp (°C)
H	**a**	xylene	65	51	180
Phenyl	**b**	xylene	68 [72]	51 [11]	240
OCH3	**c**	xylene	62 [12]	74 [9]	211
OC6H5	**d**	xylene	70	62	150
N(CH3)2	**e**	xylene	42 [31]	85 [15]	249
NH(C6H5)	**f**	xylene	75	77	223
Carbazolyl	**g**	none[b]	5	26	213
SCH3	**h**	xylene	61	30	210

[a] Data from reactions using toluene as solvent are presented in square brackets. [b] Reaction performed at 200 °C without solvent.

Table 2. Cyclic Voltammetry Results[a] **for Tetrafluoroacridines**

compound	E_p^{Red}	$\mathbf{i}_p$ ratio[b]	E_p^{Ox}
a	−1.34	0	1.91
b	−1.45	0.34	1.78
c	−1.45	0.65	1.61
e	−1.50	0.70	0.83

[a] Oxidation (E_p^{Ox}) and reduction (E_p^{Red}) potentials in V vs SCE from the oxidation and reduction peak of the CVs. On Pt, scan rate: 0.1 Vs^{-1} in AN + TBAP (0.1 M). [b] Ratio of reverse oxidation peak to reduction peak.

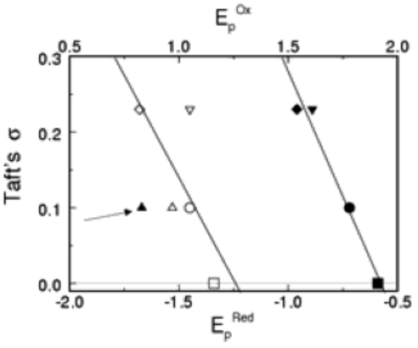


Figure 1. Taft's σ plot. Filled symbols, oxidation peaks; empty symbols, reduction peaks; **a** (square), **b** (circle), **c** (triangle down), and **e** (triangle up).

As expected, the oxidation and reduction potentials of acridines reflect the nature of substituents in position 7. As their electron-donating properties are increased moving from hydrogen to dimethylamino, the reduction potentials are increased while the oxidation potentials are reduced. In Figure 1 are plotted the oxidation and reduction potential as a function of Taft's σ for the inductive effect of the substituents.[16] Both reduction and oxidation potentials are set in two distinct rows, thus indicating a linear correlation of electrochemical properties of acridines with inductive effect of substituents.

The arrow indicates the anomalous oxidation potential of compound **e**, which is much lower than the others. This shift toward lower potentials is partially due to a sensible mesomeric contribution of dimethylamino group, and kinetically controlled electronic processes at the electrodes cannot be excluded. The acridines **b**, **c**, and **e** at room temperature show reversible or partially reversible reduction peaks as estimated by the $\mathbf{i}_p$ ratio reported in Table 2 (see Supporting Information); on the contrary **a** undergoes irreversible reduction. In all cases a prepeak (signed as α, see Supporting Information) has been observed. This prepeak is ascribed to the formation

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(13) Indeed, by using 2,4-difluoroaniline, a small amount of 1,2,3,4,7,9-esafluoroacridine was obtained after refluxing for 35 h the preformed Schiff's base in 2,4-difluoroaniline as solvent.

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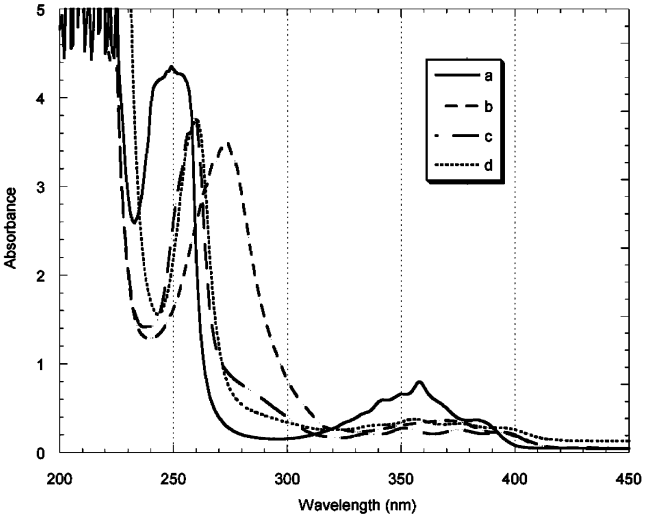

Figure 2. Absorption spectra of the synthesized compounds in CH_2Cl_2 solution (10^{-5} M).

of a complex between acridine and oxygen, already observed in previous reports for similar substrates.[15] This prepeak strongly decreases by bubbling argon through the solution before performing CV analysis. The CVs of tetrafluoroacridines displayed also irreversible oxidation peaks, only acridine **e** showed a reverse peak (β) at +0.23 V (Supporting Information) which is probably due to the reduction of condensation products obtained during the oxidation process.

C. Absorption and Fluorescence Spectra of Tetrafluoroacridines in Solution. A detailed study on the optical properties (absorption and emission) of the prepared acridines has been performed in solution in order to individuate, among them, a suitable couple for energy transfer investigation in the solid state. The absorption spectrum of tetrafluoroacridine **a** resembles the absorption spectra of acridine and anthracene (see Figure 2). This molecule has an intense high energy band near 250 nm and a second absorption band between 320 and 390 nm showing a series of vibronic replicas. The spacing between the replicas is 0.18 eV (1452 cm^{-1}), i.e., the energy of the stretching vibrational mode of C═C bond. In our case the introduction of four fluorine atoms has a modest effect on the absorption spectrum, and the absorption maxima are found at the same wavelength. The absorptions of substituted acridines (Figures 2 and 3) are differently and bathochromically shifted with respect to the parent compound **a** in relation to the electronic properties of the substituent. For compounds **b** and **h** the high-energy band (at 250 nm) is bathochromically shifted by 25 nm (corresponding to 0.45 eV), while the lower energy band (between 320 and 390 nm) is shifted by 30 nm (0.23 eV). A similar trend is also observed for acridines **c** and **d**. The acridines **e**−**g**, bearing electron-rich nitrogen substituents, show a rather different behavior: the dimethylamino group bathochromically shifts the high energy band at 250 nm by 40 nm (corresponding to 0.68 eV), while the carbazolyl group exerts a minor bathochromic effect of 30 nm on this band. Whereas the high-energy intense band at 250 nm is associated with a $\pi-\pi$ transition mainly localized in the acridine π-system, since this is present also in unsubstituted acridine, the low energy absorption band between 450 and 550 nm of **e** and **f** is a CT band due to the (partial) electron transfer from the aryl/alkyl amino moiety to the acridine moiety. Indeed, the conjugation of the nitrogen lone pair with the acridine π-system should give rise to a (intramolecular) charge transfer (CT) band in the absorption spectrum. The middle energy (320−400 nm) structured band, present in the other tetrafluoroacridines, is partially hidden below these intense bands. Compound **g** behaves in a different way. Indeed, for electronic (the nitrogen lone pair is partially delocalized over the carbazole moiety) and steric (repulsive interaction of 3,5-acridine hydrogen atoms with those in 2,7 of carbazolyl nucleus) reasons, the conjugation in the ground state between these two units is strongly depressed. In the absorption spectrum of **g**, the absorption band between 400 and 450 nm can be assigned to a charge-transfer transition. Probably the intense band between 240 and 320 nm is the superposition of two distinct bands, originated by different transitions in the π systems of acridine and carbazole.

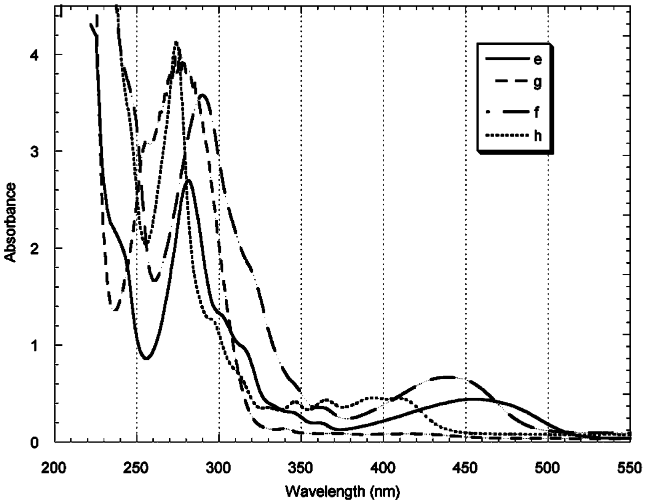

Figure 3. Absorption spectra of the synthesized compounds in CH_2Cl_2 solution (10^{-5} M).

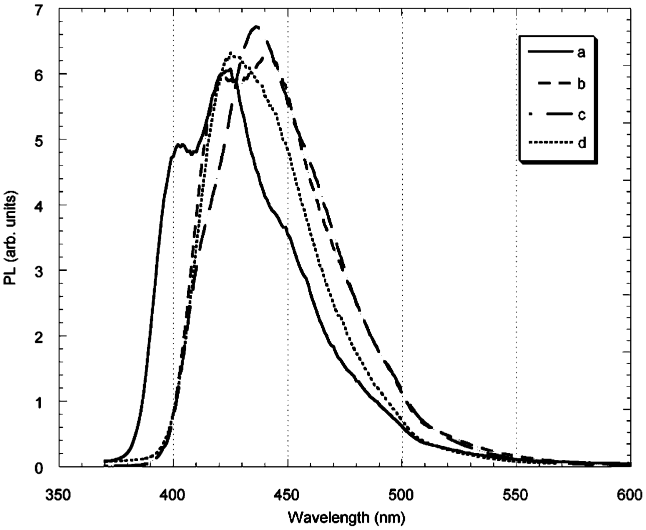

Figure 4. Fluorescence spectra of the synthesized compounds in CH_2Cl_2 solution (10^{-5} M).

The fluorescence spectra of compounds **a**−**d** are comparable (Figures 4 and 5); they exhibit a broad fluorescence band between 420 and 440 nm. For the compound **a** we observed a vibronic series (the electronic

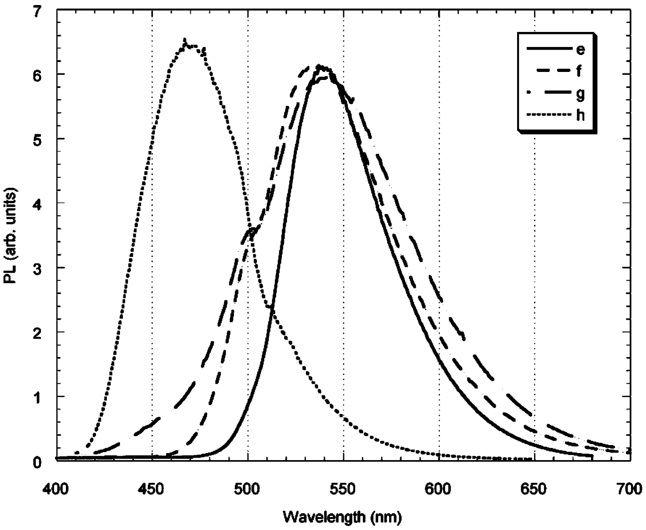

Figure 5. Fluorescence spectra of the synthesized compounds in CH_2Cl_2 solution (10^{-5} M).

transition is coupled with the C=C stretching mode), whereas a less resolved vibronic structure is observed for the other compounds (**b**−**d**). The fluorescence spectra of acridines **e**−**g** consist of a broad band with a maximum at lower energy, between 530 and 540 nm. Considering the lower-energy absorbing state of the compounds **e** and **f** is an intramolecular charge transfer state, for Kasha's rule the emission should originate from this charge-transfer excited state. The comparison with the absorption spectra for compound **g** allows us to take a glance at the nature of its excited states. The assignment of the band lying between 400 and 450 nm to a charge-transfer state is dubious, but the molecule in the excited state probably relaxes in a more planar charge-transfer state, thus the emission originates from this state, as indeed confirmed by the fluorescence spectrum, lying in the same region of compound **e** and **f**. This assignment is consistent with that reported for a similar system, 9(*p*-cyanophenyl)-carbazole.[17] The optical properties of compound **h** are peculiar; its absorption spectrum is bathochromically below 400 nm, but we do not identify any CT band. On the other side the fluorescence spectrum of this compound lies in an intermediate region between those previously analyzed and centered at 470 nm: the substitution of methoxy group (**c**) with a thiomethyl (**h**) apparently does not originate new bands in the absorption spectrum. In any case, the sulfur electron-donating properties reduce the energy difference between HOMO and LUMO, thus red-shifting both the absorption and fluorescence spectra. The fluorescence spectra of the synthesized compounds were performed in dichloromethane (10^{-5}M) and are shown in Figures 5 and 6.

These molecules show an interesting solvatochromic behavior (see Supporting Information). A modest or very low solvatochromism in their absorption spectrum is observed. For compound **e**, the band between 400 and 500 nm is red-shifted by 20 nm (0.12 eV) moving from hexane to dimethyl sulfoxide (DMSO); in hexane the low energy band presents a series of vibronic replica, whereas this series is unresolved in more polar solvents, resulting in a broad and structureless band. For compound **c,** the band between 330 and 410 nm is only 5 nm (0.05 eV) red-shifted (from hexane to DMSO); in hexane this band closely resembles the absorption spectrum of acridine where all the replicas in the corresponding band show two maxima. A strong solvatochromic effect in the fluorescence spectrum was observed for compound **e**; in hexane the fluorescence spectrum shows a structured band (replica spaced by 0.18 eV) with the maximum centered at 430 nm, while in DMSO the fluorescence is a broad band centered at 590 nm; the shift is 110 nm or 0.54 eV. For **c** the solvatochromism in the same solvents is smaller (420 nm, i.e., 0.20 eV): this difference is explainable assuming that the emitting state for **e** has a strong CT character and hence it is strongly stabilized in polar solvents, while the emitting state of **c** has a poor CT character and is then less influenced by solvent polarity.

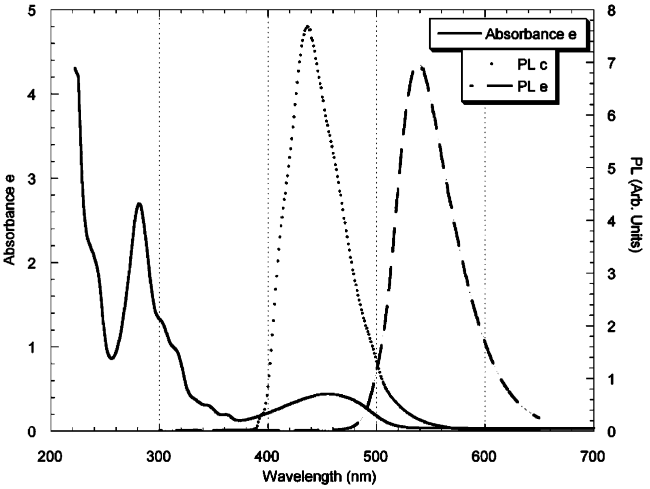

Figure 6. Spectral overlap between fluorescence of **c** and absorption of **e** in CH_2Cl_2 solution (10^{-5} M).

As mentioned in the Introduction, an efficient energy transfer between two molecules or systems can be observed when a good spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor is realized. Among the compounds analyzed so far, compounds **e** and **f** absorb between 400 and 500 nm, a spectral region where compounds **a**−**d** emit, therefore the donor should be chosen among molecules **a**−**d** and the acceptor should be either **e** or **f**. Our attention has been focused on the couple **c** (donor) plus **e** (acceptor) because they give rise to the best spectral overlap (see Figure 6). Moreover, they crystallize with the same packing motif (see after), which should help us in obtaining good blends or solid solutions.

D. X-ray Crystallographic Analysis of 1,2,3,4-Tetrafluoro-7-(*N*,*N*)dimethylaminoacridine (e). The molecular structure of **e** is reported in Figure 7 , and Table 3 lists selected bond distances and angles.[18] The molecular and solid-state structure of **e** is strictly related to those observed for the other 1,2,3,4-tetrafluoroacridines characterized in the solid state by X-ray diffraction analysis, namely the 7-methoxy[12c] (compound **c**) and 7-fluoro derivatives.[12c] In particular, comparison of the bonding features of **c** and **e** shows a close similarity between the acridinic unit, with partial localization of double bonds (C(1)−C(2), C(3)−C(4),

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[17] Samanta, A.; Saha, S.; Ishikawa, H.; Hamaguchi, H. *Chem. Lett.* **2002**, *3*, 340.

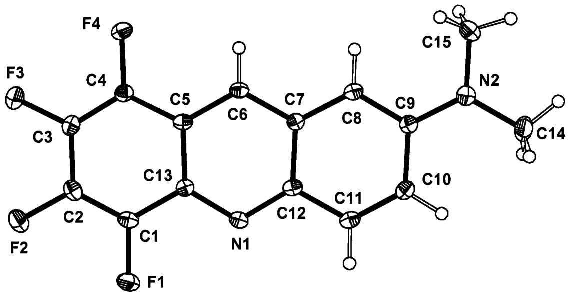

Figure 7. ORTEP drawing (ellipsoids at 30% probability level) and partial numbering scheme for 1,2,3,4-tetrafluoro-7-(*N*,*N*)dimethylaminoacridine (**e**). Hydrogen atoms were given arbitrary radii.

Table 3. Selected Bond Lengths (Å) and Angles (°) for Compound e

F(1)−C(1)	1.349(4)	C(5)−C(6)	1.390(5)
F(2)−C(2)	1.341(5)	C(5)−C(13)	1.426(5)
F(3)−C(3)	1.342(5)	C(6)−C(7)	1.389(5)
F(4)−C(4)	1.348(4)	C(7)−C(8)	1.401(5)
N(1)−C(13)	1.347(5)	C(7)−C(12)	1.430(5)
N(1)−C(12)	1.349(5)	C(8)−C(9)	1.377(5)
N(2)−C(9)	1.375(5)	C(9)−C(10)	1.431(6)
N(2)−C(15)	1.429(6)	C(10)−C(11)	1.344(5)
N(2)−C(14)	1.434(6)	C(11)−C(12)	1.415(5)
C(1)−C(2)	1.345(6)		
C(1)−C(13)	1.402(5)	C(13)−N(1)−C(12)	117.4(3)
C(2)−C(3)	1.411(6)	C(9)−N(2)−C(15)	120.2(4)
C(3)−C(4)	1.336(5)	C(15)−N(2)−C(14)	117.1(4)
C(4)−C(5)	1.408(5)	C(9)−N(2)−C(14)	122.6(4)

C(8)−C(9) and C(10)−C(11) for **e**, see Table 3). The $(CH_3)_2N$ moiety, which has been chosen to tailor the absorption and fluorescence properties, exhibits a N−C(acridine) bond distance of 1.375(5) Å, a value placed between that observed for pyramidalized N(sp^3)−C(arene) interactions (average 1.419(17) Å) and the value typical for planar N(sp^2)−C(arene) interactions (average 1.353(7) Å).[22] The actual length suggests a significant double bond character for the N(2)−C(9) interaction with the nitrogen atom close to sp^2 and a high relevance of a chinoid structure. The least squares plane through molecule **e** with exclusion of all hydrogen atoms and the $(CH_3)_2N$ group gives a rms deviation of fitted atoms of 0.0165 Å, with a maximum deviation from planarity of fitted atoms for C(8) (0.040(3) Å). Also the $(CH_3)_2N$ nitrogen atom N(2) does not deviate significantly from the acridine plane (0.041(5) Å), whereas the methyl groups are slightly off-plane (C(14) 0.098(6) Å), C(15) −0.180(6) Å) owing to a small rotation of the whole $(CH_3)_2N$ group (torsion angles: C(10)−C(9)−N(2)−C(14) 7.6(6)° and C(8)−C(9)−N(2)−C(15) 2.8(6)°) while maintaining its planarity (sum of the C−N(2)−C angles 359.9°). Other aromatic systems containing acceptor groups such as 4-aminobenzonitrile derivatives[23] can display a variety of geometries of the amino group, depending on intramolecular (e.g., steric) and intermolecular effects (e.g., optimization of packing interactions). The features described, together with the C−N(2)−C bond angles, are in accordance with a significant mesomeric donation of the dimethylamino group lone pair to the electron-withdrawing tetrafluoroacridinic nucleus, as discussed for the electronic absorption spectra. The second feature relevant to the aim of the present work is the crystal structure of molecule **e**, as the performance of our system critically depends also on the intermolecular interactions in the solid state. The packing of **e** in the crystal is best described as a head-to-tail stacking of molecules having the perfluoroarene moiety of one molecule facing the arene region of an adjacent molecule, with a distance between the stacked planes of ca. 3.43 Å. This kind of intermolecular interaction, with the same stacking distance, has been observed in the strictly related 7-methoxy derivative **c**.[12c] The perfluoroarene/arene interactions (the very nature of which is still not completely understood[24]) are relevant in the benzene/hexafluorobenzene mixed-crystal discovered in 1960[25] and they have been exploited in a number of other systems as a supramolecular synthon.[26] The stacking motif observed for 1,2,3,4-tetrafluoro-7-methoxy-acridine **c** along [100] in the triclinic space group $P\bar{1}$ or, for example, in the naphthalene/octafluoronaphthalene system,[27] closely resembles the van der Waals arrangement of two subsequent layers in hexagonal graphite, with half the C atoms in a layer eclipsed with respect to those in the next or previous layer. Also, molecule **e** displays the same stacking geometry along the [001] direction (Figure 8, middle part) owing to the presence of inversion centers (Wyckoff letter a), which relate molecular pairs of molecules sitting in general position. Moreover, either in **c** or **e** along each stacked infinite column is present a second type of stacking interaction, again related to the graphite motif but with a reduced overlap between the two adjacent molecular planes and generated by inversion centers (Wyckoff letter b; Figure 8, right side). Therefore, the **..ABAB..** stacking sequence of **e** molecules along [001] comprises two slightly different types of molecular interactions. We recall here

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(18) Crystal data for **e**, $C_{15}H_{10}F_4N_2$: monoclinic, space group $P2_1/n$ (No. 14), $a = 6.427(4)$ Å, $b = 26.783(16)$ Å, $c = 7.235(2)$ Å, $\beta = 95.92(5)°$, $V = 1239(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.578$ g cm^{-3}, final R1 value 0.0616 for 1065 independent reflections with $F_o > 4\sigma(F_o)$. Crystals of compound **e** were grown from CH_2Cl_2 solutions by slow evaporation, giving blade needle orange crystals. The data collection was performed at RT on an Enraf-Nonius CAD-4 diffractometer, using Mo Kα radiation ($\lambda = 0.71073$ Å) by the ω-scan method, within the limits $3° < \theta < 25°$. Data were corrected for Lorentz and polarization effects, absorption (empirical ψ-scans[19]), and decay (11%). The structure was solved by direct methods (SIR97[20]) and refined by full-matrix least-squares on F_o^2 (SHELX97[21]). Anisotropic displacement parameters were assigned to all nonhydrogen atoms. Hydrogen atoms were located in approximate positions by difference Fourier maps; they were introduced in the final stages of l-s refinement in idealized positions riding on their parent carbon atoms with isotropic adp's. The two methyl groups were found disordered and modeled with two sets of H atoms each, with 50% occupancy.

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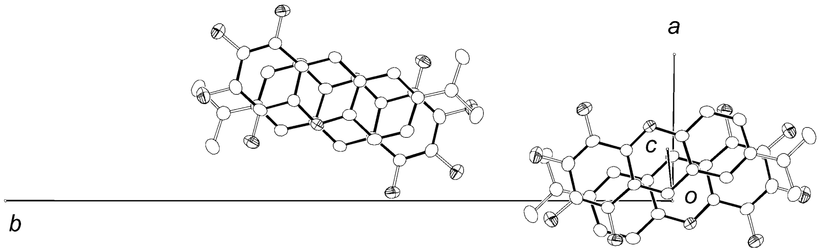

Figure 8. ORTEP drawing showing the overlap diagram by projecting onto the average molecular plane in crystals of acridine **e**. Hydrogen atoms were omitted for the sake of clarity. Stacks are viewed orthogonally to the molecular plane for the stack in the middle part of the unit cell, while the stack closer to the cell origin is slightly tilted.

that the previously described flattening of the (*N*,*N*)-dimethylamino group is functional also to the efficient packing of the molecules to build the [001] columns. Studies are in due course to analyze the reciprocal solubility of **c** in **e** and vice versa in the solid state.

E. Photophysical Properties of Donor and Acceptor in the Solid State. The study of a crystal doped with an isostructural, different molecule has a peculiar interest in the physics of molecular solids and in materials science. A chemical impurity in a single-crystal introduces new energy levels, and, if the impurity does not fit well into the lattice, it may create a distortion in the host crystal; some authors distinguish between X-traps, caused by lattice imperfection and Y-traps caused by chemical impurities.[1] In our case, the impurity (the acceptor **e**) does not strongly distort the lattice (of donor **c**) but introduces different electronic states, so the trap state is mainly due to the electronic states of the dopant.[28]

The study was then extended to the solid state by analyzing the absorption and fluorescence properties of thin films of the molecules **c** and **e** prepared by casting a solution of both molecules in the right ratio onto fused silica substrates. Absorbance measurements were performed at normal incidence in the spectral range from 800 to 190 nm (i.e., from 1.55 to 6.5 eV). Because of the high tendency of molecules to crystallize, the optical quality of the films is very poor and the absorption spectra are strongly affected by light (Rayleigh) scattering from micron-sized crystallites produced during the casting process. In any case, from the absorption spectra of the donor (**c**) we were able to detect a structured low energy band with two distinguished replicas at 422 and 388 nm. The high-energy band, observed in solution, was hidden by scattered light. The absorption spectrum of the acceptor (**e**) displays a similar behavior with a low energy structureless band at 500 nm, similar to that observed in solution. The poor optical quality of film has a minor impact on the photoluminescence (PL) measurements. The PL spectra have been recorded on both the pure component (Supporting Information) and of a blend of donor containing 5% (molar) of acceptor (Figure 9). Both molecules show a red-shifted emission in the solid with respect to the solution, as obviously expected in relation to the molecular aggregation; both spectra present broad and structureless bands, centered at 507 nm for molecule **c** and at 605 nm for **e**. The extent of the red shift is 65 nm (0.25 eV) for the acceptor and 71 nm (0.4 eV) for the donor; it is worthy of note that the red shift for the donor is roughly two times the corresponding shift of the acceptor. For both the acceptor **e** and the donor **c** a modest or no effect of the temperature on the PL has been observed (see Supporting Information). In contrast the emission of the blend has peculiar features. At 300 K it appears as a broad and structureless band centered at 530 and red-shifted by 20 nm (0.12 eV) with respect to the emission of the pure donor, whereas at 70 K only the emission of the donor is observed. On the basis of the temperature-dependent behavior of PL spectra, the emission of the blend should be related to two emitting species, populated by different mechanisms.

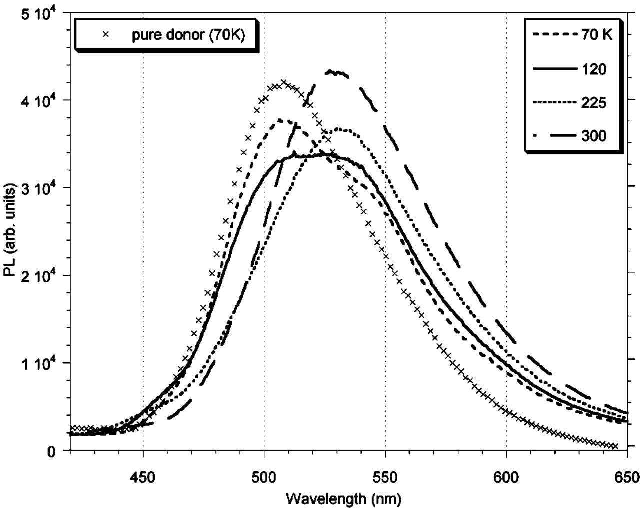

Figure 9. Photoluminescence of blend of **c** (95%) and **e** (5%).

This peculiar behavior allows us to sketch a simple model concerning the fate of the excited states. In accordance with the crystallographic analysis we can suppose that the acceptor molecules are dispersed through the crystal of donor as a substitutional impurity or at least the acceptor may form small clusters in the donor crystal; these species are reasonably the trap states responsible for the emission observed at room temperature. The peculiar temperature behavior of the photoluminescence spectrum of the blend indicates that these trap states, originated by the acceptor, are populated by hopping (at room temperature) and not by Foerster energy transfer. The fact that the emission observed at 300 K is very close to the emission of the acceptor in solution (CH_2Cl_2) strongly supports this hypothesis. At low temperature the population of the acceptor states via hopping process is inhibited and the emission is associated with the donor crystal. The mechanism of population by hopping indicates that the good spectral overlap observed for the donor−acceptor

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(28) This hypothesis is confirmed by our research, still in progress, on solid solution of **c** and **e**.

couple in solution is lost in the solid state. This means that the interaction between the acceptor and the surrounding molecules in the donor crystal is quite different with respect to the acceptor in its own crystal, so the first excited state of the acceptor (responsible for the emission) has a quite different energy: in the crystal of donor the emission is centered at 530 nm (2.34 eV), whereas in the crystal of the pure acceptor the emission is centered at 605 nm (2.05 eV), then the excited state of the acceptor is less stabilized by 0.29 eV in the donor crystal. Moreover, the emitting state attributed to the acceptor is far enough from the bottom of the excitonic band of the pure crystal to prevent the participation of its excited states in the collective states of the crystal of donor. Thus, even if the acceptor molecule has a structure similar to that of the donor one, different interactions between acceptor and donor crystal with respect to acceptor in its own crystal are present; they are responsible for the formation of a deep trap and for the observed emission. As a consequence of this, in principle it is possible, acting on the optical properties of the acceptor, to modify the emission of the donor crystal.

Conclusions

A series of new tetrafluoroacridines has been synthesized in reasonable to good yields by modifying the procedure reported in the literature. The electrochemical and optical properties have been analyzed both in solution and in the solid state. The cyclic voltammetry studies have shown interesting features; the replacement of hydrogen with fluorine atoms reduces by 0.2 V the reduction potential of acridine nucleus. Both reduction and oxidation potential are strongly influenced by the nature of substituents, and a more marked effect has been observed with the strong electron-donating dimethylamino substituent. The electrochemical properties of tetrafluoroacridines make them candidates as potential electron transporting materials, suitable to use in devices such as as OLED, OFET, and photovoltaic devices; work in this direction is in progress and the preliminary results obtained are encouraging. The X-ray analysis showed the role of fluorination on the packing of molecule **e** in the solid state; indeed, due to presence of a fluorinated part in the acridine molecule, the packing in the crystal is a head-to-tail stacking of molecules where the fluorinated moiety of one molecule faces the arene region of an adjacent molecule; the same packing, with the same stacking distance, has been observed in the strictly related 7-methoxy derivative **c**. The study performed in solution on the optical properties of tetrafluoroacridines has allowed us to individuate a promising donor−acceptor couple, studied further in the solid state. The study of the optical properties of a blend of donor (**c**) and acceptor (**e**) allowed us to take a glance at the phenomena concerning the energy transfer processes and the fate of the excited states in the solid state. The peculiar temperature behavior of the photoluminescence spectrum of a blend of donor and acceptor molecules indicates that the acceptor introduces deep trap states in the donor crystal, populated at room temperature by hopping. The emission properties of these blends are strongly influenced by the nature of these traps, and after all, by the optical properties of acceptor; this latter can be modulated by acting on the electronic properties of substituents present on the acceptor.

Experimental Section

General Information. All starting materials were purchased from commercial sources (Aldrich Chemical Co.). The amines were purified by distillation. Pentafluorobenzaldehyde was purchased from Fluorochem and used without further purification. Column chromatography was performed on Merck silica gel 60 (0.063−0.200 mm). Toluene and xylene were of analytical grade and used as received; dichloromethane for spectroscopic measurements was purchased from Aldrich (B&J Brand, suitable for pesticide analysis) and used as is. ^{1}H and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 400 spectrometer and Bruker 300, using CF_3CH_3 as internal standard for ^{19}F spectra. The UV−Vis absorption spectra of the solutions were recorded with a Perkin-Elmer Lambda 900 spectrophotometer. The fluorescence spectra of solutions were measured on an Aminco-Bowman spectrofluorometer at room temperature. Photoluminescence measurements on films were performed with a homemade apparatus using a monochromated Xe lamp as excitation light source and a nitrogen-cooled CCD camera coupled with a 190-mm polychromator for the signal detection. The sample was kept inside a cryostat during all PL measurements to control the temperature and to avoid its photooxidation. 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) as reference. Both electrodes were separated from the solution by a glassy septum. Cyclic voltammetries of 2 mM solutions were carried out at room temperature in acetonitrile (AN) + 0.1 M tetrabuthylammonium perchlorate (TBAP). AN (UVASOL Merck product) was stored and manipulated under argon pressure. TBAP (Fluka AG purum) was crystallized from methanol.

General Procedure for 1,2,3,4-Tetrafluoroacridines Synthesis (Except Compound g). To a solution of pentafluoro benzaldehyde (3.5 mmol) in xylene[29] (25 mL) wass added aniline (8 mmol) and the solution was refluxed under nitrogen atmosphere. After 20 h of reflux, another 3.5 mmol of aniline was added to the solution and the reflux continued (see Table 1 for the total refluxing time). The solvent was removed and the crude was purified by column chromatography (silica gel, CH_2Cl_2) and further by sublimation or crystallization.

1,2,3,4-Tetrafluoroacridine (a). Yield: 51%. White-yellow solid. mp 180° C (sublimation at 115 °C. 0.7 mbar). ^{1}H NMR ($CDCl_3$): d 9.03 (s, 1H), 8.34−8.31 (d, 1H, J = 8.8 Hz), 8.07−8.04 (d, 1H, J = 8.5 Hz), 7.92−7.86 (t, 1H, J = 7.85 Hz), 7.68−7.63 (t, 1H, J = 7,55 Hz). ^{19}F NMR ($CDCl_3$): d: −150.9 (t, 1F), −152,2 (t, 1F), − 152.9 (t, 1F), −158.3 (t, 1F). Anal. Calcd. for $C_{13}H_5F_4N$: C, 62.16%; H, 2.01%; F, 30.25%; N 5.58%. Found: C, 62.4%; H, 1.9%; F, 30.0%; N, 5.6%.

1,2,3,4-Tetrafluoro-7-phenylacridine (b). Yield: 51%. Yellow solid. mp 240°C (sublimation at 130 °C, 0.1 mbar). ^{1}H NMR ($CDCl_3$): d 9.05 (s, 1H), 8.41−8.38 (d, 1H, J = 9.0 Hz), 8.22−8.21 (d, 1H, J = 1.85 Hz), 8.20−8.16 (q, 1H, J1 = 9.0 Hz, J2 = 2.1 Hz), 7.78−7.76 (d, 2H, J = 6.8 Hz), 7.57−7.52 (t, 2H, J = 7.4 Hz), 7.48−7.43 (t, 1H, J = 7.2 Hz). ^{19}F NMR ($CDCl_3$) d: −150.8 (t, 1F), −152.1 (t, 1F), −153.0 (t, 1F), −158.1 (t, 1F). Anal. Calcd. for $C_{19}H_9F_4N$: C, 69.73%; H, 2.77%; F, 23.22%; N, 4.28%. Found: C, 69.5%; H, 2.6%; F, 23.1%; N, 4.2%.

1,2,3,4-Tetrafluoro-7-methoxyacridine (c). Yield: 74%. Pale yellow solid. mp 210−211 °C (sublimation at 140 °C, 0.2 mbar). ^{1}H NMR ($CDCl_3$): d 8.82 (s, 1H), 8.21−8.18 (d, 1H, J = 9.5 Hz), 7.57−7.53 (q, 1H, $J1$ = 9.4 Hz, $J2$ = 2.6 Hz), 7.18 (d, 1H, J = 2.5 Hz); 3.99 (s, 3H).; ^{19}F NMR ($CDCl_3$): d −151.9

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[29] Or toluene. See Table 1 for details.

(t, 1F), −152.7 (t, 1F), −155.3 (t, 1F), −158.5 (t, 1F). Anal. Calcd. for $C_{14}H_7F_4NO$: C, 59.80%; H, 2.51%; F, 27.02%; N, 4.98%. Found: C, 59.8%; H, 2.5%; F, 27.0%; N, 4.9%.

1,2,3,4-Tetrafluoro-7-phenoxyacridine (d). Yield: 62%. Yellow solid. mp 150 °C (sublimation at 140 °C, 0.5 mbar). ^{1}H NMR (CDCl$_3$): d 8.77 (s, 1H), 8.31−8.29 (d, 1H, $J = 6.9$ Hz), 7.73−7.70 (dd, 1H, $J1 = 6.9$ Hz, $J2 = 2.1$ Hz), 7.48−7.44 (dd, 2H, $J1 = 6.3$ Hz, $J2 = 5.7$ Hz), 7.29−7.27 (d, 1H, $J = 5.7$ Hz), 7.234−7.226 (d, 1H, $J = 2.4$ Hz), 7.18−7.16 (d, 2H, $J = 5.7$ Hz). ^{19}F NMR (CDCl$_3$): d − 150.8 (t, 1F), −151.8 (t, 1F), − 153.6 (t, 1F), − 157.3 (t, 1F). Anal. Calcd. for $C_{19}H_9F_4NO$: C, 66.48%; H, 2.64%; F, 22.14%; N, 4.08%. Found: C, 66.5%; H, 2.5%; F, 21.9%; N, 4.2%.

1,2,3,4-Tetrafluoro-7-(*N,N*)dimethylaminoacridine (e). Yield: 85%. Orange solid. mp 246∠249 °C (sublimation at 140 °C, 0.5 mbar). ^{1}H NMR (CDCl$_3$): d 8.60 (s, 1H), 8.15−8.12 (d, 1H, $J = 6.67$ Hz), 7.64−7,60 (d, 1H, $J1 = 9.7$ Hz, $J2 = 2.8$ Hz), 6.82 (d, 1H, $J = 2.85$ Hz), 3.14 (s, 6H). ^{19}F NMR (CDCl$_3$): d −152.6 (t, 1F), −153.4 (t, 1F), −157.8 (t, 1F), −159.9 (t, 1F). Anal. Calcd. for $C_{15}H_{10}F_4N_2$: C, 61.23%; H, 3.43%; F, 25.83%; N, 9.52%. Found: C, 61.1%; H, 3.3%; F, 25.5%; N, 9.5%.

1,2,3,4-Tetrafluoro-7-*N*-phenylaminoacridine (f). Yield: 77%. Orange solid. mp 223 °C (sublimation at 170 °C, 0.1 mbar). ^{1}H NMR (CDCl$_3$): d 7.88 (s, 1H), 8.22−8.19 (d, 1H, $J = 9.4$ Hz), 7.58−7.55 (dd, 1H, $J1 = 9.4$ Hz, $J2 = 2.6$ Hz), 7.43−7.42 (d 1H, $J = 2.5$ Hz), 7.40−7.38 (d, 2H, $J = 7.45$ Hz), 7.30−7.27 (d, 2H, $J = 7.5$), 7.16−7.11 (t, 1H, $J = 7.3$), 6.15 (s broad, 1H). ^{19}F NMR (CDCl$_3$): d −152.0 (t, 1F), −152.8 (t, 1F), −156.0 (t, 1F), −158.9 (t, 1F). Anal. Calcd. for $C_{19}H_{10}F_4N_2$: C, 66.67%; H, 2.94%; F, 22.20%; N, 8.18%. Found: C, 66.6%; H, 2.9%; F, 22.0%; N, 8.2%.

1,2,3,4-Tetrafluoro-7-methylthioacridine (h). Yield: 30%. Bright yellow solid mp 210 °C (crystallization from Et$_2$O). ^{1}H NMR (CDCl$_3$): d 8,75 (s, 1H), 8.10−8.08 (d, 1H, $J = 6.9$ Hz), 7.63−7.61 (dd, 1H, $J1 = 7.2$ Hz, $J2 = 1.8$ Hz), 7.53 − 7.52 (d, 1H, $J = 2$ Hz), 2.58 (s, 3H). ^{19}F NMR (CDCl$_3$): d −146.2 (m, 2F), −153.5 (m, 2F). Anal. Calcd. for $C_{14}H_7F_4NS$: C, 56.57%; H, 2.37%; F, 25.56%; N, 4.71%; S, 10.78%. Found: C, 56.5%; H, 2.3%; F, 25.4%; N, 4.7%; S, 10.7%.

***p*-Carbazolylnitrobenzene.** To *p*-fluoronitrobenzene (2124 mg, 15.05 mmol) was added carbazole (503 mg, 3.01 mmol) and potassium carbonate (2211 mg), and the orange mixture was heated at 210−215 °C for 6 h. The solid was ground, washed with water, and then extracted with CH$_2$Cl$_2$. The crude was purified by column chromatography (CH$_2$Cl$_2$/hexane 1:1 and then CH$_2$Cl$_2$) to give a bright yellow solid. Yield 87%. ^{1}H NMR (CDCl$_3$): d 8.51−8.46 (d, 2H, $J = 8.9$ Hz), 8.16−8.13 (d, 2H, $J = 7.6$ Hz), 7.82−7.77 (d, 2H $J = 8.9$ Hz), 7.51−7.49 (d, 2H, $J = 7.5$ Hz), 7.47−7.42 (dd, 2H, $J1 = 6.8$ $J2 = 8.2$), 7.37−7.32 (dd, 2H, $J1 = 7.7$, $J2 = 6.8$). Anal. Calcd. for $C_{18}H_{12}N_2O_2$: C, 74.99%; H, 4.20%; N, 9.72%. Found: C, 74.8%; H, 4.2%; N, 9.7%.

1,2,3,4-Tetrafluoro-7-carbazolylacridine (g). To pentafluorobenzaldehyde (132 mg, 0.67 mmol) was added the *p*-carbazolylaniline freshly prepared (640 mg, 2.48 mmol). The amine was prepared following a procedure reported in the literature,[14] starting from *p*-carbazolylnitrobenzene. The mixture was heated at 210 °C under nitrogen atmosphere for 5 h. The crude was purified by column chromatography (silica gel, CH$_2$Cl$_2$, and then CH$_2$Cl$_2$/hexane 7:3) to give a bright yellow solid (blue-green fluorescence in the solid at 365 nm). Yield: 26%. mp 213 °C. ^{1}H NMR (CDCl$_3$): d 9.01 (s, 1H), 8.48−8.46 (d, 1H, $J = 7.2$ Hz), 8.19 (d, 1H, $J = 1.8$ Hz), 8.12−8.10 (d, 2H, $J = 5.4$ Hz), 8.08−8.05 (dd, 1H, $J1 = 7.0$ Hz, $J2 = 1.6$ Hz), 7.49−7.47 (d, 2H, $J = 6.3$ Hz) 7.40−7.36 (t, 2H, $J = 6.2$ Hz), 7.30−7.26 (t, 2H, $J = 5.6$ Hz). ^{19}F NMR (CDCl$_3$): d −150.5 (t, 1F), −151.6 (t, 1F), −152.2 (t, 1F), −157.0 (t, 1F). Anal. Calcd. for $C_{25}H_{12}F_4N_2$: C, 72.12%; H, 2.90%; F, 18.25%; N, 6.73%. Found: C, 72.0%; H, 2.90%; F, 18.0%; N, 6.8%.

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Supporting Information Available: Cyclic voltammograms of **b** and **e**; solvatochromism of fluorescence spectra of compounds **c** and **e**; photoluminescence of film of **c** and **e** (pdf). Complete crystallographic data in CIF format for compound **e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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