Different Nature of the Interactions between Anions and HAT(CN)$_6$: From Reversible Anion−π Complexes to Irreversible Electron-Transfer Processes (HAT(CN)$_6$ = 1,4,5,8,9,12-Hexaazatriphenylene)

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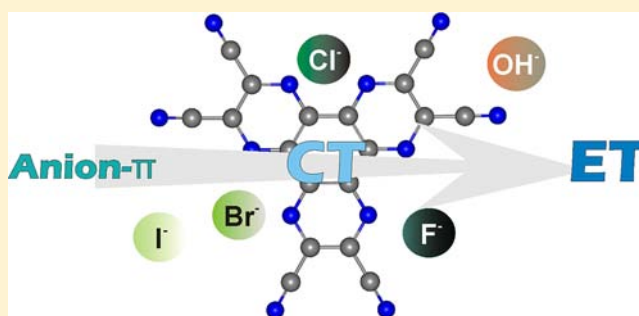[‡]Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Companys, 23, 08018 Barcelona, Spain
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Ⓢ *Supporting Information*

ABSTRACT: We report experimental evidence indicating that the nature of the interaction established between HAT(CN)$_6$, a well-known strong electron acceptor aromatic compound, with mono- or polyatomic anions switches from the almost exclusive formation of reversible anion−π complexes, featuring a markedly charge transfer (CT) or formal electron-transfer (ET) character, to the quantitative and irreversible net production of the anion radical [HAT(CN)$_6$]$^{•−}$ and the dianion [HAT(CN)$_6$]$^{2−}$ species. The preferred mode of interaction is dictated by the electron donor abilities of the interacting anion. Thus, weaker Lewis basic anions such as Br$^−$ or I$^−$ are prone to form mainly anion−π complexes. On the contrary, stronger Lewis basic F$^−$ or $^−$OH anions display a net ET process. The ET process can be either thermal or photoinduced depending on the HOMO/LUMO energy difference between the electron donor (anion) and the electron acceptor (HAT(CN)$_6$). These ET processes possibly involve the intermediacy of anion−π complexes having strong ET character and producing an ion-pair radical complex. We hypothesize that the irreversible dissociation of the pair of radicals forming the solvent-caged complex is caused by the reduced stability (high reactivity) of the radical resulting from the anion.

INTRODUCTION

The study of noncovalent, reversible interactions between anions and π-systems has gained significant recognition in the past decade due to the pivotal role of anions in many chemical and biological systems[1−4] and the involvement of π-rings in anion transport.[5] Since 2002, when the term "anion−π interaction" was used by Deyà, Frontera et al. to describe the interaction of anions with electron-deficient arenes,[6] many computational investigations involving the study of the physical nature of energetically favorable and reversible anion−π interactions have been reported.[7] Simultaneously, several experimental studies aiming for the confirmation of the existence of attractive anion−π interactions in solution and the quantification of their magnitudes were undertaken.[8−12]

Results derived from theoretical studies indicated that anion−π interactions are generally dominated by electrostatic and anion-induced polarization contributions.[6,13−15] Both theoretical and experimental investigations indicate that the magnitude of the interaction can be modulated by tuning the electrostatic component of the aromatic system. In several reports, the modulation of the strength of the anion−π interaction was achieved by installing different electron-withdrawing substituents in the aromatic system.[16−18] In

solution, the interactions of anions with neutral π-systems are generally weak and difficult to assess experimentally with good accuracy. In many cases, the anion−π interactions do not perturb the energies of the aromatic system's orbitals at the extent required for the experimental detection of changes in their absorption spectra.

On the other hand, several studies have shown that certain arenes possessing strong electron-accepting abilities and large positive quadrupole moments undergo significant changes in their absorption and emission spectra upon interaction with anions.[19,20] These anion−π interactions are associated with the observation of charge transfer (CT) bands displaying Mulliken dependence.[21,22] They are also related to π-donor/acceptor complexes in which the anion acts as donor and the π-system as acceptor.[19] The CT character of these anion−π complexes seemed to provide larger magnitudes to the interaction. Anion−π complexes with electron-transfer character (ET) have been postulated as an extreme of the energy continuum of the CT complexes.[23,24] An anion−π complex having a formal ET nature can be considered analogous to a pair of radicals in a

solvent cage. As the character of the anion−π complex changes from CT to ET type, the electrostatic nature of the interaction progressively decreases and the degree of covalent bonding (orbital mixing of donor/acceptor) progressively increases.[25] The dissociation of the solvent caged radical ion-pair produced by an anion−π complex with strong ET character is equivalent to a net ET process. Once dissociated, both radicals must be stable for the back-electron transfer to occur;[26] otherwise, the dissociation process becomes irreversible.

Interestingly, it has been demonstrated that strongly Lewis basic anions and aromatic systems featuring low reduction potentials are involved in such formal and irreversible (net) ET process.[24,27] The ET process can be either thermal or light induced and yield kinetically and thermodynamically stable, well-defined aromatic anion radicals and dianions.

In particular, Saha et al. evidenced that by tuning the electron-accepting ability (LUMO level) of a range of *N*-aryl-substituted naphthalenediimides (NDI) electron acceptors with respect to the Lewis basicity (HOMO level) of the electron-donor anions, the formation of anion/NDI complexes with CT/ET character can be switched to the generation of net ET processes.[24,28,29] The formation of discrete aromatic anion radicals or dianions in solution can be distinguished from that of supramolecular anion−π complexes with CT/ET character because the energy bands of the former, not being supramolecular aggregates, must be independent of the HOMO−LUMO energy gap. Likewise, aromatic anion radicals are EPR-active paramagnetic species, while supramolecular or covalent (Meisenheimer) anion−π complexes are usually diamagnetic.

In light of these observations, we considered that 1,4,5,8,9,12-hexaazatriphenylene **1** (HAT(CN)$_6$, Figure 1),
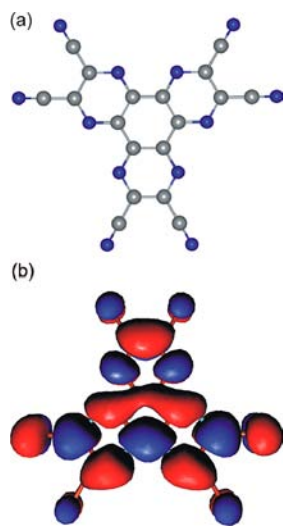

Figure 1. Structure of HAT(CN)$_6$ (a) and its computed LUMO orbitals diagram (b).

being a known strong electron acceptor, could also display a similar switching process upon interaction with anions. That is, formation of anion−π complexes with CT or formal ET character with weak donor anions undergo irreversible anion-mediated net ET processes with those having better donor properties. Previous studies by Dunbar et al. had shown the existence of CT bands in the complexation process of HAT(CN)$_6$ with several halide anions (i.e., Cl$^-$, Br$^-$, and I$^-$) using THF as solvent.[30] The corresponding anion−π complexes were assigned with a marked CT character.

Remarkably, the mathematical analysis of the UV−vis titrations performed by Dunbar et al. to assess the magnitude of the stability constant of the complexes afforded extremely high values ($K_{CT,X} = (1-4) \times 10^3$ M^{-1}) as compared to those typically determined $(1-10$ M$^{-1})$ for related complexes also displaying CT bands.[19,20]

The main aim of this work was to investigate the potential involvement of the aromatic system of HAT(CN)$_6$ **1** in anion-mediated net ET processes, either thermal or photoinduced, affording the discrete anion radical [HAT(CN)$_6$]$^{\bullet-}$ and dianion [HAT(CN)$_6$]$^{2-}$ species.

■ RESULTS AND DISCUSSION

We first investigated the spectroelectrochemical behavior of HAT(CN)$_6$ (**1**) in acetonitrile solution using nonbasic TBAPF$_6$ as supporting electrolyte to identify the spectroscopic features of radical [**1**]$^{\bullet-}$ anion ([HAT(CN)$_6$]$^{\bullet-}$) and [**1**]$^{2-}$ dianion ([HAT(CN)$_6$]$^{2-}$) upon stepwise electrochemical reduction of **1**. Cyclic voltammetry of **1** revealed two reversible redox couples with half-wave potentials at $E_{1/2} = -64$ and -450 mV vs Ag/AgCl.[31]

Application of a potential of -200 mV to a pale orange acetonitrile solution of **1** afforded a bright green solution of radical [**1**]$^{\bullet-}$ with the consequent change in the UV−vis spectrum (increase of absorption bands at 422, 684, 760 nm) (Figure 2).[32] Further reduction of the radical [**1**]$^{\bullet-}$ by applying
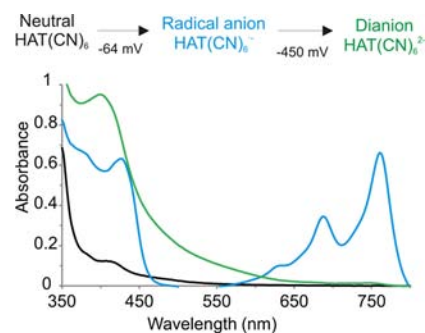

Figure 2. Spectroscopic changes of HAT(CN)$_6$ (50 μM in 0.1 M TBAPF$_6$/CH$_3$CN) upon direct electrochemical reduction. Black trace: neutral HAT(CN)$_6$. Blue trace: radical anion [HAT(CN)$_6$]$^{\bullet-}$. Green trace: [HAT(CN)$_6$]$^{2-}$ dianion.

a higher negative potential (-700 mV) produces a deep orange solution that contains mainly the [**1**]$^{2-}$ dianion species. The solution displays a distinguished UV−vis absorption spectrum with an intense absorption band centered at 394 nm (Figure 2).

The electrochemical bulk reoxidation of the anion radical [**1**]$^{\bullet-}$ to **1** proceeds uneventfully. However, the complete reoxidation of the dianion [**1**]$^{2-}$ to neutral **1** was not possible in the concentration range used for the spectroelectrochemistry experiment even applying high positive potentials (0 or +500 mV). Most likely, the dianion [**1**]$^{2-}$ is not persistent under these conditions and yields decomposition products, thus avoiding its complete reoxidation to **1** (vide infra).

Upon having determined the UV−vis spectral fingerprints for each species, we performed a series of UV−vis titrations of **1** with anions of different Lewis basicity using acetonitrile as solvent. We selected acetonitrile as the solvent to perform the titrations because THF solutions of **1** were prone to show the presence, in small amount, of the characteristic absorption bands of the radical [**1**]$^{\bullet-}$ (at 684, 760 nm).[33] Most likely, the

aromatic system of **1** is easily reduced by impurities present in the THF.

Addition of a few equivalents (1−3 equiv) of strong Lewis basic anions such as $^-$OH or F$^-$ to an acetonitrile solution of **1** provoked the appearance and increase of two well-defined absorption bands centered at 684 and 760 nm in the UV−vis spectrum (Figure 3). The maximum, relative intensity, and half-
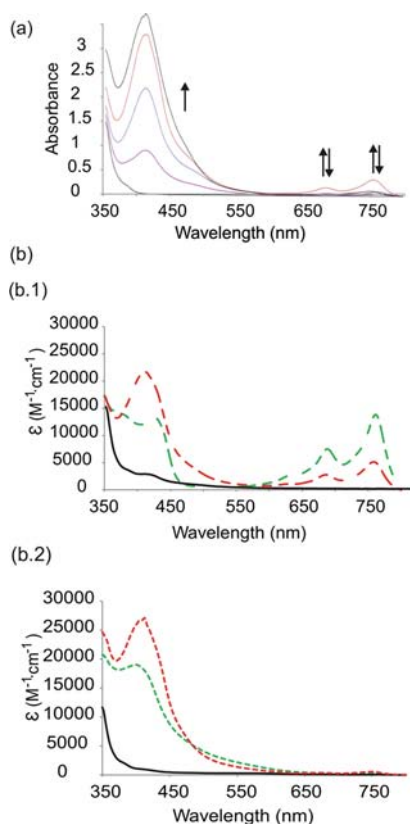

Figure 3. (a) UV−vis spectroscopic changes observed during the titration of **1** (0.13 mM, concentration constant during the titration) in acetonitrile solution with incremental amounts of TBAF (0, 0.8, 1.5, 4.5, 10 equiv). (b) Comparison of the spectroscopic features of the species $[1]^{\bullet-}$ (b.1) and $[1]^{2-}$ (b.2) generated by electrochemical (dashed green line) and chemical reduction (dashed red line). The dashed red line in (b.1) corresponds to 4.5 equiv of F$^-$ added and in (b.2) to 10 equiv of F$^-$ added. For comparison, the UV−vis spectrum of **1** is shown as a continuous black line in both figures.

band widths of these two bands were almost identical to those observed for radical $[1]^{\bullet-}$ generated by electrochemical reduction of $[HAT(CN)_6]$. The addition of increasing amounts of both anions (5−10 equiv of $^-$OH and F$^-$, respectively) induced a decrease in the intensity of the absorption bands centered at 684 and 760 nm with the concomitant increase of a new band centered at 402 nm. The spectral features of this new band perfectly correlate with the ones assigned to the dianion $[1]^{2-}$ generated by electrochemical reduction of the radical $[1]^{\bullet-}$ (Figure 3). It is worth noting that, although the chemical reduction of **1** with $^-$OH or F$^-$ mainly produces the formation of $[1]^{\bullet-}$ in the early salt additions (characteristic bands at 684 and 760 nm), the diagnostic band for the dianion (402 nm) is also present, although to a lesser extent. This finding suggested that during the chemical reduction of **1** with basic anions the exclusive formation of $[1]^{\bullet-}$ is not attainable.

The fact that, independent of the electron donor source we used ($^-$OH, F$^-$, or electrochemical reduction), the spectroscopic features of the species generated in solution were fully coincident provided strong support to its nonsupramolecular character. Anion−π complexes of **1** displaying CT bands do show a linear correlation (Mulliken dependence) between the charge-transfer energy and the donor properties (i.e., oxidation potential of the anion).[19,20,30]

We also performed an analogous UV−vis titration of **1** with a solution of TBAF also containing 1 equiv of *meso*-tetra *p*-nitrophenyl-tetramethyl calix[4]pyrrole (Figure S3).[34] The aryl-extended calix[4]pyrrole is a perfect host for the quantitative inclusion of the F$^-$ anion inside its deep aromatic cavity through hydrogen-bonding interaction with the pyrrole NHs. The fact that the F$^-$ anion is involved in a highly thermodynamically stable complex completely suppressed its enrollment in the chemical reduction of **1**. The diagnostic signals for $[1]^{\bullet-}$ and $[1]^{2-}$ were not detected at all during the titration with the F$^-$ inclusion complex. This result indicated that thermodynamically the formation of the F$^-$ inclusion complex is more favorable than the generation of the anion radical and dianion species of **1**.

Analogous titrations of **1** in acetonitrile solution with Cl$^-$, Br$^-$, and I$^-$ tetrabutylammonium salts indicated that the formation of the radical species $[1]^{\bullet-}$ took place to a much reduced extent.[35] The presence of small amounts of the radical $[1]^{\bullet-}$ can be inferred from the observation of its fingerprints bands (683 and 762 nm) showing very low intensity in the UV−vis spectra of the titrations (Figures S4−S6). In agreement with the observations of Dunbar et al. in similar titrations experiments carried out in THF as solvent, we also detected the presence of CT bands for the interaction of the halides with **1**. The relative intensity of the CT band with respect to the absorption bands assigned to $[1]^{\bullet-}$ indicated that the formation of anion−π complexes with CT character was the main process taking place in solution for the weaker Lewis basic anions.[36]

In addition to monatomic halide anions, we also evaluated if the interaction of **1** with polyatomic anions (i.e., $^-$OCN, $^-$SCN) was able to trigger net ET processes (Figure S5).[37] Incremental additions of the weak Lewis basic $^-$SCN anion to an acetonitrile solution of **1** did not provoke any sign of radical $[1]^{\bullet-}$ formation. On the contrary, the more Lewis basic $^-$OCN anion certainly produced net ET processes. The amount of $^-$OCN anion required for the production of the same levels of radical $[1]^{\bullet-}$ in solution is 20-fold larger (30 equiv) than when F$^-$ anion (1.5 equiv) is used as the electron-donor source. We hypothesized that the extent of the thermal ET depended, among other factors, that is, solvent, on the energy difference between the HOMO of the donor (anion) and the LUMO of the acceptor (**1**).

To rationalize the obtained results, we have calculated the HOMO and LUMO energies of the basic Lewis anions used in our studies and the aromatic electron acceptor compound **1** (using an acetonitrile continuum solvent model PCM).[38] This method has been successfully used to reproduce accurately the experimental solvation energies of halides in acetonitrile.[39] The thermal electron transfer from the HOMO energy level of the anion to the LUMO of the acceptor **1** will be thermodynamically favorable if the LUMO energy level of **1** lies below the HOMO energy level of the anion. As can be drawn from the data summarized in Table 1, only $^-$OH and F$^-$ HOMO levels are higher in energy than the LUMO level of **1**. These are the two anions that experimentally showed the existence of net

Table 1. Theoretically Calculated HOMO−LUMO Energy Levels in eV for 1, [1]•−, and the Anions Used in This Study[a]

	HOMO	LUMO
[**1**]	−7.54	−4.90
[**1**]•−	−4.35	−4.27
−OH	−3.27	
F−	−4.33	
HF₂−	−6.40	
Cl−	−5.25	
Br−	−5.31	
I−	−5.14	
−OCN	−4.98	
−SCN	−4.98	

[a]Calculations were performed with the SCI PCM model considering CH_3CN solvation.
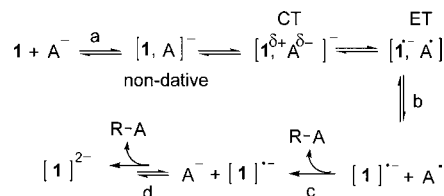
anion-induced ET processes in their interactions with **1**, yielding both the radical anion [**1**]•− and the dianion [**1**]²− depending of the number of equivalents added. The HOMO energy levels of polyatomic −OCN and −SCN anions are comparable in energy to the LUMO energy of the acceptor **1**. Taking into consideration a 1 kcal/mol as a typical error of the computed energy levels, theory predicts that thermal ET could happen (or not) from both anions. However, experimentally we observed that only the −OCN anion is capable of triggering the reduction of **1** to the anion radical [**1**]•−.

Besides the anion-mediated thermal ET, we next investigated if photoinduced electron-transfer (PET) processes from the HOMO of the anion to the SOMO−1 level of photoexcited **1** were taking place in the cases where the thermal electron transfer was mainly turned off (i.e., Cl−, Br−, I−, −SCN). We observed a slight increase in the intensity of the bands corresponding to the anion radical [**1**]•− after 5 min irradiation of an acetonitrile solution containing **1** (0.14 mM) and 60 equiv of the Br− or I− anions (Figure S8). These results pointed out that PET processes did not take place significantly from the Br− and I− anions. This observation demonstrated that the thermal/photoinduced net ET processes to **1** are not significant when Br− and I− anions are used as electron donor sources. Conversely, we detected significant CT bands in the titrations of **1** with these anions. These CT bands showed a Mulliken dependence behavior (478 and 578 nm for Br− and I−, respectively; Figures S5−S6) and were indicative of the formation of anion−π complexes in solution with CT/ET character.[21,22] We did not make any effort in determining the stoichiometry of these complexes; however, related anionic complexes formed in THF solution were assigned to a (X−)₃⊂**1**₂ stoichiometry by Dunbar et al.[30]

Remarkably, when the Cl− anion (60 equiv) was present in the solution of **1**, the photoexcitation process did not produce the bands assigned to the anion radical [**1**]•−. Instead, what we observed after the photoexcitation process was a significant increase of the diagnostic band centered at 402 nm for the dianion [**1**]²− (Figure S9).

Taken together, the results described above suggested that all of the investigated anions (A−) engage in the formation of anion−π complexes, of not determined stoichiometry, with **1**. The formed anion−π complexes had a significant CT/ET character. The electron donor properties of the anion modulate the amount of CT or formal ET character of the complex. Strong Lewis basic anions (i.e., −OH, F−, or −OCN) render

anion−π complexes with a marked formal ET character, that is, resembling a solvent caged radical ion-pair complex (Scheme 1).

Scheme 1. Schematic Representation of the Possible Different Equilibria and Irreversible Processes Occurring in the Interaction of HAT(CN)₆ (1) with Anions (A−)[a]

[a](a) Formation of the anion−π complex. The different characters are indicated using equilibria between the different complexes: non-dative, CT, and ET dative. (b) Reversible dissociation of the components of the solvent caged radical pair produced by ET within the anion−π complex. (c) Elimination of the highly reactive radical from the equilibria (A·) and irreversible formation of the stable anion-radical of the aromatic acceptor ([**1**]•−). (d) A similar series of reversible and irreversible steps could produce the dianion ([**1**]²−).[43]

The dissociation (diffusive separation) of the components of the radical pair complex [**1**•−, A•], which is analogous to a solvent caged anion−π complex with strong or formal ET character, produces net radicals: [**1**]•− and A•.[40] If one of the radicals of the pair is very reactive, that is, not persistent in solution, it renders the back-electron-transfer process irreversible. We assume that this is the case for the radical of fluorine or the cyanate, which may act as sacrificial agents reacting probably with solvent or counterions. Conversely, the anionic radical of **1** seems to be kinetically and thermodynamically more stable and is easily detected by different spectroscopic techniques (UV−vis and EPR vide infra).

On the contrary, weaker Lewis bases (i.e., Cl−, Br−, I−, −SCN) produce anion−π complexes with CT character but significantly reduced ET nature. In short, these anion−π complexes are too weak, and the distance between the donor and the acceptor is too large for an efficient formal ET.[41] Consequently, the radicals derived from the components of the anion−π complex, if any, are formed to a much lesser extent.
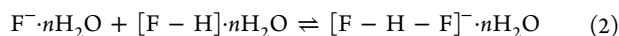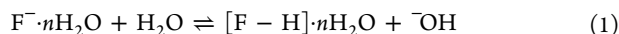
The generation of the dianion [**1**]²− is likely to occur due to a second formal ET process mediated by the anion through the intermediacy of an anion−π complex involving the anion-radical [**1**]•− as π-acceptor system. Only highly Lewis basic anions are capable to induce the second formal ET process thermally, and Cl− anion is the only one displaying this second ET by means of light-induced process (PET).[42]

Computational results are in agreement with the formation of an intermediate complex between [**1**]•− and either F− or −OH, prior to the [**1**]•− reduction to [**1**]²−. Both complexes present favorable interaction energies (−5.7 and −7.6 kcal/mol), the complex with −OH being 2 kcal/mol more favorable. Interestingly, the equilibrium distances donor−acceptor are very short (<2.3 Å, see Figure S2), which likely indicates an orbital (covalent contribution) interaction between radical [**1**]•− moiety and the anion that compensates for the electrostatic repulsion between the anionic components of the complex.[43]

The PET process observed for the Cl− anion is likely to happen when the thermal electron-transfer process is not

favored thermodynamically and the HOMO of the chloride anion has higher energy than the SOMO−1 of the photo-excited state of neutral **1***. Moreover, during the photo-excitation process, the second ET required to transform the radical anion $[\mathbf{1}]^{\bullet-}$ into the dianion $[\mathbf{1}]^{2-}$ might also be light-gated. For this reason, after photoexcitation, we only observe the band at 402 nm corresponding to the dianion $[\mathbf{1}]^{2-}$ but not the UV−vis bands for the radical (Figure S9). Photoexcitation of solutions containing mainly $[\mathbf{1}]^{\bullet-}$ previously generated by adding F⁻ or ⁻OCN anions induce the disappearance of the absorption bands of the radical anion and the emergence of diagnostic absorbance for the dianion species $[\mathbf{1}]^{2-}$.

We performed ¹⁹F NMR experiments to explore and verify the generation of radical species in the interaction of **1** with F⁻. The addition of incremental amounts of **1** to a 1 mM CD₃CN solution of tetrabutylammonium fluoride (TBAF) showed the gradual broadening and disappearance of the signal corresponding to the fluoride atoms in the bifluoride anion HF_2^- species (Figure S10). At this concentration, we were not able to detect the expected signal for hydrated fluoride in the CD₃CN solution prepared from solid trihydrated TBAF. Even though the deprotonation of water by fluoride (eq 1) is not thermodynamically favored, it is known that most organic solutions of TBAF contain the bifluoride anion. This is because any proton transfer to the fluoride ion results in the rapid formation of the thermodynamically very stable bifluoride anion (eq 2) featuring the strongest known hydrogen bond. Most likely, due to the large water content of our acetonitrile solution, the proportion of bifluoride increased drastically.[44]

$$F^- \cdot nH_2O + H_2O \rightleftharpoons [F-H] \cdot nH_2O + {}^-OH \qquad (1)$$

$$F^- \cdot nH_2O + [F-H] \cdot nH_2O \rightleftharpoons [F-H-F]^- \cdot nH_2O \qquad (2)$$

We observed that the signal for the bifluoride completely disappeared upon addition of approximately 1.2 equiv of **1**. As mentioned above, the bifluoride is in equilibrium with the hydrated fluoride. The consumption of the fluoride anion as electron donor in the thermal and ET reaction with **1** affording the highly reactive fluorine radical must be responsible for the disappearance of the fluorine signal corresponding to bifluoride (see Figure S10). Because of the water content in the CD₃CN and the fluoride/bifluoride equilibria that exist in solution, the participation of the hydroxide as electron donor cannot be ruled out. Nevertheless, the disappearance of the bifluoride corresponding signal gives strong support to the hypothesis that the hydrated fluoride can also act as electron donor of the net ET process.

On the other hand, the addition of 0.5 equiv of TBAF to a 1 mM CD₃CN solution of **1** showed a significant upfield shift (δ = −168 ppm; $\Delta\delta$ = −18 ppm) of the fluorine signal corresponding to the bifluoride species as compared to the chemical shift value measured for bifluoride in a 1 mM CD₃CN solution of TBAF (Figure S11). The signal for the fluorine atom in the hydrated fluoride species was not detected. The origin of the upfield shift for the HF_2^- signal is not known to us. We hypothesize that it could be due to the existence of a fast chemical exchange on the NMR time scale between free HF_2^- and bound HF_2^- to free **1**, which is in high excess in solution in the early stages of the titration.[45] The addition of more than 0.5 equiv of TBAF produced the gradual downfield shift of the bifluoride signal until it reached the expected chemical shift value for the free HF_2^- species (after 5 equiv of TBAF). This observation can be explained assuming that the consumption of

1 due to the net ET process and the addition of extra bifluoride provoke an increase in the concentration of the HF_2^- free species. Low temperature experiments performed in non-deuterated acetonitrile to try to clarify the putative involvement of HF_2^- binding to **1** were not conclusive but indicated the participation of HF_2^- anion in chemical exchange processes.[46] The fluorine signal corresponding to hydrated $F^- \cdot n(H_2O)$ emerged at δ = −118 ppm after the addition of 10 equiv of TBAF (Figure S11).

We also recorded ¹³C{¹H} NMR spectra during the incremental addition of TBAF to a 7 mM solution of **1** (Figure S12). After the addition of 1 equiv of TBAF, only the signals corresponding to the carbon atoms of tetrabutylammonium cation can be observed. This result suggested that species derived from the reaction of **1** with F⁻/⁻OH had a paramagnetic character as is expected for radical $[\mathbf{1}]^{\bullet-}$. In the presence of 2 and 3 equiv of TBAF, no carbon signals were detected in the aromatic region of the spectrum. After the addition of a high excess of TBAF (15 equiv), different carbon signals appeared in the chemical shift region expected for sp² carbons. Probably, these carbon signals correspond to degradation products of **1** or covalent anion complexes produced due to the high excess of the strong Lewis basic anions (Figure S12).[47] Conversely, we did not observe significant changes in the ¹³C{¹H} NMR spectra of **1** during the addition of less Lewis basic anions, (i.e., TBAI, Figure S13), only some broadening in the carbon signals.

The chemically generated radical anion $[\mathbf{1}]^{\bullet-}$ and dianion $[\mathbf{1}]^{2-}$ species (F⁻/⁻OH induced reduction by 1 and 2 equiv addition, respectively) were treated with excess of $NOBF_4$ in separate NMR tubes. The ¹³C{¹H} NMR spectrum of the solution corresponding to the reoxidation of the radical anion $[\mathbf{1}]^{\bullet-}$ displayed the carbon signals expected for **1** with intensities of approximately 80% with respect to those of **1** before experiencing chemical reduction (benzene used as internal standard, Figure S14). If the acquisition of the ¹³C{¹H} NMR spectrum of the sample is continued (2048 scans), carbon signals of low intensity are detected in the sp² region. Some of the low intensity carbon signals and their chemical shift values are coincident with those detected when 15 equiv of TBAF was added. This result provides compelling evidence that the reduction of **1** to the radical anion $[\mathbf{1}]^{\bullet-}$ induced by F⁻/⁻OH complexation is the predominant reaction pathway in solution. It also rules out the significant formation of covalent Meisenheimer (sigma) complexes, which will be responsible for the modification of the structure of **1** through S_NAr reactions. In contrast, the regeneration of **1** from the mixture containing 2 equiv of F⁻, carried out by adding more than 3 equiv of $NOBF_4$, produced a ¹³C NMR spectrum in which the signals of the carbons from regenerated **1** were of intensity similar to those assigned to reaction products (Figure S15). These findings suggest that the dianion $[\mathbf{1}]^{2-}$ species is less persistent in solution than the radical anion $[\mathbf{1}]^{\bullet-}$ and that the addition of more than 1 equiv of F⁻ provokes significant modifications of the covalent structure of **1**. In the same vein, we investigated the chemical regeneration of **1** from the solution containing 1 equiv of ⁻OH. The carbon signals for regenerated **1** were observed but to a lesser extent than in the case of F⁻ (Figure S16). Interestingly, no carbon signals for **1** were detected in the regeneration process starting from a mixture containing **1** and 2 equiv of ⁻OH (Figure S17). Most likely, the increase in concentration of the more nucleophilic ⁻OH anion is the main reason for the observed different behaviors. In addition, the lack

of detection of fluorine NMR signals that could be assigned to the degradation products of **1** produced in the presence of excess F⁻ suggests that, also in this case, the unavoidable presence of ⁻OH anion in the TBAF solution is involved in the final degradation of the structure of **1**.[48]

We also probed the interaction of **1** with TBAF using conductometric measurements. The incremental addition of **1** to an acetonitrile solution of TBAF (1 mM) induced a significant decrease in the molar conductance of the solution. This is probably due to the conversion of the F⁻/⁻OH anions into reactive radical, which are rapidly trapped by reaction with solvent molecules and the formation of the much larger anion-radical and dianion species of **1** featuring a reduced mobility. We did not observe any decrease in molar conductance in similar experiments performed with TBABr or TBAI (Figure S18).

Finally, to demonstrate the formation of the radical [**1**]•⁻ species, we carried out electron paramagnetic resonance (EPR) measurements. The titration of **1** with TBAF gradually generated the characteristic EPR signals corresponding to a paramagnetic compound, which can be assigned to [**1**]•⁻ (g = 2.00375).[49,50] The addition of incremental amounts of the TBAF salt provoked an increase in the intensity of the EPR signal with a concomitant higher definition of the hyperfine coupling structure (Figure 4a). The best simulation fit is
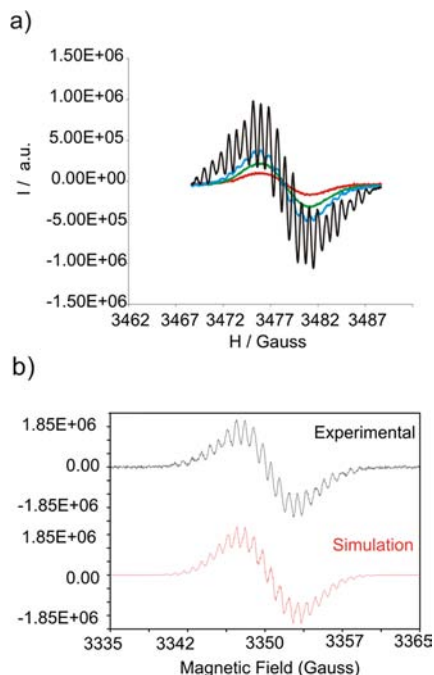

Figure 4. (a) EPR spectral changes detected for the titration of **1** (0.95 mM) with TBAF in acetonitrile solution (0.5, 1, 2, 4 equiv); and (b) experimental and simulated EPR spectra of radical anion [**1**]•⁻ molecule in CH₃CN at room temperature.

obtained considering a distortion of the planar symmetry of the anion radical molecule and as a consequence using four groups of three equivalent nitrogen atoms: $aN_A = 1.27$ G, $aN_B = 0.96$ G, $aN_C = 0.83$ G, and $aN_D = 0.75$ G with a g factor of 2.0038 (Figure 4b). We also observed a linear relationship between the intensity of the EPR signal and the number of equivalents of the TBAF salt added (Figure S19).[51]

Moreover, we performed similar studies with other halide salts of less Lewis basic anions (TBACl and TBABr) to investigate whether the formation of the anion radical [**1**]•⁻ could be detected by EPR measurements.[52] The obtained results are in good agreement with the observations made in the UV−vis experiments. In short, less basic anions do form the anion radical [**1**]•⁻ but to a much reduced extent (Figure S20) as compared to the stronger Lewis bases. To conclude with our EPR measurements, we photoexcited the acetonitrile solutions of **1** containing an excess of TBACl and TBABr salts. The existence of PET process also in these cases was detected with the EPR measurements too. Photoexcitation of the solutions during 5 min provoked a sensible increase in the intensity of the EPR signal of the thermal generated anion radical [**1**]•⁻ (Figure S20).

■ CONCLUSIONS

The present work demonstrated the different nature of the interactions that are established between a series of monatomic and polyatomic anions, having different Lewis basic strength, and the aromatic compound **1** featuring strong electron acceptor abilities and a high positive quadrupole moment. Experimental results carried out exclusively in acetonitrile solution indicated that the stronger Lewis basic anions (e.g., ⁻OH, F⁻, ⁻OCN) are involved in a net thermal electron-transfer process that takes places between the HOMO energy level of the anion and the LUMO of HAT(CN)₆. Less basic anions (Br⁻, I⁻, and ⁻SCN) interact with HAT(CN)₆ mainly producing anion−π complexes with CT character but reduced thermodynamic stabilities.

These weaker basic anions are also involved in a net thermal ET process with HAT(CN)₆ but to a very reduced extent. In the cases where the thermal ET process is turned off, it can be slightly activated by photoexcitation of the electron-accepting aromatic system. The Cl⁻ anion constitutes a special case, as it behaves as a weak basic anion under thermal conditions yielding mainly anion−π complexes with CT character on interacting with HAT(CN)₆. However, the photoexcitation of the mixture induces a quantitative PET process yielding the dianion [HAT(CN)₆]²⁻.

We have presented sound experimental evidence of the reduction process of HAT(CN)₆ mediated by the interaction with Lewis basic anions. The results obtained from UV−vis and NMR spectroscopies are in full support of our conclusion. EPR measurements have provided irrefutable evidence to the formation of radicals through the interaction of HAT(CN)₆ and suitable anions. In addition, computational calculations backed up our experimental results explaining the energetic requirements that are necessary to achieve a thermal electron transfer from the HOMO level of an anion to the LUMO of the HAT(CN)₆.

On the basis of the experimental results, we proposed a tentative explanation for the events that are involved in the interaction of anions with HAT(CN)₆. We also suggested reasons for the observed switching in the mode of interaction. The character of the initially formed anion−π complex [**1**,A]⁻ is strongly dictated by the electron donor abilities of the anion. In turn, the character of the anion−π complex controls the preferred mode interaction with the aromatic systems: anion−π supramolecular complex formation or net ET process yielding radical and dianion species of HAT(CN)₆. Our proposal is in complete agreement with the electron-transfer mechanism that is operative in neutral donor−acceptor complexes.[23]

To the best of our knowledge, this work is the first to demonstrate that $F^-/^-OH$ anions can thermally reduce $HAT(CN)_6$. Although thermodynamically the radical formation reaction is endergonic, we attributed the driving force of the equilibria toward the formation of the radical anion and dianion of $HAT(CN)_6$ to the sacrificial nature of $X^\bullet$ radicals generated, which acts as thermodynamic sink. The sacrificial reaction prevents the back-electron transfer from $[\mathbf{1}]^{\bullet-}$ to $X^\bullet$, leading to the radical formation irreversibly. In turn, $[\mathbf{1}]^{\bullet-}$ radical anion is stable in solution being converted to the final $[HAT(CN)_6]^{2-}$ dianion by means of a second ET reaction possibly mediated by the anion donor.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

General experimental methods, additional experimental and computational results discussed in the text, and their associated figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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(37) TBA(N_3) salt has also been tested, but the obtained results point to some reaction between N_3^- anion and **1**.

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(46) HF_2^- is involved in different chemical exchange processes. F^- acts as strong base yielding the highly stable bifluoride anion. Water ($TBAF + H_2O \leftrightarrow TBAHF_2 + TBAOH$) and even the solvent can be the source of the proton. In some deuterated solvents like acetonitrile, DF_2^- is also produced. We performed a low temperature $^{19}F-^{19}F$ EXSY NMR experiment of TBAF in nondeuterated acetonitrile solution, and indeed we observed chemical exchange between the fluoride (singlet) and bifluoride (doublet) signals (Figure S18).

(47) A larger number of scans (NS = 512) was necessary to obtain the signals in the $^{13}C\{^1H\}$ NMR as compared to the neutral $HAT(CN)_6$ (NS = 64).

(48) The X-ray structure of single crystals grown from a solution containing **1** and an excess of TBAF that was left unattended for several months showed the substitution of three of the six cyano groups of **1** by hydroxyl groups.

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(51) Higher amounts of salt induced a change and decrease in the EPR signal probably due to the formation of the dianion and other radical species caused by the degradation of the structure of **1**.

(52) EPR titration studies with TBAOH were also performed. However, the obtained EPR spectra are different from the ones registered with the halides (Figure S23). These differences are likely to be produced by the presence of different radical species in solution. The stronger nucleophilicity of the ^-OH anion in comparison to the halide anions favors the structural modifications of **1** through S_NAr reactions.