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# Comparative Study of Charge-Assisted Hydrogen- and Halogen-Bonding Capabilities in Solution of Two-Armed Imidazolium Receptors toward Oxoanions

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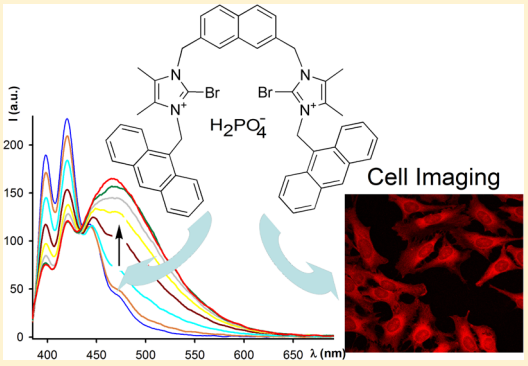
Supporting Information

**ABSTRACT:** Two-armed imidazolium-based anion receptors have been prepared. The central 2,7-disubstituted naphthalene ring features two photoactive anthracene end-capped side arms with central 2-bromoimidazolium or hydrogen-bonding imidazolium receptors. Combined emission and $^{1}H$ and $^{31}P$ NMR studies carried out in the presence of a wide variety of anions reveal that only $HP_2O_7^{3-}$, $H_2PO_4^-$, $SO_4^{2-}$, and $F^-$ anions promoted noticeable changes. The halogen receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ acts as a selective fluorescent molecular sensor for $H_2PO_4^-$ anions, since only this anion promotes the appearance of the anthracene excimer emission band, whereas it remains unchanged in the presence of the other tested anions. In addition this halogen receptor behaves as a chemodosimeter toward $HP_2O_7^{3-}$ anion, through its transformation into the corresponding bis-imidazolone after debromination by the action of the basic anion. The association constant values of the halogen-bonding complexes in a competitive solvent $CD_3CN$/MeOD (8/2) mixture with $H_2PO_4^-$ and $SO_4^{2-}$ anions are higher than those found for the hydrogen-bonding counterpart. In contrast, in the less competitive $CH_3CN$ solvent higher binding affinity for anions corresponds to the hydrogen-bonding receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$. In addition, the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ represents a useful alternative as an imaging agent in living cells in a wide range of emission wavelengths.




## INTRODUCTION

Imidazolium-based species have been used extensively in the last years in the areas of anion recognition and sensing,[1] due to the fact that imidazolium rings provide both a positive charge and a relatively acidic C2−H hydrogen bond donor unit as binding sites for anionic species. Among the well-established noncovalent intermolecular interactions, halogen bonding (XB) *"a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity"*[2] is the least exploited noncovalent interaction, especially in the solution phase.[3] It is known that XB is generally of the same order of strength as hydrogen bonding (HB) and can either compete or cooperate with HB in crystal structures. In this context, in 1999 an interesting investigation was reported on the interplay of XB with HB in solid-state organic salts.[4] Several scenarios have been found in this field; in some cases there has been shown the ability of XB to dominate over HB in driving the self-assembly processes of several cocrystals under the appropriate conditions,[5] whereas recently there has been demonstrated the complementarity and ability of HB and XB to interact orthogonally in the preparation of several cocrystals with various XB and HB acceptor molecules.[6] The bonding mechanisms of the halogen bonds XB···A and the hydrogen bonds HB···A are very similar, taking into account the electrostatic and covalent contribution. The main differences between the XB···A and the HB···A bonds is that the former are generally associated with a weaker electrostatic attraction, due to a smaller and in some cases less favorably oriented polarization; additionally the HOMO−LUMO interaction is more stabilized due to the lower energy of the $\sigma^*$ LUMO in the halogen−halogen compared with the respective hydrogen−hydrogen. When this is taken into account, the strength of the halogen bonds could be stronger or weaker than that of the analogous hydrogen bonds.[7] However, comparative studies of the anion sensing properties in solution of analogous charge-assisted XB and HB receptors remain almost unexplored.

In this context, it has been reported that in halogen- and hydrogen-bonding triazolium-[8] and imidazolium-based receptors,[9] substitution of the hydrogen atom by halogen in the anion receptor has a great influence on the anion recognition event due to electronic and geometric considerations. With the aim of acquiring more knowledge about the behavior of halogen-bonding-based receptors in solution, we report here the synthesis and a comparative study of the anion sensing

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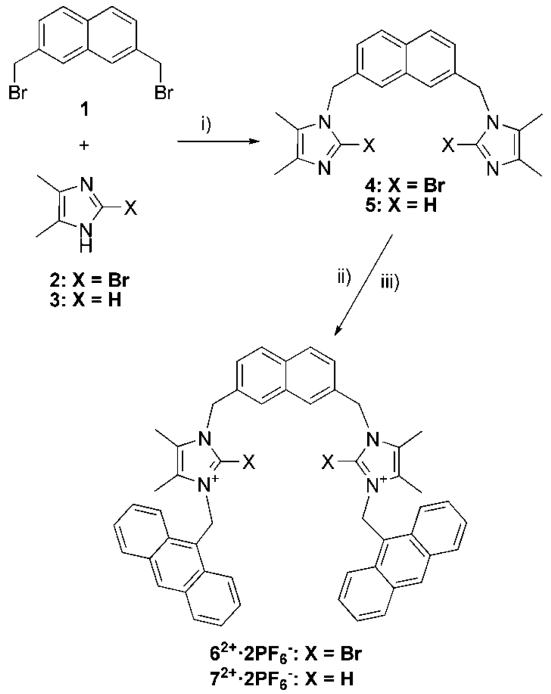
properties of a series of novel two-armed charge-assisted ditopic receptors: imidazolium and haloimidazolium bidentate receptors, which incorporate two end-capped photoactive anthracene rings as fluorescent signaling units in their host frameworks.

## RESULTS AND DISCUSSION

**Synthesis.** The bis-imidazolium receptors $\mathbf{6}^{2+}\cdot 2PF_6^-$ and $\mathbf{7}^{2+}\cdot 2PF_6^-$ were prepared by a stepwise sequence which involves initial alkylation of 2-bromo-4,5-dimethyl-1*H*-imidazole (**2**)[10] or 4,5-dimethyl-1*H*-imidazole (**3**)[11] with 2,7-bis(bromomethyl)naphthalene (**1**) in basic medium to give the corresponding bis-imidazoles **4** and **5**,[9a] respectively. Further alkylation of **4** or **5** with 9-(bromomethyl)anthracene afforded the expected halogen- or hydrogen-bonding bis-imidazolium receptors as bromide salts in moderate yield (47 and 14%, respectively). These bromide salts were readily converted by anion exchange after several washings with a saturated aqueous solution of $NH_4PF_6$ into the corresponding hexafluorophosphate salts $\mathbf{6}^{2+}\cdot 2PF_6^-$ and $\mathbf{7}^{2+}\cdot 2PF_6^-$ in almost quantitative yield (Scheme 1). All of the prepared compounds have been fully characterized using standard techniques: $^1$H NMR, $^{13}$C NMR, and FAB mass spectrometry.

**Scheme 1. Synthesis of the Halogen- and Hydrogen-Bonding Bis-Imidazolium Receptors $\mathbf{6}^{2+}\cdot 2PF_6^-$ and $\mathbf{7}^{2+}\cdot 2PF_6^-$ [a]**




[a]Reagents and conditions: (i) NaOH (1 M in $H_2O$), $CH_3CN$, reflux; (ii) 9-(bromomethyl)anthracene, $CH_3CN$, reflux; (iii) $NH_4PF_6$ in $H_2O$.

**Anion Binding Studies.** The anion sensing properties of receptors $\mathbf{6}^{2+}\cdot 2PF_6^-$ and $\mathbf{7}^{2+}\cdot 2PF_6^-$ were initially investigated by fluorescence toward the anions $HP_2O_7^{3-}$, $H_2PO_4^-$, $SO_4^{2-}$, $HSO_4^-$, $NO_3^-$, $F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $ClO_4^-$, $BF_4^-$, and $C_6H_5CO_2^-$ as tetrabutylammonium salts and the organic phosphate derivatives ATP, ADP, and AMP as sodium salts.

The emission spectra of receptors $\mathbf{6}^{2+}\cdot 2PF_6^-$ and $\mathbf{7}^{2+}\cdot 2PF_6^-$ were measured in $CH_3CN$ using an excitation wavelength at 370 nm; both receptors exhibit only the characteristic anthracene monomeric emission bands at 396, 418, and 442 nm. The hydrogen receptor $\mathbf{7}^{2+}\cdot 2PF_6^-$ exhibits a quantum yield ($\Phi$ = 0.370) which is considerably higher, almost 22 times, than that showed by the halogenated receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ ($\Phi$ = 0.017). Probably, the quenching in the fluorescence emission bands of the halogenated receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ could be attributed to an intramolecular heavy-atom effect[12] caused by the bromine atoms present in the receptor.

Evaluation of the sensing properties by fluorescence were realized by stepwise addition of increasing amounts of the previously mentioned set of anions in $CH_3CN$, except ATP, ADP, and AMP anions, which were added to water, to a solution of the corresponding receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ and $\mathbf{7}^{2+}\cdot 2PF_6^-$ in $CH_3CN$. The results reveal important differences in the sensing behavior between the halogenated receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ and the hydrogen receptor $\mathbf{7}^{2+}\cdot 2PF_6^-$.

Titration data obtained from the halogenated receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ ($c = 1 \times 10^{-5}$ M in $CH_3CN$) showed that addition of $HSO_4^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $ClO_4^-$, $BF_4^-$, and $C_6H_5CO_2^-$ anions had no effect on the emission spectrum of this receptor, whereas the addition of $HP_2O_7^{3-}$, $H_2PO_4^-$, $SO_4^{2-}$, and $F^-$ anions promoted significant changes in the emission bands of $\mathbf{6}^{2+}\cdot 2PF_6^-$. Interestingly the resulting changes were strongly dependent on the anion added, and three different responses have been observed (Figure 1).

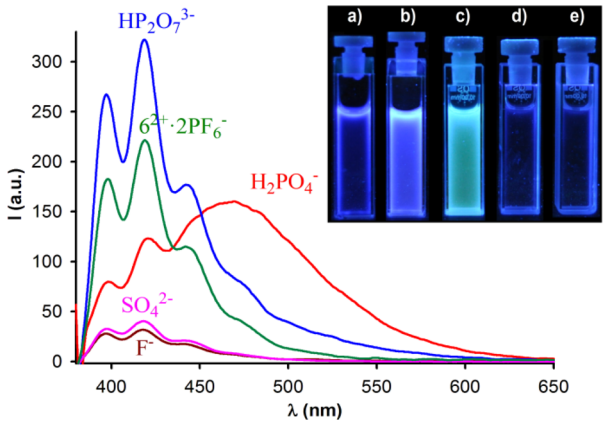



**Figure 1.** Emission spectra of the receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ ($c = 1 \times 10^{-5}$ M) in $CH_3CN$ (green line) and after the addition of excess of $HP_2O_7^{3-}$ (blue line), $H_2PO_4^-$ (red line), $SO_4^{2-}$ (pink line), and $F^-$ (brown line). Inset: visual changes in the fluorescence of receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ (a) upon the addition of (b) $HP_2O_7^{3-}$, (c) $H_2PO_4^-$, (d) $SO_4^{2-}$, and (e) $F^-$.

First, addition of increasing amounts of $SO_4^{2-}$ or $F^-$ promoted a remarkable decrease in the monomer emission bands of the receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ and no other additional spectral changes were observed (Figure 2a). Second, addition of $H_2PO_4^-$ anions promotes a progressive increase in a new broad and structureless emission band at $\lambda$ 465 nm, assigned to the anthracene excimer emission band, with a concomitant decrease in the monomer emission bands at $\lambda$ 396, 418, and 442 nm (Figure 2b). Third, addition of $HP_2O_7^{3-}$ anions induces two different effects: addition of up to 1 equiv of $HP_2O_7^{3-}$ anion causes a weak increase in the excimer emission band at $\lambda$ 465 nm along with a decrease in the monomer emission bands (Figure 2c) and subsequent addition of more than 1 equiv promotes only a continuous and remarkable increase in the monomer emission bands $\lambda$ 396, 418, and 442



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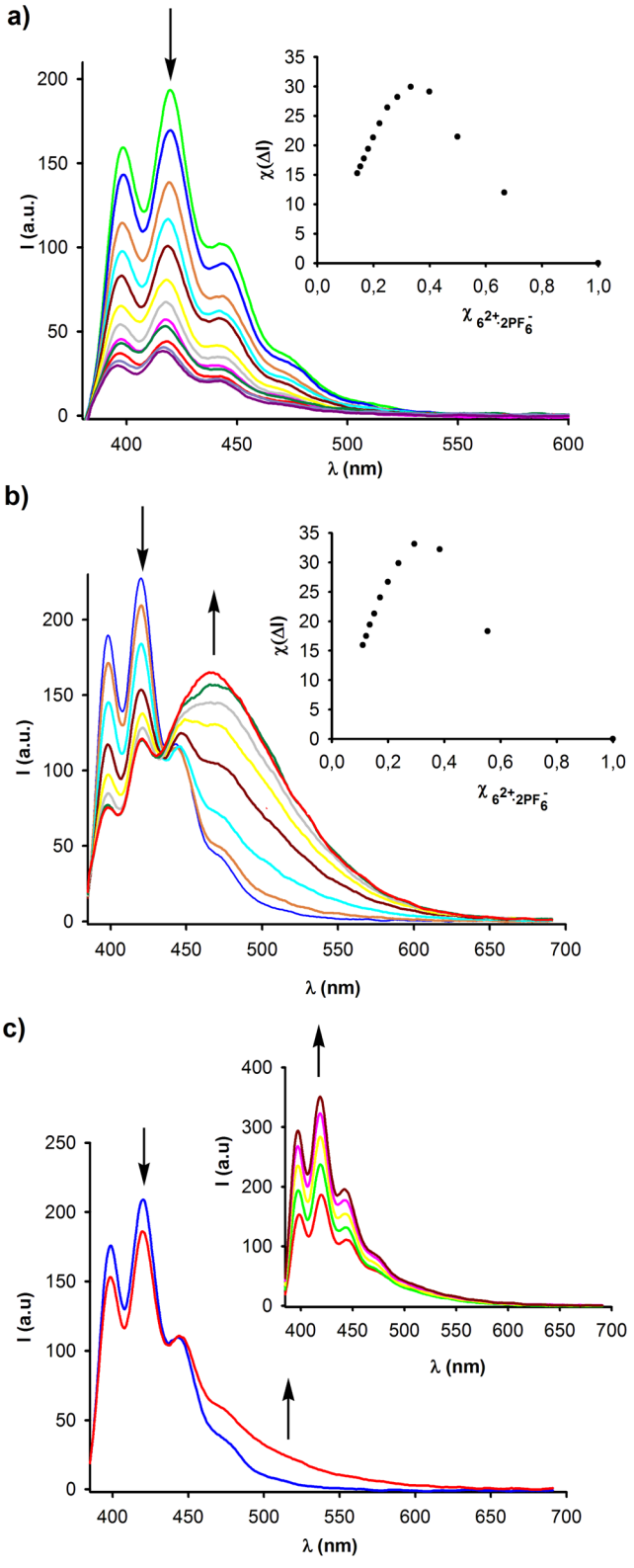


**Figure 2.** Changes in the fluorescence spectra of receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ ($c$ = 1 × $10^{-5}$ M) in $CH_3CN$ upon addition of (a) $F^-$, (b) $H_2PO_4^-$, and (c) $HP_2O_7^{3-}$. Arrows indicate the emission that increases or decreases during the titration. IIn (c) the blue line indicates the free receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ and the red line the sample after the addition of 1 equiv of anion. Inset (c): from 1 to 5 equiv of $HP_2O_7^{3-}$ added. nsets (a) and (b): Job plot experiments of receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ with $F^-$ and $H_2PO_4^-$ anions, respectively, with a maximum at 0.33 indicating a 2:1 anion:receptor stoichiometry.

nm (Figure 2c inset), the quantum yield being increased 2-fold from Φ = 0.017 to Φ = 0.037. Additionally the increase in the monomer emission bands not only is dependent on the number of equivalents added but also depends on the time, which suggests that a chemical modification could be taking place during the recognition event. In other words, the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ could be acting as a chemodosimeter; further investigations about this process will be detailed in the next sections.

The different responses observed with the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ in the presence of $HP_2O_7^{3-}$, $H_2PO_4^-$, $SO_4^{2-}$, and $F^-$ anions could be due to the fact that the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ can act through different mechanisms depending on the nature of the anion added. Thus, the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ acts by a photoinduced electron transfer (PET) mechanism in the presence of $SO_4^{2-}$ and $F^-$ anions which diminishes the intensity of the emission bands.[13] The broad emission band observed at λ 465 nm in the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ with the presence of $H_2PO_4^-$ anions could be attributed to the well-known p-stacking formation of the two anthracene moieties[14] present in the receptor after the addition of the anion as a consequence of the XB interactions between the receptor and the anions.[15]

Competition experiments were performed to test the specificity of the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ ($c$ = 1 × $10^{-5}$ M in $CH_3CN$) for $H_2PO_4^-$ anions. The intensity of the excimer emission band at λ 465 nm of the complex $\mathbf{6}^{2+}\cdot\mathbf{2H_2PO_4}^-$ remained practically unaltered with the addition of 2 equiv of $HSO_4^-$, $NO_3^-$, $F^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $ClO_4^-$, $BF_4^-$, and $C_6H_5CO_2^-$, while the presence of 2 equiv of $HP_2O_7^{3-}$ and $SO_4^{2-}$ anions promotes a weak decrease of 13 and 26%, respectively, in the intensity of the excimer band (Figure 3).

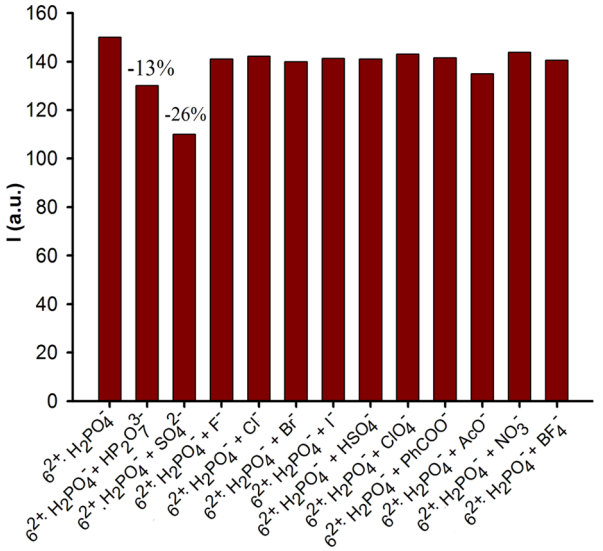


**Figure 3.** Competition experiments of the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ ($c$ = 1 × $10^{-5}$ M) in $CH_3CN$ with the addition of 2 equiv of $H_2PO_4^-$ and 2 equiv of other anions, monitoring the excimer band at λ 465 nm.

Several anion-binding experiments were also carried out by the fluorescence technique on the receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ in order to make a comparative study of sensing capabilities of the halogen-bonding receptor versus the hydrogen-bonding receptor.



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Thus, addition of the previously mentioned set of anions in $CH_3CN$, except for ATP, ADP, and AMP anions, which were added water, to the hydrogen-bonding receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ in $CH_3CN$ ($c = 1 \times 10^{-6}$ M) promotes quenching of the monomer emission bands at $\lambda$ 396, 418, and 442 nm of the receptor. The decrease in the intensity of these bands was strongly dependent on the nature of the anion added (Figure 4). Interestingly, with difference from the halogen bonding receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$, in all cases the presence of the excimer band was not detected after the addition of any anion.

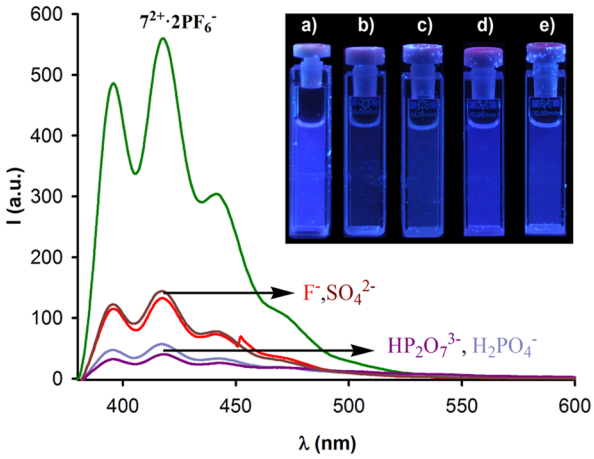


**Figure 4.** Emission spectra of the receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ ($c = 1 \times 10^{-6}$ M in $CH_3CN$) and of the samples after the addition of 10 equiv of different anions. Inset: visual changes in the fluorescence of receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ (a) upon the addition of (b) $HP_2O_7^{3-}$, (c) $H_2PO_4^-$, (d) $SO_4^{2-}$, and (e) $F^-$.

The fluorescence properties of receptors $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ and $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ and their responses after additions of several kinds of anions can be observed by the naked eye (Figure 1 inset and Figure 4 inset, respectively)

In the UV/vis spectra of the receptors $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ and $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ in $CH_3CN$ the most salient features are two intense absorption bands at $\lambda$ 230 and 255 nm, respectively, along with the characteristic absorption bands attributed to the anthracene moieties at $\lambda$ 336, 353, 370, and 390 nm. The molar absorption coefficients are slightly higher for the nonhalogenated receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ than for the halogenated receptors $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ (see the Supporting Information). The addition of increasing amounts of $HP_2O_7^{3-}$, $H_2PO_4^-$, $SO_4^{2-}$, and $F^-$ anions in $CH_3CN$ to a solution of the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ ($c = 1 \times 10^{-5}$ M) in $CH_3CN$ induced important perturbations in the absorption spectrum of the receptor. These changes were dependent on the anion added. Thus, addition of $H_2PO_4^-$ anions promotes the decrease in the high-energy bands at $\lambda$ 230 and 255 nm while the anthracene absorption bands were red-shifted by $\Delta\lambda = 2$ nm. The presence of well-defined isosbestic points at $\lambda$ 260, 365, 375, 387, and 393 nm was also observed during the titration process (Figure 5a). However, the addition of $SO_4^{2-}$ and $F^-$ anions did not modify the high-energy bands at $\lambda$ 230 and 255 nm, while the anthracene absorption bands at $\lambda$ 336, 353, 370, and 390 nm had movements opposite to that previously mentioned for $H_2PO_4^-$ anions: in other words, they were blue-shifted by $\Delta\lambda = -3$ nm. Several well-defined isosbestic points were also observed during the addition of $SO_4^{2-}$ and $F^-$ anions at $\lambda$ 351, 360, 369, 379, and 389 nm (Figure 5b).

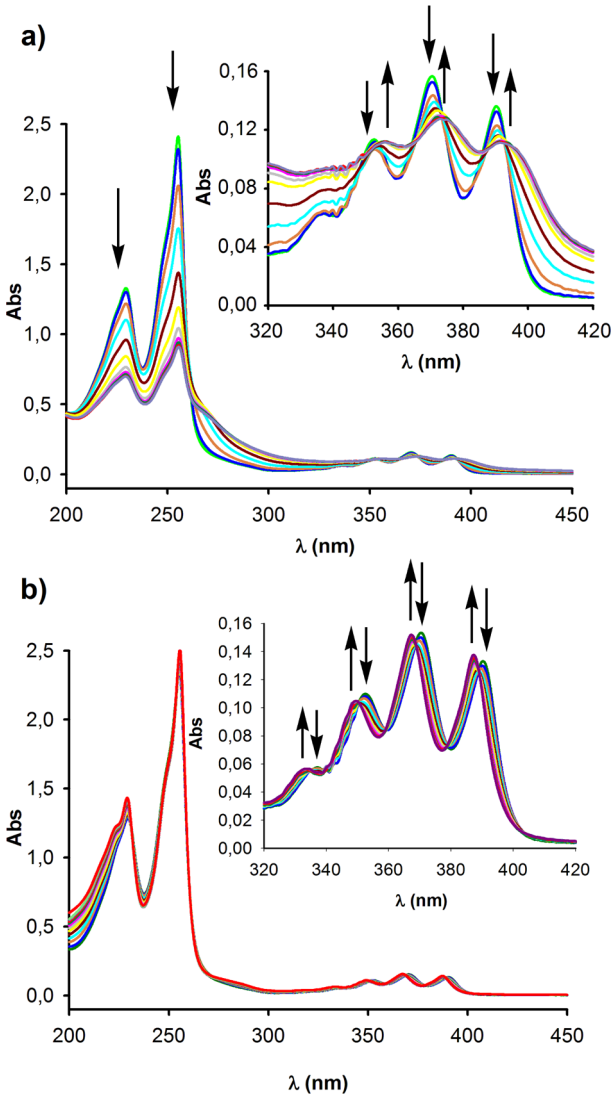


**Figure 5.** Changes in the absorption spectra of the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ ($c = 1 \times 10^{-5}$ M in $CH_3CN$) upon addition of increasing amounts of (a) $H_2PO_4^-$ and (b) $SO_4^{2-}$ anions. Arrows indicate the absorption bands that increase or decrease during the titration.

The addition of $HP_2O_7^{3-}$ causes two consecutive events. The first one, the addition of up to 1 equiv, promotes a decrease in the intensity of the high-energy bands and the anthracene absorption bands are red-shifted. The second event is observed during the addition of more than 1 equiv of the anion; now the absorption bands at $\lambda$ 230 and 255 nm remain unaltered, whereas a blue shift in the anthracene absorption bands was observed. As expected, no isosbestic points are present during the process, which clearly indicates that more than one process is taking place during the titration (see the Supporting Information). The addition of $HSO_4^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $ClO_4^-$, $BF_4^-$, $C_6H_5CO_2^-$, ATP, ADP, and AMP had no effect on the absorption spectrum of the halogen-bonding receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ even in the presence of a large excess of anions added.

The addition of the aforementioned set of anions to a solution of the hydrogen-bonding receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ in $CH_3CN$ ($c = 1 \times 10^{-5}$ M) shows that only the addition of $H_2PO_4^-$ anions promotes remarkable changes in its absorption spectrum, which were almost the same as those observed


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**Table 1. Association Constants for Receptors $6^{2+}\cdot 2PF_6^-$ and $7^{2+}\cdot 2PF_6^-$ with $HP_2O_7^{3-}$, $SO_4^{2-}$, and $H_2PO_4^-$ Anions in $CH_3CN$**

| receptor | anion | stoichiometry | $K_1$ ($M^{-1}$) | $\beta$ ($M^{-2}$) |
|---|---|---|---|---|
| $6^{2+}\cdot 2PF_6^-$ | $HP_2O_7^{3-}$ | [c] | | |
| $6^{2+}\cdot 2PF_6^-$ | $SO_4^{2-}$ | 1:1 | $8.0 \times 10^4$ (9)[a] | |
| | | | $9.8 \times 10^4$ (4)[b] | |
| $6^{2+}\cdot 2PF_6^-$ | $H_2PO_4^-$ | 1:2 | | $5.0 \times 10^{11}$ (16)[a] |
| | | | | $5.5 \times 10^{10}$ (10)[b] |
| $7^{2+}\cdot 2PF_6^-$ | $HP_2O_7^{3-}$ | 1:2 | | $8.0 \times 10^{12}$ (14)[a] |
| $7^{2+}\cdot 2PF_6^-$ | $SO_4^{2-}$ | 1:1 | $1.4 \times 10^6$ (6)[a] | |
| $7^{2+}\cdot 2PF_6^-$ | $H_2PO_4^-$ | 1:2 | | $9.8 \times 10^{11}$ (13)[a] |
| | | | | $7.5 \times 10^{10}$ (17)[b] |

[a]Calculated by fluorescence. Errors (in percent) are given in parentheses. [b]Calculated by UV−vis. Errors (in percent) are given in parentheses. [c]Chemodosimeter behavior.

previously when this anion was added to the receptor $6^{2+}\cdot 2PF_6^-$ (see the Supporting Information).

Job plot analysis of the fluorescence titration data revealed 1:1 and 1:2 receptor to anion binding stoichiometries for $SO_4^{2-}$ and $H_2PO_4^-$ anions, respectively, for the receptors $6^{2+}\cdot 2PF_6^-$ and $7^{2+}\cdot 2PF_6^-$. The calculated stoichiometry for the hydrogen bond donor receptor $7^{2+}\cdot 2PF_6^-$ with $HP_2O_7^{3-}$ anion was 1:2 receptor to anion (see Figure 2 and the Supporting Information). The stoichiometry obtained for $H_2PO_4^-$ anions could be due to the capability of the monodentate $H_2PO_4^-$ anions to form stable dimers in solution in the presence of dicationic receptors.[16] The association constant values were calculated by fitting the fluorescence and UV−vis titration data in $CH_3CN$ to the obtained host−guest binding model using the Dynafit[17] program and are collected in Table 1. Attempts to estimate the association constants $K_{11}$ and $K_{12}$ individually were unsuccessful, and only the overall association constant $\beta$ ($\beta = K_{11}K_{12}$) could be calculated for the complexes with stoichiometry 1:2.

$^1H$ NMR and $^{31}P$ NMR titration experiments were performed in $CD_3CN/CD_3OD$ (9/1), in order to get additional information about the binding mode between the receptors $6^{2+}\cdot 2PF_6^-$ and $7^{2+}\cdot 2PF_6^-$ with the previously tested anions. Halogen and hydrogen bond donor receptors $6^{2+}\cdot 2PF_6^-$ and $7^{2+}\cdot 2PF_6^-$ respectively have similar $^1H$ NMR spectra in $CD_3CN/CD_3OD$ 9/1; the only exception is the presence of an imidazolium proton $H_m$ at $\delta$ 7.52 ppm in the bis-imidazolium hydrogen bond donor receptor $7^{2+}\cdot 2PF_6^-$, which is obviously absent in the bis-bromoimidazolium $6^{2+}\cdot 2PF_6^-$. Both receptors show the same set of signals: the methyl protons located at the imidazolium rings appear at $\delta$ 2.15 and 1.85 ppm, respectively, in the receptor $6^{2+}\cdot 2PF_6^-$ and at $\delta$ 2.57 and 2.10 ppm in the receptor $7^{2+}\cdot 2PF_6^-$. The protons of the two methylenes present in the fragments naphthalene−$CH_2$−imidazolium ($H_b$) and imidazolium−$CH_2$−anthracene ($H_a$) appear as two different singlets around $\delta$ 5.55 and 6.30 ppm, respectively, and the naphthalene ($H_e$, $H_g$, and $H_f$) and the anthracene ($H_h$, $H_i$, $H_j$, $H_k$, and $H_l$) protons appear in the aromatic region in the range $\delta$ 6.91−8.77 ppm.

The most interesting feature observed during the $^1H$ NMR titration experiments was the different behavior of receptors $6^{2+}\cdot 2PF_6^-$ and $7^{2+}\cdot 2PF_6^-$ after the addition of $HP_2O_7^{3-}$ anions.

Thus, stepwise addition of $HP_2O_7^{3-}$ anions to the hydrogen bond donor receptor $7^{2+}\cdot 2PF_6^-$ promotes significant downfield shifts in the naphthalene $H_e$ protons ($\Delta\delta$ = +0.32 ppm) and in the methylene protons $H_a$ ($\Delta\delta$ = +0.21 ppm) and $H_b$ ($\Delta\delta$ = +0.17 ppm). However, the methyl protons $H_d$ were shifted significantly upfield ($\Delta\delta$ = −0.38 ppm), the maximum shift being reached after addition of 2 equiv. Further addition of a large excess of $HP_2O_7^{3-}$ anion did not induce detectable changes (Figure 6).

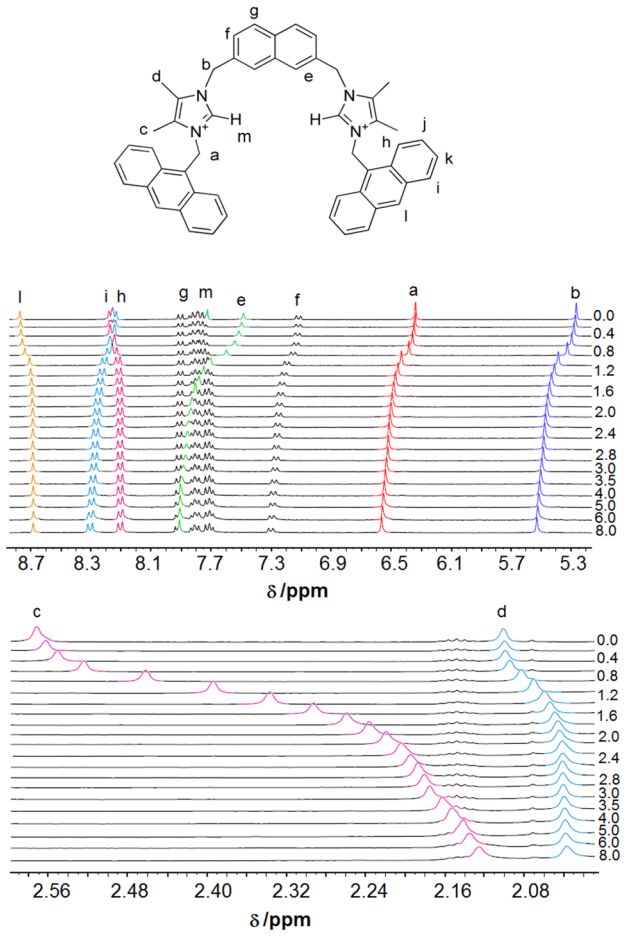


**Figure 6.** $^1H$ NMR spectral changes observed in the receptor $7^{2+}\cdot 2PF_6^-$ in $CD_3CN/CD_3OD$ (9/1, v/v) during the addition of up to 8 equiv of $HP_2O_7^{3-}$ ions.

The behavior observed during the titration experiment of the halogen bond donor receptor $6^{2+}\cdot 2PF_6^-$ with $HP_2O_7^{3-}$ anions was quite different: first of all, addition of up to 1 equiv promotes changes similar to those observed in the receptor $7^{2+}\cdot 2PF_6^-$: the signals corresponding to $H_e$, $H_a$, and $H_b$ protons were shifted downfield at $\Delta\delta$ = +0.25, +0.08, and +0.08 ppm, respectively, and the methyl protons were shifted upfield at $\Delta\delta$ = −0.06 ppm, suggesting that a recognition process is taking


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place. The addition of more than 1 equiv induced the appearance of two new sets of signals (Figure 7, peaks in blue and in red) and the progressive disappearance of the signals assigned to the complex $\mathbf{6}^{2+}\cdot\mathbf{HP_2O_7}^{3-}$. Finally, after addition of 5 equiva only one set of signals (Figure 7, peaks in red) was present in the $^1$H NMR spectrum, which clearly indicates than an intermediate species (Figure 7, blue peaks) was generated during the addition process. The titration was also monitored by mass spectrometry, which showed that the two new species were the result of the loss of one or two bromine atoms in the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ and the subsequent generation of the corresponding mono- and bis-imidazolones $\mathbf{8}^{+}\cdot\mathbf{PF_6}^-$ and **9**, respectively. Although halogen displacement in 2-haloimidazolium derivatives by the action of active methylene compounds, amines, and sulfur derivatives is well-documented,[18] conversion into the corresponding 2-imidazolones by merely the action of oxoanions under extremely mild reaction conditions is unprecedented. To this end, the bis-imidazolone **9** was prepared in bulk in 44% yield by treatment of the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ with 10 equiv of tris-(tetrabutylammonium)hydrogen pyrophosphate in acetonitrile at room temperature for 24 h.

During the course of the reaction the intermediate 2-bromoimidazolium/2-imidazolone compound $\mathbf{8}^{+}\cdot\mathbf{PF_6}^-$ was detected by $^1$H NMR spectroscopy The target molecule **9** was isolated as a solid which was fully characterized by standard techniques: $^1$H NMR, $^{13}$C NMR, and high-resolution mass spectrometry (see the Experimental Section). A tentative mechanism for this transformation could involve an initial recognition process to form the complex $\mathbf{6}^{2+}\cdot\mathbf{HP_2O_7}^{3-}$, which in the presence of an excess of $HP_2O_7^{3-}$ anion undergoes displacement of a bromine atom and concomitant cleavage of the resulting organic pyrophosphate to give the intermediate 2-bromoimidazolium/2-imidazolone $\mathbf{8}^{2+}\cdot\mathbf{2PF_6}^-$ and cyclodiphosphate anion. The intermediate $\mathbf{8}^{2+}\cdot\mathbf{2PF_6}^-$ by the action of the $HP_2O_7^{3-}$ anion undergoes O-nucleophilic attack at position 2 of the bromoimidazolium ring followed by cleavage of the pyrophosphate moiety to give the target compound **9** and cyclodiphosphate anion (Scheme 2). This mechanism is related to that previously described in the displacement of sulfur from ADP$\alpha$S and for the hydrolysis of the adenosine 5-*O*-(*S*-methyl 1-thiotriphosphate).[19] Probably, a tetraphosphate is formed through trapping of the reactive cyclodiphosphate by the $HP_2O_7^{3-}$ anion.[19b]

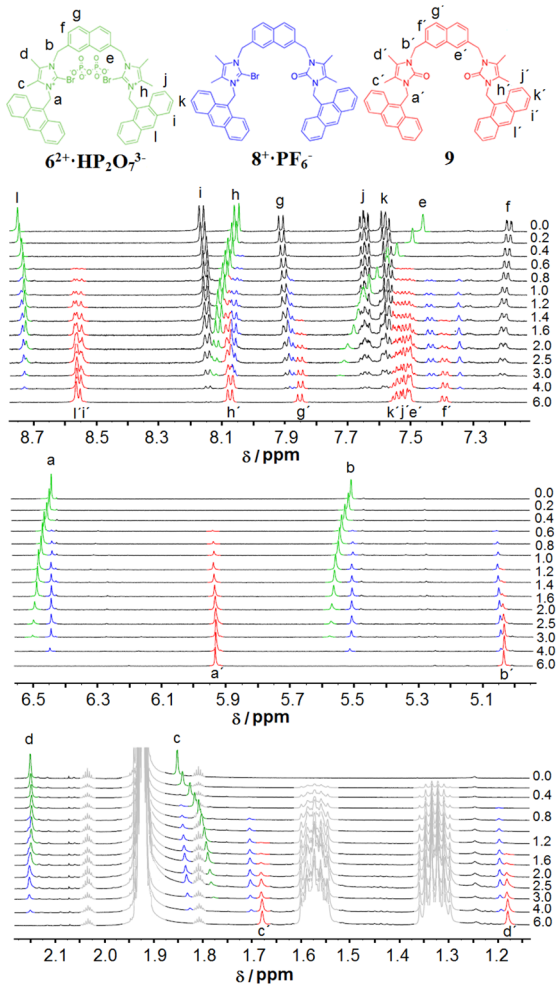


**Figure 7.** $^1$H NMR spectral changes observed in the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ in $CD_3CN/CD_3OD$ (9/1, v/v) during the addition of up to 6 equiv of $HP_2O_7^{3-}$ ions.

Stepwise addition of increasing amounts of $H_2PO_4^-$ anions to a solution of either $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ or $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ receptors in $CD_3CN/CD_3OD$ 9/1 induced similar changes in their $^1$H NMR spectra. The presence of $H_2PO_4^-$ anions promotes significant downfield shifts in the naphthalene $H_e$ protons ($\Delta\delta \approx +0.40$ ppm) and in the methylene protons $H_a$ ($\Delta\delta \approx +0.15$ ppm) and $H_b$ ($\Delta\delta \approx +0.11$ ppm). As expected, the imidazolium protons $H_m$ of the hydrogen bond donor receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ were the most affected ($\Delta\delta \approx +0.56$ ppm). On the other hand the methyl protons $H_d$ were shifted upfield by around $\Delta\delta \approx -0.13$ ppm (see the Supporting Information). The presence of $SO_4^{2-}$ anions also promotes the same changes in both receptors (Figure 8) as those observed previously during the addition of $H_2PO_4^-$ anions although to a lesser extent, while $HSO_4^-$, $NO_3^-$, $Cl^-$, $Br^-$, $I^-$, $AcO^-$, $ClO_4^-$, $BF_4^-$, and $C_6H_5CO_2^-$ did not modify the $^1$H NMR spectra of the receptors $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ and $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ even when a large excess of anions was added.

The association constants were initially calculated in the solvent mixture $CD_3CN$/MeOD (8/1), but some of the obtained association constants values were out of the accepted limit ($K_a > 10000\ M^{-1}$). This issue was solved by the utilization of the more competitive solvent mixture $CD_3CN$/MeOD (8/2), and the association constants are collected in Table 2.

The analysis of the obtained association constant values in $CH_3CN$ by UV−vis and fluorescence and in $CD_3CN$/MeOD (8/2) by $^1$H NMR reveal that the halogen-bonding bis-imidazolium receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ exhibits higher binding affinity for the tested anions than the hydrogen-bonding receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ in the more competitive solvent mixture $CD_3CN$/MeOD (8/2), which is in agreement with the most of the studies reported to date on halogen-bonding receptors in very competitive solvent mixtures.[8,9] In contrast, the hydrogen receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ shows higher binding affinity for anions than the halogen-bonding receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ in the less competitive and aprotic $CH_3CN$ solvent. Note that, as expected, the presence of methanol always decreases the association constants, moderately in the 1:1 complexes (about $10^2$ times) and strongly in the 1:2 complexes (about $10^7$ times).

Recognition events were also studied using the $^{31}$P NMR spectral changes of $H_2PO_4^-$ and $HP_2O_7^{3-}$ anions in $CD_3CN/CD_3OD$ (9/1, v/v) solution after the addition of 0.5 equiv for $H_2PO_4^-$ or 1 equiv for $HP_2O_7^{3-}$ of the receptors $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ and $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$. The $^{31}$P NMR spectrum of $HP_2O_7^{3-}$ shown a single


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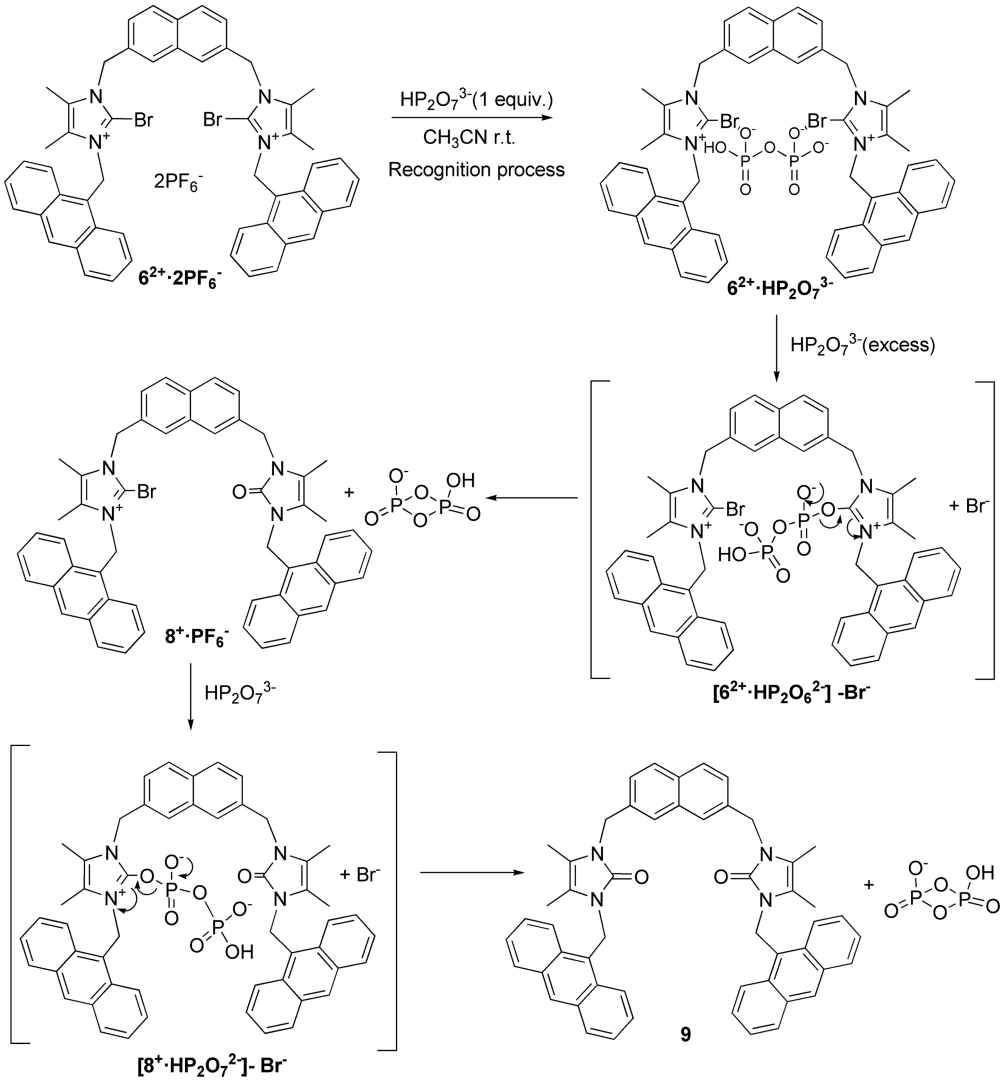
**Scheme 2. Plausible Pathway for the Conversion of the Bis(2-bromoimidazolium) Receptor $6^{2+}\cdot 2PF_6^-$ into the Bis(2-imidazolone) 9**




peak at $\delta$ −6.44 ppm, which was shifted upfield by $\Delta\delta \approx 2$ ppm after the addition of 1 equiv of the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ or $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$. The same experiment was carried out after the addition of 0.5 equiv of receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ or $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$ to a solution of $H_2PO_4^-$ in $CD_3CN/CD_3OD$ (9/1, v/v), in this case the single peak attributed to the phosphorus atom of the $H_2PO_4^-$ anion was also shifted upfield by $\Delta\delta \approx 1$ ppm. Upfield shifts of $\Delta\delta \approx -3$ ppm have been reported for hydrogenpyrophosphate trianion with other receptors.[20]

When the reaction course between the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ and 6 equiv of $HP_2O_7^{3-}$ anions was followed by $^{31}P$ NMR spectroscopy, it was found that the final spectrum displayed a sharp signal at −8.12 ppm due to a complexed $H_2PO_4^-$ anion, along with a doublet centered at −9.16 ppm attributable to the tetraphosphate and a small signal at −15.7 ppm due to the cyclodiphosphate anion.[19b] Support for the assignment of the signal at −8.12 ppm to a complexed $H_2PO_4^-$ anion is the fact that a signal similar in shape and position is found when 1 equiv of this anion is added to a solution of the bis-imidazolone **9** in $CD_3CN/CD_3OD$ (9/1, v/v).

The results of the theoretical calculations can be found in the Supporting Information.

**Cell Uptake and Imaging.** The fluorescence image of the halogen-bonding receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ was assayed using HeLa cells for biological application by confocal microscopy experiments to demonstrate the potential value of this sensor as an imaging agent in living cells.

The overlay of the bright field and fluorescence images obtained by confocal microscopy at different channels ($\lambda$ 450 ± 10, 510 ± 10, and 610 ± 10 nm) on excitation at $\lambda$ 405 nm (Figure 9) shows that the fluorescence was located in the intracellular area, indicating a good cell membrane permeability and the capability of the sensor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ to be used as an imaging agent in living cells in a wide range of emission wavelengths.

In addition, with regard to further biological application, the cytotoxicity in HeLa cells was determined by a conventional MTT assay. The results clearly showed that the receptor $\mathbf{6}^{2+}\cdot\mathbf{2PF_6}^-$ had low toxicity to the HeLa cells under the experimental conditions.

The same kinds of experiments were realized for the hydrogen-bonding receptor $\mathbf{7}^{2+}\cdot\mathbf{2PF_6}^-$. The fluorescence observed at low-energy wavelengths, especially at $\lambda$ 610 ± 10 nm, were considerably smaller (see the Supporting Informa-



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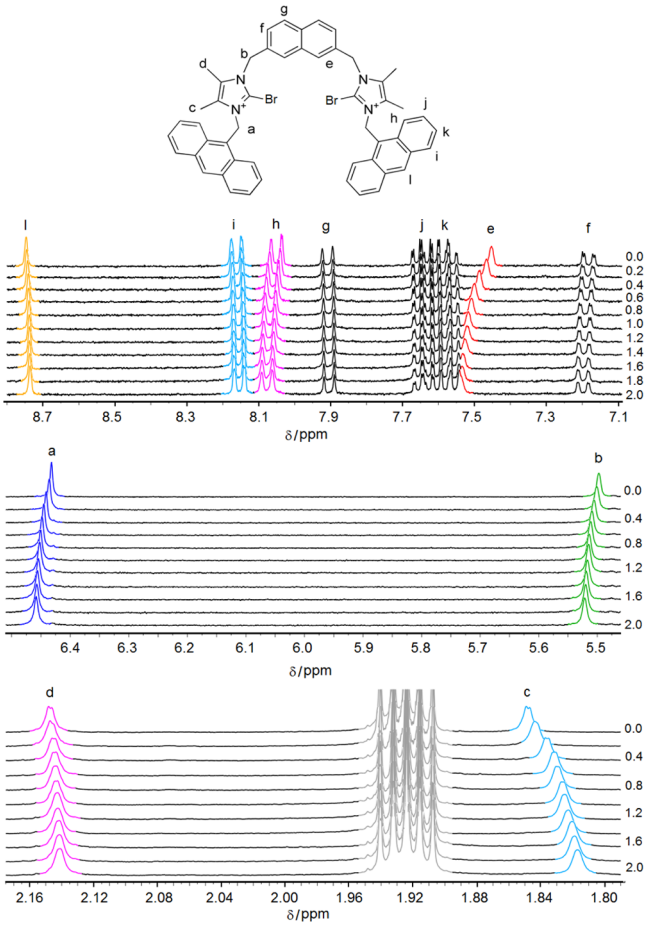


**Figure 8.** $^1$H NMR spectral changes observed in the receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ in $CD_3CN/CD_3OD$ (9/1, v/v) during the addition of up to 2 equiv of $SO_4^{2-}$ ions.

tion). This emphasized the importance of the utilization of the receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ as an imaging agent in living cells because near-infrared fluorescent dyes (>600 nm) are very attractive for biological and clinical applications due to several factors: minimum photodamage to biological samples, deep tissue penetration, and minimum interference from background autofluorescence of biomolecules in living systems.[21]

## CONCLUSION

The synthesis of novel two-armed charge-assisted anion ditopic receptors has been reported. The central 2,7-disubstituted naphthalene core incorporates two end-capped photoactive anthracene rings as fluorescent signaling units into their side arms, with central 2-bromoimidazolium (XB) or hydrogen

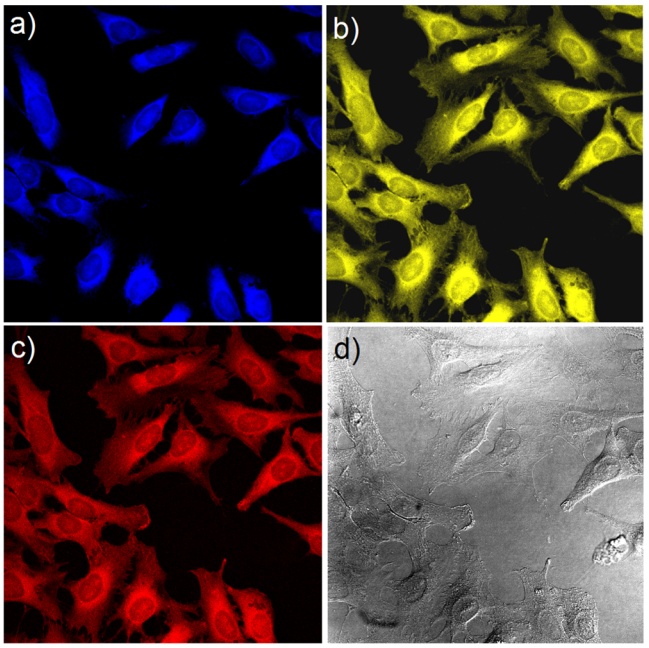


**Figure 9.** Fluorescence imaging of living HeLa cells incubated with the sensor $\mathbf{6}^{2+}\cdot 2PF_6^-$ at the different channels (a) $\lambda$ 450 ± 10 nm, (b) $\lambda$ 510 ± 10 nm, and (c) $\lambda$ 610 ± 10 nm on excitation at $\lambda$ 405 nm. (d) Bright field image of living HeLa cells incubated with the sensor $\mathbf{6}^{2+}\cdot 2PF_6^-$.

imidazolium (HB) bidentate receptors. Several anion-binding experiments have been carried out in order to make a comparative study of the sensing capabilities of the XB versus the HB receptor. Evaluation of the sensing properties by fluorescence reveals important differences in the sensing behavior between the halogenated receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$ and the hydrogen receptor $\mathbf{7}^{2+}\cdot 2PF_6^-$. In the presence of $SO_4^{2-}$ or $F^-$ anions a remarkable decrease in the monomer emission bands of the receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$was observed, whereas the XB receptor acts as a selective fluorescent molecular sensor for $H_2PO_4^-$ anion, this being the unique anion which promotes a progressive increase in a new broad and structureless emission band assigned to the anthracene excimer emission band in the receptor $\mathbf{6}^{2+}\cdot 2PF_6^-$. In addition, this receptor behaves as a chemodosimeter toward the $HP_2O_7^{3-}$ anion, through its transformation into the corresponding bis-imidazolone after debromination by the action of the basic anion. In contrast to this rich fluorescent behavior of the XB donor receptor, addition of the aforementioned anions to the HB donor receptor only promoted quenching of the monomer emission bands. $^1$H NMR titration experiments were performed in order to get additional information about the binding mode between

**Table 2. Association Constants Calculated by $^1$H NMR using the Dynafit Program for Receptors $\mathbf{6}^{2+}\cdot 2PF_6^-$ and $\mathbf{7}^{2+}\cdot 2PF_6^-$ with $HP_2O_7^{3-}$, $SO_4^{2-}$, and $H_2PO_4^-$ Anions in $CD_3CN$/MeOD (8/2)[a]**

| receptor | anion | stoichiometry | $K_1$ ($M^{-1}$) | $\beta$ ($M^{-2}$) |
|---|---|---|---|---|
| $\mathbf{6}^{2+}\cdot 2PF_6^-$ | $HP_2O_7^{3-}$ | *b* | | |
| $\mathbf{6}^{2+}\cdot 2PF_6^-$ | $SO_4^{2-}$ | 1:1 | $5.5 \times 10^3$ (4) | |
| $\mathbf{6}^{2+}\cdot 2PF_6^-$ | $H_2PO_4^-$ | 1:2 | | $9.9 \times 10^3$ (3) |
| $\mathbf{7}^{2+}\cdot 2PF_6^-$ | $HP_2O_7^{3-}$ | 1:2 | | $3.3 \times 10^5$ (6) |
| $\mathbf{7}^{2+}\cdot 2PF_6^-$ | $SO_4^{2-}$ | 1:1 | $2.2 \times 10^3$ (4) | |
| $\mathbf{7}^{2+}\cdot 2PF_6^-$ | $H_2PO_4^-$ | 1:2 | | $5.6 \times 10^3$ (4) |

[a]Errors (in percent) are given in parentheses. [b]Chemodosimeter behavior.



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the receptors $6^{2+}\cdot 2PF_6^-$ and $7^{2+}\cdot 2PF_6^-$. Halogen and hydrogen bond donor receptors have similar $^1H$ NMR spectra; the only exception is the presence of an imidazolium proton on the hydrogen bond donor receptor. Both receptors show the same set of signals, and the most interesting feature observed during the $^1H$ NMR titration experiments was the different behavior of receptors $6^{2+}\cdot 2PF_6^-$ and $7^{2+}\cdot 2PF_6^-$ after addition of $HP_2O_7^{3-}$ anions. The analysis of the obtained association constant values reveals that in the competitive solvent mixture $CD_3CN$/MeOD (8/2) the halogen-bonding complexes display values higher than those found for the hydrogen-bonding counterpart. In contrast, in the less competitive and aprotic $CH_3CN$ solvent the hydrogen receptor $7^{2+}\cdot 2PF_6^-$ shows higher binding affinity for anions than the halogen-bonding receptor.

The reported experiments using HeLa cells with the XB receptor $6^{2+}\cdot 2PF_6^-$ proved that this sensor has a good cell membrane permeability and is capable of being used as an imaging agent in living cells in a wide range of emission wavelengths; on the other hand, for the HB receptor $7^{2+}\cdot 2PF_6^-$, the observed fluorescence was much smaller.

Taking into account that the capability of a XB or HB to act as a binding site strongly depends on several factors, the assessment that the integration of a halogen atom into the anion receptor at the expense of one hydrogen-bonding receptor increases the anion recognition affinity cannot be considered as a general rule.

For these very flexible structures, localization of minima is a difficult task. The results of the theoretical calculations are not entirely satisfying, although the main tendencies of the binding energies are reproduced. The most important result is the finding that open and closed forms exist for the $6^{2+}\cdot(H_2PO_4^-)_2$ complex, justifying the existence of an excimer emission.

## EXPERIMENTAL SECTION

The reactions were performed using dried solvents, and the solvents were previously dried by a traditional method. All melting points were determined by means of a Kofler hot-plate melting-point apparatus and are uncorrected. Solution $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were recorded at 200, 300, 400, or 600 MHz. The abbreviations used in the NMR data are as follows: s (singlet), m (multiplet), and q (quaternary carbon atom). Tetramethylsilane (TMS) has been used as an internal reference to determine the chemical shifts ($\delta$) in the $^1H$ and $^{13}C$ NMR spectra. The concentrations used in the UV−vis and fluorescence titrations are as stated in the text and in the corresponding figure captions; we have used a 10 mm path length cell with the spectra background corrected before and after sequential additions of different aliquots of anions. The values of the quantum yield were calculated using anthracene as the standard ($\Phi = 0.27 \pm 0.01$) and the equation $\Phi_x/\Phi_s = (S_x/S_s)[(1 - 10^{-A_s})/(1 - 10^{-A_x})](n_s^2/n_x^2)$, where x and s indicate the unknown and standard solutions, respectively, $\Phi$ is the quantum yield, $S$ is the area under the emission curve, $A$ is the absorbance at the excitation wavelength, and $n$ is the refractive index. 3-Nitrobenzyl alcohol was used as a matrix in the mass spectra. HeLa cells were cultured in glass bottom culture dishes in Dulbecco's modified Eagle's medium (DMEM), supplemented with 10% FBS and 1000 units/mL of penicillin and 1000 $\mu$g/mL of streptomycin. The cells were incubated at 37 °C in a humidified atmosphere of 5% $CO_2$ for 24 h, and then the cells were washed with PBS several times and incubated with the receptor $6^{2+}\cdot 2PF_6^-$ (5 $\mu$M) in PBS (2 mL)/DMSO (20 $\mu$L) for 1 h at 37 °C.

**Synthesis of Bis-Bromoimidazolium Receptor $6^{2+}\cdot 2Br^-$.** To a solution of 2,7-bis(2-bromo-4,5-dimethylimidazolyl)naphthalene (**4**; 0.120 g, 0.24 mmol) in acetonitrile (25 mL) was added dropwise a solution of 9-(bromomethyl)anthracene (0.156 g, 0.58 mmol) in 40 mL of acetonitrile, and the resultant mixture was heated at reflux temperature for 72 h. The resulting precipitate was collected and washed with diethyl ether, giving the desired bis-imidazolium receptor as the bromide salt. Yield: 0.117 g (47%). Mp: 216−218 °C. $^1H$ NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.84 (s, 2H); 8.22 (d, 4H, $J$ = 9 Hz); 8.19 (d, 4H, $J$ = 9 Hz); 8.00 (d, 2H, $J$ = 8 Hz); 7.70−7.68 (m, 4 H); 7.61 (s, 2H); 7.66−7.60 (m, 4 H); 7.24 (dd, 2H, $J$ = 8 Hz, $J$ = 1.5 Hz); 6.63 (s, 4H); 5.67 (s, 4H); 2.18 (s, 6H); 1.83 (s, 6H) ppm. $^{13}C$ NMR (150 MHz, DMSO-$d_6$): $\delta$ 132.6; 132.0; 131.9; 130.9; 130.7; 130.1; 129.9; 129.7; 129.4; 128.8; 127.6; 125.5; 125.0; 124.4; 123.3; 122.9; 121.4; 50.2; 47.1; 9.9; 8.9 ppm. MS (ESI): $m/z$ calcd for $[M^{2+} + Br^-]^+$ 963.1, found 963.1. Anal. Calcd for $C_{52}H_{44}Br_4N_4$: C, 59.79; H, 4.25; N, 5.36. Found: C, 59.81; H, 4.35; N, 5.27.

**Synthesis of Bis-Bromoimidazolium Receptor $6^{2+}\cdot 2PF_6^-$.** A solution of bis-imidazolium receptor as the bromide salt $6^{2+}\cdot 2Br^-$ (0.100 g, 0.096 mmol) in $CH_2Cl_2$ (20 mL) was washed with a saturated solution of $NH_4PF_6$ in $H_2O$ and stirred for 20 min (5 × 20 mL). The organic solvent was collected and dried with anhydrous $Na_2SO_4$. The solid was separated by filtration, and the solvent was removed under reduced pressure to give the $PF_6^-$ salt in quantitative yield. Yield: 0.109 g (97%). Mp: 217−219 °C. $^1H$ NMR (300 MHz, $CD_3CN/CD_3OD$ (9/1 v/v)): $\delta$ 8.75 (s, 2H); 8.17 (d, 4H, $J$ = 8 Hz); 8.05 (d, 4H, $J$ = 8 Hz); 7.90 (d, 2H, $J$ = 8 Hz); 7.67−7.62 (m, 4 H); 7.60−7.55 (m, 4H); 7.45 (s, 2H); 7.19 (dd, 2H, $J$ = 1.7 Hz, $J$ = 8 Hz); 6.43 (s, 4H); 5.50 (s, 4H); 2.15 (s, 6H); 1.85 (s, 6H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 132.4; 132.1; 132.0; 130.9; 130.6; 130.1; 129.9; 129.7; 129.5; 128.9; 127.6; 125.5; 125.2; 124.3; 123.1; 122.7; 121.2; 50.2; 46.9; 9.8; 8.9 ppm. MS (ESI): $m/z$ calcd for $[M^{2+} + PF_6^-]^+$ 1029.2, found 1029.2. Anal. Calcd for $C_{52}H_{44}Br_2F_{12}N_4P_2$: C, 53.17; H, 3.78; N, 4.77. Found: C, 53.05; H, 3.69; N, 4.88.

**Synthesis of Bis-Imidazolium Receptor $7^{2+}\cdot 2Br^-$.** To a solution of 2,7-bis(4,5-dimethylimidazolyl)naphthalene (**5**; 0.230 g, 0.69 mmol) in acetonitrile (25 mL) was added dropwise a solution of 9-(bromomethyl)anthracene (0.497 g, 1.83 mmol) in 40 mL of acetonitrile, and the resultant mixture was heated at reflux temperature for 72 h. The resulting precipitate was collected and washed with diethyl ether, giving the desired bis-imidazolium receptor as the bromide salt. Yield: 0.110 g (14%). Mp: 240−242 °C. $^1H$ NMR (600 MHz, DMSO-$d_6$): $\delta$ 8.90 (s, 2H); 8.35 (d, 4H, $J$ = 8 Hz); 8.29 (s, 2H); 8.25 (d, 4H, $J$ = 8 Hz); 7.82 (d, 2H, $J$ = 8 Hz); 7.69−7.65 (m, 4H); 7.64−7.60 (m, 4H); 7.46 (s, 2H); 6.97 (dd, 2H, $J$ = 1.2 Hz, $J$ = 8 Hz); 6.35 (s, 4H), 5.33 (s, 4H); 2.59 (s, 6H); 2.12 (s, 6H) ppm. $^{13}C$ NMR (150 MHz, DMSO-$d_6$): $\delta$ 134.1; 132.9; 132.2; 131.8; 131.2; 130.9; 130.4; 129.5; 128.6; 127.7; 126.9; 125.8; 125.6; 124.8; 123.6; 122.0; 49.3; 43.6; 8.6; 8.1. MS (ESI): $m/z$ calcd for $[M^{2+} + Br^-]^+$ 805.3, found 805.3. Anal. Calcd for $C_{52}H_{46}Br_2N_4$: C, 70.43; H, 5.23; N, 6.32. Found: C, 70.55; H, 5.35; N, 6.23.

**Synthesis of Bis-Imidazolium Receptor $7^{2+}\cdot 2PF_6^-$.** A solution of the bis-imidazolium receptor as the bromide salt $7^{2+}\cdot 2Br$ (0.100 g, 0.113 mmol) in $CH_2Cl_2$ (20 mL) was washed with a saturated solution of $NH_4PF_6$ in $H_2O$ and stirred for 20 min (5 × 20 mL). The organic solvent was collected and dried with anhydrous $Na_2SO_4$. The solid was separated by filtration, and the solvent was removed under reduced pressure to give the $PF_6^-$ salt in quantitative yield. Yield: 0.112 g, (98%). Mp: 176−177 °C. $^1H$ NMR (400 MHz, $CD_3CN/CD_3OD$ (9/1 v/v)): $\delta$ 8.77 (s, 2H); 8.16 (d, 4H, $J$ = 8 Hz); 8.14 (d, 4H, $J$ = 8 Hz); 7.70 (d, 2H, $J$ = 8 Hz); 7.64−7.60 (m, 4H); 7.59−7.54 (m, 4H); 7.52 (s, 2H); 7.28 (s, 2H); 6.91 (dd, 2H, $J$ = 1.6 Hz, $J$ = 8 Hz); 6.14 (s, 4H); 5.06 (s, 4H); 2.57 (s, 6H); 2.10 (s, 6H) ppm. $^{13}C$ NMR (100 MHz, DMSO-$d_6$): $\delta$ 134.1; 132.9; 132.2; 131.9; 131.2; 130.9; 130.5; 129.5; 128.7; 128.6; 127.7; 127.0; 125.9; 125.7; 124.8; 123.5; 121.9; 49.3; 43.5; 8.5; 8.0 ppm. MS (ESI): $m/z$ calcd for $[M^{2+} + PF_6^-]^+$ 871.3, found 871.3. Anal. Calcd for $C_{52}H_{46}F_{12}N_4P_2$: C, 61.42; H, 4.56; N, 5.51. Found: C, 61.58; H, 4.65; N, 5.39.

**Synthesis of Bis-Imidazolone 9.** To a solution of the bis-imidazolium receptor as the bromide salt $6^{2+}\cdot 2Br^-$ (0.100 g, 0.096 mmol) in $CH_3CN$ was added tris(tetrabutylammonium)hydrogen pyrophosphate (0.768 g, 1.0 mmol), and the resultant mixture was stirred for 24 h at room temperature. The $CH_3CN$ was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (ethyl acetate) to give the desired bis-imidazolone **9**. Yield: 28 mg (44%). Mp: 196−198 °C. $^1H$ NMR (300



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MHz, DMSO-$d_6$): $\delta$ 8.68−8.65 (m, 4H); 8.64 (s, 2H); 8.13−8.10 (m, 4H); 7.89 (d, 2H, $^3J$ = 8.5 Hz); 7.59 (s, 2H); 7.57−7.52 (m, 8H); 7.41 (dd, 2H, $J$ = 1.5 Hz, $J$ = 8.5 Hz); 5.92 (s, 4H); 5.03 (s, 4H); 1.69 (s, 6H); 1.19 (s, 6H) ppm. $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 153.1; 136.7; 132.7; 131.4; 130.9; 130.3; 129.2; 128.9; 128.2; 128.1; 126.5; 125.2; 124.9; 124.6; 113.6; 113.1; 43.9; 37.7; 9.3; 8.0 ppm. HRMS: $m/z$ calcd for $[M + H]^+$ 757.3530, found 757.3543. Anal. Calcd for $C_{52}H_{44}N_4O_2$: C, 82.51; H, 5.86; N, 7.40. Found: C, 82.41; H, 5.75; N, 7.54.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01146.

$^1$H and $^{13}$C NMR spectra, $^1$H NMR, $^{31}$P NMR, fluorescence, and UV−vis anion binding studies, Job plot experiments, a theoretical calculation section which includes the computational details, Cartesian coordinates, and total energies of the complexes of the halogen bonding receptor with $SO_4^{2-}$ and $H_2PO_4^-$, and confocal microscopy images of the hydrogen bonding receptor (PDF)

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### Notes

The authors declare no competing financial interest.

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