Amidinium based ionic liquids†

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Three new series of mono- and bis-cyclic amidinium cations bearing alkyl chains of different length were synthesized. 53 salts were generated upon combining the cations with a variety of anions and their thermal behaviour was investigated. Depending on the structure and the charges state of the cyclic amidinium moiety and the nature of the anion, several of the obtained salts behaved as ionic liquids with their melting point in the range of *ca.* 25–94 °C.

Introduction

The design and discovery of ionic liquids (ILs) displaying melting points (mp) lower than 100 °C,[1,2] in particular room temperature ionic liquids (RTILs) and tasks specific ionic liquids (TSILs) have been the subject of considerable efforts over the past decade.[3–10] The interest in this class of molecules arises in part from their use as liquid media for a variety of chemical transformation and as substitutes for volatile organic solvents.

The majority of ILs belong to the family of *N*,*N*′-methyl-(alkyl)imidazolium, alkyl-pyridinium or ammonium cations associated with a variety of anions such as X^-, BF_4^-, BPh_4^-, PF_6^-, NO_3^-, $CF_3SO_3^-$, NCS^-, $N(CN)_2^-$, TfO^-, NTf_2^-, TsO^-, $AlCl_4^-$ or MX_4^-. Recently, a few amidinium-based ionic liquids have been also reported.[11,12] The many opportunities arising from all the possible combinations of cations and anions allow to tune with good precision the characteristics of ionic liquids such as melting point, viscosity, hygroscopy, dielectric constant *etc*. Consequently, this class of molecules are increasingly used in many areas such as organic chemistry, chemical engineering, material sciences, physical chemistry, analytical chemistry, biotechnology and energy storage.[13–15]

For the reasons mentioned above, the development of new classes of ionic liquids is a topic of current interest. By analogy with imidazolium cation based ionic liquids, the use of the cyclic amidinium backbone appeared to us as an interesting alternative.

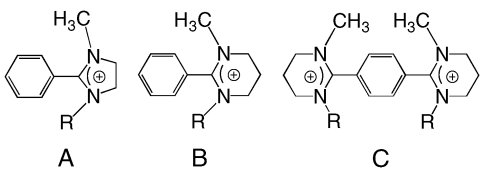
Here, we report on the design, synthesis, thermal behaviour and structural studies of three new series of mono- and bis-amidinium cations (Scheme 1) combined with a variety of anions.

Results and discussion

We have extensively used a variety of dicationic bisamidinium derivatives[16] as tectons[17] for the design and generation of charge-assisted H-bonded networks[18] in the crystalline phase by combining them with sulfonates, carboxylate, polycyanometallates[19–24] or polyoxalatometallate[25] anions. In order to obtain new families of ionic liquids based on the amidinium group, one must prevent the crystallisation processes. We thought that this could be achieved by decreasing interactions between the cationic and anionic partners through the replacement of hydrogen atoms involved in strong charge-assisted H-bonding with anions by alkyl groups. Furthermore, by rendering the amidinium group unsymmetrical through differentiated alkylation (introduction of a methyl and an alkyl groups of variable chain length), one should further reduce the crystallisation ability of the salt.

(a) Design

The design of all three series (Scheme 1) is based on the use of the benzamidine group. The rationale behind this choice is to render the cationic backbone more robust towards hydrolysis. Whereas the design of the two series A and B is based on monocationic cyclic amidinium derivatives bearing two different alkyl groups (one methyl and one alkyl chain with variable length), for the design of the third series C, a dicationic bis-cyclic amidinium backbone, for which each amidinium group bears one methyl group and one alkyl fragment of variable length, is used. As stated above, the alkylation of the monoamidines (series A and B) and the bisamidine (series C) was performed in order to prevent strong H-bonding between the cationic moiety and anions and thus to avoid the generation of crystalline materials. The double alkylation of the amidine by two different alkyl groups was performed in order to introduce dissymmetry and thus again to prevent as much as possible the crystallisation processes. The use of the methyl group was motivated by synthetic reasons since the



Scheme 1 Target N-alkylated cyclic amidinium cations, R = $CH_3(CH_2)_n$ (n = 2, 5, 11) for five-membered (A) and six-membered (B) cyclic monoamidinium and R = $CH_3(CH_2)_n$ (n = 2, 5, 11, 15) for bis-cyclic bisamidinium (C) compounds.

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monomethyl-, ethylene- and propylene-diamines are commercially available. The preparation of the bisamidinium salts (series C) is justified by the fact that only very few examples of ionic liquids based on dicationic units have been reported.[26–33] Finally, it is worth noting that, the three series spotted in this investigations can be obtained easily in large quantities and at rather low cost.

(b) Synthesis

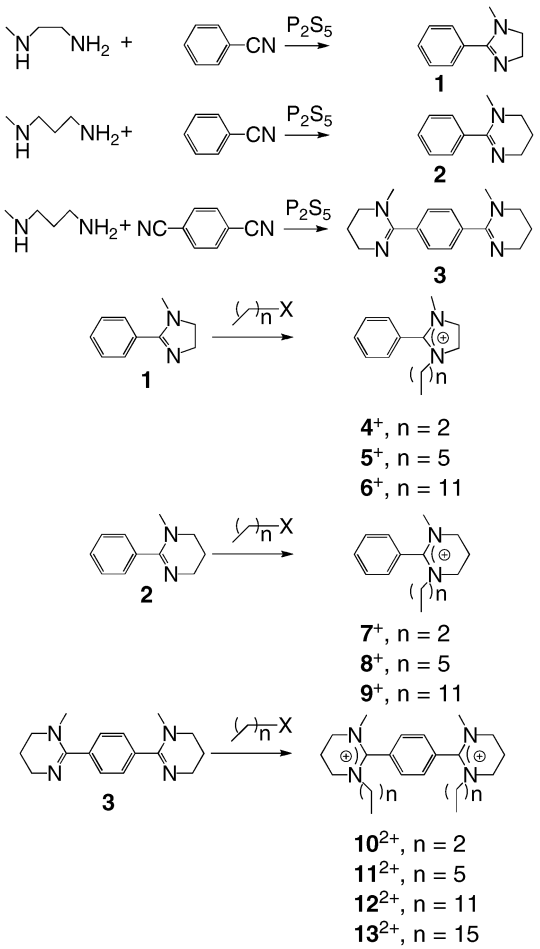
A general and versatile synthetic strategy was used for the preparation of the mono and biscationic amidinium derivatives **4–13** (Scheme 2). Following the methodology reported by Lever[34], monoamidines **1** and **2** have been prepared as their hydrochloride salts in 47 and 70% yields, respectively, upon condensation of monomethyl ethylenediamine or monomethyl propanediamine with benzonitrile in the presence of catalytic amount of P_2S_5. Using the same method, the bisamidine **3** was synthesised in 66% yield as its hydrochloride salt upon condensation of monomethyl propanediamine with 1,4-dicyanobenzene again in the presence of catalytic amount of P_2S_5.[34] The desired monoamidinium cations **4–9** have been obtained by simple condensation of the monoamidines **1** or **2** with terminal alkylhalides. In order to study the role played by the counter ion (Cl^-, Br^-, I^-, BF_4^-, BPh_4^-, PF_6^-, OTf^- (trifluoromethanesulfonate) or NTf_2 (bis(trifluoromethane)-sulfonimidate)), different salts of the cationic derivatives **4–13** have been prepared by anion metathesis. For correspondence between numbers assigned to different salts see Table 1. Both in the case of **1** and **2**, the alkylation reaction leading to the monoamidinium salts ($\mathbf{4}^+, I^-$) = **24**, ($\mathbf{5}^+, Br^-$) = **27**, ($\mathbf{6}^+, Br^-$) = **30**, ($\mathbf{7}^+, I^-$) = **33**, ($\mathbf{8}^+, Br^-$) = **38**, and ($\mathbf{9}^+, Br^-$) = **43** was carried out with iodo-1-propane, bromo-1-hexane and bromo-1-dodecane respectively. The yield of the reaction was in the 46–60% range (see Experimental section). The anion exchange proceeded in 85–99% yield in both cases. The synthesis of dicationic compounds **10–13** was achieved by condensation of **3** with terminal alkylhalides. The alkylation reaction was achieved using iodo-1-propane, bromo-1-hexane, bromo-1-dodecane and bromo-1-hexadecane. The bisamidinium salts ($\mathbf{10}^{2+}, I^-$) = **48**, ($\mathbf{11}^{2+}, Br^-$) = **53**, ($\mathbf{12}^{2+}, Br^-$) = **58** and ($\mathbf{13}^{2+}, Br^-$) = **63**, were obtained in 60–80% yield (see Experimental section). Again, the anion metathesis proceeded with almost quantitative yields.

(c) Thermal behaviour

The thermal behaviour as well as the physical state (solid, liquid) of all salts of the monocationic amidinium $\mathbf{4}^+$–$\mathbf{6}^+$, $\mathbf{7}^+$–$\mathbf{9}^+$ as well as the dicationic bisamidinium derivatives $\mathbf{10}^{2+}$–$\mathbf{13}^{2+}$ are given in Tables 2–4.

(1) Salts of monoamidinium cations 1-H$^+$ and 4$^+$–6$^+$

The chloride salt **14** and the iodide salt **24** were found to be rather hygroscopic. Among the 12 derivatives prepared in this series based on the ethylene spacer, 5 of them (**24**, **27**, **29**, **30** and **32**) are viscous liquids at room temperature (see Table 2). For the other 7 salts, the melting point was in the range of 63–162 °C. Depending on the nature of the anion used, some of the compounds were thermally stable up to 350 °C (Fig. 1).



Scheme 2 Synthetic strategies used for the preparation of $\mathbf{X}^{n+}$ (**X** = **1–13**, n = 1 or 2).

Table 1 Numbers attributed to different prepared salts. For structures of compounds **1–13** see Scheme 2

	Cl^-	Br^-	I^-	BF_4^-	BPh_4^-	PF_6^-	OTf^-	NTf_2^-
1-H$^+$	**14**				**15**	**16**		
2-H$^+$	**17**		**18**		**19**	**20**	**21**	**22**
3-2H$^+$	**23**							
4$^+$			**24**		**25**	**26**		
5$^+$		**27**			**28**	**29**		
6$^+$		**30**			**31**	**32**		
7$^+$			**33**		**34**	**35**	**36**	**37**
8$^+$		**38**			**39**	**40**	**41**	**42**
9$^+$		**43**			**44**	**45**	**46**	**47**
10^{2+}			**48**	**49**	**50**	**51**		**52**
11^{2+}		**53**		**54**	**55**	**56**		**57**
12^{2+}		**58**		**59**	**60**	**61**		**62**
13^{2+}		**63**		**64**	**65**	**66**		**67**

Table 2 Mp (°C) for **1-H$^+$**, **4$^+$–6$^+$** cations associated with different anions; L = liquid, V = viscous

	Cl^-	I^-	Br^-	BPh_4^-	PF_6^-
1-H$^+$	160 (**14**)	—	—	160 (**15**)	149 (**16**)
4$^+$	—	VL (**24**)	—	162 (**25**)	63 (**26**)
5$^+$	—	—	VL (**27**)	114 (**28**)	VL (**29**)
6$^+$	—	—	VL (**30**)	69 (**31**)	VL (**32**)

Table 3 Mp (°C) for **2**-H$^+$, **7**$^+$–**9**$^+$ cations associated with different anions (I^-, Cl^-, Br^-, PF_6^-, BPh_4^-, OTf^- and NTf_2^-) (**17–22** and **33–47**); L = liquid

	Cl^-	Br^-	I^-	BPh_4^-	PF_6^-	OTf^-	NTf_2^-
2-H$^+$	160 (**17**)	—	177 (**18**)	205 (**19**)	138 (**20**)	76 (**21**)	L (**22**)
7$^+$	—	—	88 (**33**)	119 (**34**)	93 (**35**)	L (**36**)	L (**37**)
8$^+$	—	L (**38**)	—	94 (**39**)	41–47 (**40**)	L (**41**)	L (**42**)
9$^+$	—	49 (**43**)	—	92 (**44**)	49–51 (**45**)	L (**46**)	L (**47**)

If applying the definition of the ionic liquid state (melting point below 100 °C), only compounds **26** and **31** may be of interest as ionic liquids. Indeed, the hexafluorophosphate salt of the monocation **4**$^+$ (salt **26**) and the tetraphenylborate salt of the monoamidinium **6**$^+$ (salt **31**) display melting points between 60 and 70 °C.

(2) Salts of monoamidinium cations 2-H$^+$ and 7$^+$–9$^+$

Some of the prepared salt in this series are also extremely hygroscopic. The bromide salt of **8**$^+$ (**38**), the triflate salts of **7**$^+$ (**36**), **8**$^+$ (**41**) and **9**$^+$ (**46**) as well as all the bis(trifluoromethane)sulfonimidate (NTf^-) salts of **2**-H$^+$ and **7**$^+$–**9**$^+$ were found to be liquids (see Table 3). Again, depending on the anion, some of the salts are stable up to 350 °C (Fig. 1). Interestingly, among the 21 different salts prepared, five (**17–20** and **34**) display melting points above 100 °C. For the other 16 derivatives, either they are liquids at room temperature or their melting points are in the range of 41–94 °C and thus may be considered as ionic liquids.

(3) Salts of bisamidinium dications 3-2H$^+$ and 10^{2+}–13^{2+}

As a general observation, except for the NTf_2^- salts of **10**$^{2+}$–**13**$^{2+}$ for which the melting points are below 150 °C, only one compound **57** (mp of 70 °C) may be considered as an ionic liquid. For all the other salts, high melting points were recorded (see Table 4). For these salts, some of the melting points are higher than their decomposition temperature (Fig. 1). Thus, unfortunately, among the 21 salts prepared, only one (salt **57**) may be of interest as an ionic liquid.

(d) Structural studies

For some of the salts displaying rather high melting point, we were able to grow single crystals suitable for structural analysis by X-ray diffraction methods (see crystallographic Table 5).

For the family A, only the tetraphenylborate salt of **1**-H$^+$ (**15**) (monoclinic, $P2_1/n$, Fig. 2, top) and the hexafluorophosphate salt of **4**$^+$ (**26**) (monoclinic, $C2/c$, Fig. 2, bottom) were obtained as crystalline materials. The X-ray diffraction study revealed that in both cases, the C–N distances for the cyclic amidinium moiety are in the range 1.314(2)–1.322(3) Å.

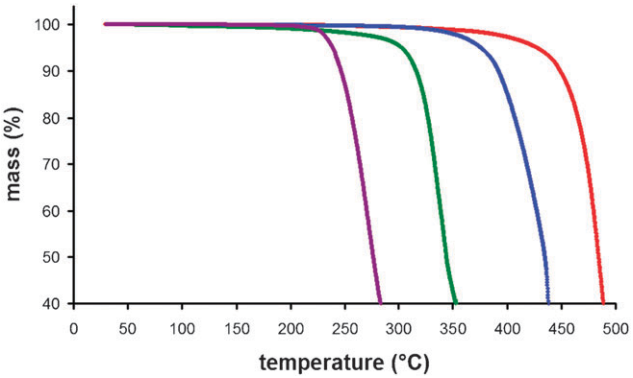


Fig. 1 TGA trace for different salts: **18** (blue), **19** (violet), **42** (red) and **44** (green).

The aromatic and the five-membered rings are not coplanar but tilted by 51°. In **26**, the propyl chain is extended with a C–C–C angles of 114.3° (see Fig. 2, bottom). In both cases, there are no specific interactions between the anionic and the cationic parts.

For the family B composed of monoamidinium cations based on the propylene spacer, crystals of the iodide (**18**, monoclinic, $P2_1/n$, Fig. 3), triflate (**20**, monoclinic, $P2_1/c$) and hexafluorophosphate (**21**, orthorhombic, $Pbca$) salts of **2**-H$^+$ and the tetraphenylborate salt of **7**$^+$ (**34**, orthorhombic, $Pna2_1$) were obtained (see crystallographic table, Table 5). The X-ray diffraction study revealed that in all cases, the C–N distances for the six-membered cyclic amidinium moiety is in the range 1.3210(17)–1.326(6) Å which is close to that mentioned above for the family A. The six-membered ring adopts a half chair conformation with the NCC angle varying between 112.0(3) and 108.05(12)°. Again, as in the case of **4**$^+$ mentioned above, the aromatic and the six-membered rings are tilted by 50°. For the iodide salt **18**, a view of the packing of cations and anions given in Fig. 2 shows weak interactions through H-bonds between amidinium and iodide with N···I distances of 3.49 and 4.53 Å.

In the case of **21**, the triflate salt of **2**-H$^+$, a strong H-bond (d_{N-O} = 2.82 Å) between the sulfonate group and the amidinium moiety of **2**-H$^+$ is observed (Fig. 4).

For the tetraphenylborate salt of **7**$^+$ (compound **34**), the C–N distances for the amidinium moiety are in the range of 1.322(2) and 1.325(2) Å. The conformation of the six-membered ring cycle is again a half chair with a NCC angle of 110.44(14)°. The aromatic ring and the six-membered cycle are almost perpendicular with a tilt angle of 78° (Fig. 5). The propyl chain is again extended with a C–C–C angle of 113.42(17)°.

Table 4 Mp (°C) for **3**-2H$^+$, **10**$^{2+}$–**13**$^{2+}$ (**23** and **48–67**) cations associated with different anions (Br^-, I^-, BF_4^-, PF_6^-, BPh_4^- and NTf_2^-); *: decomposition

	Cl^-	Br^-	I^-	BF_4^-	BPh_4^-	PF_6^-	NTf_2^-
3-2H$^+$	~250* (**23**)	—	—	—	—	—	—
10^{2+}	—	—	> 340* (**48**)	> 340* (**49**)	314–316* (**50**)	> 320* (**51**)	134–135 (**52**)
11^{2+}	—	> 280* (**53**)	—	306–308 (**54**)	> 300* (**55**)	314 (**56**)	70 (**57**)
12^{2+}	—	> 300* (**58**)	—	> 340* (**59**)	> 300* (**60**)	> 280* (**61**)	106–108 (**62**)
13^{2+}	—	> 300* (**63**)	—	> 300* (**64**)	235 (**65**)	~ 280* (**66**)	103–106 (**67**)

Table 5 Crystallographic parameters for **15**, **18**, **20**, **21**, **23**, **26**, **34**, **48** and **59** recorded at 173 K

Compound	**15**	**18**	**20**	**21**	**23**	**26**	**34**	**48**	**59**
Formula	$C_{34}H_{33}BN_2$	$C_{11}H_{15}IN_2$	$C_{11}H_{15}F_6N_2P$	$C_{12}H_{15}F_3N_2O_3S$	$C_{16}H_{24}N_4Cl_2 \cdot 4H_2O$	$C_{13}H_{19}N_2F_6P$	$C_{38}H_{41}BN_2$	$C_{22}H_{36}N_4I_2$	$C_{40}H_{72}N_4Br_2 \cdot 3H_2O$
Molecular weight	480.43	302.15	320.22	324.32	415.36	348.27	536.54	610.35	822.88
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$Pbca$	$P2_1/n$	$C2/c$	$Pna2_1$	$P2_1/n$	$P\bar{1}$
a/Å	9.7552(9)	6.60500(10)	15.4539(12)	11.0219(4)	9.8040(3)	15.8396(12)	18.620(3)	7.6986(4)	7.4346(2)
b/Å	15.9976(13)	15.5700(3)	12.1945(7)	15.3857(5)	9.3589(2)	7.3779(6)	16.793(2)	13.1654(8)	12.6309(3)
c/Å	17.3840(16)	11.7069(2)	15.6621(12)	16.9442(6)	11.3818(3)	26.074(2)	9.9862(9)	12.2445(8)	24.8045(7)
α/°	90	90	90	90	90	90	90	90	81.5990(10)
β/°	99.527(2)	97.5510(10)	113.353(2	90	95.5590(10)	92.798(2)	90	98.824(2)	88.3960(10)
γ/°	90	90	90	90	90	90	90	90	73.3400(10)
V/Å^3	2675.5(4)	1193.50(4)	2709.8(3)	2873.39(17)	1039.42(5)	3043.4(4)	3122.5(7)	1226.35(13)	2207.33(10)
Z	4	4	8	8	2	8	4	2	2
Colour	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless
Dimensions/mm^3	0.10 × 0.06 × 0.06	0.20 × 0.18 × 0.17	0.12 × 0.10 × 0.06	0.20 × 0.15 × 0.13	0.21 × 0.13 × 0.12	0.12 × 0.10 × 0.05	0.20 × 0.16 × 0.08	0.10 × 0.05 × 0.05	0.10 × 0.10 × 0.08
D_c/g cm^{-3}	1.193	1.682	1.570	1.499	1.327	1.520	1.141	1.653	1.238
$F(000)$	1024	592	1312	1344	444	1440	1152	604	880
μ/mm^{-1}	0.068	2.649	0.264	0.270	0.340	0.242	0.065	2.579	1.874
λ/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
No. data meas.	17812	18778	21182	56466	12120	12587	32310	19439	49155
No. data with $I > 2\sigma(I)$	6100	3355	7374	4217	2388	3523	6364	3545	13224
R_{int}	0.0416	0.0302	0.0934	0.0412	0.0341	0.0294	0.0452	0.0368	0.0244
R_1 ($I > 2\sigma(I)$)	0.0487	0.0286	0.0878	0.0365	0.0452	0.0523	0.0357	0.0290	0.0593
wR_2 ($I > 2\sigma(I)$)	0.1115	0.0597	0.2234	0.0910	0.1184	0.1585	0.0773	0.0762	0.1862
R_1 (all)	0.1043	0.0424	0.2109	0.0622	0.0538	0.0759	0.0539	0.0383	0.0771
wR_2 (all)	0.1414	0.0626	0.3527	0.0992	0.1248	0.1791	0.0843	0.0796	0.2004
GOF	1.016	1.050	1.012	1.074	1.048	1.028	1.013	1.054	1.035
$\Delta\rho_{max,\ min}$/e Å^{-3}	0.185, −0.210	1.387, −1.289	0.741, −0.835	0.277, −0.368	0.490, −0.442	0.615, −0.476	0.143, −0.145	1.321, −0.599	1.781, −2.258

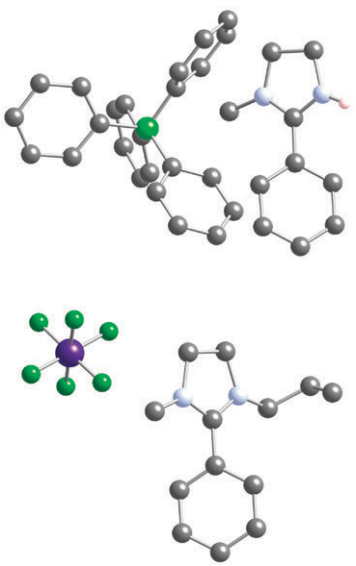


Fig. 2 A portion of the crystal structure of **15** (top) and **26** (bottom). For distances and angles see text. H-atoms are not represented for clarity.

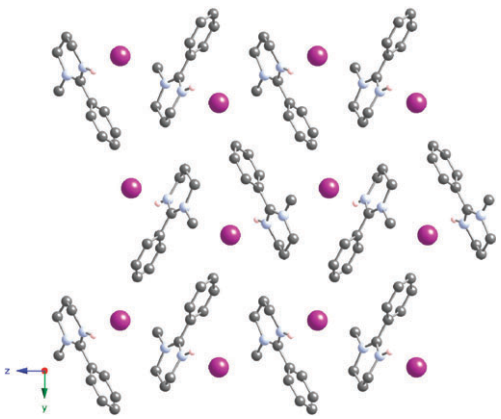


Fig. 3 A portion of the crystal structure of **18** (projection in the [100] plane) showing the presence of the H-bond. For distances and angles see text. H-atoms, except those involved in H-bonding with iodide anion, are not represented for clarity.

For the dicationic bisamidinium derivates (family C), the chloride salt of **3**-2H^{2+} (**23**), the iodide salt of **10**$^{2+}$ (**48**) and the tetrafluoroborate salt of **12**$^{2+}$ (**59**) could be obtained as crystals (see crystallographic table, Table 5).

For the hydrochloride salt of **3**$^+$ (compound **23**), in agreement with the structure of other amidinium cations, the C–N distances for **3**-2H$^+$ dication are in the range of 1.315(2)–1.322(2) Å (Fig. 6). The conformation of the two six-membered cycles is, as expected, a half chair with a NCC angle of 116.49(16)°. The aromatic ring and the cyclic amidinium cycles are not coplanar but tilted with an angle of 108.17(16) and 110.82(17)°. The packing of the cationic and anionic partners shows a hydrogen bond between the N–H centre of the amidinium dication and chloride anion (d_{N-Cl} = 3.12 Å) (see Fig. 6 bottom). The crystal contains also four H_2O molecules in the unit cell. The water molecules are H-bonded

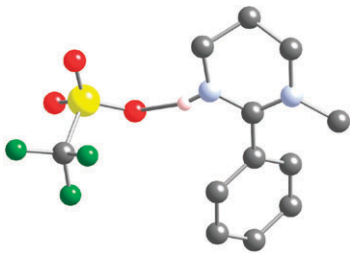


Fig. 4 A portion of the crystal structure of **21** showing the presence of an H-bond between the amidinium cation and the triflate anion. For distances and angles see text. H-atoms, except those involved in H-bonding with iodide anion, are not represented for clarity.

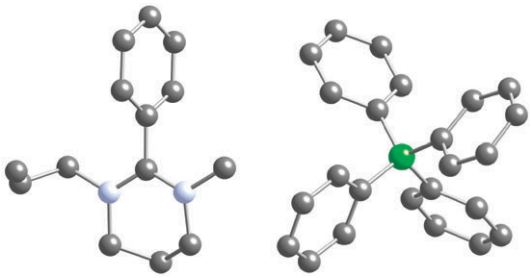


Fig. 5 A portion of the crystal structure of **34** showing the cationic and the anionic parts. For distances and angles see text. H-atoms are not represented for clarity.

with O–O distances of 2.88 and 2.86 Å, leading to a 1D polymeric network, that is connected to the ionic units through OH···Cl interactions (d_{O-Cl} = 3.18 Å) as well as through O···HN amidinium interactions (d_{O-N} = 3.30 Å).

Suitable crystals of both salts **48** and **59** have been also obtained. The X-ray analysis revealed that the anionic and cationic parts are separated without any specific interactions between them. The bisamidinium moiety of **48** (the iodide salt of **10**-$2H^{2+}$) is centrosymmetric (Fig. 7) and the C–N distances of 1.320(3) and 1.324(3) Å are again in the same range as that observed for the other cases discussed above. Both six-membered rings again adopt a half-chair conformation with a NCC angle of 110.6(3)°. As for the hydrochloride salt **23**, the aromatic cycle is tilted with respect to the two amidinium cycles with a tilt angle of 97°. The propyl chain is extended with a C–C–C angle of 112.5(2)°).

In marked contrast with the transoid conformation adopted by the dication in **48**, the bisamidinium moiety of **59** adopts the cisoid conformation in the crystalline phase (Fig. 9). The latter conformation results from the packing of the molecular units leading to interdigitation of the alkyl chains (Fig. 8). One of the two alkyl chains was found to be disordered. For the amidinium unit, the C–N distances are again in the range of 1.314(4)–1.319(4) Å. The conformation of the six-membered cycle is also a half chair with a NCC angle of 110.6(4)°. The tilt between the aromatic ring and the six-membered cycle is 89.0° which is less than those observed for **23** and **48**. The dodecyl chains are unfolded and located on the same face of the amidinium unit and in the same plane. As mentioned above, the packing of consecutive cationic units is achieved through van der Waals interaction by interdigitation of the alkyl chains (shortest C–C distances between chains belonging to

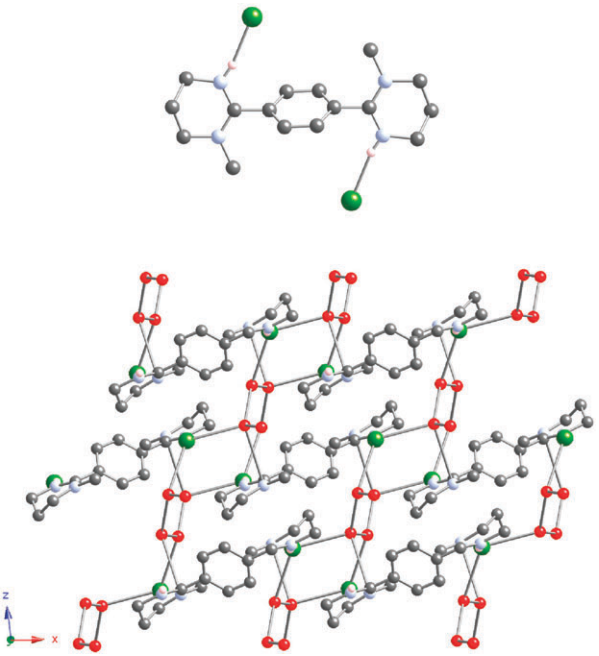


Fig. 6 A portion of the crystal structure of **23** showing the H-bond between the Cl^- anion and the amidinium moiety (top) and the packing in the [010] plane and the formation of H-bonded networks between water molecules and the ionic network (bottom). For distances and angles see text. H-atoms, except those involved in H-bonding with iodide anion, are not represented for clarity.

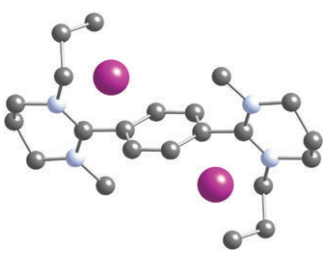


Fig. 7 A portion of the crystal structure of **48** showing the cationic and the anionic (I^-) parts. For distances and angles see text. H-atoms are not represented for clarity.

consecutive units is 4.01 Å). This mode of packing generates hydrophobic layers of *ca.* 13 Å thickness (see Fig. 9). The water molecules present in the crystal form a H-bonded network with O···O distances varying between 2.74 and 2.81 Å and are located outside the hydrophobic zones. The Br^- anions are located above the charged cycles and are interacting strongly with water molecules through H-bonds (O···Br distances in the range of 3.31–3.33 Å).

Conclusions

Three series (A, B and C, see Scheme 1) of amidinium based salts have been designed, synthesised and investigated for their thermal behaviour. The first two series (A and B) are based on a cyclic monoamidinium cation and differ only by the number of methylene groups connecting the N atoms of the amidinium group (two for A and three for B). The third family is constructed around a dicationic bicyclic backbone.

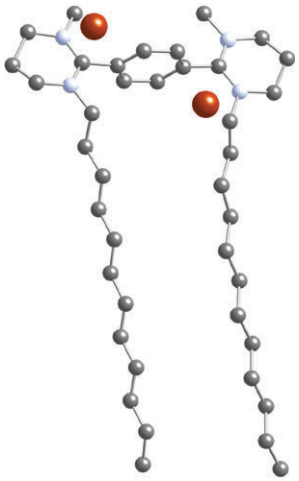


Fig. 8 A portion of the crystal structure of **59** showing the cationic and the anionic (Br^-) parts. For distances and angles see text. H-atoms are not represented for clarity.

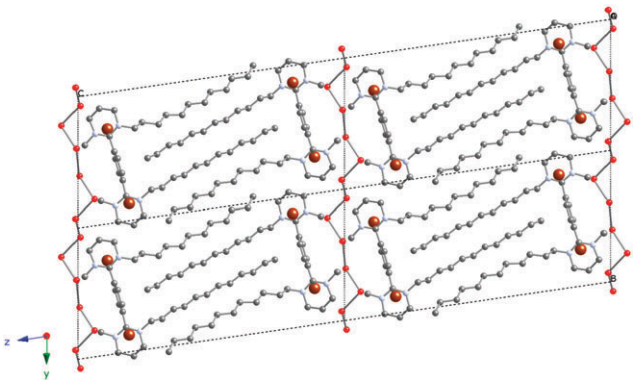


Fig. 9 A portion of the crystal structure of **59**, view in the [100] plane. For distances and angles see text.

For the first two series composed of monocationic species $\mathbf{4}^+$–$\mathbf{9}^+$, the chloride salts do not behave as ionic liquids (mp > 250 °C). As already observed for other IL,[35] the melting points are considerably lower for TfO^- and NTf_2^- anions than for the other salts. Indeed, except for the compound **21** for which the melting point is 76 °C, all other TfO^- and NTf_2^- salts (**22**, **36**, **37**, **41**, **42**, **46** and **47**) are liquid at room temperature and thus can be used as ionic liquids.

A correlation between the length of the alkyl chain and the measured melting points while using the same anion (mainly BPh_4^- and PF_6^-) shows clearly that, as expected, the variation of the melting point is inversely proportional to the chain length (Fig. 10).[36,37] This trend may be explained by the increase of the dissymmetry of the cation.[38,39]

For the dicationic series, only the salt **57** (mp = 57 °C) displays a melting points lower than 100 °C for all the other salts prepared, melting points are higher than 250 °C and usually above their decomposition temperature.

Experimental

The NMR studies were performed at 25 °C on a Bruker AC300 at 300 MHz for ^1H and at 75 MHz for ^{13}C.

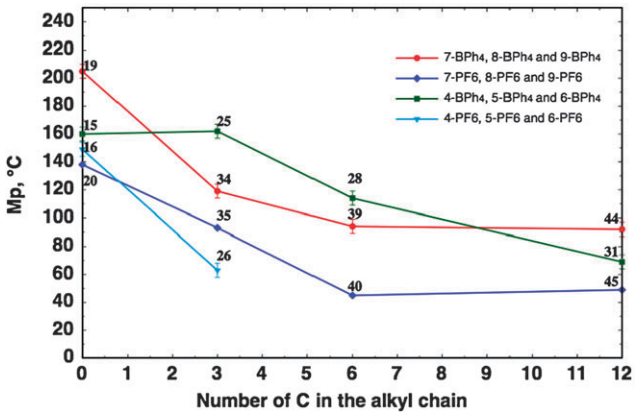


Fig. 10 Variation of the melting point (mp) as a function of the length of the alkyl chain BPh_4^- and PF_6^- salts of monocationic amidinium $\mathbf{4}^+$ and $\mathbf{7}^+$ associated with either BPh_4^- or PF_6^- anions (compounds **15**, **16**, **19**, **20**, **25**, **26**, **28**, **31**, **34**, **35**, **39**, **40**, **44** and **45**).

Thermogravimetric (TGA) studies

TGA measurements have been performed on Pyris 6 TGA Lab System (Perkin-Elmer), using a N_2 flow of 20 ml min^{-1} and a heat rate of 10 °C min^{-1}.

Single-crystal studies

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer, equipped with an Oxford Cryosystem liquid N2 device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. The structures were solved using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).[40]

Synthesis

Synthesis of 1. A saturated aqueous solution of sodium hydroxide (8 ml) was mixed with 1.99 g (10.1 mmol) of **14** dissolved in 10 ml of distilled water. After stirring for 5 min, the mixture was extracted into CH_2Cl_2 (2 × 25 ml), dried with $MgSO_4$. After filtration, the organic solvent was removed under vacuum affording the pure compound **1** in 86% yield as a slightly yellowish liquid which decomposed at 50 °C. ^1H NMR ($CDCl_3$, δ ppm): 2.75 (s, 3H, CH_3–N), 3.40–3.83 (2t, 2H, ^3J = 9.7 Hz, CH_2–N), 7.3–7.5 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 36.5 (CH_3–N), 53.2–54.1 (CH_2–N); 128.1–128.3 (CH arom, α and β), 129.7 (CH arom, γ), 131.3 (C arom), 168.2 (N–C–N). Calc. for $C_{10}H_{12}N_2$: C = 74.97%, H = 7.55%, N = 17.48%. Found: C = 74.52%, H = 7.78%, N = 17.65%.

Synthesis of 2. 8 ml of a saturated aqueous solution of sodium hydroxide was mixed with 2.15 g (12.3 mmol) of **17** dissolved in 10 ml of distilled water. After stirring for 5 min, the mixture was extracted into CH_2Cl_2 (2 × 25 ml), dried with $MgSO_4$. After filtration, the organic solvent was removed under vacuum affording the pure compound **2** in 85% yield as a slightly yellowish liquid. ^1H NMR ($CDCl_3$, δ ppm): 1.90 (q, 2H, ^3J = 5.7 Hz, $CH_2(CH_2$–$N)_2$), 3.04 (s, 3H, CH_3–N), 3.24 (t, 2H, ^3J = 5.7 Hz, CH_2–N–CH_3), 3.46 (t, 2H, ^3J = 5.7 Hz,

CH_2–NH), 7.32 (m, 5H, CH arom). ^{13}C NMR ($CDCl_3$, δ ppm): 22.0 (N–CH_2–CH_2–CH_2–N), 40.3 (CH_3–N), 44.9, 48.6 (CH_2–N), 128.0, 128.5 (CH arom), 138.0 (C arom), 159.3 (N–C–N). Calc. for $C_{11}H_{14}N_2$: C = 75.82%, H = 8.10%, N = 16.08%. Found: C = 75.24%, H = 8.35%, N = 16.05%.

Synthesis of 3. To an aqueous solution (distilled, 200 ml) of 23 (5.0 g), a saturated solution of sodium hydroxide was added until pH = 13 was reached. The white precipitate thus formed was filtered off, washed with 2 × 15 ml of water and dried under vacuum affording the pure compound **3** in 71% yield. Mp 171 °C. ^{1}H NMR (CD_3OD, δ ppm): 1.96 (q, 4H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.76 (s, 6H, CH_3), 3.39 (q, 8H, ^3J = 6.0 Hz, CH_2–N), 7.42 (s, 4H, CH arom); ^{13}C NMR (CD_3OD, δ ppm): 21.5 (N–CH_2–CH_2–CH_2–N), 39.2 (CH_3–N), 43.5 (CH_2–NH), 48.0 (CH_2–N–CH_3), 127.9 (CH arom), 137.9 (C arom), 160.0 (N–C–N). Calc. for $C_{16}H_{22}N_4 \cdot 2/3H_2O$: C = 68.05%, H = 8.33%, N = 19.84%. Found: C = 68.05%, H = 8.22%, N = 19.95%.

Synthesis of 14. A mixture of benzonitrile (7.99 g, 77.5 mmol), *N*-methyl-1,2-ethylenediamine (5.74 g, 77.5 mmol) and P_2S_5 (100 mg) was stirred and heated under argon for 4 h at 160 °C before it was evaporated to dryness. The mixture was treated with dilute aqueous HCl solution until pH 5 was reached. The solution was then washed twice with CH_2Cl_2 and the aqueous phase was recovered and evaporated to dryness. The brownish oil thus obtained was taken up in EtOH (50 ml) and heated under reflux in the presence of charcoal during 2 h. Filtration followed by evaporation and drying afforded the compound **14** in 47% yield as a very hygroscopic pale yellow solid. Mp ~160 °C (decomposition at 210 °C). ^{1}H NMR (D_2O + *t*BuOH, δ ppm): 3.12 (s, 3H, CH_3–N), 4.06 (m, 4H, CH_2–N), 7.6 (m, 4H, CH arom, α and β), 7.69–7.78 (m, 1H, CH arom, γ); ^{13}C NMR (D_2O + *t*BuOH, δ ppm): 34.5 (CH_3–N), 43.2–53.0 (CH_2–N), 123.0 (C arom), 129.1, 129.9 (CH arom, α and β), 134.1 (CH arom, γ), 167.3 (N–C–N). Calc. for $C_{10}H_{13}ClN_2 \cdot 1/4H_2O$: C = 59.70%, H = 6.76%, N = 13.92%. Found: C = 59.56%, H = 6.90%, N = 14.01%.

Synthesis of 15. To a solution of **14** (420 mg, 2.14 mmol) in distilled water (12 ml) a solution of sodium tetraphenylborate (804 mg, 2.35 mmol) in CH_2Cl_2 (25 ml) was added and stirred vigorously for 3 min. The aqueous phase was extracted with 2 × 20 ml of CH_2Cl_2 and the combined organic layers were washed with 2 × 15 ml of distilled water, dried over $MgSO_4$, filtered, evaporated and vacuum dried for 1 day. Compound **25** was obtained as a white solid in 86% yield and was recrystallised from a CH_3Cl–EtOH (13 : 1) mixture, to afford crystals suitable for X-ray studies. Mp 160 °C (decomposition at 150 °C). ^{1}H NMR ($CDCl_3$–CD_3OD (2 : 1), δ ppm): 2.65 (s, 3H, CH_3–N), 3.12 (m, 4H, CH_2–N), 6.83 (t, 4H, ^3J = 7.2 Hz, CH arom, γ (BPh_4)), 6.97 (t, 8H, ^3J = 7.2 Hz, CH arom, β (BPh_4)), 7.2–7.4 (m, 10H, CH arom, α and CH arom, α (BPh_4)), 7.49 (t, 2H, ^3J = 7.5 Hz, CH arom, β), 7.63 (t, 1H, ^3J = 7.5 Hz, CH arom, γ); ^{13}C NMR ($CDCl_3$–CD_3OD (2 : 1), δ ppm: 34.3 (CH_3–N), 42.9, 54.3 (CH_2–N), 122.0, 125.8, 136.1 (CH arom, BPh_4), 128.4, 129.7 (CH arom, α and β), 127.7 (C arom), 134.0 (CH arom, γ), 163.2, 163.8, 164.5, 165.1, 166.2 (C arom, BPh_4 and N–C–N). Calc. for $C_{34}H_{33}BN_2$: C = 85.00%, H = 6.92%, N = 5.83%; Found: C = 84.84%, H = 6.96%, N = 5.90%.

Synthesis of 16. To a solution of **14** (318 mg, 1.82 mmol) in of distilled water (5 ml) an aqueous solution (5 ml) of ammonium hexafluorophosphate (415 mg, 2.55 mmol) was added and the mixture stirred for 15 min. The white solid thus formed was filtered off, washed with water (3 × 3 ml) and dried under vacuum for 1 day affording the compound **16** as a white solid in 82% yield. For X-ray diffraction analysis, suitable colourless crystals were obtained upon slow diffusion of acetone into a water–acetone mixture containing **16**. Mp 149 °C (decomposition at 250 °C). ^{1}H NMR (($CD_3)_2O$, δ ppm): 3.28 (s, 3H, CH_3–N), 4.26 (m, 4H, CH_2–N), 7.6–7.8 (m, 5H, CH arom), 9.20 (NH); ^{13}C NMR (($CD_3)_2O$, δ ppm): 33.9 (CH_3–N), 43.0, 53.7 (CH_2–N), 122.9 (C arom), 128.7, 129.4 (CH arom, α and β), 133.5 (CH arom, γ), 167.0 (N–C–N). Calc. for $C_{10}H_{13}F_6N_2P$: C = 39.23%, H = 4.28%, N = 9.15%. Found: C = 39.13%, H = 4.04%, N = 9.19%.

Synthesis of 17. A mixture of benzonitrile (5.17 g, 50.1 mmol), *N*-methyl-1,3-propanediamine (4.42 g, 50.1 mmol) and P_2S_5 (30 mg) was stirred and heated under argon for 4 h at 160 °C before it was evaporated to dryness. The mixture was treated with dilute aqueous HCl solution until pH 5 was reached. The solution was then washed twice with CH_2Cl_2 and the aqueous phase was recovered and evaporated to dryness. The brownish oil thus obtained was taken up in EtOH (50 ml) and heated under reflux in the presence of charcoal during 2 h. After filtration and evaporation, **17** was obtained in 70% yield as a colourless oil, dried under 60 °C. Mp 160 °C (decomposition at 100 °C). ^{1}H NMR (D_2O + *t*BuOH, δ ppm): 2.17 (q, 2H, ^3J = 5.7 Hz, $CH_2(CH_2$–$N)_2$), 3.04 (s, 3H, CH_3–N), 3.51 (t, 2H, ^3J = 5.7 Hz, CH_2–N–CH_3), 3.63 (t, 2H, ^3J = 5.7 Hz, CH_2–NH), 7.60 (m, 5H, CH arom); ^{13}C NMR (D_2O + *t*BuOH, δ ppm): 19.4 (N–CH_2–CH_2–CH_2–N), 39.3, 41.1 (CH_2–N), 48.6 (CH_3–N), 128.4, 129.8 (CH arom, α and β), 129.4 (C arom), 132.8 (CH arom, γ), 162.4 (N–C–N). Calc. for $C_{11}H_{15}ClN_2$: C = 62.70%, H = 7.18%, N = 13.30%. Found: *C*: 62.17%, H 7.07%, N 12.96%.

Synthesis of 18. Compound **18** is a by-product isolated by chromatography during the synthesis of **24**. Recrystallisation from a mixture of acetonitrile–ethyl acetate afforded **18** as colourless crystals, which were analysed by X-ray diffraction on a single crystal. Mp 177–178 °C (decomposition at 350 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 2.18 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 3.10 (s, 3H, CH_3–N), 3.64 (m, 4H, CH_2–NH), 7.48–7.72 (m, 5H, CH arom); 9.24 (NH); ^{13}C NMR ($CDCl_3$, δ ppm): 19.2 (N–CH_2–CH_2–CH_2–N), 38.8, 48.8 (CH_2–N), 41.5 (CH_3–N), 128.9, 129.3 (CH arom, α and β), 127.8 (C arom), 132.6 (CH arom, γ), 161.8 (N–C–N). Calc. for $C_{11}H_{15}IN_2$ C = 43.73%, H = 5.00%, N = 9.27%. Found: C = 43.72% H = 5.06%, N = 9.28%.

Synthesis of 19. To a solution of **18** (538 mg, 1.78 mmol) in distilled water (12 ml), a solution of sodium tetraphenylborate

(670 mg, 1.96 mmol) in CH_2Cl_2 (25 ml) was added and stirred vigorously for 3 min. The aqueous phase was extracted with 2 × 20 ml of CH_2Cl_2 and the combined organic layers were washed with 2 × 15 ml of distilled water, dried over $MgSO_4$, filtered and evaporated and vacuum dried for 1 day. Compound **19** was obtained as a white solid in 96% yield. Rod-shape colourless crystals of **19** were obtained upon recrystallisation from a CH_3Cl–EtOH mixture. Mp 204–206 °C (decomposition at 220 °C). ^{1}H NMR (DMSO, δ ppm): 2.02 (q, 2H, ^3J = 5.9 Hz, $CH_2(CH_2–N)_2$), 2.89 (s, 3H, CH_3–N), 3.36–3.49 (2t, 4H, ^3J = 5.9 Hz, CH_2–N), 6.8–7.6 (m, 25H, CH arom); ^{13}C NMR (DMSO, δ ppm): 19.0 (N–CH_2–CH_2–CH_2–N), 38.9, 48.1 (CH_2–N), 41.0 (CH_3–N), 122.0, 125.8, 136.0 (C arom BPh_4); 128.6, 129.5 (C arom α and β); 129.4 (C arom); 132.4 (C arom γ); 161.3 (N–C–N); 162.9–163.5–164.2–164.8 (C arom. BPh_4). Calc. for $C_{35}H_{35}BN_2$: C = 85.01%, H = 7.13%, N = 5.67%. Found: C = 85.31%, H = 6.88%, N = 5.52%.

Synthesis of 20. To a solution of **18** (615 mg, 2.03 mmol) in distilled water (5 ml) an aqueous solution of ammonium hexafluorophosphate (663 mg, 4.07 mmol) was added and stirred for 15 min. The resulting white solid was filtered off, washed with 3 × 3 ml of water, then dried under vacuum for 1 day affording **20** as a white solid with a yield of 87%. Colourless crystals of **20** suitable for X-ray diffraction analysis, can be obtained by recrystallisation in water. Mp 138–141 °C (decomposition at 260 °C). ^{1}H NMR ($(CD_3)_2O$, δ ppm): 2.32 (q, 2H, ^3J = 5.9 Hz, $CH_2(CH_2–N)_2$); 3.17 (s, 3H, CH_3–N); 3.68–3.78 (2t, 4H, ^3J = 5.9 Hz, CH_2–NH) 7.61–7.75 (m, 5H, CH arom); 8.87 (NH); ^{13}C NMR ($(CD_3)_2O$, δ ppm): 18.8 (N–CH_2–CH_2–CH_2–N); 39.1 48.1 (CH_2–N); 40.6 (CH_3–N); 128.0 129.2 (CH arom α et β); 129.3 (C arom); 132.2 (CH arom γ); 162.0 (N–C–N). Calc. for $C_{11}H_{15}F_6N_2P$: C = 41.26%, H = 4.72%, N = 8.75%. Found: C = 40.82%, H = 4.62%, N = 8.80%.

Synthesis of 21. A solution of **2** (1.00 g, 5.74 mmol) in distilled water (3 ml) was cooled to 0 °C and then an aqueous solution (4 ml) containing trifluoromethanesulfonic acid (861 mg, 5.74 mmol) was added. After stirring for 1 h, the solvent was removed affording the compound **21** as a white solid with in 99% yield. Colourless crystals were be obtained upon diffusing diethyl ether vapours into an EtOH solution of **21** and studied by X-ray diffraction on single crystal. Mp 76 °C (decomposition at 350 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 2.13 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2–N)_2$), 3.06 (s, 3H, CH_3–N), 3.51–3.60 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.6 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 19.1 (N–CH_2–CH_2–CH_2–N), 39.0 48.4 (CH_2–N), 41.2 (CH_3–N), 128.1, 129.3 (CH arom α and β), 128.0 (C arom, 132.5 (CH arom γ), 162.2 (N–C–N). The signal for the C atom of the triflate anion could not be observed probably due to a too long relaxation time. Calc. for $C_{12}H_{15}F_3N_2O_3S$: C = 44.44%, H = 4.66%, N = 8.64%. Found: C = 44.00%, H = 4.70%, N = 8.40%.

Synthesis of 22. To a solution of **18** (684 mg, 2.26 mmol) in distilled water (5 ml) an aqueous solution (3 ml) of lithium bis(trifluoromethane)sulfonimide (670 mg, 2.26 mmol) was added. After stirring for 1 h, the mixture was decanted and the aqueous phase was removed. The colourless liquid was washed with 2 × 3 ml of distilled water and dried under vacuum at 50 °C for 30 h, affording the compound **22** in 91% yield as a colourless liquid which decomposes at 360 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 2.17 (q, 2H, ^3J = 5.8 Hz, $CH_2(CH_2–N)_2$), 3.06 (s, 3H, CH_3–N), 3.54–3.62 (2t, 4H, ^3J = 5.8 Hz, CH_2–N), 7.4–7.6 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 18.9 (N–CH_2–CH_2–CH_2–N), 39.2, 48.3 (CH_2–N), 41.3 (**C**H_3–N), 119.7 (q, CF_3, ^1J = 319.3 Hz), 127.8, 129.5 (CH arom α and β), 128.0 (C arom), 132.7 (**C**H arom γ), 161.4 (N–C–N). The signal for the C atom of the anion could not be observed probably due to a too long relaxation time. Calc. for $C_{13}H_{15}F_6N_3O_4S_2$: C = 34.29%, H = 3.32%, N = 9.23%. Found: C = 34.58%, H = 3.44%, N = 9.37%.

Synthesis of 23. 1,4-Dicyanobenzene (3.00 g, 23.4 mmol), *N*-methyl-1,3-propanediamine (4.13 g, 46.8 mmol) and P_2S_5 (10 mg) were mixed and the mixture, under Ar atmosphere, was stirred and heated to 120 °C during 4 h. After cooling, the residue was crushed and treated with an aqueous 1 M HCl solution. After stirring for 30 min, the precipitate was filtered and the volume of the mother-liquor reduced. Compound **23** was obtained in 66% yield upon recrystallisation from distilled water. Crystals thus obtained were of sufficient quality for structural studies by X-ray diffraction on single crystal. Mp ~250 °C (decomposition). ^{1}H NMR (D_2O + *t*BuOH, δ ppm): 2.20 (q, 4H, ^3J = 5.8 Hz, $CH_2(CH_2–N)_2$), 3.06 (s, 6H, CH_3), 3.54 (t, 4H, ^3J = 5.8 Hz, CH_2–N–CH_3), 3.66 (t, 4H, ^3J = 5.8 Hz, CH_2–NH), 7.77 (s, 4H, CH arom); ^{13}C NMR (D_2O + *t*BuOH, δ ppm): 19.2 (N–CH_2–CH_2–CH_2–N), 39.3 (CH_2–NH), 41.1 (CH_3–N), 48.7 (CH_2–N–CH_3), 129.5 (CH arom, 132.8 (C arom), 161.2 (N–C–N). Calc. for $C_{16}H_{24}N_4Cl_2 \cdot 4.7H_2O$: C = 44.90%, H = 7.87%, N = 13.09%. Found C = 44.81%, H = 7.82%, N = 13.43%.

Synthesis of 24. A mixture of **1** (600 mg, 3.74 mmol), 1-iodopropane (1.27 g, 7.49 mmol) and K_2CO_3 (517 mg, 3.74 mmol) in DMF (30 ml) was stirred at RT overnight. The solvent was removed and the residue was purified by chromatography (Al_2O_3, CH_2Cl_2–MeOH (97 : 3 → 96 : 4)). Compound **24**, a colourless and very hygroscopic viscous liquid, was dried at 50 °C under vacuum for 12 h was obtained in 83% yield. The latter decomposed at 280 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.80 (t, 3H, ^3J = 7.4 Hz, CH_3 propyl), 1.61 (sex, 2H, ^3J = 7.4 Hz, CH_2–CH_3), 2.98 (s, 3H, CH_3–N), 3.20 (t, 2H, ^3J = 7.4 Hz, C_2H_5–CH_2–N), 4.25 (m, 4H, CH_2–N) 7.5–7.7 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 11.1 (CH_3 propyl), 20.5 (CH_2–CH_3), 35.1 (CH_3–N), 48.2, 49.7, 50.9 (CH_2–N), 122.0 (C arom), 128.8, 129.8 (CH arom, α and β), 132.7 (CH arom, γ), 166.4 (N–C–N). Calc. for $C_{13}H_{19}N_2I$: C = 47.29%, H = 5.80%, N = 8.48%. Found: C = 47.05%, H = 6.18%, N = 8.06%.

Synthesis of 25. To a solution of **24** (212 mg, 0.64 mmol) in distilled water (12 ml) a solution of sodium tetraphenylborate (242 mg, 0.71 mmol) in CH_2Cl_2 (25 ml) was added and stirred vigorously for 3 min. The aqueous phase was extracted with 2 × 20 ml of CH_2Cl_2 and the combined organic layers were

washed with 2 × 15 ml of distilled water, dried over $MgSO_4$, filtered, evaporated and vacuum dried for 1 day. Compound **24** was obtained as a white solid in 74% yield which was recrystallised from a EtOH–CH_2Cl_2 mixture, affording suitable crystals for X-Ray diffraction. Mp 162 °C (decomposition at 160 °C). ^{1}H NMR (CD_2Cl_2, δ ppm): 0.76 (t, 3H, ^3J = 7.5 Hz, CH_3 propyl), 1.44 (sex, 2H, ^3J = 7.5 Hz, 2H, CH_2–CH_3), 2.61 (s, 3H, CH_3–N), 2.95 (t, 2H, ^3J = 7.5 Hz, C_2H_5–CH_2–N), 3.22 (m, 4H, CH_2–N), 6.89 (t, 4H, ^3J = 7.1 Hz, CH arom, γ (BPh_4)), 7.04 (t, 8H, ^3J = 7.2 Hz, CH arom, β (BPh_4)), 7.23 (d, 2H, ^3J = 7.2 Hz, CH arom, α), 7.38 (br, 8H, CH arom, α (BPh_4)), 7.63 (t, 2H, ^3J = 7.2 Hz, CH arom, β), 7.71 (t, 1H, ^3J = 7.2 Hz, CH arom, γ); ^{13}C NMR ($CDCl_3$, δ ppm): 12.4 (CH_3 propyl), 22.4 (CH_2–CH_3), 36.3 (CH_3–N), 49.2, 51.2, 51.7 (CH_2–N), 123.0 (C arom), 123.7, 127.6, 137.8 (CH arom BPh_4), 129.6, 132.1 (CH arom, α and β), 135.3 (CH arom, γ), 164.9, 165.6, 166.2, 166.9, 168.4 (C arom, BPh_4 and N–C–N). Calc. for $C_{37}H_{39}BN_2$: C = 85.05%, H = 7.52%, N = 5.39%. Found: C = 85.45%, H = 7.53%, N = 5.02%.

Synthesis of 26. To a solution of **24** (301 mg, 0.91 mmol) in of distilled water (5 ml) an aqueous solution (5 ml) of ammonium hexafluorophosphate (208 mg, 1.28 mmol) was added and the mixture stirred for 15 min. The white solid thus formed was filtered off, washed with water (3 × 3 ml) and dried under vacuum for 1 day affording the compound **16** as a white solid in 82% yield. For X-ray diffraction analysis, suitable colourless crystals were obtained upon slow diffusion of acetone into a water–acetone mixture containing **16**. Mp 62–64 °C (decomposition at 300 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.80 (t, 3H, ^3J = 7.4 Hz, CH_3 propyl), 1.60 (sex, 2H, ^3J = 7.4 Hz, CH_2–CH_3), 2.92 (s, 3H, CH_3–N), 3.15 (t, 2H, ^3J = 7.4 Hz, C_2H_5–CH_2–N), 4.11 (m, 4H, CH_2–N), 7.5–7.7 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 10.8 (CH_3 propyl), 20.3 (CH_2–CH_3), 34.3 (CH_3–N), 47.6, 49.4, 50.1 (CH_2–N), 122.1 (C arom), 128.1, 129.9 (CH arom, α and β), 132.7 (CH arom, γ), 166.2 (N–C–N). Calc. for $C_{13}H_{19}F_6N_2P$: C = 44.83%, H = 5.50%, N = 8.04%. Found: C = 44.69%, H = 5.22%, N = 8.12%.

Synthesis of 27. The same procedure described for **24** was used, using **14** (600 mg, 3.75 mmol) and 1-bromohexane (1.24 g, 7.40 mmol), as well as K_2CO_3 (501 mg, 3.75 mmol). **27** was obtained as a colourless hygroscopic viscous liquid with a yield of 51%. Mp not determined, liquid at room temperature (decomposition at 120 °C). ^{1}H NMR ($(CD_3)_2O$, δ ppm): 0.80 (t, 3H, ^3J = 7.2 Hz, CH_3 hexyl), 1.0–1.4 (m, 6H, $(CH_2)_3CH_3$), 1.55 (m, 2H, CH_2–CH_2N), 3.00 (s, 3H, CH_3–N), 3.26 (t, 2H, ^3J = 7.5 Hz, C_5H_{11}–CH_2–N), 4.27 (m, 4H, CH_2–N), 7.4–7.7 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 hexyl), 22.6, 26.2, 27.2, 31.2 (CH_3–$(CH_2)_4$–CH_2N), 35.1 (CH_3–N), 48.3, 48.5 (CH_2–N), 51.0 (C_5H_{11}–CH_2–N), 122.3 (C arom), 128.7 129.9 (CH arom α and β), 132.8 (CH arom γ), 166.7 (N–C–N). Calc. for $C_{16}H_{25}BrN_2 \cdot 1/2H_2O$: C = 57.49%, H = 7.84%, N = 8.38%. Found: C = 57.50%, H = 8.45%, N = 8.44%.

Synthesis of 28. The same procedure described for **25** was used, starting from **27** (55 mg, 0.169 mmol) and sodium tetraphenylborate (64 mg, 0.186 mmol). After recrystallisation in EtOH, **28** can be obtained either as colourless plate shaped crystals with a yield of 48%, or as an oil which solidifies after several days. Mp 114 °C (decomposition at 100 °C). ^{1}H NMR (($CDCl_3$, δ ppm): 0.84 (t, 3H, ^3J = 7.2 Hz, CH_3 hexyl), 1.0–1.4 (m, 8H, $(CH_2)_3$–CH_3), 2.48 (s, 3H, CH_3–N), 2.9 (m, 6H, CH_2–N), 6.90 (t, 4H, ^3J = 7.1 Hz, CH arom γ (BPh_4)), 7.06 (t, 8H, ^3J = 7.2 Hz, CH arom β (BPh_4)), 7.18 (d, 2H, ^3J = 7.2 Hz, CH arom α), 7.49 (br, 8H, CH arom α (BPh_4)), 7.61 (t, 2H, ^3J = 7.2 Hz, CH arom β), 7.69 (t, 1H, ^3J = 7.2 Hz, CH arom γ); ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 hexyl), 22.6, 26.1, 27.3, 31.2 (CH_3–$(CH_2)_4$–CH_2N), 34.7 (CH_3–N), 47.9, 48.0 (CH_2–N), 51.3 (C_5H_{11}–CH_2–N), 122.1, 125.9, 136.4 (CH arom BPh_4), 128.1, 130.3 (CH arom α and β), 128.9 (C arom), 133.3 (CH arom γ). Calc. for $C_{40}H_{45}BN_2$: C = 85.09%, H = 8.03%, N = 4.96%. Found: C = 85.55%, H = 8.05%, N = 4.89%.

Synthesis of 29. The same procedure described for **26** was used, starting from **27** (120 mg, 0.369 mmol) and ammonium hexafluorophosphate (66 mg, 0.406 mmol). **29** was obtained as a viscous colourless liquid, that decomposes at 250 °C) with a 71% yield. ^{1}H NMR (($CDCl_3$, δ ppm): 0.80 (t, 3H, ^3J = 7.2 Hz, CH_3 hexyl), 1.1–1.3 (m, 6H, $(CH_2)_3$–CH_3), 1.54 (m, 2H, CH_2–CH_2N), 2.93 (s, 3H, CH_3–N), 3.18 (t, 2H, ^3J = 7.5 Hz, C_5H_{11}–CH_2–N), 4.11 (m, 4H, CH_2–N), 7.4–7.7 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 hexyl), 22.5, 26.1, 27.1, 31.2 (CH_3–$(CH_2)_4$–CH_2N), 34.5 (CH_3–N), 47.9, 48.0 (CH_2–N);, 50.3 (C_5H_{11}–CH_2–N), 122.3 (C arom), 128.3, 130.0 (CH arom α and β), 132.9 (CH arom γ), 166.4 (N–C–N). Calc. for $C_{13}H_{19}F_6N_2P$: C = 44.83%, H = 5.50%, N = 8.04%. Found: C = 44.69%, H = 5.22%, N = 8.12%.

Synthesis of 30. The same procedure described for **27** was used, starting from **14** (619 mg, 3.87 mmol) and 1-bromo-dodecane (1.93 g, 7.73 mmol) as well as K_2CO_3 (534 mg, 3.87 mmol). **30** was obtained as a colourless hygroscopic viscous liquid with a yield of 60%. Mp not determined, liquid at room temperature (decomposition at 240 °C). ^{1}H NMR (($CDCl_3$, δ ppm): 0.83 (t, 3H, ^3J = 7.2 Hz, CH_3 dodecyl), 1.0–1.3 (m, 18H, $(CH_2)_9$–CH_3), 1.53 (m, 2H, CH_2–CH_2N), 2.99 (s, 3H, CH_3–N), 3.24 (t, 2H, ^3J = 7.8 Hz, $C_{11}H_{23}$–CH_2–N), 4.25 (m, 4H, CH_2–N), 7.4–7.7 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 dodecyl), 22.6, 26.3, 27.1, 28.8, 29.1, 29.3, 29.3, 29.4, 29.5, 31.8 (CH_2 n-dodecyl), 34.9 (CH_3–N), 48.1, 48.3, 50.9 (CH_2–N), 122.1 (C arom), 128.4, 128.8 (CH arom α and β), 132.7 (CH arom γ), 166.4 (N–C–N).

Synthesis of 31. The same procedure described for **25** was used, starting from **30** (196 mg, 0.339 mmol) and sodium tetraphenylborate (139 mg, 0.407 mmol). After recrystallisation in EtOH, **31** can be obtained either as colourless prismatic crystals with a yield of 60%, or as an oil which solidifies after several days. Mp 69 °C (decomposition at 220 °C). ^{1}H NMR (($CDCl_3$, δ ppm): 0.88 (t, 3H, ^3J = 6.6 Hz, CH_3 dodecyl), 1.0–1.3 (m, 20H, $(CH_2)_{10}$–CH_3), 2.43 (s, 3H, CH_3–N), 2.8 (m, 6H, CH_2–N), 6.90 (t, 4H, ^3J = 7.1 Hz, CH arom γ (BPh_4)), 7.05 (t, 8H, ^3J = 7.2 Hz, CH arom β (BPh_4)), 7.15 (d, 2H, ^3J = 7.2 Hz, CH arom α), 7.49 (br, 8H, CH arom α (BPh_4)), 7.60 (t, 2H, ^3J = 7.2 Hz, CH arom β), 7.69 (t, 1H, ^3J = 7.2 Hz, CH arom γ); ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 dodecyl),

22.7, 26.3, 27.1, 28.9, 29.3, 29.5, 29.6, 31.9 (CH_2 dodecyl), 34.6 (CH_3–N), 47.3, 47.6, 49.7 (CH_2–N), 121.8, 125.7, 136.1 (CH arom BPh_4), 125.7, 130.2 (CH arom α and β), 127.7 (C arom), 133.2 (CH arom γ). Calc. for $C_{46}H_{57}BN_2$: C = 85.16%, H = 8.86%, N = 4.32%. Found: C = 85.42%, H = 9.14%, N = 4.12%.

Synthesis of 32. The same procedure described for **26** was used, starting from **30** (215 mg, 0.525 mmol) and ammonium hexafluorophosphate (120 mg, 0.735 mmol). **32** was obtained as a viscous colourless liquid, that decomposes at 50 °C, with a 79% yield. ^{1}H NMR ($CDCl_3$, δ ppm): 0.86 (t, 3H, ^3J = 7.2 Hz, CH_3 dodecyl), 1.0–1.3 (m, 18H, $(CH_2)_9$–CH_3), 1.54 (m, 2H, CH_2–CH_2N), 2.93 (s, 3H, CH_3–N), 3.18 (t, 2H, ^3J = 7.5 Hz, $C_{11}H_{23}$–CH_2–N), 4.10 (m, 4H, CH_2–N), 7.5–7.8 (m, 5H, CH arom); ^{3}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 dodecyl), 22.7, 26.3, 27.0, 28.9, 29.3, 29.5, 29.6, 29.6, 31.9 (CH_2 n-dodecyl), 34.3 (CH_3–N), 47.7, 47.8, 50.1 (CH_2–N), 122.1 (C arom), 128.1, 129.8 (CH arom α and β), 132.7 (CH arom γ), 166.2 (N–C–N). Calc. for $C_{22}H_{37}F_6N_2P$: C = 55.69%, H = 7.86%, N = 5.90%. Found: C = 56.93%, H = 8.30%, N = 5.32%.

Synthesis of 33. A mixture of **17** (5.00 g, 27.7 mmol) and 1-iodopropane (4.88 g, 27.7 mmol) in DMF (30 ml) was stirred for 3 h at RT. The volatiles were removed by evaporation and the residue was purified by chromatography (Al_2O_3, CH_2Cl_2–MeOH (98 : 2)). The yellow oil thus obtained was taken up in MeOH (40 ml) and after addition of charcoal, the mixture was heated under reflux overnight. After filtration and evaporation, the resulting colourless oil was dried under vacuum affording **33** in 55% yield as a rather hygroscopic yellowish powder. Mp 88 °C (decomposition at 200 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.55 (t, 3H, ^3J = 7.4 Hz, CH_3 propyl), 1.45 (m, 2H, CH_2–CH_3), 2.26 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.78 (s, 3H, CH_3–N), 2.95 (t, 2H, ^3J = 7.5 Hz, C_2H_5–CH_2–N), 3.68 3.70 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.25–7.61 (m, 5H, CH arom); ^{13}C NMR (D_2O + *t*BuOH, δ ppm): 10.9 (CH_3 propyl), 19.4 (N–CH_2–CH_2–CH_2–N), 21.0 (CH_2–CH_3), 42.7 (CH_3–N), 45.4, 48.4 (CH_2–N), 56.0 (C_2H_5–CH_2–N), 127.7, 129.7 (CH arom, α and β), 128.1 (C arom), 131.5 (CH arom, γ), 162.1 (N–C–N). Calc. for $C_{14}H_{21}N_2I$: C = 48.85%, H = 6.15%, N = 8.14%. Found: C = 48.21%, H = 6.14%, N = 8.14%.

Synthesis of 34. For preparing **34**, the procedure described for the synthesis of **19** was employed using **33** (0.935 g, 2.72 mmol) and sodium tetraphenylborate (1.02 g, 2.99 mmol). After recrystallisation in ethanol, **34** was obtained in 85% yield as rod shaped colourless crystals suitable for X-ray diffraction studies. Mp 119–120 °C (decomposition at 200 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.61 (t, 3H, ^3J = 7.4 Hz, CH_3 propyl), 1.26 (m, 2H, CH_2–CH_3), 1.39 (q, 2H, ^3J = 5.9 Hz, $CH_2(CH_2$–$N)_2$), 2.27 (s, 3H, CH_3–N), 2.60 (m, 6H, CH_2–N), 6.8–7.6 (m, 25H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 10.7 (CH_3 propyl), 18.6 (N–CH_2–CH_2–CH_2–N), 21.0 (CH_2–CH_3), 41.7 (CH_3–N); 44.8, 47.7 (CH_2–N), 55.5 (C_2H_5–CH_2–N), 121.9, 125.6, 136.2 (CH arom BPh_4), 126.6, 130.2 (CH arom, α and β), 126.6 (C arom, 132.0 (CH arom, γ), 161.5 (N–C–N), 163.1, 163.7, 164.4, 165.0 (C arom BPh_4). Calc. for $C_{38}H_{41}BN_2$: C 85.06%, H 7.70%, N 5.22%. Found: C 85.26%, H 7.71%, N 5.17%.

Synthesis of 35. For the synthesis of **35**, the procedure described for **20** was followed using **33** (1.31 g, 3.82 mmol) and ammonium hexafluorophosphate (1.24 g, 7.63 mmol). Compound **35** was obtained as a white powder in 97% yield and was recrystallised either from water or a water–acetone mixture. Mp 93 °C (decomposition at 300 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.70 (t, 3H, ^3J = 7.4 Hz, CH_3 propyl), 1.54 (m, 2H, CH_2–CH_3), 2.29 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.87 (s, 3H, CH_3–N), 3.05 (t, 2H, ^3J = 7.7 Hz, C_2H_5–CH_2–N), 3.64 (2t, 4H, ^3J = 6.0 Hz, CH_2–N) 7.4–7.6 (m, 5H, CH arom, ^3J = 50 Hz, ^4J = 6.0 Hz, ^5J = 1.4 Hz); ^{13}C NMR ($CDCl_3$, δ ppm): 10.8 (CH_3 propyl), 18.9 (N–CH_2–CH_2–CH_2–N), 20.9 (CH_2–CH_3), 42.0 (CH_3–N), 45.1 48.0 (CH_2–N), 55.8 (C_2H_5–CH_2–N), 127.1, 130.0 (CH arom, α and β), 128.1 (C arom); 131.6 (CH arom, γ), 162.3 (N–C–N). Calc. for $C_{14}H_{21}F_6N_2P$: C = 46.41%, H = 5.84%, N = 7.73%. Found: C = 45.82%, H = 5.86%, N = 7.77%.

Synthesis of 36. 33 (1.20 g, 3.49 mmol) was dissolved in 7 ml of distilled water and 8 ml of an aqueous solution containing lithium triflate (598 mg, 3.83 mmol) was added. After stirring for 1 h, the mixture was extracted with 3 × 15 ml of CH_2Cl_2. The combined organic layers was washed with 8 ml of water and dried over $MgSO_4$, filtered and evaporated to dryness. The resulting colourless oil was further dried under vacuum at 40 °C for 30 h. Compound **36** was obtained in 93% yield as a colourless liquid which decomposes at 220 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.68 (t, 3H, ^3J = 7.4 Hz, CH_3 propyl), 1.54 (m, 2H, CH_2–CH_3), 2.31 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.87 (s, 3H, CH_3–N), 3.05 (t, 2H, ^3J = 7.8 Hz, C_2H_5–CH_2–N), 3.73 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.55 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 10.8 (CH_3 propyl), 19.3 (N–CH_2–CH_2–CH_2–N), 21.0 (CH_2–CH_3), 42.3 (CH_3–N), 45.3, 48.3 (CH_2–N), 55.9 (C_2H_5–CH_2–N), 127.5, 129.9 (CH arom, α and β), 128.2 (C arom, 131.6 (CH arom, γ), 162.4 (N–C–N). The signal for the C atom of the triflate anion could not be observed probably due to a too long relaxation time. Calc. for $C_{15}H_{21}F_3N_2O_3S$: C = 49.17%, H = 5.78%, N = 7.65%. Found: C = 48.66%, H = 6.26%, N = 7.69%.

Synthesis of 37. The same procedure described for **22** was followed, using **33** (687 mg, 2.87 mmol) and lithium bis-(trifluoromethane)sulfonimide (866 mg, 2.87 mmol). Compound **37** was obtained in 98% yield as a colourless liquid which decomposes at 210 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.66 (t, 3H, ^3J = 7.2 Hz, CH_3 propyl), 1.51 (m, 2H, CH_2–CH_3), 2.23 (q, 2H, ^3J = 6.2 Hz, $CH_2(CH_2$–$N)_2$), 2.81 (s, 3H, CH_3–N), 3.01 (t, 2H, ^3J = 7.8 Hz, C_2H_5–CH_2–N), 3.59 (2t, 4H, ^3J = 6.2 Hz, CH_2–N), 7.3–7.6 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 10.6 (CH_3 propyl), 18.8 (N–CH_2–CH_2–CH_2–N), 20.8 (CH_2–CH_3), 41.9 (CH_3–N), 45.2, 48.0 (CH_2–N), 55.8 (C_2H_5–CH_2–N), 119.9 (q, CF_3, ^1J = 321.6 Hz), 127.0, 129.9 (CH arom, α and β), 128.0 (C arom); 131.7 (CH arom, γ), 162.3 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion. Calc. for $C_{16}H_{21}F_6N_3O_4S_2$: C = 38.63%, H = 4.25%, N = 8.45%. Found: C = 38.70%, H = 4.26%, N = 8.45%.

Synthesis of 38. **2** (520 mg, 2.99 mmol), 1-bromohexane (987 mg, 5.98 mmol) and K_2CO_3 (412 mg, 2.99 mmol) were dissolved in 30 ml DMF and stirred overnight at RT. The solvents were then evaporated to dryness and the residue was purified by chromatography (Al_2O_3, CH_2Cl_2–MeOH (97 : 3 → 96 : 4)). The corresponding phases were evaporated affording a colourless oil which was dried at 50 °C under vacuum for 12 h. **38** was obtained as a very hygroscopic viscous liquid that decomposes at 150 °C, with a yield of 63%. ^{1}H NMR ($CDCl_3$, δ ppm): 0.66 (t, 3H, ^3J = 7.2 Hz, CH_3 hexyl), 0.8–1.3 (m, 6H, $(CH_2)_3$–CH_3), 1.42 (m, 2H, CH_2–CH_2N), 2.27 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.83 (s, 3H, CH_3–N), 3.00 (t, 2H, ^3J = 7.9 Hz, C_5H_{11}–CH_2–N), 3.73 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.6 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 13.8 (CH_3 hexyl), 19.4 (N–CH_2–CH_2–CH_2–N), 22.2, 25.8, 27.5, 30.8 (CH_3–$(CH_2)_4$–CH_2N), 42.4 (CH_3–N), 45.5, 48.5 (CH_2–N), 54.4 (C_5H_{11}–CH_2–N), 127.4, 129.7 (CH arom α and β), 128.2 (C arom), 131.5 (CH arom γ), 162.1 (N–C–N). Calc. for $C_{17}H_{27}BrN_2 \cdot 2/3H_2O$: C = 58.12%, H = 8.13%, N = 7.97%. Found: C = 58.13%, H = 8.15%, N = 8.00%.

Synthesis of 39. The same procedure described for **19** was used, starting from **38** (1.00 g, 2.95 mmol) and sodium tetraphenylborate (1.11 g, 3.24 mmol). After recrystallisation in a mixture of EtOH–$CHCl_3$, colourless crystals of **39** were obtained in 91% yield. Mp 94–95 °C (decomposition at 250 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.83 (t, 3H, ^3J = 7.2 Hz, CH_3 hexyl), 0.9–1.4 (m, 8H, $(CH_2)_4$–CH_3), 2.24 (s, 3H, CH_3–N), 2.60 (m, 6H, CH_2–N) 6.8–7.6 (m, 25H, CH arom), ^{13}C NMR ($CDCl_3$, δ ppm): 13.9 (CH_3 hexyl), 18.6 (N–CH_2–CH_2–CH_2–N), 22.3, 25.7, 27.5, 30.9 (CH_3–$(CH_2)_4$–CH_2N), 41.7 (CH_3–N), 44.8, 47.6 (CH_2–N), 54.0 (C_5H_{11}–CH_2–N), 121.9, 125.6, 136.2 (CH arom BPh_4), 126.6, 130.2 (CH arom α and β), 127.3 (C arom), 132.0 (CH arom γ), 161.3 (N–C–N), 163.1, 163.7, 164.4, 165.0 (C arom BPh_4). Calc. for $C_{41}H_{47}BN_2$: C = 85.10%, H = 8.19%, N = 4.84%. Found: C = 85.23%, H = 8.38%, N = 4.66%.

Synthesis of 40. The same procedure described for **20** was used, starting from **38** (671 mg, 1.98 mmol) and ammonium hexafluorophosphate (354 mg, 2.17 mmol). **40** was obtained as a viscous colourless liquid with a 92% yield. This liquid solidified after several days. Mp 41–47 °C (decomposition at 220 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.77 (t, 3H, ^3J = 7.2 Hz, CH_3 hexyl), 0.9–1.2 (m, 6H, $(CH_2)_3$–CH_3), 1.50 (m, 2H, CH_2–CH_2N), 2.28 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.86 (s, 3H, CH_3–N), 3.06 (t, 2H, ^3J = 7.9 Hz, C_5H_{11}–CH_2–N), 3.63 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.6 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 13.8 (CH_3 hexyl), 18.9 (N–CH_2–CH_2–CH_2–N), 22.2, 25.8, 27.3, 30.8 (CH_3–$(CH_2)_4$–CH_2N), 41.9 (CH_3–N), 45.2, 48.0 (CH_2–N), 54.3 (C_5H_{11}–CH_2–N), 127.1, 129.9 (CH arom α and β), 128.2 (C arom), 131.6 (CH arom γ), 162.2 (N–C–N). Calc. for $C_{17}H_{27}F_6N_2P$: C = 50.49%, H = 6.73%, N = 6.93%. Found: C = 50.54%, H = 6.80%, N = 6.60%.

Synthesis of 41. The same procedure described for **36** was used, starting from **38** (1.00 g, 2.95 mmol) and lithium triflate (506 mg, 3.24 mmol), affording **41** as a colourless oil, that decomposes at 230 °C, with a 92% yield. ^{1}H NMR ($CDCl_3$, δ ppm): 0.73 (t, 3H, ^3J = 7.4 Hz, CH_3 hexyl), 0.9–1.5 (m, 6H, $(CH_2)_3$–CH_3), 1.45 (m, 2H, CH_2–CH_2N), 2.25 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.83 (s, 3H, CH_3–N), 3.02 (t, 2H, ^3J = 7.9 Hz, C_5H_{11}–CH_2–N), 3.64 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.6 (m, 5H, CH arom), ^{13}C NMR ($CDCl_3$, δ ppm): 13.8 (CH_3 hexyl), 19.0 (N–CH_2–CH_2–CH_2–N), 22.2, 25.8, 27.4, 30.8 (CH_3–$(CH_2)_4$–CH_2N), 42.0 (CH_3–N), 45.2, 48.1 (CH_2–N), 54.3 (C_5H_{11}–CH_2–N), 127.2, 129.9 (CH arom α and β), 128.2 (C arom), 131.6 (CH arom γ), 162.2 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion. Calc. for $C_{18}H_{27}F_3N_2O_3S$: C = 52.93%, H = 6.66%, N = 6.86%. Found: C = 53.82%, H = 6.41%, N = 7.90%.

Synthesis of 42. The same procedure described for **22** was used, starting from **38** (827 mg, 2.44 mmol) and lithium bis(trifluoromethane)sulfonimide (770 mg, 2.68 mmol). **42** was obtained as a colourless liquid, that decomposes at 350 °C, with a 97% yield. ^{1}H NMR ($CDCl_3$, δ ppm): 0.77 (t, 3H, ^3J = 7.2 Hz, CH_3 hexyl), 0.9–1.2 (m, 6H, $(CH_2)_3$–CH_3), 1.49 (m, 2H, CH_2–CH_2N), 2.26 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.84 (s, 3H, CH_3–N), 3.01 (t, 2H, ^3J = 7.9 Hz, C_5H_{11}–CH_2–N), 3.63 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.7 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 13.8 (CH_3 hexyl), 18.9 (N–CH_2–CH_2–CH_2–N), 22.2, 25.8, 27.4, 30.8 (CH_3–$(CH_2)_4$–CH_2N), 42.0 (CH_3–N), 45.2, 48.0 (CH_2–N), 54.4 (C_5H_{11}–CH_2–N), 119.9 (q, CF_3), 127.0 130.0 (CH arom α and β), 128.0 (C arom), 131.7 (CH arom γ), 162.3 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion. Calc. for $C_{19}H_{27}F_6N_3O_4S_2$: C = 42.29%, H = 5.04%, N = 7.79%. Found: C = 42.51%, H = 5.09%, N = 7.61%.

Synthesis of 43. The same procedure described for **38** was used, starting from **17** (4.37 g, 25.1 mmol) and 1-bromododecane (2.49 g, 50.1 mmol), as well as K_2CO_3 (3.46 g, 25.1 mmol). **43** was obtained as a colourless hygroscopic viscous liquid which solidified in a fridge after several days. Yield = 87%. Mp ~49 °C (decomposition at 200 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.83 (t, 3H, ^3J = 7.2 Hz, CH_3 dodecyl), 0.9–1.4 (m, 20H, $(CH_2)_{10}$–CH_3), 1.49 (m, 2H, CH_2–CH_2N), 2.34 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.90 (s, 3H, CH_3–N); 3.08 (t, 2H, ^3J = 7.9 Hz, C_5H_{11}–CH_2–N), 3.81 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.7 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.0 (CH_3 dodecyl), 19.4 (N–CH_2–CH_2–CH_2–N), 22.6, 26.1, 27.5, 28.6, 29.1, 29.2, 29.3, 29.4, 29.5, 31.8 (CH_3–$(CH_2)_{10}$–CH_2N), 42.4 (CH_3–N), 45.5–48.5 (CH_2–N), 54.4 ($C_{11}H_{23}$–CH_2–N), 127.4, 129.7 (CH arom α and β), 128.2 (C arom), 131.5 (CH arom γ) 162.1 (N–C–N). Calc. for $C_{23}H_{39}BrN_2 \cdot H_2O$: C = 62.57%, H = 9.36%, N = 6.35%. Found: C = 62.54%, H = 9.65%, N = 6.16%.

Synthesis of 44. The same procedure described for **19** was used, starting from **43** (494 mg, 1.17 mmol) and sodium tetraphenylborate (439 mg (1.28 mmol). The crude product was redissolved in 40 ml of a mixture of EtOH–$CHCl_3$ (1 : 1) affording **43** as a white solid after slow evaporation of $CHCl_3$. Mp 91–93 °C (decomposition at 250 °C). ^{1}H NMR ($CDCl_3$, δ ppm): 0.90 (t, 3H, ^3J = 6.8 Hz, CH_3 dodecyl), 1.0–1.4 (m, 20H, $(CH_2)_{10}$–CH_3), 2.25 (s, 3H, CH_3–N), 2.60 (m, 6H,

CH_2–N) 6.8–7.6 (m, 25H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.2 (CH_3 dodecyl), 18.6 (N–CH_2–CH_2–CH_2–N), 22.7, 26.0, 27.6, 28.8, 29.3, 29.3, 29.4, 29.6, 29.6, 31.9 (CH_3–$(CH_2)_{10}$–CH_2N), 41.7 (CH_3–N), 44.8, 47.6 (CH_2–N), 54.0 ($C_{11}H_{23}$–CH_2–N), 121.9, 125.6, 136.2 (CH arom BPh_4), 126.6, 130.2 (CH arom α and β), 127.3 (C arom), 132.0 (CH arom γ), 161.3 (N–C–N), 163.1 163.7, 164.4, 165.0 (C arom BPh_4). Calc. for $C_{47}H_{59}BN_2$: C = 85.17%, H = 8.97%, N = 4.23%. Found: C = 85.92%, H = 9.06%, N = 4.00%.

Synthesis of 45. The same procedure described for **20** was used, starting from **43** (809 mg, 1.91 mmol) and ammonium hexafluorophosphate (343 mg, 2.10 mmol). **45** was obtained as a viscous colourless liquid with a 96% yield. Mp 49–51 °C (decomposition at 200 °C). ^1H NMR ($CDCl_3$, δ ppm): 0.86 (t, 3H, ^3J = 6.9 Hz, CH_3 dodecyl), 0.9–1.3 (m, 18H, $(CH_2)_9$–CH_3), 1.50 (m, 2H, CH_2–CH_2N), 2.28 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.86 (s, 3H, CH_3–N), 3.05 (t, 2H, ^3J = 7.8 Hz, C_2H_5–CH_2–N), 3.64 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.6 (m, 5H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 dodecyl), 18.9 (N–CH_2–CH_2–CH_2–N), 22.7, 26.2, 27.4, 28.7, 29.2, 29.3, 29.4, 29.5, 29.5, 31.9 (CH_3–$(CH_2)_{10}$–CH_2N), 42.0 (CH_3–N), 45.2, 48.0 (CH_2–N), 54.3 (C_5H_{11}–CH_2–N), 127.1, 129.9 (CH arom α and β), 128.2 (C arom), 131.6 (CH arom γ), 162.2 (N–C–N). Calc. for $C_{23}H_{39}F_6N_2P$: C = 56.55%, H = 8.05%, N = 5.73%. Found: C = 56.22%, H = 9.04%, N = 5.72%.

Synthesis of 46. The same procedure described for **36** was used, starting from **43** (1.92 g, 4.53 mmol) and lithium triflate (778 mg, 4.99 mmol), affording **36** as a colourless oil, that decomposes at 350 °C, with a 95% yield. ^1H NMR ($CDCl_3$, δ ppm): 0.83 (t, 3H, ^3J = 6.9 Hz, CH_3 dodecyl), 0.9–1.3 (m, 18H, $(CH_2)_9$–CH_3), 1.47 (m, 2H, CH_2–CH_2N), 2.26 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.85 (s, 3H, CH_3–N), 3.04 (t, 2H, ^3J = 7.8 Hz, C_2H_5–CH_2–N), 3.67 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.50 (m, 5H, CH arom), ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 dodecyl), 19.2 (N–CH_2–CH_2–CH_2–N), 22.7, 26.2, 27.5, 28.7, 29.0, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9 (CH_3–$(CH_2)_{10}$–CH_2N), 42.1 (CH_3–N), 45.2, 48.1 (CH_2–N), 54.3 ($C_{10}H_{21}$–CH_2–N), 127.2, 129.9 (CH arom α and β), 128.2 (C arom), 131.6 (CH arom γ), 162.3 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion. Calc. for $C_{24}H_{39}F_3N_2O_3S$: C = 58.51%, H = 7.98%, N = 5.69%. Found: C = 58.50%, H = 8.48%, N = 5.66%.

Synthesis of 47. The same procedure described for **22** was used, starting from **43** (1.72 g, 4.06 mmol) and lithium bis-(trifluoromethane)sulfonimide (1.28 mg, 4.47 mmol). **47** was obtained as a colourless liquid, that decomposes at 200 °C, with a 84% yield. ^1H NMR ($CDCl_3$, δ ppm): 0.84 (t, 3H, ^3J = 6.9 Hz, CH_3 dodecyl), 0.9–1.3 (m, 18H, $(CH_2)_9$–CH_3), 1.48 (m, 2H, CH_2–CH_2N), 2.26 (q, 2H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.84 (s, 3H, CH_3–N), 3.04 (t, 2H, ^3J = 7.9 Hz, $C_{10}H_{21}$–CH_2–N), 3.63 (2t, 4H, ^3J = 6.0 Hz, CH_2–N), 7.4–7.6 (m, 5H, CH arom), ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 dodecyl), 19.0 (N–CH_2–CH_2–CH_2–N), 22.6, 26.1, 27.4, 28.7, 28.9, 29.2, 29.3, 29.4, 29.5, 31.9 (CH_3–$(CH_2)_{10}$–CH_2N), 42.0 (CH_3–N), 45.3, 48.1 (CH_2–N), 54.4 ($C_{10}H_{21}$–CH_2–N), 119.9 (q, CF_3), 127.0 130.0 (CH arom α and β), 128.0 (C arom), 131.7 (CH arom γ), 162.3 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion. Calc. for $C_{25}H_{39}F_6N_3O_4S_2$: C 48.14%, H 6.30%, N 6.74%. Found: C 48.57%, H 6.13%, N 6.38%.

Synthesis of 48. 3 (1.0 g, 3.7 mmol) and 1-iodopropane (1.26 g, 7.4 mmol) of were dissolved in 40 ml of dry DMF and the mixture was heated at 70 °C overnight under argon. After cooling, the white solid was filtered off, washed with 2 × 15 ml of diethyl ether, then dried under vacuum. The compound was recrystallised from distilled water to afford colourless crystals of **48**, suitable for X-ray diffraction (yield 79%). Mp > 340 °C. ^1H NMR (D_2O + *t*BuOH, δ ppm): 0.68, 0.69 (2t, 6H, ^3J = 7.2 Hz, CH_3 propyl), 1.57 (m, 4H, CH_2–CH_3), 2.25 (q, 4H, ^3J = 5.8 Hz, $CH_2(CH_2$–$N)_2$), 2.87, 2.90 (2s, 6H, CH_3–N), 3.09, 3.11 (2t, 4H, ^3J = 7.8 Hz, C_2H_5–CH_2–N), 3.64, 3.66 (2t, 8H, ^3J = 5.8 Hz, CH_2–N) 7.80, 7.81 (2s, 4H, CH arom); ^{13}C NMR (D_2O + *t*BuOH, δ ppm): 10.6, 10.7 (CH_3), 19.3 (N–CH_2–CH_2–CH_2–N), 21.0, 21.1 (CH_2–CH_3), 42.2 (CH_3–N), 45.9, 46.0 (CH_2–NPr), 48.7, 48.8 (CH_2–N–CH_3), 56.2, 56.3 (C_2H_5–CH_2–N), 129.7 (CH arom), 131.8 (C arom), 161.3 (N–C–N). Calc. for $C_{22}H_{36}N_4I_2$: C = 43.29%, H = 5.95%, N = 9.18%. Found: C = 41.63%, H = 5.95%, N = 9.11%.

Synthesis of 49. The same procedure described for **20** was used, starting from **48** (117 mg, 0.192 mmol) and sodium tetrafluoroborate (142 mg, 0.233 mmol), which affords colourless prismatic crystals of **49** (yield 65%). Mp > 340 °C. ^1H NMR (DMSO, δ ppm): 0.60, 0.64 (2t, 6H, ^3J = 7.2 Hz, CH_3 propyl), 1.48 (m, 4H, CH_2–CH_3), 2.17 (m, 4H, $CH_2(CH_2$–$N)_2$), 2.79, 2.83 (2s, 6H, CH_3–N), 2.99 (m, 4H, C_2H_5–CH_2–N), 3.58, 3.60 (2t, 8H, ^3J = 6.0 Hz, CH_2–N), 7.84, 7.86 (2s, 4H, CH arom); ^{13}C NMR (DMSO, δ ppm): 10.6 10.7 (CH_3), 18.5 (N–CH_2–CH_2–CH_2–N), 20.3, 20.4 (CH_2–CH_3), 41.6, 41.7 (CH_3–N), 45.1, 45.2 (CH_2–NPr), 47.9, 48.0 (CH_2–N–CH_3), 55.0 (C_2H_5–CH_2–N), 128.9 (CH arom), 131.0 (C arom), 160.2 (N–C–N). Calc. for $C_{22}H_{36}B_2F_8N_4{\cdot}1/2H_2O$: C = 49.01%, H = 6.92%, N = 10.39%. Found C = 48.78%, H = 6.78%, N = 10.43%.

Synthesis of 50. 48 (60 mg, 0.097 mmol), dissolved in a minimum of distilled water was mixed with 2 ml of an aqueous solution containing sodium tetraphenylborate (67 mg, 0.195 mmol) and stirred for 1 h. The resulting white solid was filtered off, then recrystallised in a mixture of ethanol–water to afford **50** as a white powder (yield 68%). Mp 315 °C. ^1H NMR (DMSO, δ ppm): 0.60, 0.64 (2t, 6H, ^3J = 7.5 Hz, CH_3 propyl), 1.46 (m, 4H, CH_2–CH_3), 2.15 (q, 4H, ^3J = 5.9 Hz, $CH_2(CH_2$–$N)_2$), 2.77, 2.81 (2s, 6H, CH_3–N), 2.98 (m, 4H, CH_2–N), 3.56, 3.58 (2t, 8H, ^3J = 5.9 Hz, CH_2–N), 6.79 (t, 8H, ^3J = 7.5 Hz, CH arom, γ BPh_4), 6.92 (t, 16H, ^3J = 7.5 Hz, CH arom, β BPh_4), 7.17 (br, 16H, CH arom, α BPh_4), 7.82, 7.83 (2s, 4H, CH arom), ^{13}C NMR (DMSO, δ ppm): 10.6 (CH_3 propyl), 18.5 (N–CH_2–CH_2–CH_2–N), 21.4 (CH_2–CH_3), 41.6, 41.7 (CH_3–N), 45.2 48.0 (CH_2–N), 55.0 (C_2H_5–CH_2–N), 121.5, 125.2, 128.8 (CH arom BPh_4), 135.5 (CH arom amidine), 131.0 (C arom), 161.1 (N–C–N), 162.4, 163.0, 163.7, 164.3 (C arom, BPh_4). Calc. for $C_{70}H_{76}B_2N_4$: C = 84.50%,

H = 7.70%, N = 5.63%. Found C = 84.78%, H = 7.58%, N = 5.42%.

Synthesis of 51. **48** (100 mg, 0.162 mmol) dissolved in a minimum of distilled water was mixed with 1 ml an aqueous solution containing of ammonium hexafluorophosphate (53 mg, 0.325 mmol) and stirred for 1 h. The resulting white solid was filtered off, then recrystallised in distilled water to afford colourless crystals of **51**, suitable for X-ray diffraction analysis (yield 57%). Mp >320 °C. ^{1}H NMR (DMSO, δ ppm): 0.61, 0.64 (2t, 6H, ^3J = 7.2 Hz, CH_3 propyl), 1.48 (m, 4H, CH_2–CH_3), 2.17 (m, 4H, $CH_2(CH_2$–$N)_2$), 2.79, 2.83 (2s, 6H, CH_3–N), 3.00 (m, 4H, C_2H_5–CH_2–N), 3.59, 3.61 (2t, 8H, ^3J = 6.0 Hz, CH_2–N), 7.85, 7.86 (2s, 4H, CH arom), ^{13}C NMR (DMSO, δ ppm): 10.7 (CH_3), 18.5 (N–CH_2–CH_2–CH_2–N), 20.4 (CH_2–CH_3), 41.7, 41.8 (CH_3–N), 45.1, 45.2 (CH_2–NPr), 47.9, 48.0 (CH_2–N–CH_3), 55.1 (C_2H_5–CH_2–N), 129.2 (CH arom), 131.0 (C arom), 160.5 (N–C–N). Calc. for $C_{22}H_{36}P_2F_{12}N_4$: C = 40.87%, H = 5.61%, N = 8.67%. Found: C = 39.81%, H = 5.69%, N = 8.18%.

Synthesis of 52. The same procedure described for **51** was used, starting from **48** (247 mg, 0.405 mmol) and lithium bis(trifluoromethane)sulfonimide (290 mg, 1.01 mmol). After recrystallisation in a water–acetone mixture, **52** was obtained as a white solid with a yield of 61%. Mp 134–135 °C. ^{1}H NMR ($(CD_3)_2CO$, δ ppm): 0.73 (t, 6H, ^3J = 6.9 Hz, CH_3 propyl), 1.65 (m, 4H, CH_2–CH_3), 2.36 (q, 4H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 3.03, 3.04 (2s, 6H, CH_3–N), 3.26 (m, 4H, C_2H_5–CH_2–N), 3.78, 3.81 (2t, 8H, ^3J = 6.0 Hz, CH_2–N), 8.05 (s, 4H, CH arom); ^{13}C NMR ($(CD_3)_2CO$, δ ppm): 10.6, 10.7 (CH_3 propyl), 19.4 (N–CH_2–CH_2–CH_2–N), 21.3, 21.4 (CH_2–CH_3), 42.2, 42.3 (CH_3–N), 46.2, 46.3 (CH_2–N-propyl), 49.0, 49.0 (CH_2–N–CH_3), 56.3, 56.4 (C_2H_5–CH_2–N), 121.0 (q, CF_3, ^1J = 317 Hz), 130.0 (CH arom), 132.4 (C arom), 161.7 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion. Calc. for $C_{25}H_{36}F_{12}N_6O_8S_4$: C = 34.06%, H = 3.96%, N = 9.17%. Found C = 33.76%, H = 3.98%, N = 9.16%.

Synthesis of 53. **3** (1.50 g, 5.56 mmol) and 1-bromohexane (1.93 g, 11.7 mmol) were dissolved in 40 ml of dry DMF and the mixture was heated at 70 °C for 5 days under argon. After cooling, the white solid was filtered off, washed with 2 × 15 ml of diethyl ether, then dried under vacuum, affording **53** as a very hygroscopic white solid with a yield of 68%. Mp > 280 °C. ^{1}H NMR (D_2O + *t*BuOH, δ ppm): 0.75, 0.79 (2t, 6H, ^3J = 7.2 Hz, CH_3 hexyl), 0.9–1.2 (m, 12H, $(CH_2)_3$–CH_3), 1.55 (m, 4H, CH_2–CH_2–N), 2.24 (q, 4H, ^3J = 5.8 Hz, $CH_2(CH_2$–$N)_2$), 2.88–2.89 (2s, 6H, CH_3–N), 3.12, 3.15 (2t, 4H, ^3J = 7.5 Hz, C_5H_{11}–CH_2–N), 3.62, 3.65 (2t, 8H, ^3J = 5.8 Hz, CH_2–N), 7.82 (s, 4H, CH arom); ^{13}C NMR (D_2O + ^{t}BuOH, δ ppm): 13.9 (CH_3 hexyl), 19.3 (N–CH_2–CH_2–CH_2–N), 22.3, 22.4 (CH_2–CH_3), 25.6, 26.0, 27.3, 27.5, 30.8, 30.9, 31.0 (C_2H_5–$(CH_2)_3$–CH_2–N), 42.2 (CH_3–N), 46.0 (CH_2–N-hexyl), 48.8 (CH_2–N–CH_3), 54.6, 54.7 (C_5H_{11}–CH_2–N), 129.7 (CH arom), 131.6 (C arom), 161.2 (N–C–N). Calc. for $C_{28}H_{48}Br_2N_4{\cdot}1.4H_2O$: C = 53.74%, H = 8.18%, N = 8.95%. Found: C = 53.61%, H = 8.12%, N = 9.10%.

Synthesis of 54. The same procedure described for **51** was used, starting from **53** (117 mg, 0.166 mmol) and sodium tetrafluoroborate (100 mg, 0.911 mmol). After recrystallisation in water, **54** was obtained as a white powder with a yield of 60%. Mp 306–308 °C. ^{1}H NMR (DMSO, δ ppm): 0.76, 0.79 (2t, 6H, ^3J = 7.2 Hz, CH_3 hexyl), 0.9–1.2 (m, 12H, $(CH_2)_3$–CH_3), 1.47 (br, 4H, CH_2–CH_2–N), 2.16 (br, 4H, $CH_2(CH_2$–$N)_2$), 2.78, 2.81 (2s, 6H, CH_3–N), 3.02 (m, 4H, C_5H_{11}–CH_2–N), 3.57, 3.59 (2t, 8H, ^3J = 6.3 Hz, CH_2–N), 7.87 (s, 4H, CH arom); ^{13}C NMR (DMSO, δ ppm): 13.7 (CH_3 hexyl), 18.5 (N–CH_2–CH_2–CH_2–N), 21.8, 21.9 (CH_2–CH_3), 25.1, 25.5, 26.7, 26.9, 30.3, 30.6 (C_2H_5–$(CH_2)_3$–CH_2–N), 41.4, 41.7 (CH_3–N), 45.2, 47.9 (CH_2–N-hexyl and CH_2–N–CH_3), 53.4, 53.5 (C_5H_{11}–CH_2–N), 128.8 (CH arom), 131.1 (C arom), 160.1 (N–C–N). Calc. for $C_{28}H_{48}B_2F_8N_4{\cdot}1/2H_2O$: C = 53.95%, H = 7.92%, N = 8.99%. Found: C = 54.00%, H = 7.88%, N = 8.98%.

Synthesis of 55. The same procedure described for **50** was used, starting from **53** (50 mg, 0.083 mmol) and sodium tetraphenylborate (60 mg, 0.175 mmol). **55** was obtained as a white solid with a yield of 77%. Mp >300 °C. ^{1}H NMR (DMSO, δ ppm): 0.76, 0.80 (2t, 6H, ^3J = 7.5 Hz, CH_3 hexyl), 0.9–1.2 (m, 12H, N–CH_2–$(CH_2)_3$–C_2H_5), 1.46 (br, 4H, CH_2–CH_3), 2.14 (br, 4H, $CH_2(CH_2$–$N)_2$), 2.76, 2.79 (2s, 6H, CH_3–N), 3.00 (m, 4H, CH_2–N), 3.55, 3.57 (2t, 8H, ^3J = 6.0 Hz, CH_2–N), 6.79 (t, 8H, ^3J = 7.5 Hz, CH aromγ BPh_4), 6.92 (t, 16H, ^3J = 7.5 Hz, CH arom, β BPh_4), 7.17 (br, 16H, CH arom, α BPh_4), 7.83 (s, 4H, CH, arom); ^{13}C NMR (DMSO, δ ppm): 13.7 (CH_3 hexyl), 18.5 (N–CH_2–CH_2–CH_2–N), 21.8, 21.9 (CH_2–CH_3), 25.1, 25.5, 26.7, 26.9, 30.3, 30.6 (C_2H_5–$(CH_2)_3$–CH_2–N), 41.7 (CH_3–N), 45.2 (CH_2–N-hexyl), 47.9 (CH_2–N–CH_3), 53.4, 53.5 (C_5H_{11}–CH_2–N), 121.5, 125.3, 128.8 (CH arom, BPh_4), 131.0 (C arom), 135.5 (CH arom, amidine), 160.0 (N–C–N), 162.4, 163.0, 163.6, 164.3 (C arom BPh_4). Calc. for $C_{76}H_{88}B_2N_4$: C = 84.59%, H = 8.22%, N = 5.19%. Found: C = 84.80%, H = 8.12%, N = 5.01%.

Synthesis of 56. The same procedure described for **51** was used, starting from **53** (50 mg, 0.083 mmol) and ammonium hexafluorophosphate (27 mg, 0.166 mmol). After recrystallisation in water, colourless crystals of **56** were obtained with a yield of 59%. Mp 313–315 °C. ^{1}H NMR ($(CD_3)_2O$, δ ppm): 0.78, 0.82 (2t, 6H, ^3J = 7.2 Hz, CH_3 hexyl), 1.0–1.3 (m, 12H, $(CH_2)_3$–CH_3), 1.66 (m, 4H, CH_2–CH_2–N), 2.36 (q, 4H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 3.01, 3.02 (2s, 6H, CH_3–N), 3.28 (m, 4H, C_5H_{11}–CH_2–N), 3.76, 3.81 (2t, 8H, ^3J = 5.7 Hz, CH_2–N), 8.04, 8.05 (2s, 4H, CH arom); ^{13}C NMR ($(CD_3)_2O$, δ ppm): 14.2, 14.3 (CH_3 hexyl), 19.7 (N–CH_2–CH_2–CH_2–N), 23.1, 23.2 (CH_2–CH_3), 26.6, 26.9, 28.2, 28.4, 31.8, 32.0 (C_2H_5–$(CH_2)_3$–CH_2–N), 42.6, 42.7 (CH_3–N), 46.6 (CH_2–N-hexyl), 49.3 (CH_2–N–CH_3), 55.2, 55.3 (C_5H_{11}–CH_2–N), 130.3 (CH arom), 132.7 (C arom), 161.9 (N–**C**–N). Calc. for $C_{28}H_{48}F_{12}N_4P_2{\cdot}1.5H_2O$: C = 44.39%, H = 6.78%, N = 7.39%. Found: C = 44.10%, H = 6.58%, N = 7.55%.

Synthesis of 57. The same procedure described for **52** was used, starting from **53** (196 mg, 0.326 mmol) and lithium bis(trifluoromethane)sulfonimide (234 mg, 0.816 mmol). After recrystallisation in a water–acetone mixture, **57** was obtained

as a white solid with a yield of 68%. Mp 70 °C. ^{1}H NMR ($(CD_3)_2CO$, δ ppm): 0.78, 0.82 (2t, 6H, ^3J = 6.9 Hz, CH_3 hexyl), 1.0–1.3 (m, 12H, $(CH_2)_3$–CH_3), 1.66 (m, 4H, CH_2–CH_2–N), 2.36 (q, 4H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 3.03 (s, 6H, CH_3–N), 3.29 (m, 4H, C_2H_5–CH_2–N), 3.77, 3.82 (2t, 8H, ^3J = 6.0 Hz, CH_2–N), 8.06, 8.07 (2s, 4H, CH arom); ^{13}C NMR ($(CD_3)_2CO$, δ ppm): 14.1, 14.2 (CH_3 hexyl), 19.9 (N–CH_2–CH_2–CH_2–N), 23.1, 23.1 (CH_2–CH_3), 26.6, 26.9, 28.2, 28.4, 31.8, 32.0 (C_2H_5–$(CH_2)_3$–CH_2–N), 42.6, 42.7 (CH_3–N), 46.7 (CH_2–N-hexyl), 49.4 (CH_2–N–CH_3), 55.2, 55.3 (C_5H_{11}–CH_2–N), 121.1 (q, CF_3), 130.4 (CH arom), 132.7 (C arom), 161.9 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion. Calc. for $C_{32}H_{48}F_{12}N_6O_8S_4$: C = 38.40%, H = 4.83%, N = 8.40%. Found C = 38.02%, H = 4.99%, N = 8.37%.

Synthesis of 58. The same procedure described for **53** was used, starting from **23** (1.50 g, 5.56 mmol) and 1-bromododecane (2.77 g, 11.1 mmol) (reaction time = two days). The compound was recrystallised from a 1 : 1 water–acetone mixture, affording colourless crystalline needles of **58**, suitable for X-ray diffraction, with a yield of 48%. Mp > 300 °C (decomposition at 200 °C). ^{1}H NMR (MeOD, δ ppm): 0.89 (t, 6H, ^3J = 6.8 Hz, CH_3 dodecyl), 1.09–1.26 (m, 36H, CH_3–$(CH_2)_9$–C_2H_4–N), 1.59 (q, 4H, ^3J = 7.5 Hz, $C_{10}H_{21}$–CH_2–CH_2N), 2.30 (q, 4H, ^3J = 6.0 Hz, $CH_2(CH_2$–$N)_2$), 2.90 2.92 (2s, 6H, CH_3–N), 3.13 3.15 (2t, 4H, ^3J = 7.5 Hz, $C_{11}H_{23}$–CH_2–N), 3.69 3.71 (2t, 8H, ^3J = 6.0 Hz, CH_2–N) 7.95 (s, 4H, CH arom); ^{13}C NMR (D_2O + *t*BuOH, δ ppm): 13.0 (CH_3 dodecyl), 18.6 (N–CH_2–CH_2–CH_2–N), 22.3 (CH_2–CH_3), 26.0, 26.4, 27.3, 27.4, 28.7, 29.0, 29.0, 29.1, 29.1 29.2, 29.3, 29.4, 31.7 (C_2H_5–$(CH_2)_9$–CH_2–N), 41.2, 41.3 (CH_3–N), 45.4 (CH_2–N-dodecyl), 48.2 (CH_2–N–CH_3), 54.2 ($C_{11}H_{23}$–CH_2–N), 129.2 (CH arom), 131.6 (C arom), 160.7 (N–C–N). Calc. for $C_{40}H_{72}Br_2N_4{\cdot}3H_2O$: C = 58.38%, H = 9.55%, N = 6.81%. Found: C = 58.12%, H = 10.10%, N = 6.82%.

Synthesis of 59. The same procedure described for **49** was used, starting from **58** (400 mg (0.520 mmol) and sodium tetrafluoroborate (114 mg, 1.04 mmol). **59** was obtained as a white powder with a yield of 48%. Mp > 300 °C (decomposition at 240 °C). ^{1}H NMR (DMSO, δ ppm): 0.84, 0.85 (2t, 6H, ^3J = 6.6 Hz, CH_3 dodecyl), 0.99, 1.21 (2m, 36H, CH_3–$(CH_2)_9$–C_2H_4–N), 1.45 (br, 4H, $C_{10}H_{21}$–CH_2–CH_2N), 2.16 (br, 4H, $CH_2(CH_2$–$N)_2$), 2.77, 2.81 (2s, 6H, CH_3–N), 3.00 (m, 4H, $C_{11}H_{23}$–CH_2–N), 3.57, 3.59 (2t, 8H, ^3J = 6.3 Hz, CH_2–N), 7.85 (s, 4H, CH arom); ^{13}C NMR (DMSO, δ ppm): 13.9 (CH_3 dodecyl), 18.5 (N–CH_2–CH_2–CH_2–N), 22.1 (CH_2–CH_3), 25.5, 25.9, 26.8, 27.1, 28.3, 28.6, 28.7, 28.8, 29.0, 29.1, 31.3 (C_2H_5–$(CH_2)_9$–CH_2–N), 41.4, 41.7 (CH_3–N), 45.2 (CH_2–N-dodecyl), 47.9 (CH_2–N–CH_3), 53.5 ($C_{11}H_{23}$–CH_2–N), 128.8 (CH arom), 131.0 (C arom), 160.0 (N–C–N). Calc. for $C_{40}H_{72}B_2F_8N_4{\cdot}1/2H_2O$: C = 61.39%, H = 7.16%, N = 9.27%. Found: C = 61.35%, H = 7.01%, N = 9.57%.

Synthesis of 60. The same procedure described for **50** was used, starting from **58** (80 mg, 0.104 mmol) and sodium tetraphenylborate (75 mg, 0.219 mmol). **60** was obtained as a white powder with a yield of 83%. Mp > 300 °C (decomposition at 240 °C). ^{1}H NMR (DMSO, δ ppm): 0.85 (t, 6H, ^3J = 6.6 Hz, CH_3 dodecyl), 0.9–1.3 (m, 36H, CH_3–$(CH_2)_9$–C_2H_4–N), 1.43 (br, 4H, $C_{10}H_{21}$–CH_2–CH_2N), 2.11 (br, 4H, $CH_2(CH_2$–$N)_2$), 2.72, 2.76 (2s, 6H, CH_3–N), 2.96 (m, 4H, $C_{11}H_{23}$–CH_2–N), 3.52, 3.53 (2t, 8H, ^3J = 6.0 Hz, CH_2–N), 6.80 (t, 8H, ^3J = 7.5 Hz, CH aromγ BPh_4), 6.93 (t, 16H, ^3J = 7.5 Hz, CH arom, β BPh_4), 7.18 (br, 16H, CH arom, α BPh_4), 7.76, 7.77 (2s, 4H, CH arom); ^{13}C NMR (DMSO, δ ppm): 13.9 (CH_3 dodecyl), 18.5 (N–CH_2–CH_2–CH_2–N), 22.1 (CH_2–CH_3), 25.5, 25.9, 26.8, 27.1, 28.2, 28.6, 28.7, 28.8, 29.0, 29.1, 31.3 (C_2H_5–$(CH_2)_9$–CH_2–N), 41.4, 41.7 (CH_3–N), 45.2 (CH_2–N-dodecyl), 47.9 (CH_2–N–CH_3), 53.5 ($C_{11}H_{23}$–CH_2–N), 121.5, 125.3, 128.8 (CH arom, BPh_4), 130.1 (C arom), 135.5 (CH arom, amidine), 160.0 (N–C–N), 162.4, 163.0, 163.7, 164.3 (C arom BPh_4). Calc. for $C_{88}H_{112}B_2N_4$: C = 84.73%, H = 9.05%, N = 4.49%. Found: C = 84.30%, H = 9.20%, N = 4.08%.

Synthesis of 61. **58** (200 mg, 0.260 mmol), dissolved in a minimum of distilled water was mixed with 0.5 ml of an aqueous solution containing ammonium hexafluorophosphate (85 mg, 0.520 mmol) and stirred for 1 h. The resulting white solid was filtered off, washed with 3 × 1 ml of water, then dried under vacuum affording **61** as a white solid with a yield of 57%. Mp > 280 °C (decomposition).^{1}H NMR (DMSO, δ ppm): 0.84, 0.85 (2t, 6H, ^3J = 6.6 Hz, CH_3 dodecyl), 0.9 1.3 (2m, 36H, CH_3–$(CH_2)_9$–C_2H_4–N), 1.46 (br, 4H, $C_{10}H_{21}$–CH_2–CH_2N), 2.16 (br, 4H, $CH_2(CH_2$–$N)_2$), 2.77, 2.81 (2s, 6H, CH_3–N), 3.00 (m, 4H, $C_{11}H_{23}$–CH_2–N), 3.57, 3.59 (2t, 8H, ^3J = 6.3 Hz, CH_2–N), 7.86 (s, 4H, CH arom); ^{13}C NMR (DMSO, δ ppm): 13.9 (CH_3 dodecyl), 18.5 (N–CH_2–CH_2–CH_2–N), 22.1 (CH_2–CH_3), 25.5, 25.9, 26.8, 27.1, 28.3, 28.6, 28.7, 28.8, 29.0, 29.1, 31.3 (C_2H_5–$(CH_2)_9$–CH_2–N), 41.4, 41.7 (CH_3–N), 45.2 (CH_2–N–dodecyl), 47.9 (CH_2–N–CH_3), 53.5 ($C_{11}H_{23}$–CH_2–N), 128.8 (CH arom), 131.0 (C arom), 160.0 (N–C–N). Calc. for $C_{40}H_{72}F_{12}N_4P_2{\cdot}H_2O$: C = 52.39%, H = 8.13%, N = 6.11%. Found: C = 51.99%, H = 7.70%, N = 6.12%.

Synthesis of 62. The same procedure described for **52** was used, starting from **58** (397 mg, 0.482 mmol) and lithium bis(trifluoromethane)sulfonimide (346 mg, 1.20 mmol). **62** was obtained as a white solid with a yield of 86%. Mp 106–108 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.86 (t, 6H, ^3J = 6.6 Hz, CH_3 dodecyl), 0.95–1.35 (m, 36H, CH_3–$(CH_2)_9$–C_2H_4–N), 1.50 (br, 4H, $C_{10}H_{21}$–CH_2–CH_2N), 2.31 (br, 4H, $CH_2(CH_2$–$N)_2$), 2.85, 2.87 (2s, 6H, CH_3–N), 3.04, 3.07 (2t, 4H, ^3J = 7.2 Hz, $C_{11}H_{23}$–CH_2–N), 3.65 (br, 8H, CH_2–N), 7.87, 7.88 (2s, 4H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.1 (CH_3 dodecyl), 18.7 (N–CH_2–CH_2–CH_2–N), 22.6 (CH_2–CH_3), 26.6, 27.5, 28.7, 28.9, 29.3, 29.3, 29.4, 29.4, 29.5, 29.5, 29.6, 31.9 (C_2H_5–$(CH_2)_9$–CH_2–N), 41.9, 42.1 (CH_3–N), 45.4 (CH_2–N-dodecyl), 48.2 (CH_2–N–CH_3), 54.7 ($C_{11}H_{23}$–CH_2–N), 119.9 (q, CF_3), 129.3 (CH arom), 131.2 (C arom), 160.8 (N–C–N). Probably, owing to a too long relaxation time, no ^{13}C signal was observed for the anion.

Calc. for $C_{44}H_{72}F_{12}N_6O_8S_4$: C = 45.19%, H = 6.21%, N = 7.19%. Found: C = 44.87%, H = 6.30%, N = 7.06%.

Synthesis of 63. The same procedure described for **48** was used, starting from **23** (1.50 g, 5.56 mmol) and 1-bromohexadecane (2.77 g, 11.1 mmol) (reaction time = two days). The compound was recrystallised from a 1 : 1 water–acetone mixture, affording colourless crystalline needles of **63** with 66% yield. Mp >300 °C (decomposition). ^{1}H NMR (MeOD, δ ppm): 0.89 (t, 6H, ^3J = 6.8 Hz, CH_3 hexadecyl), 1.08–1.27 (m, 52H, CH_3–$(CH_2)_{13}$–C_2H_4–N), 1.59 (q, 4H, ^3J = 7.5 Hz, $C_{14}H_{29}$–CH_2–CH_2N), 2.30 (q, 4H, ^3J = 6.0 Hz, $CH_2(CH_2$–N$)_2$), 2.90, 2.92 (2s, 6H, CH_3–N), 3.16, 3.18 (2t, 4H, ^3J = 7.5 Hz, $C_{15}H_{31}$–CH_2–N), 3.69, 3.71 (2t, 8H, ^3J = 6.0 Hz, CH_2–N), 7.95 (s, 4H, CH arom); ^{13}C NMR (MeOD, δ ppm): 13.0 (CH_3 hexadecyl), 18.6 (N–CH_2–CH_2–CH_2–N), 22.3 (CH_2–CH_3), 26.0, 26.4, 27.4, 29.0, 29.0, 29.4, 29.4, 31.7 (C_2H_5–$(CH_2)_{13}$–CH_2–N), 41.2 (CH_3–N), 45.4 (CH_2–N-hexadecyl), 48.2 (CH_2–N–CH_3), 54.2 ($C_{15}H_{31}$–CH_2–N), 129.2 (CH arom), 131.6 (C arom), 160.7 (N–C–N). Calc. for $C_{48}H_{88}Br_2N_4{\cdot}1/2H_2O$: C = 64.77%, H = 10.08%, N = 6.29%. Found: C = 64.98%, H = 10.59%, N = 6.29%.

Synthesis of 64. 63 (267 mg, 0.303 mmol) dissolved in 100 ml of distilled water at 55 °C was mixed with 3 ml of an aqueous solution containing sodium tetrafluoroborate (115 mg, 1.045 mmol) and stirred for 1 h. The resulting white solid was filtered off, washed with 2 × 5 ml of water, then dried under vacuum affording **64** as a white solid with a yield of 68%. Mp >300 °C (decomposition at 240 °C). ^{1}H NMR (DMSO, δ ppm): 0.85 (t, 6H, ^3J = 6.6 Hz, CH_3 hexadecyl), 0.9–1.3 (m, 52H, CH_3–$(CH_2)_{13}$–C_2H_4–N), 1.46 (br, 4H, $C_{14}H_{29}$–CH_2–CH_2N), 2.16 (q, 4H, ^3J = 5.7 Hz, $CH_2(CH_2$–N$)_2$), 2.77, 2.81 (2s, 6H, CH_3–N), 3.0 (t, 4H, ^3J = 7.5 Hz, $C_{15}H_{31}$–CH_2–N), 3.57, 3.59 (2t, 8H, ^3J = 6.3 Hz, CH_2–N), 7.86 (s, 4H, CH arom). The compound was not characterized by NMR ^{13}C because of its insolubility in usual solvents. Calc. for $C_{48}H_{88}B_2F_8N_4{\cdot}H_2O$: C = 63.15%, H = 9.94%, N = 6.26%. Found: C = 63.21%, H = 9.77%, N = 6.03%.

Synthesis of 65. The same procedure described for **50** was used, starting from **63** (157 mg, 0.178 mmol) and sodium tetraphenylborate (203 mg, 0.593 mmol). **65** was obtained as a white powder with a yield of 43%. Mp 235 °C. ^{1}H NMR (DMSO, δ ppm): 0.85 (t, 6H, ^3J = 6.6 Hz, CH_3 hexadecyl), 0.85–1.26 (m, 52H, CH_3–$(CH_2)_{13}$–C_2H_4–N), 1.44 (br, 4H, $C_{14}H_{29}$–CH_2–CH_2N), 2.12 (br, 4H, $CH_2(CH_2$–N$)_2$), 2.74, 2.77 (2s, 6H, CH_3–N), 2.97, 2.99 (2t, 4H, ^3J = 7.5 Hz, $C_{15}H_{31}$–CH_2–N), 3.54 (br, 8H, CH_2–N), 6.79 (t, 8H, ^3J = 7.5 Hz, CH arom, γ, BPh_4), 6.92 (t, 16H, ^3J = 7.5 Hz, CH arom, β, BPh_4), 7.18 (br, 16H, CH arom, α, BPh_4), 7.79 7.80 (2s, 4H, CH arom); ^{13}C NMR (DMSO, δ ppm): 13.9 (CH_3 hexadecyl), 18.5 (N–CH_2–CH_2–CH_2–N), 22.1 (CH_2–CH_3), 26.0, 27.0, 28.7, 28.7, 28.8, 29.1, 31.3, (C_2H_5–$(CH_2)_{13}$–CH_2–N), 41.7 (CH_3–N), 45.2 (CH_2–N-hexadecyl), 47.9 (CH_2–N–CH_3), 53.5 ($C_{15}H_{31}$–CH_2–N), 121.5, 125.3, 128.8 (CH arom, BPh_4), 131.0 (C arom), 135.5 (CH arom, amidine), 160.0 (N–C–N), 162.4, 163.0, 163.7, 164.3 (C arom, BPh_4). Calc. for $C_{96}H_{128}B_2N_4{\cdot}H_2O$: C = 83.69%, H = 9.51%, N = 4.07%. Found: C = 83.70%, H = 9.16%, N = 3.71%.

Synthesis of 66. 63 (100 mg (0.113 mmol), dissolved in 2 ml of methanol, was mixed with 3 ml of a methanolic solution containing ammonium hexafluorophosphate (50 mg, 0.307 mmol) and stirred for 1 h. The resulting white solid was filtered off, washed with 2 × 3 ml of methanol, then dried under vacuum affording **66** as a white solid with a yield of 98%. Mp ~280 °C (decomposition at 230 °C). ^{1}H NMR (DMSO, δ ppm): 0.85 (t, 6H, ^3J = 6.6 Hz, CH_3 hexadecyl), 0.8–1.3 (m, 52H, CH_3–$(CH_2)_{13}$–C_2H_4–N), 1.45 (q, 4H, ^3J = 7.5 Hz, $C_{14}H_{29}$–CH_2–CH_2N), 2.16 (q, 4H, ^3J = 6.0 Hz, $CH_2(CH_2$–N$)_2$), 2.77, 2.80 (2s, 6H, CH_3–N), 3.0 (t, 4H, ^3J = 7.8 Hz, $C_{15}H_{31}$–CH_2–N), 3.57, 3.59 (2t, 8H, ^3J = 6.3 Hz, CH_2–N), 7.86 (s, 4H, CH arom). The compound was not characterized by ^{13}C NMR because of its insolubility in usual solvents. Calc. for $C_{48}H_{88}F_{12}N_4P_2{\cdot}2H_2O$: C = 55.05%, H = 8.86%, N = 5.35%. Found: C = 54.85%, H = 8.60%, N = 5.60%.

Synthesis of 67. 63 (274 mg, 0.311 mmol), dissolved in 20 ml of distilled water, was mixed with 3 ml of an aqueous solution containing lithium bis(trifluoromethane)sulfonimide (223 mg, 0.777 mmol). After 1 h stirring, the resulting white solid was filtered off, washed with 2 × 5 ml of water, then dried under vacuum affording **66** as a white solid with a yield of 71%. Mp 103–106 °C. ^{1}H NMR ($CDCl_3$, δ ppm): 0.86 (t, 6H, ^3J = 6.6 Hz, CH_3 hexadecyl), 0.95–1.32 (m, 52H, CH_3–$(CH_2)_{13}$–C_2H_4–N), 1.50 (br, 4H, $C_{14}H_{29}$–CH_2–CH_2N), 2.30 (br, 4H, $CH_2(CH_2$–N$)_2$), 2.83, 2.86 (2s, 6H, CH_3–N), 3.03, 3.05 (2t, 4H, ^3J = 7.5 Hz, $C_{15}H_{31}$–CH_2–N), 3.63 (br, 8H, CH_2–N), 7.86, 7.87 (2s, 4H, CH arom); ^{13}C NMR ($CDCl_3$, δ ppm): 14.0 (CH_3 hexadecyl), 18.7 (N–CH_2–CH_2–CH_2–N), 22.7 (CH_2–CH_3), 26.6, 27.5, 28.7, 28.9, 29.3, 29.4, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9 (C_2H_5–$(CH_2)_{13}$–CH_2–N), 41.8, 42.0 (CH_3–N), 45.4 (CH_2–N-hexadecyl), 48.1 (CH_2–N–CH_3), 54.7 ($C_{15}H_{31}$–CH_2–N), 119.9 (q, CF_3), 129.2 (CH arom), 131.3 (C arom), 160.7 (N–C–N). Calc. for $C_{52}H_{88}F_{12}N_6O_8S_4$: C = 48.74%, H = 6.92%, N = 6.56%. Found: C = 48.56%, H = 7.01%, N = 6.38%.

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