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Photophysical properties of some newly synthesised *N*-perfluoroacylpyridiniumaminides

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Abstract

Having established an easy approach to a new class of pyridinium-1-aminides bearing an *N*-perfluoroacyl residue, we studied the influence of the polarity of the solvent on the maximum absorption in the UV/vis spectra. *N*-perfluoroacyl-pyridinium-1-aminides have a strong interaction with the solvent determining negative solvatochromic effects which have been correlated with the $E_T(30)$ polarity parameters. Some relative quantum yields of the title aminides as fluorescence emitters are also reported and they show an interesting structure dependence. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Solvatochromism; Fluoroscence; UV/vis spectra; Pyridine; Fluorine

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1. Introduction

After Dimroth used a pyridinium *N*-phenolate betaine dye to establish his solvent polarity scale [1,2]. many other dyes were synthesized and their solvatochromic properties studied [3–7]. Perfluorinated chains are known to impart unique physical and chemical properties to molecules (electron distribution and conformation) and to bulk materials (thermal and chemical stability, surface tension and viscosity) [8].

Having established an easy access to a new class of pyridinium-1-aminides bearing a perfluorinated residue on the aminide nitrogen, we decided to investigate their structure and properties deeming that the presence of the perfluoroalkyl chain could induce specific and useful features. The mass spectra fragmentation under El and FAB conditions [9] and the crystalline organization [10] have already been reported. In this paper we describe the synthesis and the UV/vis spectra of some new *N*-perfluoroacyl-pyridinium-1-aminides. A comparison between their behaviour and that of the starting pyridines, or corresponding *N*-oxides, is presented and some relative quantum yields as fluorescence emitters are also reported.

2. Experimental

2.1. General

^1H and ^{19}F NMR spectra were recorded on a Bruker AC 250L spectrometer and TMS and $CFCl_3$ were used as internal standards. Chemical ionisation mass spectra were registered with a Finnigan Mat TSQ 70 using CH_4 as an impact gas. IR spectra were recorded on a Perkin–Elmer 2000 FT-IR in KBr pellet. A detailed procedure is described for compounds obtained starting from (*E*)-1,2-bis-(4-pyridyl)ethene (**5b**) and the same conditions were used for the preparation of the other pyridine derivatives. Melting points were measured in open capillary tubes and are uncorrected. Flash chromatographies were performed with silica gel 60 (60–200 μm, Merck); thin layer chromatographies (TLC) were performed with glass sheets coated with silica gel 60 F_{254}, (E. Merck, Darmstadt). 4,4′-Bipyridine *N*-oxide (**7a**) and 4,4′-bipyridine *N*,*N*-dioxide (**10a**) were identified through comparison with authentic samples and by comparison with the data reported in the literature [11]. Spectral data of compounds **3a–c** [13] and **3d** [14] have already been reported. Excitation spectra were carried out on a Jasco UVIDEC-510 spectrophotometer using solutions 10^{-4} M ca. in the appropriate solvent. Fluorescence spectra were carried out on a Jasco FP-770 spectrofluorimeter at room

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temperature; solutions of the same absorbance (0.35) were used to determine the relative quantum yields.

2.2. General procedure for the preparation of N-perfluorobutanoylpyridinium-1-aminides and pyridine N-oxides with perfluoro-cis-2-n-butyl-3-n-propyloxaziridine

To a solution of (*E*)-l,2-bis-(4-pyridyl)ethene (**5b**) (455 mg, 2.5 mmol) in chloroform (4 ml) was added a solution of the oxaziridine **1** (1.234 g, 2.75 mmol) in $CFCl_3$ (1.5 ml) at −60°C The reaction was stirred for 30 min at the same temperature, then it was quenched by adding of perfluorotributylamine. The resulting mixture was stirred, then allowed to warm to room temperature. The perfluorinated layer was extracted with AcOEt and combined organics were evaporated under reduced pressure. The residue was flash chromatographed (AcOEt–MeOH, 9 : 1) to give the *N*-(perfluorobutanoyl)-4-[2-(*E*)-(4-pyridyl)ethenyl] pyridinium-1-aminide (**6b**) (412 mg, 42% yield) and the 4-[2-(*E*)-(4-pyridyl)ethenyl] pyridine *N*-oxide (**7b**) (228 mg, 46% yield). Treatment of the *N*-oxide **7b** under the same conditions brought to the formation of (*E*)-l,2-di-(4-pyridyl)ethene-*N*, *N′*-dioxide (**l0b**, 38% yield) and (*E*)-2-(1-oxidopyridin-1-ium-4-yl)-1-(*N*-(perfluorobutanoyl)-pyridinium-1-aminide-4-yl)ethene (**9b**, 39% yield). Treatment of the *N*-perfluorobutanoyl-aminide (**6b**) with the oxaziridine **1** gave the aminide-oxide **9b** (33% yield) and the *N*,*N′*-bis(perfluorobutanoyl)-(*E*)-1,2-(dipyridinium-1,1′,-diaminide-4,4′-diyl) ethene (**8b**) (759 mg, 49% yield).

*N-(Perfluorobutanoyl)-4-[2-(E)-(4-pyridyl)ethenyl] pyridinium-1-aminide (**6b**)*. mp 145°C ($CHCl_3$, yellow crystals); IR ν: 1229, 1638 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$): δ: 7.35 (d, 2H, $J = 15.4$ Hz, CH=), 7.45 (s, 2H, br s, H-3′), 7.79 (d, 2H, $J = 7.2$ Hz, H-3), 8.73 (d, 4H, $J = 7.2$ Hz, H-2 and H-2′); ^{19}F (235 MHz, $CDCl_3$) δ, −81.8 (t, 3F, $J = 9$ Hz, CF_3), −120.0 (q, 2F, $J = 9$ Hz, CF_2), −128.0 (br s, 2F, CF_2), MS (m/z) 394 (M + l), 224, 181; anal calcd for $C_{16}H_{10}F_7N_3O$: C 48.9, H 2.6, F 33.8, N 10.7; found C 49.0, H 2.5, F 33.7, N 10.7. *4-[2-(E)-(4-Pyridyl)ethenyl]pyridine N-oxide (7b)*. mp 125°C ($CHCI_3$); IR ν: 1230 cm^{-1}; ^1H NMR (250 MHz, $CDCI_3$): δ: 7.10 and 7.20 (d, 2H, $J = 15.4$ Hz, CH=CH), 7.40 (d, 2H, $J = 6.2$ Hz, H-3′), 7.41 (d, 2H, $J = 7.2$ Hz, H-3), 8.20 (d, 2H, .$J = 7.2$ Hz, H-2); 8.63 (d, 2H, $J = 6.2$ Hz, H-2′); MS (m/z): 198 (M), 115; anal calcd for $C_{12}H_{10}N_2O$: C 72.7, H 5.1, N 14.1; found C 72.6, H 5.2, N 14.2.

*N,N′-Bis(perfluorobutanoyl)-(E)-1,2-(dipyridinium-1,1′-diaminide-4,4′-diyl)ethene (**8b**)*. mp 192°C (CH_3CN/THF, yellow crystals); IR ν: 1228, 1634 cm^{-1};^1H NMR (250 MHz, CD_3CN): δ: 7.69 (s, 2H, CH7=CH), 7.98 (d, 4H, $J = 7.0$ Hz, H-2, H-3), 8.66 (d, 4H, $J = 9$ Hz, −123.3 (br s, 2F); MS (El, m/z): 604 (M), 224; anal calcd for $C_{20}H_{10}F_{14}N_4O_2$: C 39.75, H 1.67, F 44.01, N 9.27; found C 39.82, H 1.75, F 43.95, N 9.19.

*(E)-2-(1-Oxidopyridin-1-ium-4-yl)- 1-(N-(perfluorobutanoyl)-pyridinium- 1-aminide-4-yl)ethene (**9b**)*. mp 182–184°C (CH_3CN/THF, yellow crystals); IR ν: 1235, 1266, 1635 cm^{-1};^1H NMR (250 MHz, $CDCl_3$): δ 7.16–7.36 (AB system, 2H, CH=CH), 7.47 (d, 2H, $J = 7.2$ Hz, H-3′), 7.77 (d, 2H, $J = 72$ Hz, H-3), 8.23 (d, 2H, $J = 7.2$ Hz, H-2′), 8.71 (d, 2H, $J = 7.2$ Hz, H-2);^{19}F (235 MHz, $CDCl_3$): δ: −81.8 (t, 3F, $J = 9$ Hz), −119.9 (q, 2F, $J =$ Hz), −128.0 (br s, 2F); MS (El, m/z): 409 (M), 224; anal calcd for $C_{16}H_{10}F_7N_30_2$: C 46.96, H 2.46, F 32.49, N 10.27; found C 47.05, H 2.53, F 32.05, N 10.23.

*(E)-1,2-Di-(4-pyridyl)ethene-N,N′-dioxide (**10b**)*. ^1H NMR (250 MHz, $CDCI_3$) δ: 7.14 (s, 2H, CH=CH), 7.50 (d, 4H, $J = 7.1$ Hz, H-3), 8.22 (d, 4H, $J = 7.1$ Hz, H-2); MS (m/z): 215 (M + l); anal calcd for $C_{12}H_1N_20_2$: C 67.28, H 4.70, N 13.07; found C 67.05, H 4.53, N 13.23.

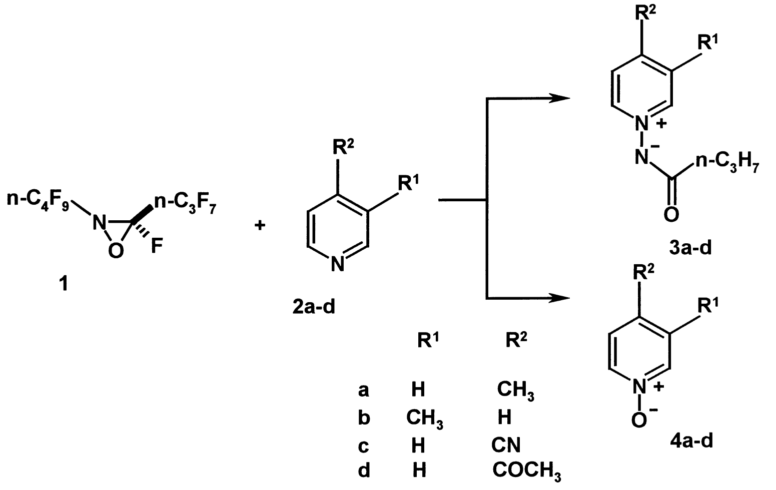
*N-Perfluorobutanoyl-4,4′-bipyridin-1-ium-1-aminide (**6a**)*. 311 mg, 40% yield; mp 148°C ($CHCl_3$); IR ν: 1229, 1643 cm^{-1}; ^1H NMR (250 MHz, $CDCI_3$): δ: 7.60 (d, 2H, $J = 6.6$ Hz, H-3′), 7.99 (d, 2H, $J = 6.6$ Hz, H-3), 8.85–8.90 (m, 4H, H-2 and H-2′); ^{19}F (235 MHz, $CDCl_3$): δ: −81.8 (t, 3F, $J = 9$ Hz), −120.0 (q, 2F, $J = 9$ Hz), −128.0 (br s, 2F); MS (CI, CH_4, m/z): 367 (M + 1), 198; anal calcd for $C_{14}H_8F_7N_3O$: C 45.8, H 2.2, N 11.4; found C 45.6, H 2.2, N 11.6.

*NN′-Bis(perfluorobutanoyl)-4,4′-bipyridine- 1,1′-diium-1,1′-diaminide (**8a**)*. 564 mg, 41% yield; mp 263°C ($CHCI_3$); IR ν: 1226, 1637 cm^{-1}; ^1H NMR (250 MHz, CD_3CN) δ: 8.05 (d, 4H, $J = 7.2$ Hz), 9.10 (d, 4H, $J = 7.2$ Hz); ^{19}F (235 MHz, CD_3CN): δ: −81.8 (t, 6F, $J = 9$ Hz), −120.0 (q, 4F, $J = 9$ Hz), −127.9 (br s, 4F); MS (m/z): 579 (M + 1); anal calcd for $C_{18}H_8F_{14}N_40_2$: C 37.4, H 1.4, N 9.7; found C 37.3, H 1.4, N 9.7.

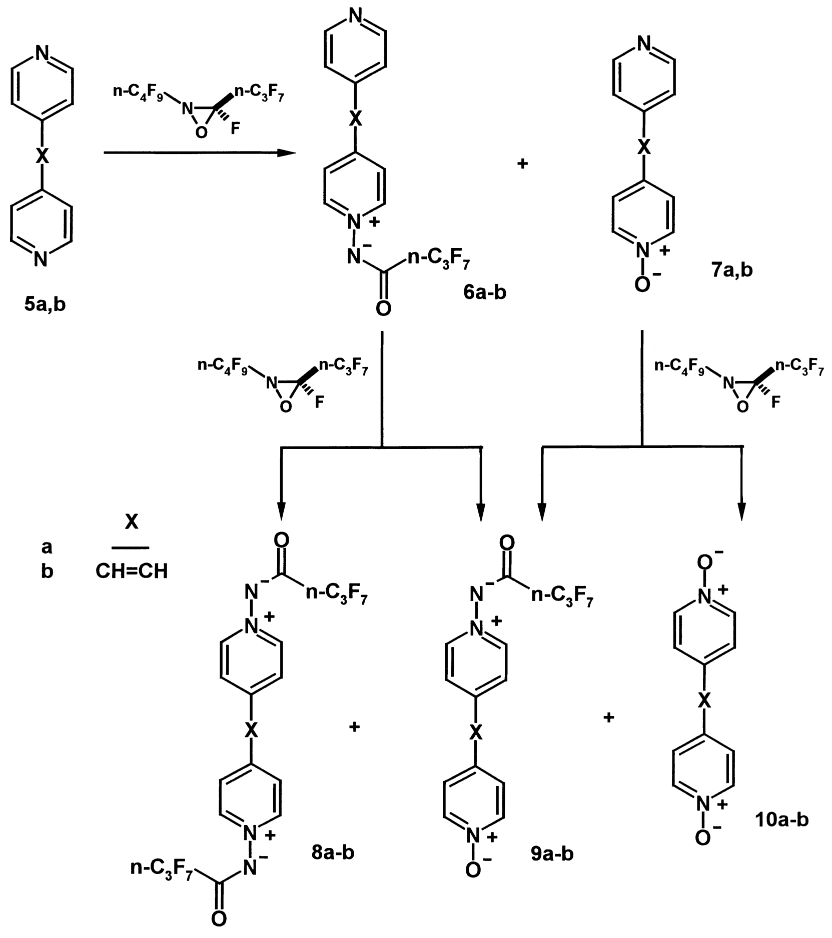
*4-(1-Oxidopyridin-1-ium-4-yl)-N-(perfluorobutanoyl)-pyridinium-1-aminide (**9a**)*. 413 mg, 42% yield; mp 200°C ($CHCI_3$); IR ν: 1277, 1652 cm^{-1};^1H NMR (250 MHz, $CDCI_3$): δ: 7.65 (d, 2H, J = 7.5 Hz), 7.91 (d, 2H, J = 7.2 Hz), 8.35 (d, 2H, J = 7.5 Hz), 8.87 (d, 2H, J = 7.2 Hz), ^{19}F (235 MHz, CD_3CN) δ: −81 8 (t, 3F, J = 8 Hz), −120.0 (q, 2F, J = 8 Hz), −128.0 (br s, 2F); MS (El, m/z) 383 (M), 214, 172; anal calcd for $C_{14}H_8F_7N_3O_2$: C 43.9, H 2.1, N 11.0; found C 44.0, H 2.2, N 10.8.

3. Results and discussion

When some pyridine derivatives **2a–d** were reacted with perfluoro-*cis*-2-*n*-butyl-3-*n*-propyloxaziridine **1** [15–19], a mixture of corresponding *N*-(perfluorobutanoyl)pyridinium-1-aminides **3a–d** and *N*-oxides **4a–d** was produced (Scheme 1) [12–14]. Similarly, reaction of 4,4′-bipyridine (**5a**) with one equivalent of the oxaziridine 1 afforded a mixture of the corresponding *N*-aminide **6a** (55% yield) and *N*-oxide **7a** (35% yield) (Scheme 2). Further reaction of the mono-*N*-aminide **6a** with one equivalent of oxaziridine **1** afforded the *N,N′* diaminide **8a** (55% yield) and the *N*-aminide-*N′*-oxide **9a** (35% yield). This latter compound was isolated along with the *N,N′*-dioxide **l0a** also when



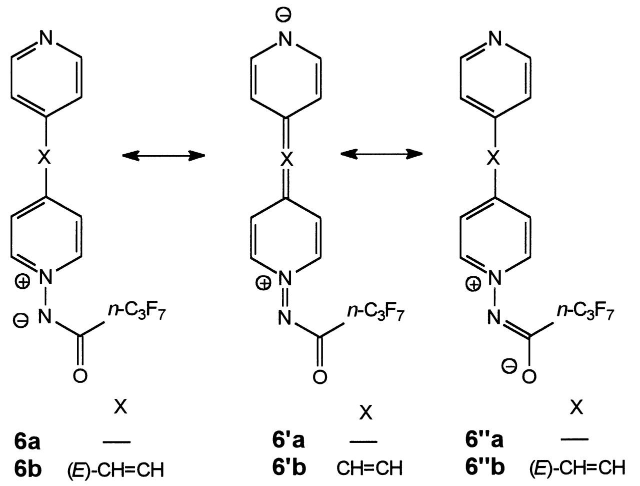
Scheme 1.



Scheme 2.

the mono-*N*-oxide **7a** was reacted with the oxaziridine **1**. The difunctionalized derivatives **8a–10a** were alternatively obtained in one step by treating the 4,4′-bipyridine (**5a**) with two equivalents of the oxaziridine **1**. A quite parallel behaviour was shown by the (*E*)-l,2-(4,4′-dipyridyl)ethene (**5b**). All the mono- and di-functionalized compounds described above were obtained in pure form through flash-chromatography on silica gel and are stable in the air and at room temperature.

In Schemes 1 and 2 the *N*-aminides **3**, **6**, **8**, and **9** have been written as the mesomeric forms bearing the negative charge on the aminide nitrogen. However, other resonance



Scheme 3.

hybrids have to be considered in order to describe correctly these aminides (Scheme 3). For the dipyridyl systems derived from **5a**, and **5b**, a considerable contribution of *p*-quinonoid forms [20] such as **6′a**, **b**, which localize the charge on the residue in the *para* position of the pyridine ring and lead to an appreciable electronic interactions between the two pyridine rings [21], is suggested by the batochromic effect observed moving from pyridyl to dipyridyl systems. The longest wavelength UV/visible absorption (in chloroform) occurs at $\lambda_{max} = 278$ nm for the 3-methyl-pyridinium-1-aminide **3b** and at $\lambda_{max} = 338$ and 350 nm for **6a** and **6b**, respectively. Moreover, an increased contribution of the forms bearing the negative charge on the acyl oxygen (**6″a**, **b** structures) due to the presence of the fluorinated chain is suggested by mass spectra fragmentations [9].

In general, the presence on the acyl carbon of residues which can distribute the negative charge located on the nitrogen atom is a prerequisite for the stability of the *N*-aminide moiety and in fact the *N*-perfluoroacyl-aminides described here are definitely more stable than the corresponding *N*-acyl analogues [22]. Resonance hybrids similar to those described above exist also for the monopyridyl aminides **3a–d** and for the diaminides **8a**, **b**. In the case of these latter compounds, a particularly extended delocalization results which determines a particular sensitivity to modifications of the dielectric environment.

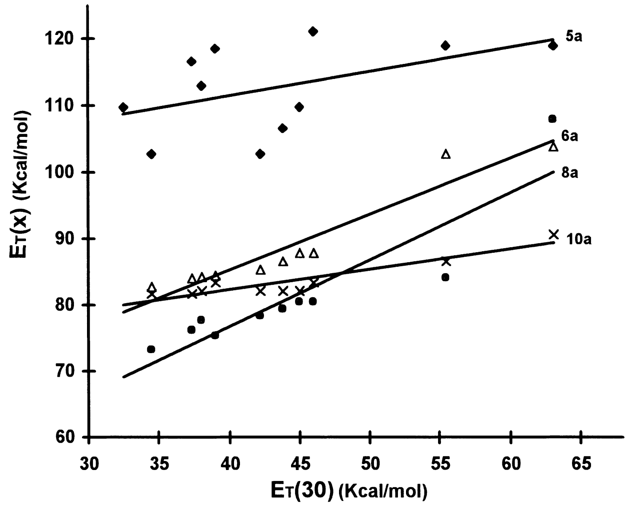


Fig. 1. Correlation between the log-wavelength UV/vis absorption maxima (measured in $E_T(x)$) of (*E*)-1,2.bis-(pyridyl)ethene derivatives and the polarity of the solvent (measured with the $E_T(30)$ parameter).

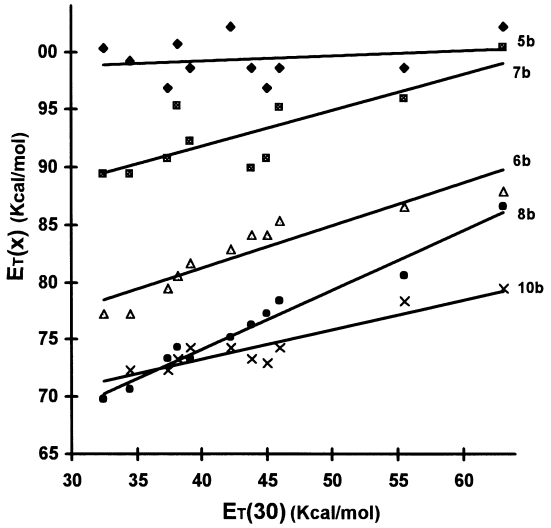


Fig. 2. Correlation between the long-wavelength UV/vis absorption maxima (measured in E_T(x)) of 4,4′-bipyridine derivatives and the polarity of the solvent (measured with the $E_T(30)$ parameter).

On decreasing the polarity of the solvent, the long-wavelength UV/visible absorption of dipyridyl derivatives **6**, **8**, and **9** show a negative solvatochromic effect. A similar behaviour has been shown by other pyridinium aminides [23]. For starting materials **5a**, **b** the corresponding solvent-induced hypsochromic band shift is nearly non-existent and single values are quite scattered (as revealed by the poor value of the statistical parameter R^2). The shift is minor for the mono-*N*-oxides **7a**, **b** and di-*N*,*N′*-oxides **10a**, **b**. Differently, *N*-aminides **6a**, **b**, *N*,*N′*-diaminides **8a**, **b**, and *N*-aminide-*N′*-oxides **9a**, **b** all show a quite substantial solvatochromic effect. For instance, the long-wavelength maximum of bis-dipyridylethylene-*N*-aminide **6b** and 4,4′-dipyridyl-*N*,*N′*-diaminibde **9a** is at $\lambda_{max} = 370$ and 390 nm in tetrachloromethane and at $\lambda_{max} = 325$ and 265 nm in water, respectively. The good linear correlation between the long-wavelength UV/visible absorption maxima and the polarity of the solvents (measured with the Dimroth-Reichardt $E_T(30)$ parameter) is indicated clearly in Figs. 1 and 2 for some derivatives of the 4,4′-dipyridyl series and bis 1,2-dipyridylethylene series, respectively (for a better comparison of the data, the maxima values of absorption spectra were converted in $E_T(x)$ (Kcal mol^{-1}) according to the equation: $E_T(x) = 28591/\lambda$ (nm). Full data for the solvatochroinic effect of dipyridyl and bis-pyridylethene deriva-

Table 1
$E_T(x)$ values (Kcal mol^{-1}) corresponding to absorption maxima of UV spectra of 4,4′-bipyridine derivatives **4a-9a**

Solvent	$E_T(30)$	**5a**	**6a**	**7a**	**8a**	**9a**	**10a**
$CC1_4$	32.5	10997		89.35			
C_6H_6	34.5	102.85	82.87	89.35	73.31	76.24	81.69
THF	37.4	116.70	84.09	90.77	76.24	77.27	81.69
AcOEt	38.1	113.01	84.34	95.30	77.69	78.33	82.16
$CHCI_3$	39.1	118.63	84.59	92.23	75.24	78.33	83.36
Acetone	42.2	102.85	85.35		78.33	78.98	82.16
DMF	43.8	106.68	86.64	89.91	79.42	78.98	82.16
DMSO	45	109.97	87.97	90.77	80.54	79.42	82.16
CH_3CN	46	121.15	87.97	95.30	80.54	80.54	83.36
MeOH	55.5	119.13	102.85	95.94	84.09	84.59	86.64
H_2O	63.1	119.13	103.97	100.32	107.89	89.35	90.77
a[a]		0.361	0.864	0.313	1.01	0.438	0.306
b[a]		97.09	51.5	79.32	36.36	60.74	70.7
(R^2)[a]		0.238	0.923	0.674	0.820	0.967	0.856

[a] a, b, and R^2 values are the slope, the intercept, and the correlation coefficient, respectively, in the equation of the line $y = ax + b$ correlating the maximum of the long-wavelength absorption (y variable, as measured with $E_T(x)$ values) with the polarity of the solvent (x variable, as measured with Dimroth $E_T(30)$ parameter).

Table 2
$E_T(x)$ values (Kcal mol^{-1}) corresponding to absorption maxima of UV spectra of (*K*)-1,2-bis-(4-pyridyl)ehtylene derivatives **4b–9b**

Solvent	$E_T(30)$	**5b**	**6b**	**7b**	**8b**	**9b**	**l0b**
CCl_4	32.5	100.32	77.27	89.35	69.73	68.89	
C_6H_6	34.5	99.27	77.27	89.35	70.60	71.48	72.38
THF	37.4	96.92	79.42	90.77	73.31	72.38	72.38
AcOEt	38.1	100.67	80.54	95.30	74.26	72.94	73.31
$CHCI_3$	39.1	98.59	81.69	92.23	73.31	73.31	74.26
Acetone	42.2	102.11	82.87		75.24	74.26	74.26
DMF	43.8	98.59	84.09	89.91	76.24	72.94	73.31
DMSO	45	96.92	84.09	90.77	77.27	73.31	72.94
CH_3CN	46	98.59	85.35	95.14	78.33	75.24	74.26
MeOH	55.5	98.59	86.64	95.94	80.54	78.33	78.33
H_2O	63.1	102.11	87.97	100.32	86.64	82.87	79.42
a[a]		0.044	0.368	0.312	0.517	0.393	0.257
b[a]		97.4	66.5	79.3	53.5	57.1	63.0
(R^2)[a]		0.051	0.866	0.677	0.970	0.933	0.864

[a] a, b, and R^2 values are the slope, the intercept, and the correlation coefficient, respectively, in the equation of the line $y = ax + b$ correlating the maximum of the long-wavelength absorption (y variable, as measured with $E_T(x)$ values) with the polarity of the solvent (x variable, as measured with Dimroth $F(30)$ parameter).

Table 3
Fluorescence relative quantum yields (Φ_{Fr}) of bis-pyridylethene derivatives[a]

Φ_{Fr}	Compound					
	8b	**9b**	**6b**	**(10b)**[b]	**5b**	**7b**
	314	22	18	8	4	1

[a] Solution absorbance in acetonitrile was adjusted to the same value (0.2) diluting mother solutions of each compound.

[b] Decomposition occurred during the measurement.

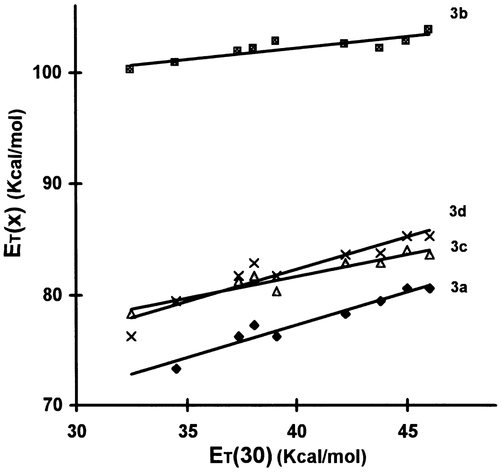


Fig. 3. Correlation between the long-wavelength UV/vis absorption maxima (measured in E_T(x)) of *N*-(perfluorobutanoyl)pyridinium-1-aminides **3a–d** and the polarity of the solvent (measured with the $E_T(30)$ parameter).

tives are listed in Tables 1 and 2, respectively. The negative solvatochromism for *N*-aminides **6**, **8**, and **9** is consistent with a dipole moment smaller in the excited state than in the ground state. Charge transfer to the heterocyclic ring occurs on light absorption and the resultant double-bond character of the *N*-aminide moiety is increased in the excited state as compared to the ground state.

Pyridine betaines [24] and pyridine organometallic derivatives [25] have recently received much attention due to their negative solvatochromic behavior and negative second-order nonlinear optical (NLO) responses. The same holds for some merocyanine dyes [26–28] which contain pyridine arrays whose electron distribution can be depicted through quinonoid and betaine resonance structures resembling closely the 6, 6′, and 6″ forms. In general, electronic delocalization and polarization in organic molecular motifs can originate second-order NLO properties and a correlation exists between solvatochromic behaviour and second-order NLO responses. Thus, mono- and di-aminides derived from 4,4′-dipyridyl (**5a**) or *trans*-l,2-bis-(4-pyridyl)ethylene (**5b**), possibly modulated with convenient substituents [29] are likely to be endowed with interesting NLO properties. Another interesting photon manipulating ability shown by the perfluoroacyl-*N*-aminides **6**, **8**, and **9** is related to their emission spectra. All of the studied compounds show no phosphorescence at 77 K and the only detected emission was fluorescence. For the *N*,*N*′-diaminide **8b** the emission maximum lies at λ = 455 nm and its position is unaffected by the solvent used, thus, confirming the less dipolar character of the excited state [23]. Relative emission quantum yields of bis-pyridylethylene derivatives at room temperature are reported in Table 3. The trend proves the ability of the *N*-perfluoroaminide moiety to promote fluorescence and the highest emission is given by *N*,*N*′-diaminide **8b**. Possibly, this may be due to the decreased accessibility of alternative deactivation processes. While a rapid decomposition of *N*,*N*′-dioxide **l0b** occurred on recording the emission spectrum, the *N*,*N*′-diaminide **8b** was stable under the same conditions. An absolute quantum yield of $4 \times 10^{-3}$was reported for bis-pyridylethene **5b** in non-polar solvents [30].

Table 4
$E_T(x)$ values (Kcal mol^{-1}) corresponding to absorption maxima of UV spectra of pyridinium-aminides **3a–d**

Solvent	$E_T(30)$	**3a**	**3b**	**3c**	**3d**
Cd$_4$	32.5		100.25	78.33	76.24
C_6H_6	345	73.31	100.95		79.42
THf	374	76.24	101.87	81.22	81.69
AcOEt	38.1	77.27	102.11	81.69	82.87
CHCI$_3$	39.1	76.24	102.85	80.31	81.69
Acetone	42.2	78.33	102.59	82.87	83.60
DMF	43.8	79.42	102.11	82.87	83.78
DMSO	45	80.54	102.84	84.09	85.35
CH_3CN	46	80.54	103.88	83.60	85.35
a[a]		0.589	0.201	0.395	0.586
b[a]		53.7	94.2	65.9	58.9
(R^2)[a]		0.942	0.773	0.895	0.893

[a] a, b, and R^2 values are the slope, the intercept, and the correlation coefficient, respectively, in the equation of the line $y = ax + b$ correlating the maximum of the long-wavelength absorption (y variable, as measured with $E_T(x)$ values) with the polarity of the solvent (x variable, as measured with Dimroth $E_T(30)$ parameter).

Assuming the same value in acetonitrile solution, an absolute quantum yield of at least 0.3 can be calculated for the *N*,*N*′-diaminide **8b**.

Also, the maxima values of the monopyridyl aminides **3a**–**d** correlate fairly well with $E_T(30)$ (Fig. 3 and Table 4). The sensitivity of the maximum wavelength shift to the solvent polarity is, however, smaller than that observed for the aminide derivatives obtained from dipyridyl compounds **5a**, **b**. Moreover, in Fig. 3 lines with a greater slope also have a larger R^2 value, thus, revealing that the greater the solvatochromic effect of perfluoroacyl-aminides **3** is, the better its correlation with $E_T(30)$.

In conclusion, comparing the solvatochromic behaviour of starting dipyridyl compounds **5** with those of corresponding *N*-oxides **7** and **10** and *N*-aminides **6** and **8** proves the effectiveness of the perfluoroacylaminide moiety in inducing solvatochromic and fluorescence properties. The behaviour of monopyridyl aminides **3** confirms this ability and also shows how the particularly extended delocalization of dipyridyl derivatives **5**–**10** plays a key role in determining the extent of the observed effects.

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