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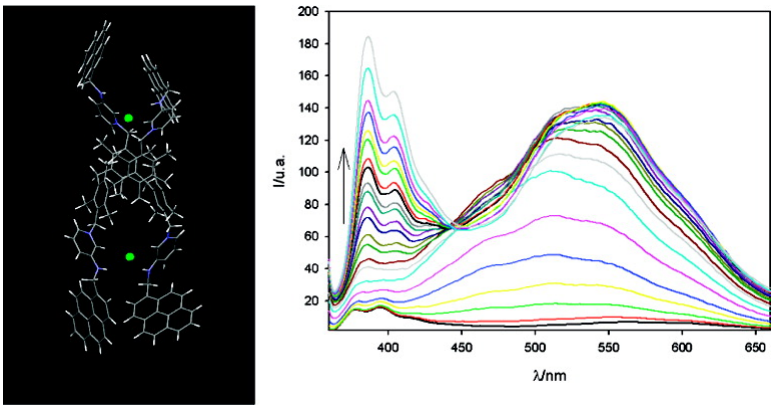

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Induced Fit Interanion Discrimination by Binding-Induced Excimer Formation

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Abstract: The synthesis, photophysical, and anion-binding properties of a series of di-, tri-, and tetrapodal anion-binding hosts based on aminopyridinium units with pyrenyl reporter groups are described. The ditopic mesitylene-derived calix[4]arene-based host **4** binds strongly to dicarboxylates, particularly malonate, in a 2:1 anion:host ratio but is essentially nonemissive in the presence of all anions except chloride because of intramolecular quenching by the pyridinium units. Addition of chloride results in a conformational change, giving an initial increase in emission assigned to intramolecular excimer formation. Further chloride addition also results in an increase in the intensity of the pyrenyl monomer emission as chloride binding reduces the acceptor ability of the pyridinium groups. This behavior is not exhibited by control compounds **5** and **6**, which lack the ditopic geometry and calixarene spacer unit; however, tripodal **6** forms 1:2 anion:host complexes with a range of anions.

Introduction

The binding and sensing of simple anions such as chloride is particularly topical.[1−24] A typical molecular sensor involves an analyte binding moiety coupled to a signaling group such as a fluorophore or redox-active substituent via a spacer capable of signal transduction.[25,26] Alternatively, a ternary indicator displacement mechanism may be employed.[27] It is a double challenge to both produce selective receptors and transduce the selective binding into an observable signal. While rigidly preorganized receptors such as macrobicycles[9,28] can give highly selective binding, effective sensing is often achieved in both natural and artificial systems by arrays of more flexible, differential receptors that respond to varying degrees to each analyte.[29−32] Flexible receptors offer the interesting possibility of *induced fit signal transduction* in which analyte binding results in a conformational change that brings about signal generation (e.g., Ca^{2+} binding by calmodulin[33,34]). The interest-

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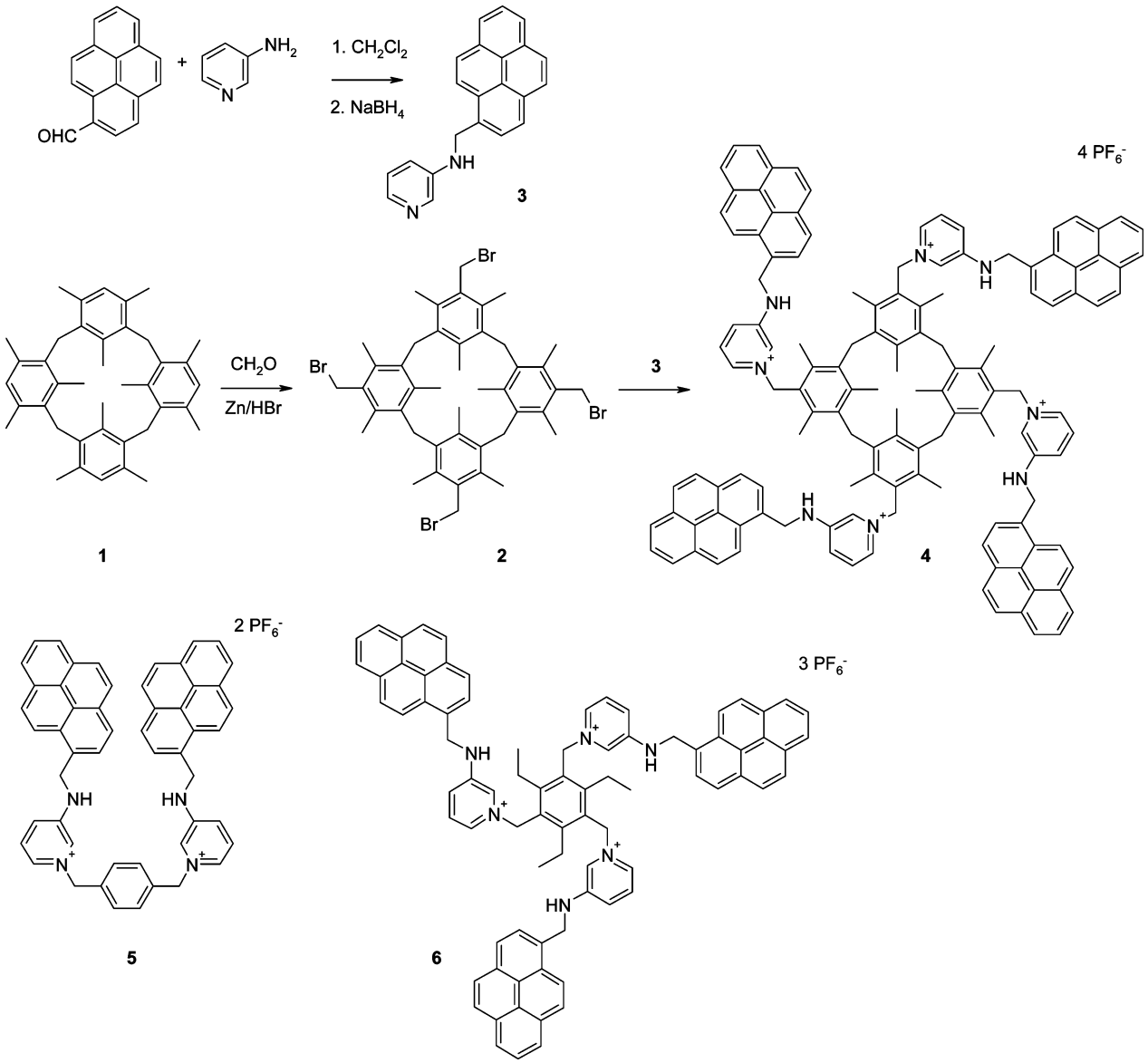
Scheme 1. Preparation of New Tetrapod Host **4** and Structural Formulas of Hosts **5** and **6**



ing point about this mechanism is that it is only analytes that result in the appropriate conformational change that will result in signal generation, *even if they are not the strongest bound by the receptor*. Thus, a relatively unselective receptor may still prove highly effective at sensing particular anions because of the differential conformational changes induced by different analytes. We applied this concept in the redox sensing of anions[35−37] using the flexible triethylbenzene scaffold, a very versatile platform for constructing small, flexible tripodal anion and cation receptors.[8,29,31,38−45] We explored in detail the anion-induced conformational changes in these kinds of receptors,[19,46] and Duan et al. used conformational flexibility in these systems in both redox and fluorescent sensing.[7,47] We also examined flexible anion hosts based on inorganic cores,[48−50] and we recently described the extension of our work to much larger calix[4]arene scaffolds.[51] We now report a flexible calixarene-based fluorescent anion sensor and its comparison with related

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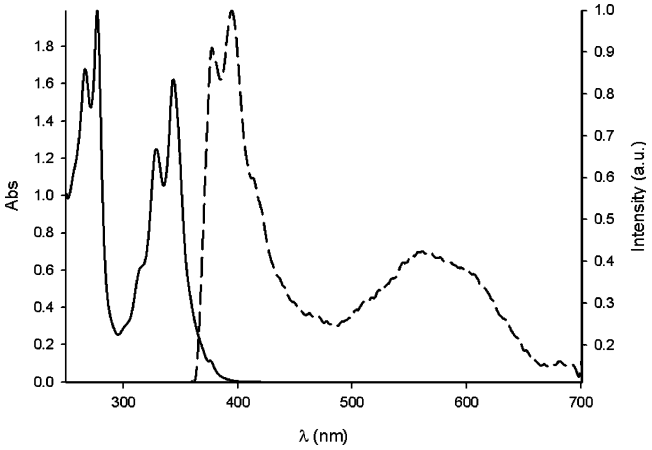

Figure 1. Absorption and fluorescence (λ_{exc} = 340 nm; solid and dashed lines, respectively) spectra of **4**·4PF_6^- in CH_3CN solution.

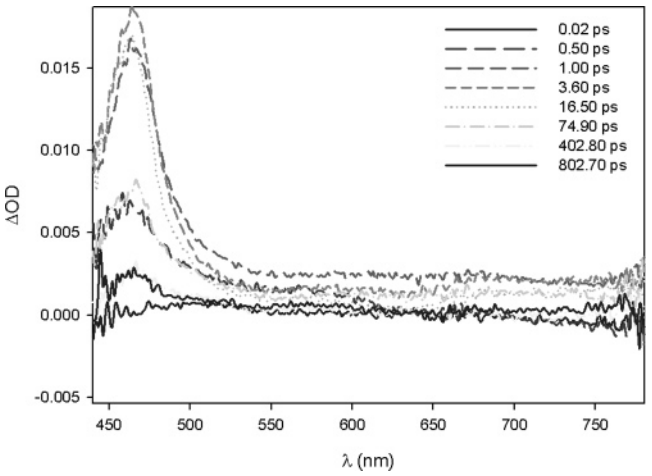

Figure 2. Transient absorption spectrum (λ_{exc} = 266 nm) of **4**·4PF_6 in CH_3CN solution at room temperature. Decay at 465 nm.

di- and tripodal systems and show that conformational change is a key factor in signal generation.

Results and Discussion

Syntheses. The mesitylene-derived calix[4]arene (**1**)[52,53] is locked in the 1,3-alternate conformation.[54] It has been used as a scaffold for coordination polymers and in organometallic hosts for anions.[55−57] Compound **1** was readily bromomethylated by action of formaldehyde in the presence of Zn/HBr to give the tetra(bromomethyl) derivative, **2**. Compound **2** was reacted with pyren-1-ylmethyl-pyridin-3-yl-amine (**3**, prepared by analogy with related ligands[46] as shown in Scheme 1) to give the target compound **4** in 81% yield as the tetrabromide. Metathesis with KPF_6 cleanly yielded the analogous hexafluorophosphate salt. The related di- and tripodal hosts, **5** and **6**, were prepared in a similar fashion starting from α,α′-dibromo-*p*-xylene and 1,3,5-tri(bromomethyl)-2,4,6-triethylbenzene.[41]

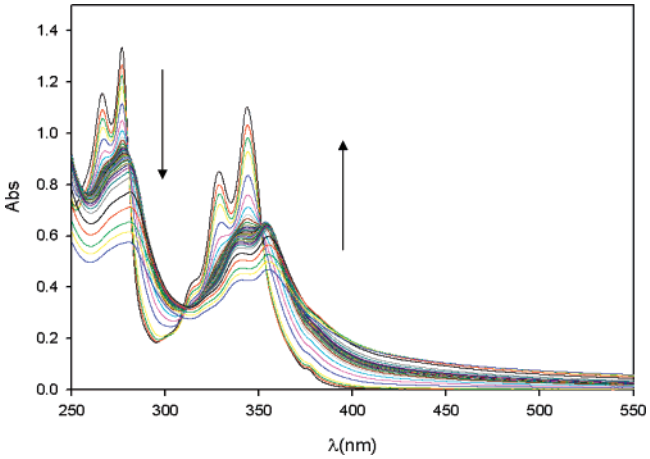

Figure 3. Absorption spectra of **4**·4PF_6^- (9.2×10^{-6} M) in CH_3CN and upon addition of increasing amounts of Cl^- up to 50 equiv.

Table 1. Binding Constants (log β) of Receptors **4**−**6** as the PF_6^- Salts with Various Anions Obtained from UV−vis Titration in Acetonitrile with Anions Added as NBu_4^+ Salts[a]

anion/receptor	stoichiometry (host:guest)	4	5	6
Cl^-	2:1		9.2 ± 0.3	12.1 ± 0.4
	1:1	4.2 ± 0.2	4.2 ± 0.1	5.7 ± 0.3
	1:2	7.7 ± 0.4		
Br^-	2:1		<4	11.7 ± 0.1
	1:1	3.6 ± 0.4	3.2 ± 0.2	5.1 ± 0.4
	1:2	7.0 ± 0.1		
NO_3^-	2:1	low	low	low
	1:1			
	1:2			
CH_3COO^-	2:1		12.7 ± 0.2	11.6 ± 0.3
	1:1	3.8 ± 0.2	6.0 ± 0.3	5.5 ± 0.2
	1:2	5.6 ± 0.2	10.5 ± 0.3	<4
$CH_2CH_2(COO)_2^{2-}$	2:1			10.5 ± 0.6
	1:1	5.5 ± 0.1	5.0 ± 0.2	5.3 ± 0.3
	1:2	11.2 ± 0.2		<4
$CH_2(COO)_2^{2-}$	2:1			10.0 ± 0.3
	1:1	5.2 ± 0.1	5.4 ± 0.2	4.7 ± 0.3
	1:2	11.2 ± 0.2		

[a] Titrations were carried out at 25 °C. Binding constants were assessed using Specfit.[64]

Photophysical Properties of the Hosts. The photophysical properties of **4**−**6** as the hexafluorophosphate salts were studied in acetonitrile solution. The absorption spectra of **4**−**6** are almost superimposable, all showing two sets of bands in the 250−300 and 300−400 nm region, similar to the spectrum of pyrene itself in the same experimental conditions.[58] In these hosts, however, the absorption band in the 300−400 nm region is broader and less intense with a small tail above 380 nm which is not present in the parent chromophore. This behavior can be attributed to small intramolecular interactions among the different pyrene units at the ground state and/or to the occurrence of a charge-transfer transition between the pyrene and the pyridinium groups.

In contrast, the fluorescence spectra of all the hosts are very different from those typically presented by pyrene derivatives. In particular, the band at ca. 400 nm typical of the pyrene monomer is, in all cases, much less intense. The quantum yields for **4**·4PF_6, **5**·2PF_6, and **6**·3PF_6 are $\Phi = 1.4 \times 10^{-3}$, 2.0×10^{-3}, and 1.4×10^{-3}, respectively, while that for pyrene itself

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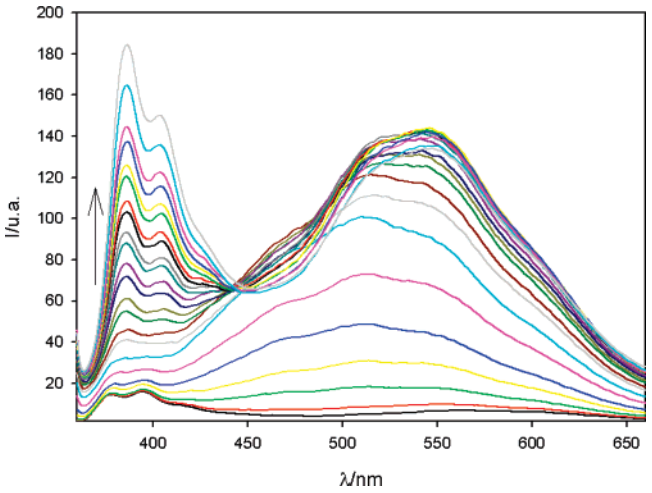

Figure 4. Fluorescence spectra (λ_{exc} = 343 nm) of **4**·4PF_6^- (1.3×10^{-5} M) in CH_3CN upon addition of increasing amounts of Cl^- up to 50 equiv.

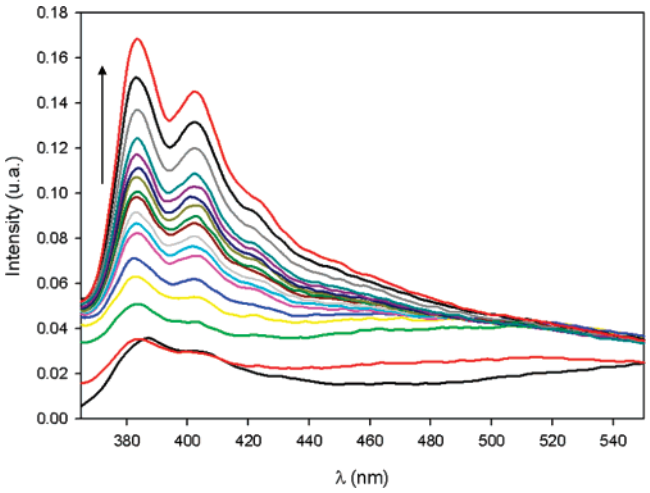

Figure 6. Fluorescence (λ_{exc} = 340 nm) spectra of **4**·4PF_6^- and upon increasing amounts of acetate anions in acetonitrile solution.

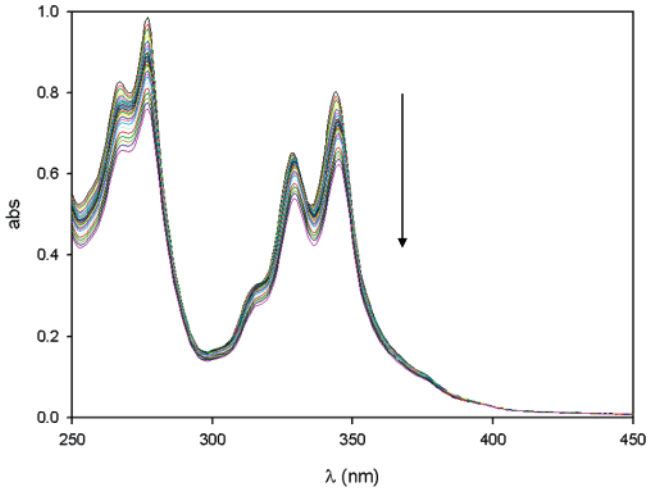

Figure 5. Absorption spectra of **6**·4PF_6 (8.2×10^{-6} M) in CH_3CN and upon addition of increasing amounts of Cl^- up to 20 equiv.

in aerated solution is 0.07.[59] Only for **4**·4PF_6, the fluorescence spectrum contains an additional, very weak, and unstructured band in the 500−620 nm region (Figure 1). Interestingly, the maximum of this band is red shifted by ca. 80 nm relative to the excimeric band of pyrene itself,[59,60] consistent with formation of an intramolecular exciplex involving the pyridinium ion. The excited-state lifetimes are also very short for **4**−**6** (τ < 0.3 ns for all compounds, compared to 18 ns for pyrene in aerated solution), ruling out the possibility of formation of intermolecular excimers or exciplexes.

The strong quenching of the fluorescence in the hosts is most probably due to a photoinduced electron-transfer (PET) process from the excited state of the pyrenyl moiety to one of the electron-deficient pyridinium ions. Together with the favorable redox potentials of the different units ($E_{red}(P^+/P)$ of pyrene = +1.16 V vs SCE;[61] $E_{red}(P^+/P)$ of pyridinium = −1.2 V vs SCE[62]) and the energy of the singlet excited state of the chromophore ($E^{\circ\circ}$ = 3.26 eV), this assignment is supported by the evidence of a band centered at 465 nm in the transient absorption spectrum of all the compounds (e.g., Figure 2 for **4**·4PF_6) that can be attributed to the pyrene cation.[63]

Anion Binding. Anion binding of chloride, bromide, nitrate, acetate, malonate, and succinate by **4**−**6** was studied by means of UV−vis and fluorescence titrations in acetonitrile. The association constants derived from these experiments, fitted using the Specfit software,[64] are gathered in Table 1.

For all three hosts, addition of nitrate did not cause any appreciable change in the absorption or fluorescence spectra, indicating that the association constant is too small to observe any complexation process in our experimental conditions or that formation of the adduct does not cause any appreciable change in the structure of the hosts. However, observation of changes in the NMR spectrum upon addition of this anion (see below) supports at least for host **6** the latter hypothesis.

From the spectroscopic point of view, addition of all the other anions to **4** results in significant changes in the absorption spectra (Figure 3) for all of the anions studied. Only in the case of addition of chloride, however, is there an appreciable effect on the emission spectrum (Figure 4). In particular, the absorption bands typical of the pyrene chromophore undergo a bathochromic shift and an intensity decrease, while an increase in the absorbance in the 350−550 nm region is observed. The absence, typically observed for this host, of clear isosbestic points suggests multiple binding processes.

We attribute these changes to formation of dimeric pyrene derivatives in the ground state, indicating that complexation with anions leads to a conformational change of the host structure in which the pyrene moieties are interacting in pairs. With all anions, formation of both 1:1 and 1:2 (host:guest) adducts was observed. For both malonate and succinate the second equilibrium constant is higher than the first one, indicating that complexation of the first anion can favor complexation of the

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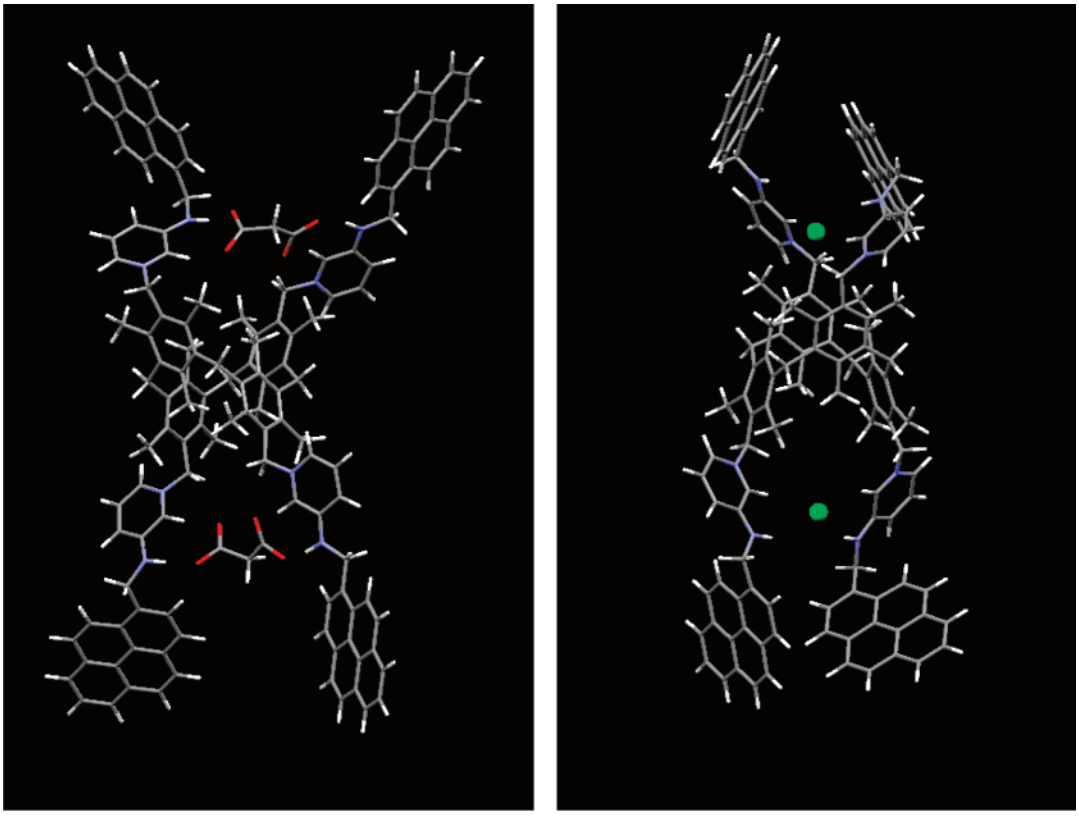

Figure 7. DFT-calculated models of host **4** bound to 2 equiv of (a) malonate and (b) chloride.

second anion on the opposite site of the calixarene ring through allosteric conformational changes (Table 1).

In contrast, much smaller changes in the absorption spectra were observed for **5** and in **6** (e.g., see Figure 5 for the example of the titration of **6** with chloride), resulting in a less pronounced decrease of the typical bands of pyrene in all the monitored spectral region (and for this reason, no isosbestic points are observed) and in the lack of the increase of the absorbance above 380 nm.

In particular, this latter finding indicates that anion complexation does not lead to formation of strong ground-state dimers of pyrene, in contrast to the results obtained for **4**. For both **5** and **6** hosts formation of 1:1 adducts was observed, accompanied by formation of 2:1 adducts, in contrast to the ditopic **4** which readily forms 1:2 (host:guest) complexes. For **6** in particular there appears to be a strong tendency for two hosts to wrap around a single anionic guest.

As far as selectivity is concerned, host **4** has a slightly higher association constant for chloride among the monovalent anions, but it is noteworthy that the association constant for dicarboxylates is at least an order of magnitude higher than halides despite the fact that a fluorescent response is only observed upon chloride binding. In contrast, host **6** shows the highest association constants (for 1:1 and 2:1 adducts) for chloride, while **5** binds strongly to acetate.

As far as the fluorescence spectra are concerned, in general addition of anions to solutions containing receptors **5** and **6** does not lead to significant changes. However, in the case of **4**, an increase of the emission intensity of *both* the monomer and the excimer bands is observed upon addition of chloride. This in contrast to related pyrene systems in which conformational changes result in an increase in the intensity of the excimer band and a corresponding *decrease* in the emission of the monomer emission.[3,65] On addition of fewer than 20 equiv of the anion, the spectrum shows an intensity increase and a significant blue shift of the nonstructured, low-energy band (Figure 4). In these conditions, this band shows a shape typical of the excimeric form of pyrene, in agreement with the data obtained by the spectrophotometric titrations. This attribution is also supported by computational studies (see below). Upon addition of further equivalents of chloride, a further modest increase of the intensity of this band occurs, concomitant with a red shift and an increase of the fluorescence of the monomeric form of pyrene. The increase of the overall fluorescence intensity can be ascribed to the diminishing acceptor properties of the pyridinium ion while interacting with the anion, hence increasing the energy of the charge-separated state and reducing the efficiency of the electron-transfer process. The fact that the excimer emission grows in intensity first suggests that chloride binding occurs in between a pair of pyridinium arms, bringing the pyrenyl groups into close proximity. The subsequent growth of pyrene monomer emission suggests that further chloride binding (which has a lower binding constant) occurs at the second binding site but is unable to bring the pyrenyl groups into close proximity, either because chloride binding is only to a single arm or because the 'pinching' of the opposite side of the molecule pulls the arms too far apart.

(65) Schazmann, B.; Diamond, D. *New J. Chem.* **2007**, *31*, 587−592.

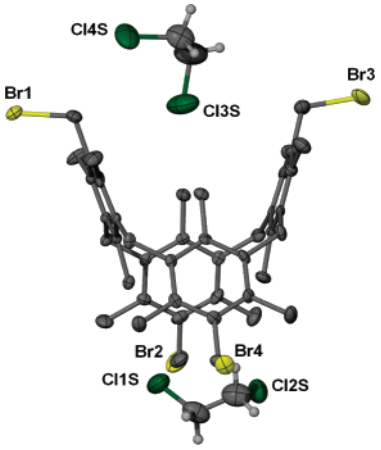

Figure 8. X-ray structure of **2**·2$C_2H_4Cl_2$, showing the 1,3-alternate conformation and solvent molecule inclusion. Host hydrogen atoms have been omitted for clarity.

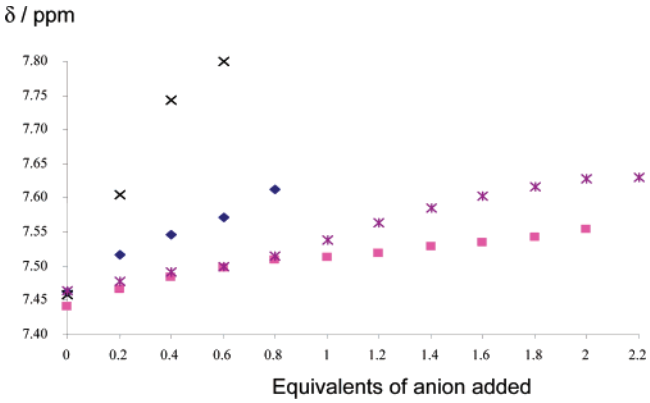

Figure 9. ^{1}H NMR spectroscopic titration data up to the solubility limit of **4**·4PF_6^- with tba chloride (squares), tba succinate (stars), tba acetate (diamonds), and tba malonate (crosses) in acetone-d_6, following the NH resonance.

In contrast, upon addition of bromide and acetate it is only the monomeric band in the 380−400 nm region that increases in intensity (Figure 6). Similarly, malonate and succinate cause only negligible changes in the spectra, and the fluorescence remains quenched despite the very strong binding of these anions. There is also no change in fluorescence spectra upon addition of F^-, HPO_4^{2-}, or triflic acid. Hence, it is apparent that while anion binding induces an increase in pyrene monomer emission, it is the particular conformational changes induced by binding of only Cl^- (that also induces the largest changes in the absorption spectrum) in the cleft between the two pyridinium arms that brings the pyrene moieties close enough together to allow excimer emission.

Computational and Structural Studies. We sought to confirm the proposed binding geometry and hence excimer formation in the case of Cl^- by means of DFT calculations. The DFT-calculated structures of the 2:1 complexes of malonate and chloride with tetracation **4** are shown in Figure 7. The calculations reproduce well the NH···anion and CH···anion interactions observed in previous studies on related systems.[19,36] The host is sufficiently flexible to accommodate both anions within the two molecular clefts, consistent with the observed high affinity for both guests. It is clear from the models, however, that the average distance between the pyrene groups in the case of the chloride groups is significantly lower in the case of the chloride complex and might readily result in partial overlap of the pyrene moieties in solution due to the small size and high negative charge density of the chloride anions. Stacking interactions between the pyrene groups may also contribute to an additional stabilization energy of the complex. In contrast, in the malonate case the pyrene groups are well separated and malonate binding appears to remove the possibility of close approach of the pyrenyl groups.

Unfortunately it proved impossible to obtain an X-ray crystal structure of any salts of **4**. However, compound **2** was characterized by X-ray crystallography as a 1:2 solvate with 1,2-dichloroethane, Figure 8. The structure establishes the 1,3-alternate geometry and shows that the bromomethyl groups are directed toward the outside of the macrocycle. Bond lengths and angles are within normal ranges. The two dichloroethane guest molecules are situated on either side of the macrocycle in differing orientations. In one case the chlorine substituent Cl3S penetrates the macrocycle cavity, while on the other side the solvent molecule lies in a cleft at the top of the host molecule. Despite these different inclusion modes, however, the host adopts approximate S_4 symmetry. Overall packing appears to be dominated by CH···π interactions[66] from the acidic guest methylene moieties to the aromatic rings on adjacent molecules.

Solution Behavior by ^{1}H NMR Spectroscopic Titration. To corroborate the spectrophotometric data, the solution anion-binding behavior of **4**−**6** as hexafluorophosphate salt was studied by ^{1}H NMR spectroscopic titration. Host **4** is soluble in acetonitrile and acetone; however, on addition of tetrabutylammonium (tba) salts of chloride, bromide, or malonate it readily precipitates, preventing determination of reliable binding constants at NMR concentrations. However, the initial shape of the titration isotherm gives some indication of differences in magnitude of binding constants between selected anions (Figure 9). The large change in chemical shift upon binding tba malonate seen previously in related calixarenes[51] is consistent with the spectrophotometric data and again suggests a good match between the anion and the ditopic host. The basicity of the carboxylate groups accounts for the large change in chemical shift. Chloride and bromide bind very similarly in acetone; the bromide data almost overlap the chloride data and hence are omitted for clarity. However, in acetonitrile chloride apparently binds more strongly.

The anion-binding behavior of hosts **5** and **6** was also studied by ^{1}H NMR spectroscopic titration. Like **4**, the dipodal host **5** readily precipitates from acetonitrile and DMSO solution on addition of the tetrabutylammonium salts of a range of halide anions, and hence, no quantitative data could be obtained by this method. In the case of tetrabutylammonium acetate, however, the host remained soluble in acetonitrile solution up to ca. 2.5 mol equiv, giving $\Delta\delta = 2.84$ ppm.

The anion-binding properties of tripodal host **6** proved remarkable and radically different to **4** and **5** and those of the closely related anthracenyl analogue and other similar systems.[46] On titration of **6** with tetrabutylammonium salts of Cl^-, Br^-, NO_3^-, $MeCO_2^-$, $CF_3SO_3^-$, and succinate^{2-} no precipitation was observed. In all cases except succinate a distinct change in gradient was observed in the ^{1}H NMR titration isotherms at a

(66) Nishio, M. *Crystengcomm* **2004**, *6*, 130−158.

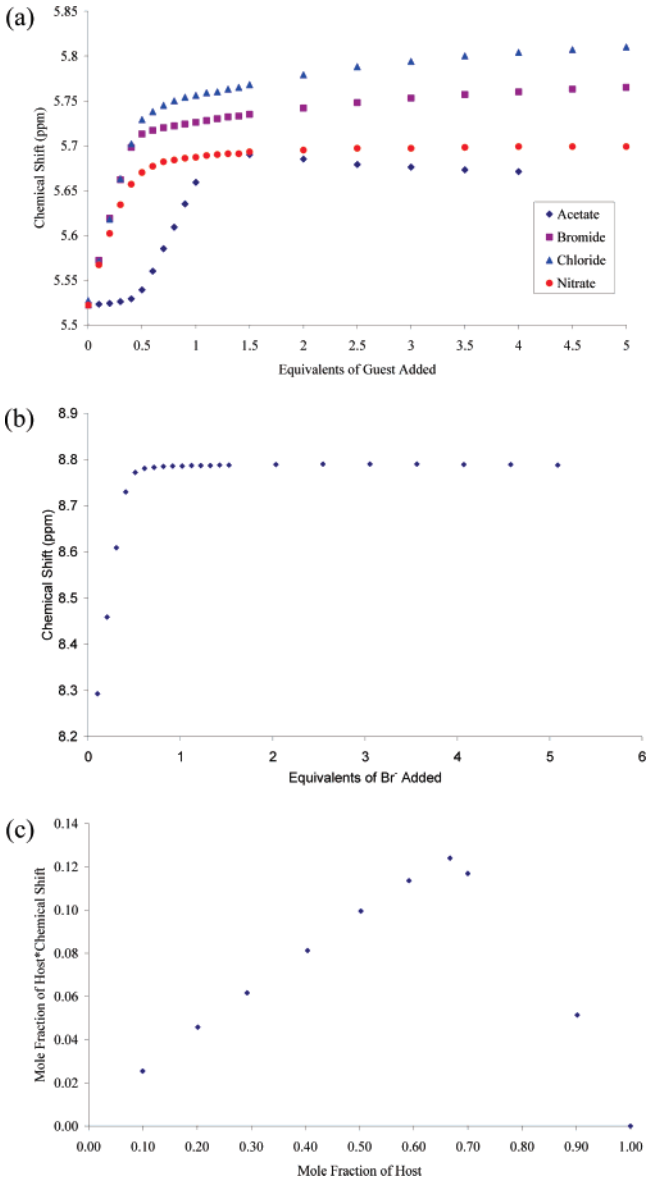

Figure 10. ^{1}H NMR titration data for anion binding by host **6** in acetonitrile-d_3 solution: (a) titration isotherm following methylene resonance at 5.52 ppm for all anions, (b) CH_2NH resonance on addition of $NBu_4^+Br^-$, and (c) Job plot for $NBu_4^+Br^-$ by showing 2:1 host:guest stoichiometry.

host:anion of 2:1, suggesting the surprising encapsulation of a single anion by two host molecules. This 2:1 ratio was confirmed by Job plot analysis in the case of Cl^- and Br^-. A cumulative plot along with representative data for Br^- is shown in Figure 10. Analysis of the titration data for multiple nuclei proved very challenging, with titration isotherms suggesting the presence of multiple equilibria comprising formation of 2:1, 1:1, and 1:2 host:guest complexes. The sharpness of the isotherm gradients suggests very strong binding in the case of all of the anions studied except triflate (i.e., tetrabutylammonium salts of Cl^-, Br^-, NO_3^-, $MeCO_2^-$, and succinate^{2-}). As illustrated by Figure 10a, the data for acetate is atypical and clearly indicative of more than one binding process involving different conformational characteristics in which the chemical shift of the methylene resonance at 5.52 ppm (plotted in Figure 10a) is not greatly affected by addition of the first equivalent of anion. Related behavior has been observed in similar systems.[46] In general, binding constants proved too high and equilibria too complex to analyze quantitatively by NMR methods, and binding constants were assessed spectrophotometrically.

The possibility of self-association of the tripodal compound **6** was assessed by an ^{1}H NMR spectroscopic dilution study from 1.6 to 26 mM (see Supporting Information). Over this concentration range the resonance assigned to the NH proton shifted from 7.11 to 6.94 ppm in a nonlinear fashion, suggesting some degree of dimerization even in the absence of added anion. The negative chemical shift change with increasing concentration and hence increasing dimer concentration implies decreased hydrogen-bonding interaction with anions and solvent on dimerization and/or increased shielding due to the orientation of the pyrenyl groups in the dimer. At lower concentrations such as those used in the photophysical studies this dimerization is insignificant, however. The absorbance is linear with concentration between 10^{-6} and 10^{-4} M, and this supports the fact that dimerization (that should lead to pyrene−pyrene intermolecular interactions and so to a change in absorbance) is very low under these conditions. Thus, the self-association does not influence the anion-binding experiments, and anion association measurements at different concentrations (from 3×10^{-6} to 3×10^{-5} M) give the same results within experimental error.

Conclusions

We report three new potential molecular anion sensors based on aminopyridinium di-, tri-, and tetrapodal hosts equipped with pyrenyl reporter groups. The conformational, associative, and sensing properties of the hosts are highly dependent on the spacing and disposition of the binding and sensing components and hence on the size and shape of the core organizing scaffold. The pyrenyl-substituted aminopyridinium binding and sensing unit is fluorescence quenched as a result of pyrene-pyridinium charge-transfer interactions in the excited state, and hence, hosts **5** and **6** do not exhibit a fluorescence response to anion binding. The wider disposition of the anion-binding groups in ditopic host **4** means that the compound is selective in binding terms for dicarboxylates, particularly malonate, which can span the gap between pairs of aminopyridinium arms. However, it is the smaller but more weakly bound chloride anion that is able to induce a conformation reorganization that brings adjacent pyrenyl groups into close enough proximity in the ground state to allow formation of an emissive excimer upon excitation and hence a fluorescent response upon chloride binding. Receptor **4** is thus a very interesting example of a sensor that is *selective* for dicarboxylates but *discriminates* chloride in terms of its fluorescent response. Ditopic host **4** exhibits a modest positive allosteric enhancement in binding a second equivalent of dicarboxylates, while halide binding is negatively cooperative presumably because the binding of the first equivalent of the small halide ions opens out the second binding pocket. Host **6** in particular shows a marked tendency to dimerize in the presence of halide anions, but this process does not result in any particular fluorescent response.

Experimental Section

Syntheses. All purchased starting materials were of commercial quality and used without further purification. Solvents were used as obtained unless mentioned otherwise. Dichloromethane was dried using

calcium hydride. Compound **1** and 1,3,5-tri(bromomethyl)-2,4,6-triethylbenzene were prepared by the literature methods.[41,52]

Pyren-1-ylmethyl-pyridin-3-yl-imine. Pyrene-1-carboxyldehyde (2.0 g, 86.9 mmol) was weighed out (in a glove box) and then dissolved in degassed dichloroethane (100 mL); 3-aminopyridine (0.81 g, 86.85 mmol) and $MgSO_4$ were added. The reaction was stirred under reflux for 25 h under N_2. The solvent was removed under reduced pressure, and the crude reaction mixture was redissolved in diethyl ether. Undissolved material was filtered off. The crude imine was then purified by precipitating out the solid from the reaction mixture by placing the flask in an acetone and dry ice bath. Yield: 2.2 g, 71.89 mmol, 82%. ^{1}H NMR ($CDCl_3$, *J*/Hz, δ/ppm): δ 7.43 (dd, 1H, J = 4.8, 8.2, Py**H**), 7.72 (ddd, 1H, J = 1.4, 2.6, 8.2, Py**H**), 8.10 (t, 1H, J = 7.6, Ar**H**), 8.15 (d, 1H, J = 8.8, Ar**H**), 8.22 (d, 1H, J = 8.8, Ar**H**), 8.28−8.31 (m, 4H, Ar**H**), 8.57 (dd, 1H, J = 1.4, 4.8, Py**H**), 8.69 (d, 1H, J = 2.6, Py**H**), 8.78 (d, 1H, J = 8.0, Ar**H**), 9.09 (d, 1H, J = 9.6, Ar**H**), 9.51 (s, 1H, C**H**). ES+ MS: m/z = 307 $[M + H]^+$. IR (ν/cm^{-1}): 1612 *s* (CH═N). Anal. Calcd for $C_{22}H_{14}N_2$: C, 86.25; H, 4.60; N, 9.14. Found: C, 86.04; H, 4.49; N, 8.60.

Pyren-1-ylmethyl-pyridin-3-yl-amine (**3**). Pyren-1-ylmethyl-pyridin-3-yl-imine (2.0 g, 6.5 mmol) was dissolved in MeOH (700 mL), and 3 mol equiv of $NaBH_4$ was added slowly. The reaction mixture was stirred for 2 h. 2 M HCl was added until the pH was 3 followed by 2 M NaOH until the pH was 9. The solvent was then removed under reduced pressure, and during the process orange crystals of pure amine appeared which were separated. Further removal of MeOH followed by extraction into CH_2Cl_2 and washing with water resulted in crude amine, which was washed with diethyl ether to remove any remaining unreacted aldehyde. Yield: 1.32 g, 4.3 mmol, 66%. ^{1}H NMR ($CDCl_3$, *J*/Hz, δ/ppm): δ 4.05 (s,br, 1H, N**H**), 4.89 (2H, J = 4.8, C**H$_2$**), 6.88 (ddd, 1H, J = 1.6, 2.8, 8.4, Py**H**), 7.01 (dd, 1H, J = 4.8, 8.4, Py**H**), 7.92 (dd, 1H, J = 1.6, 4.8, Py**H**), 7.90−7.94 (m, 2H, Ar**H**), 7.96 (d, 2H, J = 1.4, Ar**H**), 8.04 (d, 1H, J = 8.4, Ar**H**), 8.06 (d, 2H, J = 3.2, Ar**H**), 8.09 (d, 1H, J = 1.6, Py**H**), 8.11 (t, 1H, J = 1.2, Ar**H**), 8.17 (d, 1H, J = 9.2, Ar**H**). ES+ MS: m/z = 309 $[M + H]^+$. IR (ν/cm^{-1}): 3419 m (NH). Anal. Calcd for $C_{22}H_{16}N_2 \cdot 0.75\ H_2O$: C, 82.08; H, 5.47; N, 8.70. Found: C, 81.90; H, 4.99; N, 8.49.

*Tetra[3-(pyren-1-ylmethylamino)pyridium-mesityl]calixarene Bromide Salt (**4**·4Br$^-$).* Bromomethylated calix[4]arene **1** (0.146 g, 0.16 mmol) was dissolved in CH_2Cl_2 (50 mL), and 5 equiv (excess) of pyren-1-ylmethyl-pyridin-3-yl-amine **3** (0.249 g, 0.81 mmol) dissolved in CH_2Cl_2 (50 mL) was added. A precipitate formed within 0.5 h. The reaction was stirred at room temperature for 48 h. The precipitate was then separated on a Büchner funnel and thoroughly washed with dichloromethane followed by sonication in more fresh dichloromethane. The obtained solid was then washed with diethyl ether and dried in vacuo. Yield: 0.29 g, 0.14 mmol, 81%. ^{1}H NMR (DMSO-d_6, *J*/Hz, δ/ppm): 0.64 (s, 12H, C**H$_3$**), 2.04 (s, 24H, C**H$_3$**), 3.95 (s, 8H, ArC**H$_2$**Ar), 5,07 (br, 8H, C**H$_2$**), 5,73 (s, 8H, C**H$_2$**), 7.71 (br, 4H, Py**H**), 7.75−7.79 (br, 4H, Py**H**), 7.84 (br, 4H, Py**H**), 7.87 (br, 4H, N**H**), 7.96 (br, 4H, Ar**H**), 7.98 (br, 4H, Ar**H**), 8.07 (t, J = 7.6, 4H, Ar**H**), 8.15 (s, 4H, Py**H**), 8.22 (d, J = 8.0, 8H, Ar**H**), 8.26−8.35 (m, 16H, Ar**H**). ES$^+$-MS: m/z = 453 $[M - 4Br]^{4+}$.

*Tetra[3-(pyren-1-ylmethylamino)pyridium-mesityl]calixarene Hexafluorophosphate Salt (**4**·4PF$_6^-$).* Compound **4** as the tetrabromide salt was dissolved in a 1:1 acetonitrile/water mixture, and 10 equiv of $NaPF_6$ was added. The reaction mixture was stirred for 2 h. A green precipitate appeared within 0.5 h. The precipitate was separated on a Büchner funnel under suction and washed several times with diethyl ether. ^{1}H NMR (CD_3CN, *J*/Hz, δ/ppm): −0.001 (s, 12H, C**H$_3$**), 1.63 (s, 24H, C**H$_3$**), 2.94 (s, 8H, ArC**H$_2$**Ar), 4.93 (d, J = 5.6, 8H, C**H$_2$**), 5.29 (s, 8H, C**H$_2$**), 6.41 (t, J = 5.6, 4H, N**H**), 7.03 (br, s, 4H, Py**H**), 7.54 (br, 4H, Ar**H**), 7.56 (br, 4H, Ar**H**), 7.72 (d, J = 7.6, 4H, Ar**H**), 7.76 (ddd, J = 2.0, 6.4, 9.2, 4H, Py**H**), 7.91 (t, J = 7.6, 4H, Ar**H**), 7.99 (br, 4H, Py**H**), 8.01 (d, J = 7.6, 4H, Ar**H**), 8.08 (s, 4H, Py**H**), 8.10−8.13 (m, 16H, Ar**H**). ES$^+$-MS: m/z = 1051 $[M - 2PF_6]^{2+}$, 653 $[M - 3PF_6]^{3+}$, 453 $[M - 4PF_6]^{4+}$. Anal. Calcd for $C_{132}H_{116}P_4F_{24}\ 2H_2O$: C, 65.23; H, 4.97; N, 4.61. Found: C, 65.05; H, 4.78; N, 4.30. IR (ν/cm^{-1}): 3411s (NH).

*α,α′-Bis(pyren-4-yl-methyl-pyridinium-3-ylamine)-p-xylene Hexafluorophosphate (**5**).* Pyren-4-yl-methyl-pyridinium-3-ylamine (0.48 g, 1.6 mmol) and α,α′-dibromo-*p*-xylene (0.20 g, 0.77 mmol) were dissolved in dichloromethane (100 mL). This solution was placed under reflux for 2 h. After this time the solution was cooled, and a solid was formed. This solid was collected by filtration and found to be the desired product as the bromide salt (0.53 g, 0.59 mmol, 77%). ^{1}H NMR (CD_3CN, 500 MHz, δ/ppm, *J*/Hz): 8.4−7.6 (30H, m, Ar & Py); 6.47 (2H, bs, NH); 5.28 (4H, s, CH_2); 5.12 (4H, d, J = 5.4, CH_2). ES + MS: 800 $[M - Br]^+$, 360 $[M - 2Br]^{2+}$. Anal. Calcd for $C_{52}H_{40}N_4Br_2$: C, 70.92; H, 4.58; N, 6.36. Found: C, 70.18; H, 4.99; H, 6.70. The bromide salt (0.39 g, 0.45 mmol) was dissolved in methanol (50 mL) with an excess of NH_4PF_6 (1.45 g, 8.9 mmol). This solution was warmed to ∼35 °C to aid the solubility of the bromide salt and stirred for 2 h. After this time the solution was cooled, and an off-white precipitate formed. The solid was collected by filtration, washed with methanol, and found to be the desired product. (0.26 g, 0.26 mmol, 58%). ^{1}H NMR (CD_3CN, 400 MHz, δ/ppm, *J*/Hz): 8.4−7.6 (30H, m, Ar & Py); 6.48 (2H, bs, NH); 5.27 (4H, s, CH_2); 5.10 (4H, d, J = 4.0, CH_2). ES + MS: 865 $[M - PF_6]^+$, 360 $[M - 2PF_6]^{2+}$. Anal. Calcd for $C_{52}H_{40}N_4(PF_6)_2$: C, 61.79; H, 3.99; N, 5.54. Found: C, 61.14; H, 3.69; N, 5.09.

1,3,5-Tris(pyren-4-yl-methyl-pyridinium-3-ylamine)-2,4,6-triethylbenzene Hexafluorophosphate (**6**). Pyren-4-yl-methyl-pyridinium-3-ylamine (0.30 g, 0.98 mmol) and 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (0.14 g, 0.32 mmol) were dissolved in dichloromethane (100 mL), and the resulting solution was stirred at room temperature for 20 h. After this time the solvent was removed under reduced pressure to yield the bromide salt as a yellow oil (0.40 g, 0.29 mmol, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm, *J*/Hz): 8.82 (3H, s, Py); 8.50 (3H, s, Py); 8.0−7.6 (27H, m, Ar); 7.46 (3H, dd, J = 6.0, 2.75, Py); 7.05 (3H, d, J = 7.8, Py); 5.87 (3H, s, CH_2); 4.72 (6H, s, CH_2); 2.49 (6H, t, J = 7.0, CH_2); 1.01 (9H, d, J = 7.0, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz, δ/ppm): 128.85, 128.58, 128.21, 127.78, 127.60, 127.39, 126.26, 125.62, 125.47, 125.29, 125.02, 124.85, 124.61, 58.05, 44.90, 24.81, 15.52. ES + MS: 1286 $[M - Br]^+$, 603 $[M - 2Br]^{2+}$, 375 $[M - 3Br]^{3+}$. The bromide salt (0.40 g, 0.29 mmol) was dissolved in dichloromethane (100 mL), and excess NH_4PF_6 (0.53 g, 3.26 mmol) dissolved in methanol (25 mL) was added. The solution was stirred at room temperature for 2 h. After this time, the solution was concentrated, and a yellow precipitated formed. The solid was collected by filtration, washed with methanol, and found to be the desired product (0.33 g, 0.21 mmol, 65%). ^{1}H NMR (CD_3CN, 500 MHz, δ/ppm, *J*/Hz): 8.3−7.4 (39H, m, Ar/Py); 7.04 (3H, bs, NH); 5.51 (6H, s, CH_2); 4.79 (6H, s, CH_2); 2.41 (6H, br s, CH_2); 1.98 (9H, br s, CH_3). ^{13}C{^{1}H} NMR (CD_3CN, 125 MHz, δ/ppm): 131.4, 131.1, 130.7, 129.6, 128.7, 128.5, 127.9, 127.5, 126.5, 125.7, 124.9, 124.4, 122.7, 57.7, 44.8, 23.9, 14.4. ES + MS: 1415 $[M - PF_6]^+$, 635 $[M - 2PF_6]^{2+}$, 375 $[M - 3PF_6]^{3+}$. Anal. Calcd for $C_{81}H_{69}N_6(PF_6)_3$: C, 62.31; H, 4.45; N, 5.38. Found: C, 62.45; H, 4.17; N, 5.67.

Crystallographic Details. Crystal data for **2**·2$C_2H_4Cl_2$: $C_{48}H_{60}Br_4Cl_4$, M = 1098.40, yellow block, 0.80 × 0.70 × 0.60 mm^3, monoclinic, space group *I*2/*a* (No. 15), a = 15.3492(3), b = 17.7650(4), c = 34.5444(7) Å, β = 90.0280(10)°, V = 9419.5(3) Å,^{3} Z = 8, D_c = 1.549 g/cm^3, F_{000} = 4448, Nonius KappaCCD, Mo Kα radiation, λ = 0.71073 Å, T = 120(2)K, $2\theta_{max}$ = 52.0°, 28 185 reflections collected, 9239 unique (R_{int} = 0.1505). Final GooF = 1.013, R1 = 0.0642, wR2 = 0.1291, R indices based on 5365 reflections with $I > 2\sigma(I)$ (refinement on F^2), 518 parameters, 0 restraints. Lp and absorption corrections applied, μ = 3.678 mm^{-1}.

Photophysical Measurements. The fluorescence spectra were recorded with an Edinburgh FLS920 equipped with a Hamamatsu R928P photomultiplier. The same instrument equipped with a PCS900 PC card was used for the time-correlated single-photon counting

experiments. All the photophysical measurements were performed in aerated acetonitrile solutions.

Spectrophotometric Titration. Stability constants were determined by fitting the absorption spectra recorded during the titration of the hosts and the tetrabutylammonium salts of the different anions; a solution of the host species of known concentration typically 5−15 μM was used. The data were fitted with the global analysis program SPECFIT.[64]

Transient Absorption Experiments. Femtosecond time-resolved experiments were performed using a pump−probe spectrometer based on the Spectra-Physics Hurricane Ti:sapphire system as laser source and the Ultrafast Systems Helios spectrometer.[67] The pump pulse (266 nm) was generated by a second- and third-harmonics generator (Ultrafast Systems Apollo femtosecond harmonics generator). The probe pulse was obtained by continuum generation on a sapphire plate (useful spectral range, 450−800 nm). Effective time resolution ca. 300 fs, temporal chirp over the white-light 450−750 nm range ca. 200 fs, and temporal window of the optical delay stage 0−1000 ps.

NMR Titrations. ^{1}H NMR titration experiments were carried out at room temperature using a Varian Inova-500 spectrometer operating at 500 MHz (Durham University). All chemical shifts are reported in ppm relative to TMS as an internal reference. A solution of the host species of known concentration typically 0.5−1.5 mM was made up in an NMR tube using the appropriate deuterated solvent (0.5 mL). Solutions of the anions, as tba salts, were made up in volumetric flasks (2.0 mL) with a concentration 5 times greater than that of the host. The guest solution was typically added in 10 μL aliquots, representing 0.1 equiv of the guest with respect to the host. Larger aliquots were used in some cases where no inflection of the trace was evident. Spectra were recorded after each addition, and chemical shift data were recorded for typically 3−4 independent resonances.

DFT Calculations. Geometry optimizations were performed using the B3LYP hybrid density functional with the STO-3G basis, except on the atoms forming the cavities, where the 6-31+G* basis set was used. The hydrogen atoms in the cavities were further augmented with an extra diffuse sp shell. The central anions (Cl^- and malonate) used the 6-311++G** basis. Geometry optimization was started at similar host conformations. All computations were performed using the Gaussian program.[68]

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Supporting Information Available: Plot of the dilution study and full ref 64; absorption and fluorescence spectra of **5** and **6**; summary of the photophysical properties of the new hosts; crystallographic information file for the structure of **2**·$2C_2H_4Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

JA711012D

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