at 25 °C which could not be measured directly. Each rate constant was determined at least in duplicate, and the deviation was smaller than ±3%. The mean values of these data are listed in Table I.

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Synthesis of New Amphiphilic Perfluoroalkylated Bipyridines

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General and versatile synthetic methods have been developed for the preparation of a large variety of 2,2′-bipyridines bearing two various perfluoroalkylated side chains with an ester or a methylene junction in the 4,4′-positions, e.g., 4,4′-bis[[2″-(*F*-alkyl)ethenyl]alkyl]-2,2′-bipyridines, 4,4′-bis[[[(*F*-alkyl)alkyl]oxy]carbonyl]-2,2′-bipyridines, and 4,4′-bis[[[[2″-(*F*-alkyl)ethenyl]alkyl]oxy]carbonyl]-2,2′-bipyridines.

Introduction

An area of growing interest lies in the use of ligands and their transition-metal complexes exhibiting amphiphilic properties capable of being inserted into interfacial films, membranes, liposomes, and other organized supramolecular systems. A more important objective is to develop novel chemistry based on membrane-mediated processes in relatively simple systems. Such organized systems have been utilized in reactivity control, photochemical solar energy conversion and storage, transport, and drug encapsulation and providing unique environments for substrates and enzymes.[1]

Our goal is to develop metal complexes which may be transported by vesicles (or liposomes) or by injectable fluorocarbon emulsions to be used simultaneously as drug delivery systems and as artificial oxygen carriers. In order to achieve this goal, it was necessary to synthesize new highly amphiphilic ligands bearing, in particular, perfluoroalkylated side chains. Such derivatives may find several potential applications, namely in therapy for the transport and targeting of drugs based on transition-metal complexes and in the constitution of functionalized dispersed systems which may operate as catalytic microreactors.

We describe here the preparation of a new class of amphiphilic ligands in which the coordinating head consists of a bipyridine moiety and the hydrophobic part of two hydrocarbon chains of various lengths terminated by highly perfluoroalkylated tails.

The presence of the bipyridine head on these new compounds opens up a large field of applications. Very few organic ligands have received more attention than 2,2′-bipyridine and its analogues. Bipyridine ligands are widely used in coordination chemistry and catalysis.[2] The interest in such ligands stems, in particular, from their exceptional photoredox properties and from the peculiar photochemical and photophysical properties exhibited by several of their transition-metal complexes.[3] Elaborate systems exploiting such properties have indeed emerged, especially in redox electrocatalysis[4] and light-induced electron-transfer reactions that convert solar energy into chemical energy.[5] Furthermore, several 2,2′-bipyridine–metal complexes were found to be endowed with antimicrobial,[6] antifungal,[7] and antineoplasmic[8] activity.

The perfluoroalkylated tails are intended to increase the hydrophobic and fluorophilic character of these amphiphilic ligands, hence of their transition-metal complexes, to facilitate, respectively, their incorporation into liposomes and into oxygen-delivering fluorocarbon emulsions. The encapsulation into liposomes of a drug usually improves its therapeutic index, hence its efficiency, by reducing its toxicity, prolonging its intravascular persistence, and modifying its biodistribution.[9] Furthermore, the incorporation of a drug in fluorocarbon emulsions is expected to combine the numerous advantages of drug encapsulation with the capacity of the fluorocarbon to deliver oxygen in radio-[10] and chemoresistant[11] tumors, thus enhancing the tumoricidal effects of radiations or of cytotoxic drugs. Such a synergistic effect has been shown in the treatment of tumors with alkylating agents, antimetabolites, and antibiotics used in conjunction with fluorocarbon emulsions.[12] In addition, the use of fluorocarbon emulsions in therapy as drug delivery systems is particularly attractive in view of their high intravascular persistence and

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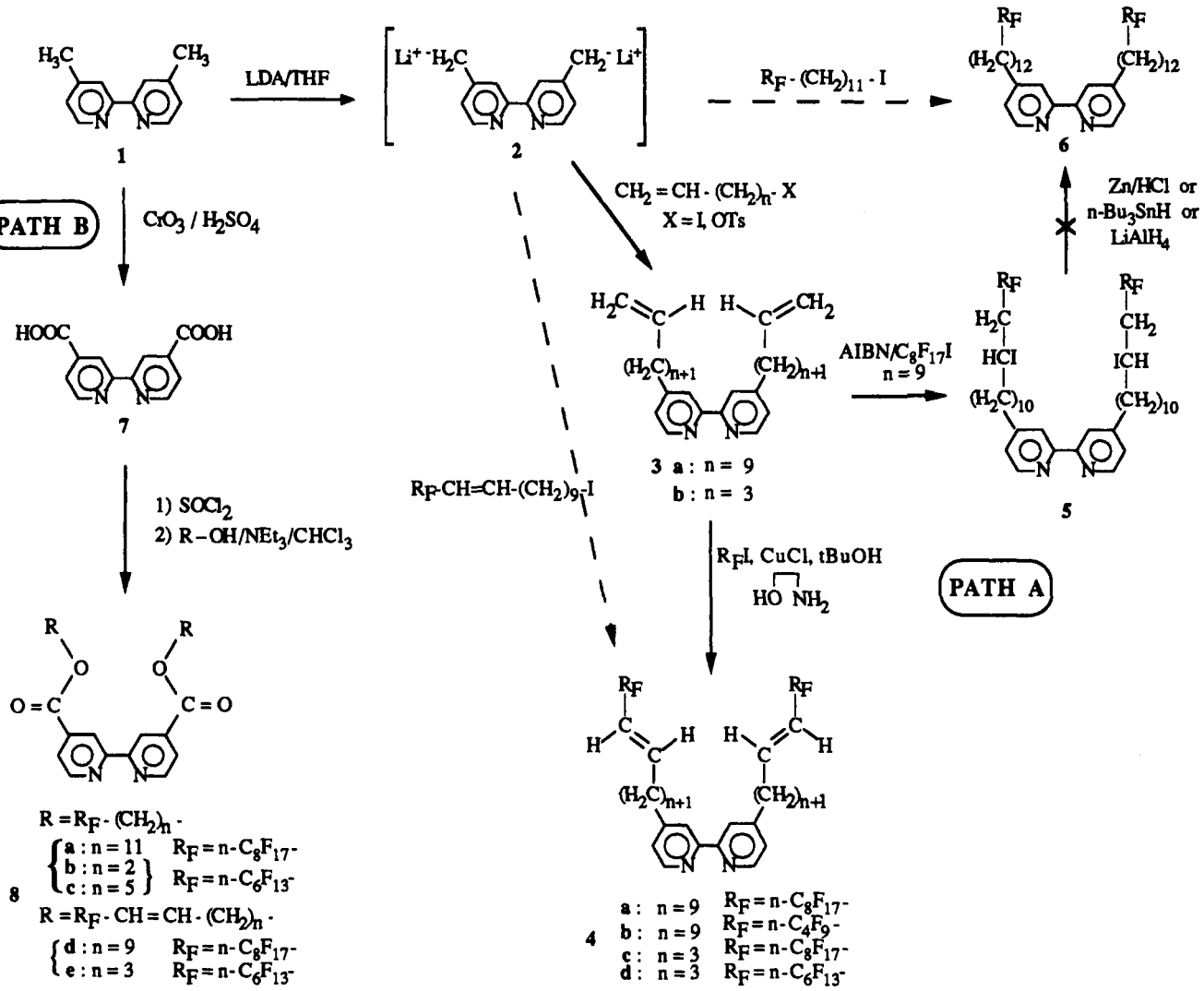
Scheme I. Synthesis of 4,4′-Bis[[2″-(*F*-alkyl)ethenyl]alkyl]-2,2′-bipyridines 4a–d, 4,4′-Bis[[[(*F*-alkyl)alkyl]oxy]carbonyl]-2,2′-bipyridines 8a–c, and 4,4′-Bis[[[[2″-(*F*-alkyl)ethenyl]alkyl]oxy]-carbonyl]-2,2′-bipyridines 8d–e



their great tendency to concentrate around tumors.[13]

This paper is devoted to the synthesis and characterization of a series of 4,4′-bis[[2″-(*F*-alkyl)ethenyl]alkyl]-2,2′-bipyridines (compounds **4**), of 4,4′-bis[[[(*F*-alkyl)alkyl]oxy]carbonyl]-2,2′-bipyridines **8a–c**, and of 4,4′-bis-[[[[2″-(*F*-alkyl)ethenyl]alkyl]oxy]carbonyl]-2,2′-bipyridines **8d,e**. Their coordination chemistry toward platinum and palladium,[14] the incorporation into liposomes,[15] and the cytotoxic activity[16] of the resulting complexes will be reported elsewhere. We also discuss our preliminary attempts to prepare 4,4′-bis[(*F*-alkyl)]alkyl]-2,2′-bipyridines such as **6**.

Results and Discussion

In anticipation of their future applications, it was desirable that the new perfluoroalkylated amphiphilic ligands possess a modular structure to allow stepwise adjustment of their properties and of those of their transition-metal complexes (e.g., their fluorophilicity, lipophilicity and consequently hydrophobicity). Aiming at these goals, it was necessary, for the preparation of such ligands, to develop flexible synthetic strategies. The ligands described here (Scheme I) have a hydrophilic 2,2′-bipyridine head connected in 4 and 4′, through a methylene (path A, compounds **4a–d**) or an ester junction (path B, compounds **8a–e**), to a highly hydrophobic fragment consisting of an unsaturated (**4a–d** and **8d–e**) or saturated (**8a–c**) hydrocarbon spacer, ended by a linear perfluoroalkyl tail of variable length. These two routes to perfluoroalkyl-substituted bipyridines appear to be capable of being generalized to any desired length of the perfluoroalkyl tail and of the spacer between the functional tail and the ring.

Both the reaction pathways were envisaged from the same starting compound, i.e., 4,4′-dimethyl-2,2′-bipyridine, **1**, which is the most versatile, inexpensive, and easily available source of 2,2′-bipyridine derivatives.

Synthesis of the 4-4′-Bis[[2″-(*F*-alkyl)ethenyl]alkyl]bipyridines 4. Over the past few years, several methods[17–22] have been described for the preparation of long-chain bis(alkyl)bipyridines. A very flexible way of

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introducing a functionalized side chain into 2,2′-bipyridine utilizes the reaction of the dianion **2**, formed from **1** and various strong bases (BuLi, $NaNH_2$, $LiN(i\text{-}Pr)_2$), with alkyl halides (or alkyl tosylates) or functionalized hydrocarbon halides. In order to obtain, in one step, the 4,4′-bis-[[2″-(*F*-alkyl)ethenyl]alkyl]-2,2′-bipyridines **4** we therefore performed the reaction between **2** and a perfluoroalkylated iodide, e.g., $C_8F_{17}CH{=}CH(CH_2)_9I$. However, it led to a complex mixture of products from which compound **4a** could be isolated only in very low yields (<10%).

An alternative consisted in introducing a double-bond-terminating side-chain on the bipyridine, the perfluoroalkyl tail being grafted to the double bond in a subsequent step (Scheme I, path A). This strategy has furthermore the advantage of being more versatile as it uses the same intermediate **3** for the synthesis of various perfluoroalkylated substituted bipyridines **4** (and also of derivatives such as **6**, vide infra) differing by their perfluoroalkyl tail length. The reaction between the dianion **2** and the α,ω-alkenyl iodides led, as expected, to the functionalized disubstituted bipyridines as the major product (50–70% yield), besides the monosubstituted ones as shown by the ^1H NMR spectra of the crude reaction mixture (presence of a singlet at 2.36–2.40 ppm corresponding to the 4′-methyl group). The addition of a linear perfluoroalkyl iodide (R_FI) on a terminal $CH_2{=}CH-$ double bond may be performed with high yields by various processes. One of the most attractive ways[23] is the modified method of Burton and Kehoe[24] in a two-step one-pot reaction, which would afford from **3**, after radical addition of R_FI initiated by CuCl/ethanolamine, a compound of type **5**, and then, after dehydroiodination in the presence of an excess of base, the perfluoroalkyl unsaturated bis[[2″-(*F*-alkyl)ethenyl]alkyl]-bipyridine derivatives **4** (mainly of *E* configuration). Thus, when this method was applied to **3**, the addition of the R_F group to both its double bonds and subsequent HI elimination led to ligands **4** (isolated as white crystalline materials) in yields ranging from 50 to 80%. According to ^{19}F NMR which shows more particularly the presence of two resonances for the CF_2 α to the double bonds, each of the isolated compounds **4a–d** consisted of a mixture of isomers differing in the configuration of their two double bonds. The most abundant one has its two double bonds in the *E* configuration and is accompanied by its *Z*/*E* and/or *Z*/*Z* isomers: the *E*/*Z* CF_2 integration ratio of nearly 9/1 indicates that the *E*/*E* to *E*/*Z* + *Z*/*Z* ratio is higher than or equal to 80/20. The pure *E*/*E* compounds can be obtained after successive recrystallizations (only the *E* CF_2 resonance is detected by ^{19}F NMR).

Synthesis of the 4,4′-Bis[(*F*-alkyl)alkyl]bipyridines 6. The preparation of 4,4′-bis[(*F*-alkyl)alkyl]-2,2′-bipyridines containing saturated hydrocarbon spacers between the bipyridine ring and the perfluoroalkyl tails (compound **6**), avoiding the above problem of the *E*/*Z* isomers, has been investigated. However, none of our experiments proved effective in the synthesis of such derivatives.

Thus, the one-step direct access to **6** starting from **2** and the perfluoroalkylated iodide, $C_8F_{17}(CH_2)_{11}I$, led to a complex mixture from which the expected compound (present in very low amount) could not be isolated.[25] Most probably, it is the basic or reducing character of the dianion **2** together with the acidic character of the CF_2CH_2 protons which are responsible for side reactions. It thus appeared that the direct alkylation of **2** either by α,ω-(perfluoroalkyl)alkyl iodides or by α,ω-[2-(perfluoroalkyl)ethenyl]alkyl iodides (vide supra) was not a valid strategy for the preparation of perfluoroalkylated side-chain bipyridines.

The two-step preparation starting from intermediate **3a**, e.g., addition of R_FI on the two double bonds of **3a** in the presence of α,α'-azobisisobutyronitrile[23] (AIBN), afforded, in step one, effectively the expected adduct **5** in good yields (71%). However, the reduction of the C–I bond in **5** using various reductors ($LiAlH_4$, $n\text{-}Bu_3SnH$), including the most widely used Zn/HCl/ethanol system for the reduction of R_FCH_2CHI- derivatives, was complex, and the desired compound **6** could never be obtained. More work is currently under way aiming at the reduction of **5** into **6**.

Synthesis of the Bis[[[(*F*-alkyl)alkyl]oxy]-carbonyl]bipyridines and Bis[[[[2″-(*F*-alkyl)-ethenyl]alkyl]oxy]carbonyl]bipyridines. The preparations of the perfluoroalkylated ligands with an ester linkage (path B, compounds **8**) are easily achieved in high yields from the diacid **7** and the corresponding perfluoroalkylated alcohol[26–28] using standard methods.[29] The main difficulty of this synthetic scheme lies in the preparation of the diacid **7** from **1**. Indeed, the tedious synthesis of the diacid **7** through the oxidation of **1** with aqueous potassium permanganate[30–33] occurred in variable yields which did not exceed 50%. Furthermore, its purification from other acidic products that are formed simultaneously is difficult because of the very low solubility in most solvents. The pure diacid **7** is obtained in nearly quantitative yields (90%) by carrying out the oxidation of **1** with CrO_3/H_2SO_4 as described for the oxidation of 2,2′,6,6′-tetramethyl-4,4′-bipyridine.[29] The diacid **7** was further purified and characterized as its dimethyl ester, avoiding the tedious recrystallization from hot concentrated HNO_3 solutions. After hydrolysis of the diester, the diacid **7** was recovered and isolated at an analytical purity level. The overall yield in **7** from **1** was 90%.

Experimental Section

General. Analytical TLC were performed on precoated silica gel 60 F_{254} plates (Merck) with UV detection (254 nm) or by charring with a fluoresceine–ethanol solution. Silica gel 60 (Merck, 70–230 mesh) columns were used for preparative separations. Melting points, determined with a Reichert apparatus, are uncorrected. IR spectra were recorded on a Bruker IFS spectrometer as KBr disks for the crystalline samples and as films for the neat liquids. ^1H, ^{13}C (Chemical shifts measured in deuterated solvents are given in ppm from Me_4Si) and ^{19}F (Internal reference $CFCl_3$) NMR spectra were recorded on Bruker CW 80, WH 90 or AC 200 spectrometers.

Reactions under anhydrous conditions were performed under dry argon. Tetrahydrofuran (THF), chloroform, methylene dichloride, pyridine, and diisopropylamine were distilled and dried

(23) Another attractive way would have been the two-step sequence reaction developed by Brace (Brace, N. O. *J. Org. Chem.* **1971**, *36*, 1904; *J. Org. Chem.* **1962**, *27*, 4491), which consists in (i) the radical addition of R_FI on **3** initiated by α,α'-azobisisobutyronitrile (AIBN) leading to compounds of type **5** followed by (ii) HI elimination under the action of a base.

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(34) The unreacted expensive iodo-F-alkane can be recovered unchanged by distillation of the crude reaction mixture and washing with water to eliminate *t*-BuOH.

according to standard procedures. The perfluoroalkylated alcohols—5-(*F*-hexyl)pentanol,[26] 5-(*F*-hexyl)-4-pentenol (*Z*/*E* mixture),[26] 11-(*F*-octyl)-10-undecenol (*Z*/*E* mixture),[27] 11-(*F*-octyl)undecanol[28]—were prepared according to published procedures, and 2-(*F*-hexyl)ethanol was a gift from ATOCHEM. These alcohols were recrystallized from hexane or distilled before use. 4,4'-Dimethyl-2,2'-bipyridine (Aldrich) was dried under reduced pressure prior to use, and *p*-toluenesulfonyl chloride (TsCl) was recrystallized from chloroform/pentane. The perfluoroalkyl iodides (n-$C_8F_{17}I$, n-$C_6F_{13}I$, and n-C_4F_9I) were distilled in the dark and under oxygen-free argon before use. All other reagents were used as received from commercial sources. 11-(*F*-Octyl)-1-iodoundecane and 11-(*F*-octyl)-1-iodo-10-undecene were obtained, respectively, from 11-(*F*-octyl)undecan-1-ol and 11-(*F*-octyl)-10-undecen-1-ol in the same way as described below for the preparation of the α,ω-alkenyl iodides.[33]

Synthesis of the ω-Alkenyl 1-Tosylates and Iodides. 10-Undecenyl *p*-toluenesulfonate and 4-pentenyl *p*-toluenesulfonate were prepared in nearly quantitative yields, according to standard published procedures, from 10-undecen-1-ol and 4-penten-1-ol, respectively, and TsCl in dry pyridine. The iodide analogues were obtained quantitatively from the tosylates by Ts/I exchange in an acetone solution containing an excess of NaI.

10-Undecenyl *p*-Toluenesulfonate. IR (film, cm^{-1}): 1641, 1599 (C=O), 1180 (S=O). ^1H NMR (80 MHz, $CDCl_3$): δ 1.35 (br, s, 12 H, $(H_2C)_{3-9}$), 1.45–2.20 (m, 4 H, $(H_2C)_{2,10}$), 2.45 (s, 3 H, H_3C), 4.05 (t, $^3J_{H,H}$ = 6 Hz, 2 H, $(H_2C)_1$), 4.9–5.1 (m, 2 H, H_2C=), 5.6–6.07 (m, 1 H, HC=), 7.39 (d, $^3J_{H,H}$ = 8 Hz, 2 H, H_{meta}), 7.82 (d, $^3J_{H,H}$ = 8 Hz, 2 H, H_{ortho}).

4-Pentenyl *p*-Toluenesulfonate. IR (film, cm^{-1}): 1645, 1599 (C=C), 1180 (S=O). ^1H NMR (80 MHz, $CDCl_3$): δ 1.60–2.20 (m, 4 H, $(H_2C)_{2,3}$), 2.43 (s, 3 H, H_3C), 4.02 (t, $^3J_{H,H}$ = 6 Hz, 2 H, $(H_2C)_1$), 4.78–5.14 (m, 2 H, H_2C=), 5.44–6.07 (m, 1 H, HC=), 7.30 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H_{meta}), 7.77 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H_{ortho}).

11-Iodo-1-undecene. Bp 52 °C (2×10^{-2} mmHg). IR (film, cm^{-1}): 1641 (C=C). ^1H NMR (80 MHz, $CDCl_3$): δ 1.22–1.56 (m, 12 H, $(H_2C)_{3-9}$), 1.62–2.27 (m, 4 H, $(H_2C)_{2,10}$), 3.22 (t, $^3J_{H,H}$ = 6 Hz, 2 H, $(H_2C)_1$), 4.85–5.10 (m, 2 H, H_2C=), 5.31–5.97 (m, 1 H, HC=).

5-Iodo-1-pentene. Bp: 150 °C (760 mmHg). IR (film, cm^{-1}): 1643 (C=C). ^1H NMR (80 MHz, $CDCl_3$): δ 1.63–2.22 (m, 4 H, $(H_2C)_{2,3}$), 3.17 (t, $^3J_{H,H}$ = 6 Hz, 2 H, $(H_2C)_1$), 4.96–5.16 (m, 2 H, H_2C=), 5.34–5.97 (m, 1 H, HC=).

Synthesis of the Bis(ω-alkenyl)bipyridines 3. 4,4'-Di(11''-dodecenyl)-2,2'-bipyridine (3a). A solution of n-butyllithium 1.6 M in hexane (45.6 mL, 72.9 mmol, 2.65 equiv) was added, via a syringe, to a solution of diisopropylamine (10 mL, 72.9 mmol, 2.65 equiv) in tetrahydrofuran (24 mL) at 0 °C. The solution was stirred at 0 °C for 1 h and 4,4'-dimethyl-2,2'-bipyridine (1) (5 g, 27.5 mmol, 1 equiv) in 150 mL of tetrahydrofuran was then added dropwise. The dark red-orange mixture was stirred at 0 °C for 3 h. Then, 11-iodo-1-undecene (15.4 g, 55 mmol, 2 equiv) in 40 mL of tetrahydrofuran was added slowly via a syringe at 0 °C. The solution which turned green was stirred for 3 h at the same temperature. The reaction was quenched by addition of 10 mL of methanol, and a clear yellow-brown solution was obtained which was poured into cold water and then extracted by diethyl ether (3 × 100 mL). The residue, after removal of ether, was chromatographied on silica gel. Elution with a chloroform/pentane (1:1) mixture allows the separation of the unreacted iodide derivative. The expected compound was eluted with chloroform and, after evaporation and recrystallization from hexane, white crystals of **3a** (6.93 g, 14.18 mmol, 52% yield) were obtained: Mp = 60 °C. IR (KBr, cm^{-1}): 1639 (HC=CH_2), 1591, 1553 (bipy). ^1H NMR (80 MHz, $CDCl_3$): δ 1.20 (br, s, 28 H, $(H_2C)_{3''-9''}$), 1.48–2.21 (m, 8 H, $(H_2C)_{2'',10''}$), 2.66 (t, $^3J_{H,H}$ = 7.2 Hz, 4 H, $(H_2C)_{1''}$), 4.78–5.14 (m, 4 H, H_2C=), 5.47–6.07 (m, 2 H, HC=), 7.06 (dd, $^3J_{ortho}$ = 5.6 Hz, $^4J_{meta}$ = 1.5 Hz, 2 H, $H_{5,5'}$), 8.27 (br s, 2 H, $H_{3,3'}$), 8.52 (d, $^3J_{ortho}$ = 5.6 Hz, 2 H, $H_{6,6'}$).

4,4'-Di(5''-hexenyl)-2,2'-bipyridine (3b). The procedure as described above was applied to diisopropylamine (10 mL, 71.5 mmol) in 20 mL of tetrahydrofuran, n-butyllithium 1.6 M in hexane (44.72 mL, 71.5 mmol), a solution of 1 (5 g, 27 mmol) in 70 mL of tetrahydrofuran, and 4-pentenyl *p*-toluenesulfonate (18.8 g, 75.6 mmol)—or 5-iodo-1-pentene—in 75 mL of tetrahydrofuran. The residue obtained was chromatographed on silica gel first with pentane/methylene dichloride (1:1) and (1:3) mixture and then with methylene dichloride/methanol (100 − *x*: *x*, *x* = 0–4%) as eluents. All the fractions containing the desired compound were combined and evaporated to give a colorless oil consisting of **3b** (5.47 g, 17.1 mmol, 63%). IR (film, cm^{-1}): 1639 (HC=CH_2), 1595, 1555 (bipy). ^1H NMR (80 MHz, $CDCl_3$): δ 1.34–2.16 (m, 12 H, $(H_2C)_{2''-4''}$), 2.68 (t, $^3J_{H,H}$ = 7 Hz, 4 H, $(H_2C)_{1''}$), 4.78–5.12 (m, 4 H, H_2C=), 5.47–6.03 (m, 2 H, HC=), 7.10 (dd, $^3J_{ortho}$ = 6 Hz, $^4J_{meta}$ = 1.5 Hz, 2 H, $H_{5,5'}$), 8.22 (br, s, 2 H, $H_{3,3'}$), 8.50 (d, $^3J_{ortho}$ = 6 Hz, 2 H, $H_{6,6'}$).

Synthesis of the Bis[ω-[2-(*F*-alkyl)ethenyl]alkyl]bipyridines 4. 4,4'-Bis[12''-(*F*-octyl)-11''-dodecenyl]-2,2'-bipyridine (4a). Procedure 1. Compound **3a** (4.7 g, 9.66 mmol, 1 equiv), *F*-octyl iodide (17.85 g, 32.69 mmol, 3.4 equiv), ethanolamine (2.5 mL, 28.98 mmol, 3 equiv), 2-methyl-2-propanol (10 mL), and CuCl (620 mg, 2.98 mmol, 0.3 equiv) were refluxed for 30 h under oxygen-free argon. The brown crude product obtained was extracted with methylene dichloride and washed with an aqueous solution of NaCN (1% w/v) and with three 100-mL portions of water. The yellow resulting organic solution was concentrated under reduced pressure to give a brown solid, which was further purified by silica gel chromatography using methylene dichloride and methylene dichloride–methanol (98:2) as the developing eluents. The white crystals obtained consisting in **4a** were recrystallized from methylene dichloride (10.1 g, 7.6 mmol, 79% yield). IR (KBr, cm^{-1}): 1676 (C=C), 1599, 1547 (bipy), 1223, 1252 (CF), 970 (HC=CH *E*). ^1H NMR (80 MHz, $CDCl_3$): δ 1.32 (br s, 28 H, $(H_2C)_{3''-9''}$), 1.60–1.94 (m, 4 H, $(H_2C)_{2''}$), 1.95–2.45 (m, 4 H, $(H_2C)_{10''}$), 2.69 (t, $^3J_{H,H}$ = 7.6 Hz, 4 H, $(H_2C)_{1''}$), 5.25–5.87 (m, 2 H, $HCCF_2$), 6.15–6.60 (m, 2 H, *H*C=CHCF_2), 7.13 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.5 Hz, 2 H, $H_{5,5'}$), 8.25 (br s, 2 H, $H_{3,3'}$), 8.54 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$). ^{19}F NMR (84.7 MHz, $CDCl_3$): δ −82.5 (3 F), −105.1, −112.8 (2 F, CF_2CH=, (*Z*/*E* 10/90)), −123.5 (6 F), −124.4 (2 F), −125.3 (2 F), −127.8 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 28.1., 29.0, 29.5, 30.5 (4s, $(CH_2)_{3''-10''}$), 32.1 (s, $(CH_2)_{2''}$); 35.6 (s, $CH_2)_{1''}$), 116.9 (t, $^2J_{C,F}$ = 23 Hz, =$CHCF_2$), 121.4 (s, $C_{3,3'}$); 123.4 (s, $C_{5,5'}$), 143.4 (t, $^3J_{C,F}$ = 9 Hz, CH=CHF_2), 149.0 (s, $C_{4,4'}$), 153.0 (s, $C_{6,6'}$), 156.0 (s, $C_{2,2'}$). Anal. Calcd for $C_{50}H_{50}F_{34}N_2$: C, 45.43; H, 3.80; F, 48.75; N, 2.11. Found: C, 45.58; H, 3.98; F, 48.47; N, 2.12.

Procedure 2. When the same procedure as described for the preparation of **3a** was applied to a dark red-orange tetrahydrofuran (40 mL) solution of **2** obtained from diisopropylamine (0.36 mL, 2.57 mmol), n-butyllithium 1.6 M in hexane (1.61 mL, 2.57 mmol), and **1** (217 mg, 1.18 mmol) and to a solution of $C_8F_{17}CH$=C-$H(CH_2)_9I$ (1.84 g, 2.64 mmol) in 20 mL of tetrahydrofuran at −40 °C, a pale blue to violet solution was obtained. Workup and chromatography as described in procedure 1 led to **4a** (125 mg, 0.094 mmol, 8% yield).

4,4'-Bis[12''-(*F*-butyl)-11''-dodecenyl]-2,2'-bipyridine (4b). The procedure 1 described above when applied to **3a** (6.25 g, 12.18 mmol), *F*-butyl iodide (14.93 g), ethanolamine (2.3 mL), 2-methyl-2-propanol (12 mL), and CuCl (280 mg) gives, after chromatography and recrystallization, white crystals of **4b** (7 g, 7.6 mmol, 62% yield). IR (KBr, cm^{-1}): 1676 (C=C), 1597, 1547 (bipy), 1234 large (CF), 972 (HC=CH *E*). ^1H NMR (80 MHz, $CDCl_3$): δ 1.12 (br s, 28 H, $(H_2C)_{3''-9''}$), 1.58–1.91 (m, 4 H, $(H_2C)_{2''}$), 2.01–2.34 (m, 4 H, $(H_2C)_{10''}$), 2.65 (t, 4 H, $^3J_{H,H}$ = 8 Hz, $(H_2C)_{1''}$), 5.24–5.94 (m, 2 H, =$HCCF_2$), 6.20-6.68 (m, 2 H, *H*C=CHCF_2), 7.11 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.5 Hz, $H_{5,5'}$), 8.23 (br, s, 2 H, $H_{3,3'}$), 8.55 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$). ^{19}F NMR (84.7 MHz, $CDCl_3$): δ −82.8 (3 F), −108.6, −113.1 (2 F, CF_2CH=, (*Z*/*E* 12/88)), −126 (2 F), −127.5 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 28.0, 28.9, 29.1, 29.3, 29.4, 29.5, 30.5 (all s, $(CH_2)_{3''-10''}$), 32.0 (s, $(CH_2)_{2''}$), 35.6 (s, $(CH_2)_{1''}$), 116.7 (t, $^2J_{C,F}$ = 23 Hz, =$CHCF_2$), 121.3 (s, $C_{3,3'}$), 123.9 (s, $C_{5,5'}$), 143.2 (t, $^3J_{C,F}$ = 9 Hz, CH=CHF_2), 149.0 (s, $C_{4,4'}$), 152.9 (s, $C_{6,6'}$), 156.3 (s, $C_{2,2'}$). Anal. Calcd for $C_{42}H_{50}F_{18}N_2$: C, 54.54; H, 5.45; F, 36.97; N, 3.03. Found: C, 54.41; H, 5.36; F, 36.29; N, 2.72.

4,4'-Bis[6''-(*F*-octyl)-5''-hexenyl]-2,2'-bipyridine (4c). The process 1 as described for the preparation of **4a**, when applied to **3b** (4.31 g, 13.44 mmol), *F*-octyl iodide (24.96 g, 45.72 mmol), ethanolamine (2.43 mL, 40.32 mmol), 2-methyl-2-propanol (13 mL), and CuCl (400 mg, 4 mmol), led after chromatography on silica gel ($CHCl_3$/methanol (100 − *x*: *x*, *x* = 0–5%) as eluents) and recrystallization from hexane to **4c** as white crystals (7.76

g, 6.71 mmol, 50% yield). IR (KBr, cm^{-1}): 1660 (C=C), 1590, 1556, (bipy), 1250, 1205, 1151 (CF), 972 (HC=CH *E*). ^1H NMR (200 MHz, $CDCl_3$): δ 1.52 (tt, $^3J_{H3'',H2''} = {}^3J_{H3'',H4''}$ = 7 Hz, 4 H, $(H_2C)_{3''}$), 1.74 (tt, $^3J_{H2'',H1''} = {}^3J_{H2'',H3''}$ = 7 Hz, 4 H, $(H_2C)_{2''}$), 2.16–2.25 (m, 4 H, $(H_2C)_{4''}$), 2.72 (t, ^3J = 7.4 Hz, 4 H, $(H_2C)_{1''}$), 5.50–5.70 (m, 2 H, =$HCCF_2$), 6.32–6.46 (m, 2 H, *H*C=$CHCF_2$), 7.12 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.3 Hz, 2 H, $H_{5,5'}$), 8.26 (br s, 2 H, $H_{3,3'}$), 8.57 (d, $^3J_{ortho}$ = 5 Hz, $H_{6,6'}$). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −81.5 (3 F), −106.9, −111.9 (2 F, CF_2CH= (*Z*/*E* 10/90)), −122.0 (2 F), −122.2 (4 F), −123.3 (2 F), −124.0 (2 F), −126.8 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 27.7, 29.7 (both s, $(CH_2)_{2''-3''}$); 31.8 (s, $(CH_2)_{4''}$); 35.2 (s, $(CH_2)_{1''}$), 117.4 (t, $^2J_{C,F}$ = 23 Hz, =$CHCF_2$), 121.3 (s, $C_{3,3'}$), 123.8 (s, $C_{5,5'}$), 142.7 (t, $^3J_{C,F}$ = 9 Hz, *C*H=$CHCF_2$), 149.2 (s, $C_{4,4'}$), 152.1 (s, $C_{6,6'}$), 156.4 (s, $C_{2,2'}$). Anal. Calcd for $C_{38}H_{26}F_{34}N_2$: C, 39.46; H, 2.26; F, 55.85; N, 2.42. Found: C, 39.75; H, 2.45; F, 56.22; N, 2.07.

4,4'-Bis[6''-(*F*-hexyl)-5''-hexenyl]-2,2'-bipyridine (4d). The process as described above was applied to **3b** (2.67 g, 8.34 mmol), *F*-hexyl iodide (18.64 g, 28.36 mmol), ethanolamine (1.51 mL, 25.0 mmol), 2-methyl-2-propanol (12 mL), and CuCl (250 mg, 2.5 mmol) and gave, after chromatography on silica gel (with hexane/methylene dichloride 100 − *x*: *x*, *x* = 10–100%, then methylene dichloride/methanol 100 − *x*: *x*, *x* = 0–10% as eluents) and recrystallization from methylene dichloride/hexane (1:2), white crystals consisting of **4d** (4.43 g, 4.63 mmol, 56% yield). IR (KBr, cm^{-1}): 1670 (C=C), 1595, 1555 (bipy), 1236, 1198, 1148 (CF), 970 (HC=CH *E*). ^1H NMR (200 MHz, $CDCl_3$): δ 1.52 (tt, $^3J_{H3'',H2''} = {}^3J_{H3'',H4''}$ = 7 Hz, 4 H, $(H_2C)_{3''}$), 1.73 (tt, $^3J_{H2'',H1''} = {}^3J_{H2'',H3''}$ = 7 Hz, 4 H, $(H_2C)_{2''}$), 2.13–2.25 (m, 4 H, $(H_2C)_{4''}$), 2.72 (t, ^3J = 7.4 Hz, 4 H, $(H_2C)_{1''}$), 5.50–5.70 (m, 2 H, =$HCCF_2$), 6.30–6.50 (m, 2 H, *H*C=$CHCF_2$), 7.13 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{5,5'}$), 8.24 (br s, 2 H, $H_{3,3'}$), 8.57 (d, $^3J_{ortho}$ = 5 Hz, $H_{6,6'}$). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −81.5 (3 F), −111.9, −114.0 (2 F, CF_2CH= (*Z*/*E* 8/92)) −122.0 (2 F), −123.6 (2 F), −124.0 (2 F), −126.8 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 27.7, 29.7 (both s, $(CH_2)_{2'',3''}$), 31.8 (s, $(CH_2)_{4''}$), 35.2 (s, $(CH_2)_{1''}$), 117.4 (t, $^2J_{C,F}$ = 23 Hz, =CCF_2), 121.4 (s, $C_{3,3'}$), 123.9 (s, $C_{5,5'}$), 142.7 (t, $^3J_{C,F}$ = 9 Hz, *C*H=$CHCF_2$), 149.2 (s, $C_{4,4'}$), 152.2 (s, $C_{6,6'}$), 156.3 (s, $C_{2,2'}$). Anal. Calcd for $C_{34}H_{26}F_{26}N_2$: C, 42.69; H, 2.74; F, 51.63; N, 2.92. Found: C, 42.33; H, 2.74; F, 52.63; N, 2.94.

Synthesis of 4,4'-Dicarboxy-2,2'-bipyridine (7). The diacid **7** was prepared according to the method published for the preparation of 2,2',6,6'-tetracarboxy-4,4'-bipyridine,[26] with some modifications. Compound **1** (8.0 g, 43.42 mmol) was dissolved in concentrated H_2SO_4 (100 mL). After the solution was cooled at 0 °C, CrO_3 (26 g, 260.52 mmol, 6 equiv) was added in small portions during 1 h. The mixture which turned blue-green was heated to 75 °C for 4 h, stirred 10 h at room temperature, and finally poured into a mixture of ice/water. The green precipitate was separated by centrifugation and washed several times with water. This green powder was then suspended in water, and KOH was added under vigourous stirring until the solution was basic. The blue insoluble residual powder was filtered and washed with water. The aqueous solution was acidified with HCl to precipitate the diacid **7** which was filtered, washed with water, methanol, and diethyl ether, and dried (10 g, 95% yield). The diacid, which is insoluble in most solvents, was further purified and characterized as its soluble dimethyl ester. Thus, the powder obtained was suspended in methanol (400 mL) and 2 mL of concd. H_2SO_4 and then refluxed until total solubilization. After 48 h, the solution was evaporated to dryness, and the crude product was extracted with chloroform and washed with water until neutrality. Evaporation of chloroform led to a white powder consisting of 4,4'-bis(methoxycarbonyl)-2,2'-bipyridine, which was recrystallized from chloroform/methanol (1:1) (10.6 g, 39 mmol, 90% yield). IR (KBr, cm^{-1}): 1732 (C=O), 1589, 1556 (bipy), 1440 (CH_3). ^1H NMR (80 MHz, $CDCl_3$): δ 3.99 (s, 6 H, CH_3), 7.86 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.5 Hz, 2 H, $H_{5,5'}$), 8.81 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$), 8.96 (br s, 2 H, $H_{3,3'}$). The diester (10.6 g, 39 mmol) was dissolved in methanol and hydrolyzed with an aqueous NaOH solution (5.3 g, 132.08 mmol, 4 equiv). The solvents were evaporated, and the residue (9 g, 33.08 mmol) was then dissolved in water; the precipitate formed after acidification of the solution by concd HCl was filtered, washed with water, methanol, and then diethyl ether, and dried to give the pure diacid **7** as a white powder (10.4 g, 42.66 mmol, 100% yield). The spectroscopic data recorded on this sample were identical to those reported in the literature.[30]

Synthesis of the Bis[[[ω-(*F*-alkyl)alkyl]oxy]carbonyl]- and Bis[[[ω-[2-(*F*-alkyl)ethenyl]alkyl]oxy]carbonyl]bipyridines 8. 4,4'-Bis[[[11''-(*F*-octyl)undecyl]oxy]carbonyl]-2,2'-bipyridine (8a). The diacid **7** (525 mg, 2.15 mmol) was suspended in $SOCl_2$ (8 mL, 43 mmol, 20 equiv) and refluxed under dry oxygen-free argon until complete solubilization of the diacid (about 20 h). The excess of $SOCl_2$ was removed by vacuum distillation, and the resulting powder was dissolved in dry chloroform (10 mL) and added dropwise to a chloroform solution (30 mL) of 11-(*F*-octyl)undecan-1-ol (3.1 g, 5.2 mmol, 2.5 equiv) and NEt_3 (1.2 mL, 8.6 mmol, 4 equiv). The mixture was refluxed for 4 h and stirred at room temperature for 12 h. After removal of chloroform, the powder obtained was washed with water, filtered, and recrystallized from methylene dichloride to give white crystals consisting of **8a** (3 g, 2.16 mmol, 100% yield). IR (KBr, cm^{-1}): 1738 (C=O), 1598, 1560, (bipy), 1256, 1148 (CF). ^1H NMR (200 MHz, $CDCl_3$): δ 1.42 (br s, 32 H, $(H_2C)_{3''-10''}$), 1.78 (t, $^3J_{H,H}$ = 6.8 Hz, 4 H, $(H_2C)_{2''}$), 2.02 (tt, $^3J_{H,H}$ = 7 Hz, $^3J_{H,F}$ = 15 Hz, 4 H, $(H_2C)_{11''}$), 4.32 (t, $^3J_{H,H}$ = 6.8 Hz, 4 H, $(H_2C)_{1''}$), 7.78 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.4 Hz, 2 H, $H_{5,5'}$), 8.75 (d, 2 H, $^3J_{ortho}$ = 5 Hz, $H_{6,6'}$), 8.84 (br s, $^4J_{meta}$ = 1.4 Hz, 2 H, $H_{3,3'}$). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −81.7 (3 F), −114.5 (2 F, CF_2CH_2), −122.1 (6 F), −123.0 (2 F), −123.9 (2 F), −126.5 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 20.0 (t, $^3J_{C,F}$ = 4 Hz, $(CH_2)_{10''}$), 25.8, 28.5, 29.0, 29.1, 29.3 (5s, $(CH_2)_{2''-9''}$), 30.9 (t, $^2J_{C,F}$ = 22 Hz, $(CH_2)_{11''}$), 66.1 (s, $(CH_2)_{1''}$), 120.6 (s, $C_{3,3'}$), 123.2 (s, $C_{5,5'}$), 139.4 (s, $C_{4,4'}$), 150.0 (s, $C_{6,6'}$), 156.5 (s, $C_{2,2'}$), 165.3 (s, C=O). Anal. Calcd for $C_{50}H_{50}F_{34}N_2O_4$: C, 43.23; H, 3.63; F, 46.50; N, 2.02. Found: C, 43.02; H, 3.65; F, 46.27; N, 2.07.

All the other compounds **8b–8e** have been obtained, as white crystals, in nearly quantitative yields using this procedure.

4,4'-Bis[[2''-(*F*-hexyl)ethoxy]carbonyl]-2,2'-bipyridine (8b). IR (KBr, cm^{-1}): 1732 (C=O), 1593, 1560 (bipy), 1242, 1142 (CF). ^1H NMR (200 MHz, $CDCl_3$): δ 2.68 (tt, $^3J_{H,F}$ = 18 Hz, $^3J_{H,H}$ = 6.5 Hz, 4 H, $(H_2C)_{2''}$), 4.72 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, $(H_2C)_{1''}$), 7.87 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.6 Hz, 2 H, $H_{5,5'}$), 8.86 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$), 8.97 (br s, 2 H, $H_{3,3'}$). ^{19}F NMR (188.8 MHz, $CDCl_3$): δ −81.2 (3 F), −113.8 (2 F, CF_2CH_2), −122.3 (2 F), −123.3 (2 F), −123.9 (2 F), −126.6 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 30.8 (t, $^2J_{C,F}$ = 22 Hz, $(CH_2)_{2''}$), 57.7 (s, $(CH_2)_{1''}$), 120.7 (s, $C_{3,3'}$), 123.2 (s, $C_{5,5'}$), 138.1 (s, $C_{4,4'}$), 150.3 (s, $C_{6,6'}$), 156.7 (s, $C_{2,2'}$), 164.8 (s, C=O). Anal. Calcd for $C_{28}H_{14}F_{26}N_2O_4$: C, 36.13; H, 1.51; F, 52.75; N, 2.99. Found: C, 36.04; H, 1.55; F, 52.80; N, 2.69.

4,4'-Bis[[[5''-(*F*-hexyl)pentyl]oxy]carbonyl]-2,2'-bipyridine (8c). IR (KBr, cm^{-1}): 1730 (C=O), 1597, 1560 (bipy), 1252, 1140 (CF). ^1H NMR (200 MHz, $CDCl_3$): δ 1.53–1.77 (m, 8 H, $(H_2C)_{3'',4''}$), 1.89 (t, $^3J_{H,H}$ = 7 Hz, 4 H, $(H_2C)_{2''}$), 2.10 (tt, $^3J_{H,H}$ = 7 Hz, $^3J_{H,F}$ = 15 Hz, 4 H, $(H_2C)_{5''}$), 4.43 (t, $^3J_{H,H}$ = 7 Hz, 4 H, $(H_2C)_{1''}$), 7.91 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.6 Hz, 2 H, $H_{5,5'}$), 8.88 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$), 8.95 (br s, 2 H, $H_{3,3'}$). ^{19}F NMR (188.8 MHz, $CDCl_3$): δ −81.3 (3 F), −114.9 (2 F, CF_2CH_2), −122.4 (2 F), −123.4 (2 F), −124.0 (2 F), −126.6 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 20.0, 25.7, 28.4 (3s, $(CH_2)_{2''-4''}$), 30.8 (t, $^2J_{C,F}$ = 22.5 Hz, $(CH_2)_{5''}$), 65.5 (s, $(CH_2)_{1''}$), 120.6 (s, $C_{3,3'}$), 123.3 (s, $C_{5,5'}$), 138.8 (s, $C_{4,4'}$), 150.2 (s, $C_{6,6'}$), 156.6 (s, $C_{2,2'}$), 165.2 (s, C=O). Anal. Calcd for $C_{34}H_{26}F_{26}N_2O_4$: C, 40.01; H, 2.57; F, 48.48; N, 2.74. Found: C, 38.98; H, 2.51, F, 48.34; N, 2.73.

4,4'-Bis[[[11''-(*F*-octyl)-10''-undecenyl]oxy]carbonyl]-2,2'-bipyridine (8d). IR (KBr, cm^{-1}): 1730 (C=O), 1676 (C=C), 1593, 1560 (bipy), 1263, 1153 (CF), 977 (HC=CH *E*). ^1H NMR (200 MHz, $CDCl_3$): δ 1.34 (br s, 28 H, $(H_2C)_{3'',9''}$), 1.82 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, $(H_2C)_{2''}$), 2.19–2.35 (m, 4 H, $(H_2C)_{10''}$), 4.41 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, $(H_2C)_{1''}$), 5.41–5.77 (m, 2 H, $HCCF_2$), 6.33–6.54 (m, 2 H, *H*C=$CHCF_2$), 7.89 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{5,5'}$), 8.86 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$), 8.97 (br s, 2 H, $H_{3,3'}$). ^{19}F NMR (188.8 MHz, $CDCl_3$): δ −81.2 (3 F), −107.0, −111.7 (2 F, CF_2CH=, (*Z*/*E* 13:87)), −121.9 (2 F), −122.4 (4 F), −123.2 (2 F), −123.9 (2 F), 126.6 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 25.9, 27.9, 28.5, 28.8, 29.0, 29.1, 29.2, 29.3 (all s, $(CH_2)_{3''-10''}$), 31.9 (s, $(CH_2)_{2''}$), 66.0 (s, $(CH_2)_{1''}$), 116.7 (t, $^2J_{C,F}$ = 23 Hz, =$CHCF_2$), 120.5 (s, $C_{3,3'}$), 123.2 (s, $C_{5,5'}$), 139.0 (s, $C_{4,4'}$), 143.2 (t, $^3J_{C,F}$ = 9 Hz, *C*H=$CHCF_2$), 150.0 (s, $C_{6,6'}$), 156.5 (s, $C_{2,2'}$), 165.2 (s, C=O). Anal. Calcd for $C_{50}H_{46}F_{34}N_2O_4$: C, 43.62; H, 3.35; F, 46.64; N, 2.04. Found: C, 43.26; H, 3.25; F, 47.19; N, 2.04.

4,4'-Bis[[[5''-(*F*-hexyl)-4''-pentenyl]oxy]carbonyl]-2,2'-bipyridine (8e). IR (KBr, cm^{-1}): 1734 (C=O), 1676 (C=C), 1597,

1564 (bipy), 1246, 1144 (CF), 975 (HC=CH *E*). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.99 (tt, $^3J_{H2'',H3''}$ = $^3J_{H2'',H1''}$ = 7 Hz, 4 H, $(H_2C)_{2''}$), 2.31-2.52 (m, 4 H, $(H_2C)_{3''}$), 4.41 (t, $^3J_{H,H}$ = 6.5 Hz, 4 H, $(H_2C)_{1''}$), 5.51-5.90 (m, 2 H, $HCCF_2$), 6.40-6.59 (m, 2 H, HC=$CHCF_2$), 7.85 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 1.5 Hz, 2 H, $H_{5,5'}$), 8.82 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$), 8.94 (br s, 2 H, $H_{3,3'}$). ^{19}F NMR (188.8 MHz, $CDCl_3$): δ -81.6 (3 F), -107.3, -111.8 (2 F, CF_2CH=, (*Z*/*E* 14:86), -122.0 (2 F), -123.8 (2 F), -124.2 (2 F), -126.6 (2 F). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 27.2, 28.6 (both s, $(CH_2)_{2'',3''}$), 64.8 (s, $(CH_2)_{1''}$), 118.6 (t, $^2J_{C,F}$ = 23 Hz, =$CHCF_2$), 120.6 (s, $C_{3,3'}$), 123.3 (s, $C_{5,5'}$), 138.8 (s, $C_{4,4'}$), 141.7 (t, $^3J_{C,F}$ = 9 Hz, CH=$CHCF_2$), 150.2 (s, $C_{6,6'}$), 156.6 (s, $C_{2,2'}$), 165.1 (s, C=O). Anal. Calcd for $C_{34}H_{22}F_{26}N_2O_4$: C, 40.17; H, 2.18; F, 48.59; N, 2.76. Found: C, 40.08; H, 2.13; F, 48.38; N, 2.69.

Synthesis of 4,4'-Bis[12''-(*F*-octyl)-11''-iodododecyl]-2,2'-bipyridine (5). **3a** (740 mg, 2.04 mmol), *F*-octyl iodide (2.98 g, ~3 equiv) and α,α'-azobisisobutyronitrile AIBN (25 mg, 0.02 equiv) were heated at 80 °C under oxygen-free argon for 12 h. Then, the crude product was extracted with methylene dichloride and washed with water before filtration, evaporation, chromatography on SiO_2 with methylene dichloride/methanol 0.5% as eluents, and recrystallization from methylene dichloride to give the expected compound **5** as white crystals (2.29 g, 1.47 mmol, 71% yield). ^{1}H NMR (80 MHz, $CDCl_3$): δ 1.45 (br s, 32 H, $(H_2C)_{2''-8''}$), 1.70-2.05 (m, 8 H, $(H_2C)_{10'',12''}$), 2.71 (t, $^3J_{H,H}$ = 7 Hz, 4 H, $(H_2C)_{1''}$), 4.35 (tt, $^3J_{H,H}$ = 7.5 Hz, 2 H, $(HCI)_{11''}$), 7.12 (dd, $^3J_{ortho}$ = 5 Hz, $^4J_{meta}$ = 2 Hz, 2 H, $H_{5,5'}$), 8.27 (d, $^4J_{meta}$ = 2 Hz, 2 H, $H_{3,3'}$), 8.58 (d, $^3J_{ortho}$ = 5 Hz, 2 H, $H_{6,6'}$).

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Registry No. 1, 1134-35-6; **3a**, 140464-50-2; **3b**, 140464-51-3; (*E*)-**4a**, 140464-53-5; (*Z*)-**4a**, 140464-52-4; (*E*)-**4b**, 140464-55-7; (*Z*)-**4b**, 140464-54-6; (*E*)-**4c**, 140464-57-9; (*Z*)-**4c**, 140464-56-8; (*E*)-**4d**, 140464-58-0; (*Z*)-**4d**, 140605-03-4; **5**, 140464-66-0; **7**, 6813-38-3; **7** dimethyl ester, 71071-46-0; **8a**, 140464-59-1; **8b**, 140464-60-4; **8c**, 140464-61-5; (*E*)-**8d**, 140464-63-7; (*Z*)-**8d**, 140464-62-6; (*E*)-**8e**, 140464-65-9; (*Z*)-**8e**, 140464-64-8; 10-undecenyl tosylate, 51148-67-5; 4-pentenyl tosylate, 19300-54-0; perfluorooctyl iodide, 507-63-1; perfluorobutyl iodide, 423-39-2; 11-(perfluorooctyl)undecanol, 1512-02-3; 2-(perfluorohexyl)ethanol, 647-42-7; 5-(perfluorohexyl)pentanol, 134052-02-1; (*Z*)-11-(perfluorooctyl)-10-undecenol, 135131-74-7; (*E*)-11-(perfluorooctyl)-10-undecenol, 135131-50-9; (*Z*)-5-(perfluorohexyl)-4-pentenol, 135131-75-8; (*E*)-5-(perfluorohexyl)-4-pentenol, 135131-51-0; 11-iodo-1-undecene, 7766-49-6; 5-iodo-1-pentene, 7766-48-5.

Electron Transfer Photoinduced Cleavage of Acetals. A Mild Preparation of Alkyl Radicals[1]

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Electron transfer from 2-alkyl- and 2,2-dialkyldioxolanes as well as from open-chain ketals to singlet excited benzene-1,2,4,5-tetracarbonitrile (TCNB) is followed by fragmentation of the donors radical cation to yield alkyl radicals and dialkoxy carbocations. The first species are trapped by TCNB to yield alkylbenzenetricarbonitriles (substitution of a second cyano group can be obtained sequentially) and in a minor path are reduced to alkanes, while the latter ones react with nucleophiles to give ortho acid derivatives. In view of the results of radical clock experiments, it is assumed that part of the process is a concerted (radical cation cleavage–addition to the aromatic) reaction, while another part involves the free-radical cation. On the other hand, intersystem crossing from the singlet radical ion pair to the triplet manifold causes cleavage of the acetal to the corresponding carbonyl derivative. This reaction offers a mild method for the preparation of alkyl radicals via C-C bond cleavage.

Photoinduced electron transfer reactions have been extensively investigated in recent years and the condition for the efficiency of such processes is prevailence of chemical reactions over energy-wasting back electron transfer within the primary radical ion pair.[2] An important class of such reactions is the fragmentation of a radical cation, $X-Y^{\bullet+}$ (arising from electron transfer to the excited acceptor A*). Such a reaction may lead to an

$$A^* + XY \rightarrow A^{\bullet-} + XY^{\bullet+} \quad (1)$$

$$XY^{\bullet+} \rightarrow X^{\bullet} + Y^+ \quad (2)$$

efficient global process since one of the radical ions is rapidly subtracted from the equilibrium. Indeed, of the species formed from the cleavage of $XY^{\bullet+}$, the cation is trapped by a nucleophile Nu^-, and the neutral radical is

$$Y^+ + Nu^- \rightarrow Y-Nu \quad (3)$$

either reduced by the radical anion (thus completing the sensitizing cycle and regenerating ground state A, eq. 4), and then e.g. protonated (eq 5), or alternatively is trapped by a radical trap Rad (eq 6, A and $A^{\bullet-}$ obviously present in solution are expected to act in this role, and other traps may purposedly be added). Observed reactions involve,

$$X^{\bullet} + A^{\bullet-} \rightarrow X^- + A \quad (4)$$

$$X^- + H^+ \rightarrow XH \quad (5)$$

$$X^{\bullet} + Rad \rightarrow products \quad (6)$$

besides deprotonation,[3] cleavage of carbon–carbon,[3a-d,5]

(1) This is contribution no. 100 from the Photochemical Unit, The University of Pavia, and is dedicated to the memory of Prof. S. Pietra (deceased January 1990), who founded it in 1971.

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