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An Internal Fluorescent Probe Based on Anthracene to Evaluate Cation–Anion Interactions in Imidazolium Salts

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Abstract: A series of fluorescent imidazolium-based salts containing the cation $[AnCH_2MeIm]^+$ (in which An = anthracene and Im = the imidazolium cation) with Cl^-, BF_4^-, PF_6^-, $SO_3CF_3^-$, $[N(CN)_2]^-$, $[N(SO_2CF_3)_2]^-$, or $PhBF_3^-$ anions have been prepared and characterized. X-ray diffraction analysis of four of the salts reveals a number of C–H···X-type (X = O, N, F) hydrogen bonds between the hydrogen atoms from the imidazolium ring and in some cases from the anthracene ring with the electronegative atoms of the anions. Additionally, C–H···π interactions can be found in all the salts analyzed by X-ray diffraction, whereas π–π stacking is observed only in the salt containing the phenyltrifluoroborate anion. Fluorescence emission analysis in acetonitrile shows that the fluorescence of these salts varies significantly according to the nature of the anion, and correlates to the extent of ion pairing present in solution. Photodimerization of these salts was observed, and in one case a dimer has been isolated and characterized by X-ray crystallography.

Keywords: fluorescence · imidazolium salts · ionic liquids · structure elucidation

Introduction

The design and synthesis of functionalized imidazolium salts, many of which may be classified as ionic liquids, are driven by the need for a greater understanding of the fundamental physical and chemical properties of low melting point salts and the desire to modify them for specific applications.[1] The general design approach is to add functional groups or their precursors to the cation scaffold to impart the salt with specific chemical properties.[2] The anion moiety is then varied to tune the physicochemical properties of the salt, with the aim of producing low melting point ionic liquids (ILs).[3,4,5] However, this is a simplistic approach and the cations and anions can interact to give rise to unpredictable interactions and consequently unpredictable properties. Controlling these interactions will be important in the rational design of functionalized room-temperature ionic liquids (RTILs). It is, therefore, not surprising that the study of the interactions between the cations and anions in imidazolium salts by using both experimental[6] and theoretical[7,8] methods, and in some cases a combination of the two,[9,10] is of considerable interest.

The imidazolium unit is interesting from a structural perspective because it is able to elicit a range of cation–anion interactions. For example, the acidic C–H proton at the 2-position of the ring is often involved in hydrogen-bonding interactions with other cation and anion units (Figure 1), and these interactions have been investigated by using NMR spectroscopic methods,[11] and infrared spectroscopy and initio calculations indicate that there is linear relationship between the interaction energies and the intermolecular

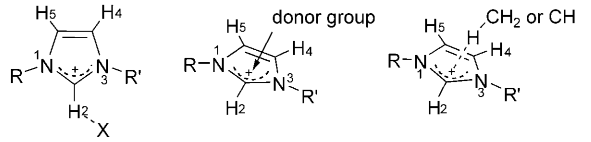

Figure 1. C–H···X, σ–π, and C–H···π interactions in imidazolium salts (X = O, N, F).

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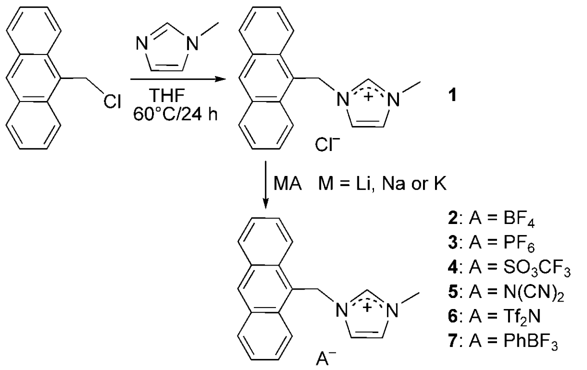
stretching frequencies of the cations and anions in the ionic liquids.[12]

In addition to the hydrogen-bonding interactions, the heterocyclic delocalized ring is also able to form π-donor interactions with other groups.[13,14] We previously reported that the introduction of different functional groups leads to the disruption of the hydrogen network within the imidazolium salt[15,16] and can be exploited to influence the physical properties of these salts.[12,13]

Systematic investigations on high melting point imidazolium salts remain fairly unexplored despite the fact that these solid salts have interesting properties and applications. For example, the relatively high melting point imidazolium salt 1-butyl-3-methylimidazolium chloride, [Bmim][Cl], can dissolve cellulose much more effectively than the corresponding room-temperature ionic liquids such as [Bmim][BF_4] and [Bmim][PF_6].[17] Solid-phase acidic imidazolium salts are superior to acidic RTILs in acid-catalyzed esterification reactions[18] in terms of catalytic turnover and recycling.[19,20,21] We were, therefore, interested in tethering an anthracene group to the imidazolium scaffold because anthracene is a strong π–π* emitter with emission characteristics that are sensitive to the local environment.[22,23] Owing to their versatile photophysical and photochemical properties, anthracene-containing compounds have been previously employed as fluorescent probes in many applications.[24,25] The emission from the anthracene chromophores in the molecule could be used to signal environmental effects that could help to delineate inter/intramolecular interactions. Moreover, the fluorescence of anthracene-based compounds may be controlled by the addition of inorganic salts. In this paper we describe the synthesis and characterization of a series of anthracene-functionalized imidazolium salts. Our strategy is to incorporate an anthracene moiety into the imidazolium unit, which can act as an internal probe providing insights into cation–anion interactions in the solid state and in solution. We investigate the cation–anion interactions with special focus on the hydrogen bonding in the solid state by means of single-crystal X-ray diffraction analysis and also study the influence of anions on the fluorescence of the imidazolium salts in solution.

Results and Discussion

The synthesis of the anthracene-derivatized imidazolium chloride salt **1** (Scheme 1) by using the well documented quarternization procedure[26,27] is straightforward and takes place in near-quantitative yield. The presence of the bulky hydrophobic anthracene ring makes **1** only moderately hydrophilic, unlike many imidazolium halides. Indeed, common imidazolium salts such as 1-butyl-3-methyl imidazolium halides dissolve in water, whereas **1** is only slightly soluble in water. Subsequent metathesis of the chloride ion in **1** with various anions such as $NaBF_4$, KPF_6, $LiSO_3CF_3$, Na[$N(CN)_2$], Li[$N(SO_2CF_3)_2$], and $LiPhBF_3$ affords the new imidazolium salts **2**–**7** in good yield.[28] All salts are solid at room temperature with only **5** melting below 100 °C, and consequently it can be classified as an ionic liquid according to the generally accepted definition.[29]



Scheme 1. Syntheses of imidazolium salts **1**–**7**.

The protons on the imidazolium ring in **1** are clearly observed in the ^{1}H NMR spectrum (CD_3CN); the signals of the protons at the 4- and 5-positions of the ring are found at 7.32 and 7.26 ppm, respectively, and the more acidic 2-position proton at 8.58 ppm. In **2**–**7**, in which the Cl^- anion has been replaced by less nucleophilic anions, the signals of the hydrogen atom at the 2-position are observed at significantly lower frequencies at approximately 8.8 ppm, whereas the frequencies of other hydrogen atoms in the ring remain essentially unchanged. In **1**–**7** the hydrogen atoms on the anthracene ring display one singlet at approximately 8.1 ppm, two doublets at approximately 8.30 and 8.20 ppm, and two triplets at approximately 7.65 and 7.70 ppm (J(H,H) = 7.0 Hz). These values do not change significantly as the anions are varied. Combined, these data indicate the ion pairing persists in the CD_3CN solvent, at least to some extent, and the main contact is between the anion and the ring proton at the 2-position as expected.[30,31] In addition, the IR spectra of salts **2**–**7** show characteristic absorptions of the imidazolium ring. It has been reported that ionic liquids tend to form cation–anion aggregates and these aggregates have been investigated by ESIMS.[32,33] As expected, in the ESIMS spectra of **2**–**7** in diluted acetonitrile (ca. 1 ppm) signals at m/z 273 representing the cation [$AnCH_2MeIm$]$^+$ are observed in the positive mode. As the concentration increases, anion–cation aggregates in the form $[(\text{cation})_n(\text{anion})_{n-1}]$ ($n = 2,3$) are also observed.[32] Moreover, if the anthracene salt **2** [$AnCH_2MeIm$][BF_4] was mixed with another IL such as 1-ethyl-3-methylimidazolium tetrafluoroborate [EmIm][BF_4], then an aggregate of formula [($AnCH_2MeIm$)(EmIm)(BF_4)] at m/z of 471 was observed. Similar phenomena were observed for **3**–**7**.[33]

To probe the cation and anion interactions in the solid state, crystals of **1**, **3**, **4**, and **7** were obtained (see the Experimental Section for details) and analyzed by single-crystal X-ray diffraction. In the solid state of salt **1** there are two molecules forming a dimeric structure in the asymmetric unit and in **7** there are six molecules in the asymmetric unit. In salts **3** and **4** there is only one molecule in the asymmetric

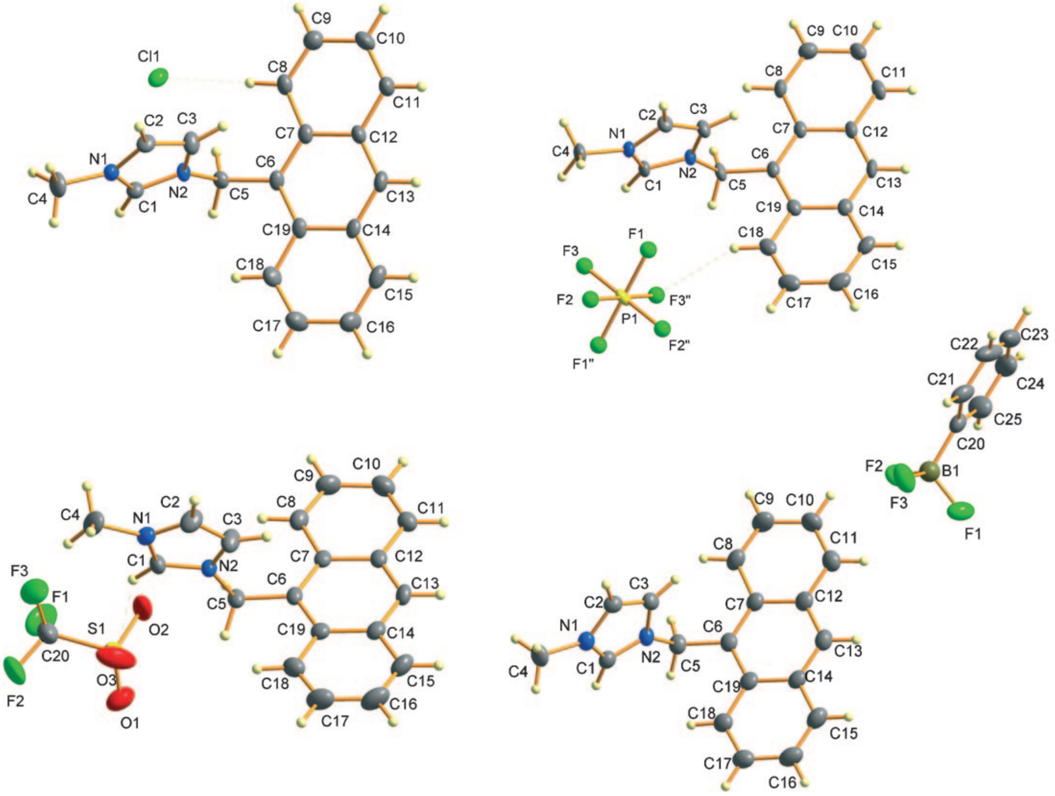


Figure 2. ORTEP representations of **1** (top, left), **3** (top, right), **4** (bottom, left), and **7** (bottom, right). In **1** there are two molecules and in **7** there are six molecules in the asymmetric unit. One molecule has been selected in each case for clarity. Ellipsoids are drawn at the 50% probability level.

Table 1. Crystallographic data for **1**, **3**, **4**, **7**, and **8**.

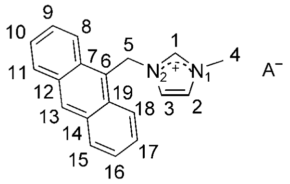
	1	**3**	**4**	**7**	**8**
formula	$[C_{19}H_{17}N_2]Cl{\cdot}0.5(CH_2Cl_2)$	$[C_{19}H_{17}N_2]PF_6$	$[C_{19}H_{17}N_2]SO_3CF_3$	$[C_{19}H_{17}N_2]C_6H_5BF_3$	$[C_{38}H_{34}N_4][N(SO_2CF_3)_2]_2$
M_r	351.26	418.32	422.42	418.26	1106.99
crystal system	triclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P2_12_12$	$P2_1/c$	$P\bar{1}$	$C2/c$
a [Å]	10.5194(8)	13.5199(9)	12.5508(10)	12.688(2)	16.6429(10)
b [Å]	10.9824(12)	22.9389(18)	12.5583(9)	13.468(2)	11.8891(8)
c [Å]	15.9190(18)	5.8824(4)	12.9236(9)	28.876(4)	22.7869(15)
α [°]	72.625(10)	90	90	88.435(13)	90
β [°]	79.860(8)	90	111.770(7)	77.583(14)	93.021(5)
γ [°]	83.695(7)	90	90	61.903(12)	90
V [Å^3]	1724.6(3)	1824.3(2)	1891.7(2)	4235.5(12)	4502.6(5)
Z	4	4	4	8	4
ρ_{calcd} [g cm^{-3}]	1.353	1.523	1.483	1.312	1.633
$F(000)$	732	856	872	1744	2256
μ [mm^{-1}]	0.378	0.216	0.225	0.095	0.322
T [K]	140(2)	100(2)	140(2)	100(2)	140(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
total reflns	10488	30641	10668	71239	13108
unique reflns	5331	3207	3327	14710	3807
$[I>2\sigma(I)]$	2826	2735	2443	11346	2227
data/restraints/parameters	5331/0/426	3207/37/274	3327/0/263	14710/0/1122	3807/0/326
R[a] $[I>2\sigma(I)]$	0.0547	0.0428	0.0400	0.0571	0.0395
$wR2$[a] (all data)	0.1368	0.0943	0.1038	0.1482	0.0694
GooF[b]	0.889	1.098	1.007	1.104	0.864

[a] $R=\Sigma||F_o|-F_c||/\Sigma|F_o|$, $wR2=\{\Sigma[w(F_o^2-F_c^2)2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [b] $\text{GooF}=\{\Sigma[w(F_o^2-F_c^2)2]/(n-p)\}^{1/2}$ in which n is the number of data and p is the number of refined parameters.

unit. Crystallographic data for **1**, **3**, **4**, and **7** are listed in Table 1 and their structures are shown in Figure 2.

Key parameters involving the imidazolium and anthracene moieties of **1**, **3**, **4**, and **7** are listed in Table 2. Imidazo-

Table 2. Selected bond lengths [Å] and angles [°] for **1**, **3**, **4**, and **7**.



	1[a]	3	4	7[b]
N1−C1	1.34	1.332(4)	1.315(3)	1.33
N1−C2	1.37	1.375(4)	1.363(3)	1.38
N1−C4	1.47	1.477(4)	1.468(3)	1.47
N2−C1	1.33	1.341(4)	1.329(3)	1.33
N2−C3	1.37	1.377(4)	1.374(3)	1.38
C2−C3	1.35	1.353(5)	1.340(3)	1.35
N2−C5	1.49	1.488(4)	1.484(2)	1.49
C5−C6	1.52	1.517(4)	1.507(3)	1.51
N1-C1-N2	109	108.2(3)	109.26(2)	109
C1-N1-C2	109	109.3(3)	108.51(2)	109
C1-N2-C3	108	108.2(3)	107.52(2)	109
N2-C5-C6	112	111.8(3)	112.68(2)	112

[a] Average value of two different moieties in the asymmetric cell. [b] Average value of six different moieties in the asymmetric cell.

lium-based compounds including some carbene complexes that have the anthracene moiety have been reported previously,[34,35] but structural data of salts containing imidazolium cations with various bulky anions have not been systematically investigated.

Bond parameters in **1**, **3**, **4**, and **7** are quite similar to those observed in other 1,3-dialkylimidazolium salts.[36] However, among all the salts the metrics of **4** differ slightly from those of **1**, **3**, and **7**. The N1−C1, N1−C2, N1−C4, C2−C3, and C5−C6 bond lengths in **4** with the $CF_3SO_3^-$ anion are the shortest among those in the series. It is probable that the differences in bond lengths in **1**, **3**, **4**, and **7** originate from the different (global) strength of hydrogen-bonding interactions between the anion and the hydrogen atoms in the imidazolium ring. Slight differences in the bond parameters of the anthracene ring in this series of salts are less easily rationalized and probably correspond to slight differences in electronics and packing effects.

Hydrogen-bonding interactions in imidazolium salts have been extensively studied as they influence cation–anion interactions and thus govern not only the physical properties of the salts but the chemistry that takes places in them. Both spectroscopic[11,12] and single-crystal X-ray diffraction studies have been used to provide information on hydrogen bonding,[9,37,38] often in combination with theoretical studies such as DFT[39,40,41] and ab initio calculations.[12]

In **1** there are many intermolecular C−H···Cl contacts in which the strongest interactions are C1−H1···Cl1′ and C20−H20B···Cl1^{iv} (Figure 3 and Table 3). In salt **3** there are some intermolecular C−H···F hydrogen bonds and the H···F distances are generally shorter than those of H···Cl found in **1** (Table 4). In **4** there are only two strong intermolecular C−

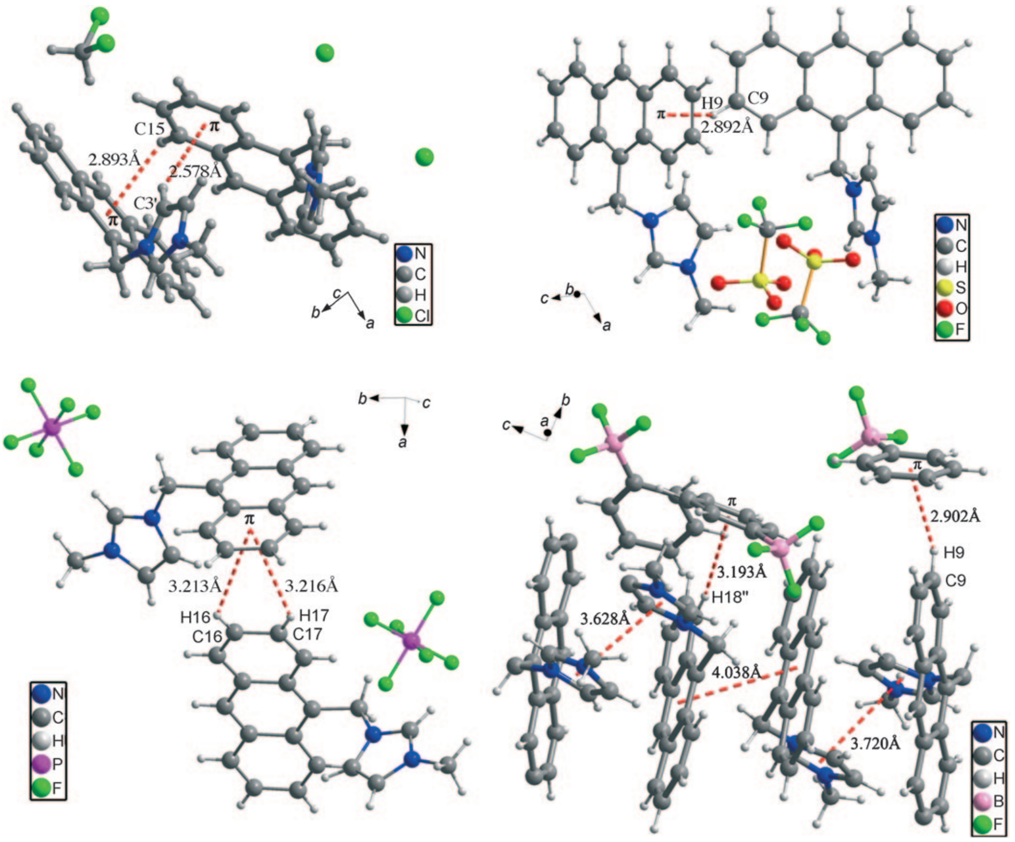


Figure 3. C−H···π interactions in **1** (top left), **3** (bottom left), **4** (top right), and π–π interactions in **7** (bottom right).

Table 3. Hydrogen-bond lengths [Å] and angles [°] for **1**[a].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∢D–H···A
C1–H1···Cl1′	0.950	2.560	3.401(5)	147.0
C1′–H1′···Cl1^{i}	0.950	2.720	3.403(5)	129.0
C2–H2···Cl1^{ii}	0.950	2.660	3.541(5)	155.0
C2′–H2′···Cl1′^{iii}	0.950	2.680	3.487(5)	144.0
C4′–H4B′···Cl1′^{iii}	0.980	2.800	3.712(6)	154.0
C5′–H5A′···Cl1′^{i}	0.990	2.800	3.600(5)	138.0
C5–H5A···Cl1	0.990	2.620	3.505(5)	149.0
C5–H5B···Cl1′	0.990	2.740	3.590(5)	144.0
C8–H8···Cl1	0.950	2.770	3.712(5)	169.0
C9′–H9′···Cl1^{iv}	0.950	2.750	3.617(5)	152.0
C20–H20B···Cl1^{iv}	0.990	2.560	3.425(6)	146.0
C3′–H3′···π	0.950	2.578	3.348(5)	138.4(4)
C15–H15···π	0.950	2.893	3.506(5)	123.3(4)

[a] Symmetry codes: i) $x, 1+y, z$; ii) $2-x, 1-y, -z$; iii) $-{}^{1}\!/_{2}-x, {}^{1}\!/_{2}-y, -z$; iv) $-1+x, 1+y, z$.

Table 4. Hydrogen-bond lengths [Å] and angles [°] for **3**[a].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∢D–H···A
C1–H1···F2^{i}	0.950	2.490	3.403(3)	162.0
C2–H2···F4	0.950	2.360	3.279(5)	163.0
C4–H4A···F5^{ii}	0.980	2.420	3.357(6)	161.0
C4–H4B···F6	0.980	2.480	3.351(3)	148.0
C16–H16···π ^{iii} (C7–12)	0.950	3.213	3.790(3)	120.9(4)
C17–H17···π ^{iii} (C7–12)	0.950	3.216	3.795(3)	121.2(4)

[a] Symmetry codes: i) $1-x, 1-y, z+1$; ii) $2-x, 1-y, z+1$; iii) $x-0.5, 1.5-y, 1-z$.

H···O hydrogen bonds with the H1···O3 and H2···O2 distance being 2.31 and 2.36 Å, respectively (Table 5). Surprisingly, there are no C–H···F interactions despite the presence of the CF_3 groups in **4**. In **7** numerous intermolecular C–H···F hydrogen bonds are observed and the H···F distances are in the range of 2.21–2.55 Å (Table 6).

Table 5. Hydrogen-bond lengths [Å] and angles [°] for **4**[a].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∢D–H···A
C1–H1···O3	0.950	2.310	3.101(3)	140.0
C2–H2···O2^{i}	0.950	2.360	3.267(3)	161.0
C9–H9···π^{ii}	0.950	2.892	3.605(3)	132.7(4)

[a] Symmetry codes: i) $x, 3/2-y, z-{}^{1}\!/_{2}$; ii) $x, 3/2-y, {}^{1}\!/_{2}+z$.

The absorption and emission of anthracene-based molecules is strongly dependent on the structure of the compound,[42] on the external environment such as the solvent, or on the presence of quenching agents.[43] Usually, the fluorescence of anthracene-based systems is quenched by inorganic anions, a phenomenon used in selective anion sensing.[44,45] For example, this phenomenon is caused by addition of inorganic salts containing halides and other anions.[46] Indeed, numerous recognition systems based on anthracene derivatives have been reported,[43,44,47] usually involving the introduction of a functional group at the anthracence backbone, which can interact with a specific anion, thereby modifying the emission intensity. In the reported systems, cation–anion interactions play an important role because electron transfer from the donor (anion) to the excited acceptor (the anthracene-containing cation) is strongly influenced by minor changes in the structure of the anthracene moiety. Most research has focused on the synthesis of neutral anthracene derivatives with comparatively few studies on anthracenes derivatized with charged groups. Recent studies on ionic liquids have shown that imidazolium salts are very sensitive to the nature of the anion,[44,45] which strongly influences the strength of the cation–anion interactions. Consequently, the fluorescence emission of **2**–**7** was studied in acetonitrile at a concentration of $c=3.5\times10^{-5}$ M. Among the salts, the combination of **6** with the Tf_2N^- anion exhibits the highest intensity, whereas **4**, which has a triflate anion, has the lowest intensity (Figure 4). The quenching effect of the anions is related to the structure of the receptors and to their affinity for the anions. Electronic and steric effects of the anions both influence the emission of the salts in the solvent. Electronegative groups on the anion should reduce the electron density on the cation, leading to lower fluorescence emission. Sterically encumbered anions often suppress

Table 6. Hydrogen-bond lengths [Å] and angles [°] for **7**[a].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∢D–H···A
C1–H1···F1^{i}	0.950	2.470	3.115(4)	125.0
C4′–H4A′···F2″^{i}	0.980	2.400	3.275(4)	148.0
C2–H2···F1“^{i}	0.950	2.320	3.083(5)	137.0
C2′–H2′···F2^{ii}	0.950	2.290	3.089(4)	141.0
C2″–H2″···F2#^{iii}	0.950	2.270	3.079(5)	142.0
C4′–H4C′···F1^{ii}	0.980	2.420	3.374(4)	164.0
C4–H4C···F1^{ii}	0.980	2.550	3.412(5)	147.0
C4″–H4A″···F2′^{iv}	0.980	2.410	3.275(4)	147.0
C4″–H4B″···F3#^{iii}	0.980	2.520	3.493(5)	173.0
C2#–H2#···F1′^{iv}	0.950	2.210	3.044(5)	146.0
C4#–H4A#···F3#^{iii}	0.980	2.450	3.308(5)	146.0
C4#–H4B#···F2′^{iv}	0.980	2.510	3.474(5)	167.0
C16′–H16′···F1′	0.950	2.500	3.417(4)	161.0
C9–H9···π(C20′–25′)	0.950	2.902	3.712(3)	143.8(4)
C18–H18···π(C20″–25″)	0.950	3.193	4.129(3)	168.7(4)

[a] Symmetry codes: i) $x-1, y, z$; ii) $1-x, 1-y, -z$; iii) $1-x, 1-y, 1-z$; iv) $1+x, y-1, z$.

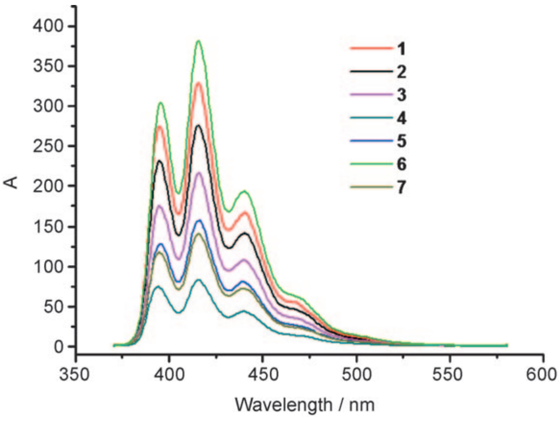


Figure 4. Emission spectra of imidazolium salts **1**–**7** in MeCN ($c=3.5\times10^{-5}$ M).

cation–anion interactions, leading to increased fluorescence emission. Because compounds **2**–**7** contain the same cation, the difference of the intensities of the emission can be regarded as entirely an anion effect, clearly reflecting the strength of the cation–anion pairing with the anthracene part of the cation. Indeed, the observed intensities match well with the crystallographic data. In the solid state of **4**, the $CF_3SO_3^-$ ion interacts most strongly with the cation, leading to greatest ion pairing in solution and resulting in a lower fluorescence emission. In **6**, which contains the weakly interacting Tf_2N^- anion,[48] the highest fluorescence emission is observed. For the remaining salts the intensities of fluorescence emission lie between those of **4** and **6**.

An interesting feature of anthracene derivatives is their ability to undergo photodimerization when irradiated with UV light.[49] The dimerization reaction has even been used as a fluorescent probe.[50] In principle, anthracene-based monomers can dimerize to form *cis* head-to-head, (9,9′ and 10,10′) or *trans* head-to-tail (9,10′ and 9′,10) photodimers.[51] Imidazolium salts have been reported to form *trans* dimers only.[52] In solution, **2**–**7** undergo photodimerization in normal light. The reaction is very slow, taking up to several weeks at room temperature to form mixtures that are difficult to separate. In the case of **6**, dimer **8** was isolated in crystalline form in low yield. The structure of **8** was confirmed by single-crystal X-ray diffraction and was shown to comprise a *trans* dimer (Figure 5).

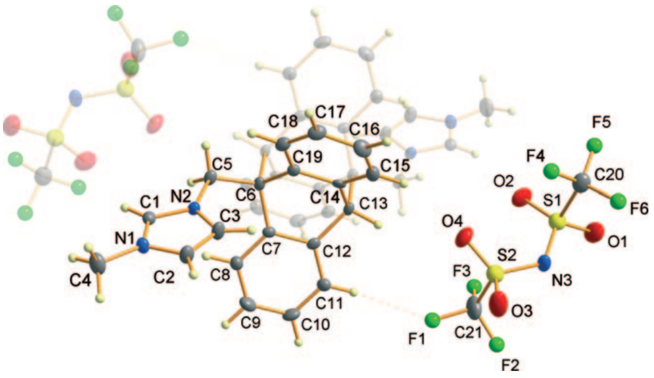


Figure 5. Structure of **8** in the solid state and selected bond lengths [Å] and angles [°]: N1–C1 1.319(3), N1–C2 1.375(3), N1–C4 1.455(3), N2–C1 1.337(3), N2–C3 1.379(3), N2–C5 1.478(3); C1-N1-C2 108.1(2), C1-N1-C4 127.0(2), C2-N1-C4 124.9(2), C1-N2-C3, 107.1(2), C1-N2-C5 122.8(2), C3-N2-C5 129.9(2), N1-C1-N2 109.8(3). Ellipsoids are drawn at the 50% probability level.

Owing to the highly flexible nature of the Tf_2N^- anion, ionic liquids that contain this anion often form room-temperature ionic liquids with very low crystallization temperatures. This makes a systematic structural analysis difficult. In a handful of known examples of imidazolium salts with Tf_2N^- anions, two C–S bonds in the anion usually adopt a *transoid* conformation,[37,38] and only few examples with *cisoid* conformations are known.[53] In the solid state of **8**, the Tf_2N^- anion adopts a *transoid* conformation with the C–S···C–S dihedral angle being 124.7°. The cation–anion interactions in **8** are, in general, stronger than in other structures with the shortest C–H···O, C–H···N, C–H···F distances being 2.31, 2.59, and 2.53 Å, respectively (Table 7). No π–π interactions are present in **8**, presumably owing to the combined presence of the less symmetrical cation and bulky Tf_2N^- anion.

Table 7. Hydrogen-bond lengths [Å] and angles [°] for **8**[a].

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∢D–H···A
C1–H1···O2	0.950	2.310	3.219(3)	160.0
C4–H4A···F1^{i}	0.980	2.530	3.370(3)	143.0
C4–H4C···O2^{ii}	0.980	2.540	3.348(3)	139.0
C8–H8···N2	0.950	2.590	3.051(3)	110.0
C3–H3···π(C14–19)	0.950	3.044	3.782(3)	135.7(4)
C2–H2···π ^{iii}(C7–12)	0.950	2.563	3.478(3)	161.9(4)

[a] Symmetry codes: i) $x-{}^1/_2$, $y-{}^1/_2$, z; ii) $-x$, y, ${}^1/_2-z$, iii) ${}^1/_2+x$, ${}^1/_2+y$, z.

Conclusion

In summary, a series of anthracene-based imidazolium salts with the fluorescent anthracene moiety have been prepared. Four of the salts have been analyzed by X-ray diffraction analysis, revealing a number of C–H···X-type (X = O, N, F) hydrogen bonds between the hydrogen atoms of the imidazolium ring, and in some cases revealing bonding between the anthracene ring with the electronegative atoms of the anions. Although C–H···π interactions can be found in all of the salts, π–π stacking is observed only in salts containing the $PhBF_3^-$ anion. Fluorescence emission analysis shows that the fluorescence of these salts varies significantly according to the nature of the anion, which can be correlated in a qualitative manner to the degree of ion pairing.

Experimental Section

General methods and materials: The reagents 1-methylimidazole and 9-chloromethylanthracene were purchased from Fluka and KPF_6, $NaBF_4$, $Na[N(CN)_2]$, $LiSO_3CF_3$, $Li[N(SO_2CF_3)_2]$, and $LiPhBF_3$ were purchased from Aldrich and all materials were used as received. The synthesis of **1** was performed under an inert atmosphere by using a modified method to that reported.[26] All other compounds were prepared without precautions to exclude air or moisture. IR spectra were recorded on a Perkin–Elmer FT-IR 2000 system. UV/Vis spectra were recorded in quartz cells by using a Jasco V-550 spectrophotometer at 25 °C. Emission spectra were recorded with an excitation wavelength close to the absorption maximum of the S_0–S_1 transition ($\lambda = 380$ nm). NMR spectra were recorded on a Bruker DMX 400 by using $SiMe_4$ for ^1H as the external standard at 20 °C. ESIMS were recorded on a ThermoFinnigan LCQ™ Deca XP Plus quadrupole ion-trap instrument with samples diluted in acetonitrile as described elsewhere.[54] Samples were infused directly into the source at 5 μL min^{-1} by using a syringe pump, the spray voltage was set at 5 kV, and the capillary temperature was set to 50 °C.

Synthesis of [AnCH$_2$MeIm][BF$_4$] (2): A mixture of **1** (0.310 g, 0.001 mol) and $NaBF_4$ (0.110 g, 0.001 mol) in acetone (15 mL) was stirred at room temperature in the dark for 24 h. The reaction mixture was then filtered and the solvent was removed under reduced pressure to afford a yellow solid. The solid was dissolved in dichloromethane (30 mL) and stored at

−22 °C for 24 h. After filtration the solvent was removed to give the product (yield = 70 %). M.p. 160 °C; ^{1}H NMR (CD_3CN): δ = 8.80 (s, 1 H; 2-imiH), 8.30 (d, J = 8.0 Hz, 2 H; AnH), 8.24 (d, J = 8.0 Hz, 2 H; AnH), 8.10 (s, 1 H; AnH), 7.70 (t, J = 8.0 Hz, 2 H; AnH), 7.65 (t, J = 8.0 Hz, 2 H; AnH), 7.45 and 7.35 (s, 2 × 1 H; 4,5-imiH), 6.49 (s, 2 H; CH_2An), 4.12 ppm (s; CH_3); IR (neat): $\tilde{\nu}$ = 3160, 3118 (C−H aromatic), 2977, 2938 (C−H aliphatic), 1573, 1469 cm^{-1} (C=C); ESIMS (CH_3CN): m/z: positive ion: 273 $[M]^+$; negative ion: 87 $[BF_4]^-$; elemental analysis calcd (%) for $C_{19}H_{17}BF_4N_2$ (360.1620): C 63.36, H 4.76, N 7.78; found: C 63.41, H 4.78, N 7.75.

Synthesis of [AnCH$_2$MeIm][PF$_6$] (3): A mixture of **1** (0.309 g, 0.001 mol) and KPF_6 (0.184 g, 0.001 mol) in water (15 mL) was stirred at room temperature in the dark for 4 h. The reaction mixture was then filtered and the solid product was washed with water (2 × 5 mL) and air dried (yield = 89 %). M.p. 200 °C; ^{1}H NMR (CD_3CN): δ = 8.82 (s, 1 H; 2-imiH), 8.33 (d, J = 8.0 Hz, 2 H; AnH), 8.26 (d, J = 8.0 Hz, 2 H; AnH), 8.11 (s, 1 H; AnH), 7.70 (t, J = 8.0 Hz, 2 H; AnH), 7.64 (t, J = 8.0 Hz, 2 H; AnH), 7.44 and 7.35 (s, 2 × 1 H; 4,5-imiH), 6.46 (s, 2 H; CH_2An), 4.15 ppm (s; CH_3); IR (neat): $\tilde{\nu}$ = 3166, 3119 (C−H aromatic), 2975, 2937 (C−H aliphatic), 1569, 1467 cm^{-1} (C=C); ESIMS (CH_3CN): m/z: positive ion: 273 $[M]^+$; negative ion: 145 $[PF_6]^-$; elemental analysis calcd (%) for $C_{19}H_{17}F_6N_2P$ (418.3216): C 54.55, H 4.10, N 6.70; found: C 54.63, H 4.14, N 6.71.

Synthesis of [AnCH$_2$MeIm][OTF] (4): A mixture of **1** (0.309 g, 0.001 mol) and $LiSO_3CF_3$ (0.156 g, 0.001 mol) in dichloromethane (30 mL) was stirred at room temperature in the dark for 24 h. The reaction mixture was then filtered and the solvent was removed under reduced pressure to afford a yellow solid. The solid was dissolved in dichloromethane (30 mL) and stored at −22 °C for 24 h. After filtration and removal of the solvent the product was obtained as a pale-yellow solid (yield = 72 %). M.p. 170 °C; ^{1}H NMR (CD_3CN): δ = 8.84 (s, 1 H; 2-imiH), 8.34 (d, J = 8.0 Hz; 2 H, AnH), 8.27 (d, J = 8.0 Hz, 2 H; AnH), 8.12 (s, 1 H; AnH), 7.72 (t, J = 8.0 Hz, 2 H; AnH), 7.66 (t, J = 8.0 Hz, 2 H; AnH), 7.46 and 7.36 (s, 2 × 1 H; 4,5-imiH), 6.47 (s, 2 H; CH_2An), 4.16 ppm (s; CH_3); IR (neat): $\tilde{\nu}$ = 3160, 3099 (C−H aromatic), 2976, 2936 (C−H aliphatic), 1568, 1465 cm^{-1} (C=C); ESIMS (CH_3CN): m/z: positive ion: 273 $[M]^+$; negative ion: 149 $[SO_3CF_3]^-$; elemental analysis calcd (%) for $C_{20}H_{17}F_3N_2O_3S$ (422.4287): C 56.87, H 4.06, N 6.63; found: C 56.91, H 4.08, N 6.65.

Synthesis of [AnCH$_2$MeIm][(N(CN)$_2$] (5): A mixture of **1** (0.309 g, 0.001 mol) and $Na[N(CN)_2]$ (0.156 g, 0.001 mol) in dichloromethane (20 mL) was stirred at room temperature in the dark for 24 h. The reaction mixture was then filtered and the solvent was removed under reduced pressure to afford a yellow solid. The solid was dissolved in dichloromethane (20 mL) and stored at −22 °C for 24 h. After filtration, the solvent was removed under vacuum to afford the product (yield = 71 %). M.p. 90 °C; ^{1}H NMR (CD_3CN): δ = 8.86 (s, 1 H; 2-imiH), 8.36 (d, J = 8.0 Hz, 2 H; AnH), 8.29 (d, J = 8.0 Hz, 2 H; AnH), 8.15 (s, 1 H; AnH), 7.74 (t, J = 8.0 Hz, 2 H; AnH), 7.69 (t, J = 8.0 Hz, 2 H; AnH), 7.48 and 7.38 (s, 2 × 1 H; 4,5-imiH), 6.48 (s, 2 H; CH_2An), 4.19 ppm (s, CH_3); IR (neat): $\tilde{\nu}$ = 3161, 3111 (C−H aromatic), 2969, 2919 (C−H aliphatic), 1557, 1455 cm^{-1} (C=C); ESIMS (CH_3CN): m/z: positive ion: 273 $[M]^+$; negative ion: 66 $[N(CN)_2]^-$; elemental analysis calcd (%) for $C_{21}H_{17}N_5$ (339.3995): C 74.32, H 5.05, N 20.63; found: C 74.39, H 5.08, N 20.65.

Synthesis of [AnCH$_2$MeIm][Tf$_2$N] (6): A mixture of **1** (0.309 g, 0.001 mol) and $LiN(SO_2CF_3)_2$ (0.287 g, 0.001 mol) in water (15 mL) was stirred at room temperature in the dark for 24 h. The reaction mixture was then filtered and the solid was washed with water (2 × 2 mL) to afford the product (yield = 95 %). M.p. 121 °C; ^{1}H NMR (CD_3CN): δ = 8.88 (s, 1 H; 2-imiH), 8.38 (d, J = 8.0 Hz, 2 H; AnH), 8.31 (d, J = 8.0 Hz, 2 H; AnH), 8.17 (s, 1 H; AnH), 7.77 (t, J = 8.0 Hz, 2 H; AnH), 7.71 (t, J = 8.0 Hz, 2 H; AnH), 7.51 and 7.41 (s, 2 × 1 H; 4,5-imiH), 6.51 (s, 2 H; CH_2An), 4.22 ppm (s; CH_3); IR (neat): $\tilde{\nu}$ = 3160, 3110 (C−H aromatic), 2972, 2921 (C−H aliphatic), 1561, 1457 cm^{-1} (C=C); ESIMS (CH_3CN): m/z: positive ion: 273 $[M]^+$; negative ion: 280 $[N(SO_2CF_3)_2]^-$; elemental analysis calcd (%) for $C_{21}H_{17}F_6N_3O_4S_2$ (553.5061): C 45.57, H 3.10, N 7.59; found: C 45.60, H 3.12, N 7.61.

Synthesis of [AnCH$_2$MeIm][PhBF$_3$] (7): A mixture of **1** (0.309 g, 0.001 mol) and $LiPhBF_3$ (0.287 g, 0.001 mol) in water (10 mL) was stirred at room temperature in the dark for 24 h. The reaction mixture was then filtered and the solid was washed with water (2 × 2 mL) to afford the product (yield = 90 %). M.p. 240 °C; ^{1}H NMR (CD_3CN): δ = 8.85 (s, 1 H; 2-imiH), 8.35 (d, J = 8.0 Hz, 2 H; AnH), 8.30 (d, J = 8.0 Hz, 2 H; AnH), 8.15 (s, 1 H; AnH), 7.76 (t, J = 8.0 Hz, 2 H; AnH), 7.70 (t, J = 8.0 Hz, 2 H; AnH), 7.68 (t; PhH), 7.50 and 7.40 (s, 2 × 1 H; 4,5-imiH), 7.35–7.25 (m, 4 H; PhH), 6.50 (s, 2 H; CH_2An), 4.20 ppm (s; CH_3); IR (neat): $\tilde{\nu}$ = 3163, 3113 (C−H aromatic), 2975, 2919 (C−H aliphatic), 1560, 1455 cm^{-1} (C=C); ESIMS (CH_3CN): m/z: positive ion: 273 $[M]^+$; negative ion: 144 $[C_6H_5BF_3]^-$; elemental analysis calcd (%) for $C_{25}H_{22}BF_3N_2$ (418.2693): C 71.79, H 5.30, N 6.70; found: C 71.88, H 5.32, N 6.71.

Synthesis of [(AnCH$_2$MeIm)$_2$][Tf$_2$N]$_2$ (8): A solution of **6** (0.555 g, 0.001 mol) in dichloromethane (15 mL) was stirred at room temperature for 6 days. The solvent was removed under reduced pressure and the remaining solid was washed with acetyl acetate (2 mL). The solid was recrystallized from dichloromethane and diethyl ether to afford the pure product (yield = 11 %). M.p. 260 °C; ^{1}H NMR (CD_3CN): δ = 8.80 (s, 2 H; 2-imiH), 8.35 (d, J = 8.0 Hz; 4 H, AnH), 8.30 (d, J = 8.0 Hz, 4 H; AnH), 7.76 (t, J = 8.0 Hz, 4 H; AnH), 7.70 (t, J = 8.0 Hz, 4 H; AnH), 7.50 and 7.40 (s, 2 × 2 H; 4,5-imiH), 6.50 (s, 4 H; CH_2An), 5.70 (s, 2 × 1 H), 4.20 ppm (s, 6 H; 2 × CH_3); IR (neat): $\tilde{\nu}$ = 3160, 3110 (C−H aromatic), 2970, 2900 (C−H aliphatic), 1558, 1451 cm^{-1} (C=C); ESIMS (CH_3CN): m/z: positive ion: 273 $[{}^1\!/_2M]^+$; negative ion: 280 $[N(SO_2CF_3)_2]^-$; elemental analysis calcd (%) for $C_{42}H_{34}F_{12}N_6O_8S_4$ (1107.0122): C 45.57, H 3.10, N 7.59; found: C 45.63, H 3.11, N 7.63.

Structure determination in the solid state: Relevant details for the structure refinements of **1**, **3**, **4**, **7**, and **8** are compiled in Table 1 and selected bond lengths and angles are given in Table 2 and the caption of Figure 5. For **1**, **4**, and **8** data collection was performed on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD at 140(2) K and data reduction was performed by using CrysAlis RED.[55] For **3** and **7** data collection was carried out on a Bruker Nonius APEX II CCD at 100(2) K and data reduction performed by using Eval CCD.[56] Structural solutions were performed by using SiR92[57] except for **7**, which was performed with SHELXS-97.[58] Structural refinement was carried out by using the SHELXTL software package, and graphical representations of the structures were made with Diamond. The structures were solved by direct methods and refined by full-matrix least-squares refinement (against F^2) with all non-hydrogen atoms refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions by using the riding model and were refined isotropically. Disorder for the hexafluorophosphate anion was modeled for **3** by means of the split model and by fixing the occupancy factor to 0.65 for the first site and to 0.35 for the second site. For **7**, the twin law (100/1$\bar{1}$0/10$\bar{1}$) was applied by using the TWIN command implemented in SHELXTL. Empirical absorption corrections were applied for **1**, **4**, and **8** by using DELABS,[59] and **3** and **7** by using SADABS.[60] CCDC-775848 (**1**), -775849 (**3**), -775850 (**4**), -775851 (**7**) and 775852 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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