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Syntheses of the first *N*-mono- and *N*,*N*′-dipolyfluoroalkyl-4,4′-bipyridinium compounds

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Reactions of 4,4′-bipyridine (1) with excess of polyfluoroalkyl iodides (2a–d) at 100–110 °C, under neat conditions, led to the formation of monoquaternary salts (3a–d) in > 90% yields. Salts 3a–d were metathesized with $LiN(SO_2CF_3)_2$ either in water or water/acetone mixtures to form ionic liquids (4a–d), respectively, in > 88% yields. When 1 was reacted with 2.5 equivalent of 2a–c in DMF at 110 °C, the diquaternary salts 5a–c were formed in > 85% yields. Alternatively, 5a–c were also synthesized by heating a mixture of 3a–c and 2a–c (1.25 equivalent) in DMF. The metathesis reaction of 5a–c with $LiN(SO_2CF_3)_2$ produced dicationic ionic liquids (6a–c) in > 86% yield.

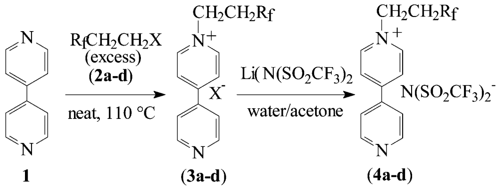
For the first time *N*-monopolyfluoroalkyl and *N*,*N*′-dipolyfluoroalkyl mono and diquaternary salts of 4,4′-bipyridine have been synthesized. A large variety of 4,4′ dialkyl-substituted diquaternary and polyquaternary salts of 4,4′-bipyridine are known.[1]

Some of these diquaternary salts have been evaluated for antibacterial activity,[1b] and as electron relays for the photoreduction of water.[1c] There are reports of a number of 2,2′-bipyridine compounds bearing two various polyfluoroalkylated side chains with an ester or a methylene spacer in the 4,4′ positions.[2] Since quaternization of the *C*-polyfluoroalkylated bipyridines was not reported, the properties of such salts are unknown. However, it was shown recently that the pyridine derivative, $2,6\text{-}NC_5H_3(CH_2CH_2C_8F_{17})_2$, can be quaternized with triflic acid to form a pyridinium triflate that is reported to exhibit a liquid crystalline phase that becomes an ionic liquid at high temperature (166.0/170.1 °C).[3] Several of these dipolyfluoroalkylated pyridines or bipyridines play a role in the catalytic aerobic oxidation of alcohols to aldehydes and ketones,[2c,4] and epoxidation of *trans*-stilbene.[2b]

While not the case for alkyl substitution, of the few reports detailing polyfluoroalkyl substituents,[2–4] the latter is invariably bonded to the carbon atom(s) of the pyridine or bipyridine ring. Now we report the high yield syntheses of the first *N*-mono- and *N*,*N*′-dipolyfluoroalkyl-4,4′-bipyridinium mono- and diquaternary salts, many of which fall into the ionic liquid class (mp < 100 °C) even when each of the fluorine-containing substituents is as large as C_8F_{17}.[5] This is particularly true when bis(trifluoromethanesulfonyl)amide is the anion. However, comparing the melting points of the dipolyfluoroalkyl bipyridinium triflates with that of the dipolyfluoroalkyl pyridinium triflate reported above shows that the bipyridinium compounds in general melt lower. Additionally, the yields of both the mono- and dipolyfluorosubstituted bipyridines are consistently higher than those obtained for the *C*-substituted pyridines.[3]

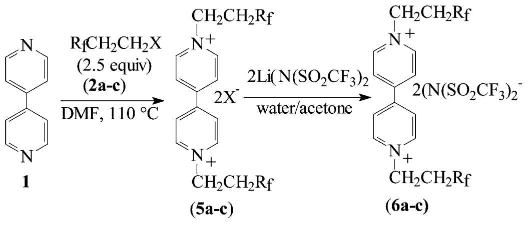
Initially the reaction of 4,4′-bipyridine was carried out with an excess of perfluoroalkyl halides under conditions expected to lead to the formation of diquaternary salts. However, only monoquaternary species were obtained. In a sealed glass tube, bipyridine (**1**) (2 mmol) was heated with excess of 1-bromo-1H,1H,2H,2H-3-fluoropropane (**2a**) at 100 °C for 24 h to give the monoquaternary salt (**3a**) as an insoluble product. After removing the unreacted excess **2a** under vacuum, **3a** remained in 95% yield. Under similar reaction conditions, **1** also was reacted with other 1-iodo-1H,1H,2H,2H-perfluoroalkanes (**2b–d**) at ~ 110 °C for 24 h to give monoquaternary salts (**3b–d**) in > 90% yields (Scheme 1). Under neat conditions, no diquaternary salts were formed. This is not surprising since the monoquaternary salts are insoluble in the perfluoroalkyl halides. Room temperature reactions of quaternary salts (**3a–d**) with $LiN(SO_2CF_3)_2$ either in water or water–acetone mixtures (1:0.5) at room temperature led to the formation of ionic liquids (**4a–d**) in > 88% yields (Scheme 1)

The preparation of diquaternary salts with perfluoroalkylated groups bonded to both nitrogen atoms of bipyridine was accomplished by utilizing a solvent to solubilize the monoquaternary bipyridinium products making them available for further reaction with the perfluoroalkyl halides. Reaction of bipyridine (**1**) with 2.25 equivalents of perfluoroalkyl halides (**2a–c**) readily produced the diquaternary salts (**5a–c**) in > 90% isolated yield (Scheme 2). Alternatively, **5a–c** were also synthesized in comparable yields by heating (105 °C, 24 h) a mixture of **3a** with **2a,3b** with **2b** and **3c** with **2c** (1:1.25) in DMF. While it was possible to introduce higher R_f groups, *e.g.* C_8F_{17}, $C_{10}F_{21}$, onto both the nitrogen atoms of the bipyridine ring, the products were insoluble in all polar, non-polar and/or



	Rf	X		Rf	X		Rf	Y	m.p (°C)
2a	CH_2F	Br	**3a**	CH_2F	Br	**4a**	CH_2F	$N(SO_2CF_3)_2$	62
2b	CF_3	I	**3b**	CF_3	I	**4b**	CF_3	$N(SO_2CF_3)_2$	67
2c	C_6F_{13}	I	**3c**	C_6F_{13}	I	**4c**	C_6F_{13}	$N(SO_2CF_3)_2$	52
2d	C_8F_{17}	I	**3d**	C_8F_{17}	I	**4d**	C_8F_{17}	$N(SO_2CF_3)_2$	94

Scheme 1



	Rf	X		Rf	X		Rf	Y	m.p. (°C)
2a	CH_2F	Br	**5a**	CH_2F	Br	**6a**	CH_2F	$N(SO_2CF_3)_2$	64
2b	CF_3	I	**5b**	CF_3	I	**6b**	CF_3	$N(SO_2CF_3)_2$	96
2c	C_6F_{13}	I	**5c**	C_6F_{13}	I	**6c**	C_6F_{13}	$N(SO_2CF_3)_2$	149

Scheme 2

fluorinated solvents tried. However, satisfactory elemental analyses were obtained. The diquaternary salts (**5a–c**) were also metathesized with $LiN(SO_2CF_3)_2$ to produce the dicationic ionic liquid products (**6a–c**) in good isolated yields (Scheme 2).† ‡

All of the mono- and diquaternary salts and ionic liquids are water and air stable. Their solubilities in polar and non-polar solvents are a function of the perfluoroalkyl chain and the cationic charge. Quaternary salts, **3a,b** are soluble in acetone and water. **3c** is only partially soluble in water but soluble in acetone whereas **3d** is soluble in acetone but insoluble in water. Diquaternary salts (**5a,b**) are insoluble in acetone but soluble in DMF and water. Compound **5c** was only soluble in DMF and DMSO and insoluble in acetone and water. All the mono- and dicationic ionic liquids (**4a–c, 6a–c**) are soluble in acetone. Most of the salts melt at < 100 °C. Compounds **4a–c, 6a–c** were thermally stable to 340 °C as determined by DSC.

In summary, the syntheses of the first *N*-mono- and *N,N′*-dipolyfluoroalkyl bipyridinium quaternary salts and ionic liquids in good isolated yields are described. Depending on reaction conditions, either mono- or diquaternary salts can be obtained that meet the melting point demand of an ionic liquid when metathesized with $LiN(SO_2CF_3)_2$. These materials are anticipated to have value as solvents where markedly reduced coordinating characteristics and liquid ranges starting at lower temperatures are desired.

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Notes and references

† *General procedure for the synthesis of* **3a–d** *and* **4a–d***:* 2,2′-Bipyridine (**1**) (2 mmol) and $R_fCH_2CH_2I$ (**2a–d**) (5 mmoL) were mixed at room temperature in a 50 mL Schlenk tube. After cooling to −195 °C, the tube was evacuated and closed. The reaction mixture was heated at 110 °C for 24 h. The quaternary salt is insoluble in $R_fCH_2CH_2I$. Excess $R_fCH_2CH_2I$ was recovered by removing *in vacuo*. Quaternary salts with $R_f = CH_2F$, CF_3, C_4F_9, C_6F_{13} (**3a–c**) were obtained analytically pure whereas **3d** ($R_f = C_8F_{17}$) was purified by crystallization from acetone. These salts (**3a–d**) were dissolved in a mixture of water and acetone (1:0.5) and treated with 1.25 equivalents aqueous solution of $LiN(SO_2CF_3)$. After 6 h, acetone was removed at reduced pressure and the insoluble products (**4a–d**) were separated by filtration from water.

3d: Yield: 90%; IR (KBr pellet): 3024, 1639, 1595, 1544, 1409, 1200, 1147, 1074, 955, 810, 704, 660 cm^{-1}; ^{19}F NMR (acetone-d_6): δ −82.07 (t, 3F, $J = 9.5$ Hz), −113.96 (m, 2F), −112.49 (m, 2F), −122.79 (m, 4F), −123.62 (m, 2F), −124.23 (m, 2F), 127.10 (m, 2F); ^{1}H NMR (acetone-d_6): δ 3.52 (tt, 2H, $J = 11.6$ Hz, $J = 7.2$ Hz), 5.38 (t, 2H, $J = 7.2$ Hz), 8.10 (d, 2H, $J = 7.3$ Hz), 8.81 (d, 2H, $J = 6.6$ Hz), 8.98 (d, 2H, $J = 7.5$ Hz), 9.76 (d, 2H, $J = 6.6$ Hz); ^{13}C NMR (acetone-d_6): δ 32.5 (t, $J = 23.0$ Hz), 54.2, 110–123.0 (overlapped quartets with multiplets), 122.6, 126.8, 141.9, 147.1, 152.1, 155.5. Anal. Calcd. for $C_{20}H_{12}F_{17}IN_2$: C, 32.90; H, 1.66. Found: C, 32.74; H, 1.74%. **4c:** Yield, 92%, (KBr pellet): 3075, 1644, 1602, 1549, 1525, 1495, 1467, 1411, 1349, 1193, 1057, 965, 870, 815, 791, 740 cm^{-1}; ^{19}F NMR (acetone-d_6): δ −80.35 (s, 6F), −82.16 (tt, 3F, $J = 9.5$ Hz, $J = 2.3$ Hz), −114.19 (m, 2F), −122.78 (m, 2F), −123.82 (m, 2F), −124.43 (m, 2F), 127.18 (m, 2F); ^{1}H NMR (acetone-d_6): δ 3.39 (ttt, 2H, $J = 11.5$ Hz, $J = 7.1$ Hz, $J = 2.5$ Hz), 5.37 (t, 2H, $J = 7.2$ Hz), 8.02 (s, broad, 2H), 8.74 (d, 2H, $J = 6.7$ Hz), 8.91 (s, broad, 2H), 9.47 (d, 2H, $J = 6.7$ Hz); ^{13}C NMR (acetone-d_6): δ 31.5 (t, $J = 20.8$ Hz), 53.6, 110–122 (overlapped quartets with multiplets), 126.2, 141.1, 146.2, 151.2, 151.5, 155.0. Anal. Calcd. for $C_{20}H_{12}F_{19}N_3O_4S_2$: C, 30.36; H,1.54. Found: C, 30.61; H, 1.79%. **4d:** Yield, 90%, (KBr pellet): 3070, 1645, 1602, 1549, 1469, 1414, 1250, 1211, 1150, 1033, 962, 835, 704 cm^{-1}; ^{19}F NMR (acetone-d_6): δ −75.16 (s, 6F), −76.87 (tt, 3F, $J = 9.5$ Hz, $J = 2.3$ Hz), −109.00 (m, 2F), −117.44 (m, 2F), −117.71 (m, 4F), −118.55 (m, 2F), 119.10 (m, 2F), 122.01 (m, 2F); ^{1}H NMR (acetone-d_6): δ 3.31 (tt, 2H, $J = 11.6$ Hz, $J = 7.2$ Hz), 5.27 (t, 2H, $J = 7.2$ Hz), 8.01 (d, 2H, $J = 7.3$ Hz), 8.66 (d, 2H, $J = 6.8$ Hz), 8.55 (d, 2H, $J = 7.4$ Hz), 9.38 (d, 2H, $J = 6.7$ Hz); ^{13}C NMR (acetone-d_6): δ 32.1 (q, $J = 22.5$ Hz), 54.2, 110–122 (overlapped quartets with multiplets), 123.0, 126.9, 142.3, 146.7, 146.8, 151.5, 155.3. Anal. Calcd. for $C_{22}H_{12}F_{23}N_3O_4S_2$: C, 29.90; H,1.37. Found: C, 30.00; H, 1.58%.

‡ **6b:** Yield, 88%, (KBr pellet): 3076, 1641, 1561, 1508, 1458, 1405, 1343, 1228, 1058, 1005, 971, 873, 831, 791, 734 cm^{-1}; ^{19}F NMR (acetone-d_6): δ −65.38 (t, 6F, $J = 10.4$ Hz), −79.85 (s, 12F); ^{1}H NMR (acetone-d_6): δ 3.39 (tt, 4H, $J = 7.2$ Hz, $J = 3.5$ Hz), 5.37 (t, 4H, $J = 7.2$ Hz), 8.97 (d, 4H, $J = 6.9$ Hz), 9.63 (d, 4H, $J = 6.9$ Hz); ^{13}C NMR (acetone-d_6): δ 35.0 (q, $J = 29.8$ Hz), 56.1, 121.0 (q, $J = 319.9$ Hz), 126.7 (q, $J = 275.1$), 128.4, 147.6, 151.5. Anal. Calcd. for $C_{20}H_{16}F_{18}N_4O_8S_4$: C, 26.38; H,1.77. Found: C, 26.30; H, 1.80%.

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