

# New Host Molecules with Imidazoliums as Functional Arms: Syntheses and Anion Recognition

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The bridged tri-imidazoliums  $3 \cdot 3X^- - 5 \cdot 3X^-$  ( $X^- = PF_6^-, Br^-, I^-$ ) and bis-imidazoliums  $6 \cdot 2PF_6^-$  were synthesized by *N*-quaternization of imidazole derivative **1** in acetonitrile under reflux. UV spectroscopic titration experiments showed that the halide salts and hexafluorophosphate salts of these imidazoliums exhibited good recognition toward anions in water and in acetonitrile, respectively.

**Keywords**    anion recognition, imidazolium, synthesis, UV titration, supramolecular chemistry

## Introduction

Anion species play important roles in both chemical and biochemical processes. Anion recognition is becoming one of the main fields of supramolecular chemistry.<sup>1</sup> During the last two decades considerable efforts have been devoted to develop host-guest systems for anionic species, however, anion supramolecular chemistry was relatively slow to develop in comparison with the host-guest chemistry of cations and neutral molecules. The selective recognition of anionic guest species is still very challenging because of the intrinsic properties of anions.<sup>2</sup>

The interests in anion recognition are mainly directed towards synthetic hosts based on positively charged moieties. 1,3-Bisubstituted imidazole, namely imidazolium, is expected to be a novel binding subunit for anions through electrostatic interaction and unconventional C—H $\cdots$ X<sup>-</sup> hydrogen bonding.<sup>3</sup> However, the reasoned stud-

ies dealing with the unique imidazolium compounds for anion recognition are still quite rare.<sup>4</sup> For example, the anion recognition ability of tripodal anion receptor  $2 \cdot 3 PF_6^-$  with halide anions in deuterated acetonitrile was investigated,<sup>3a</sup> but no molecular recognition of imidazolium compounds for anions in water was reported. In addition, it is still necessary to develop new host-guest systems for anion selective recognition too. We have focused our interests on the designs, syntheses and applications of imidazolium compounds.<sup>5</sup> Herein we report the syntheses of new triply-bridged imidazolium salts  $3 \cdot 3X^- - 5 \cdot 3X^-$  ( $X^- = PF_6^-, Br^-, I^-$ ) and bis-imidazolium salt  $6 \cdot 2 PF_6^-$  (Scheme 1), and the anion recognition in water and in acetonitrile using these imidazolium salts, respectively.

## Results and discussion

*Designes and syntheses of hosts  $3 \cdot nX^- - 6 \cdot nX^-$  ( $X^- = PF_6^-, Br^-, I^-$ ;  $n = 2, 3$ )*

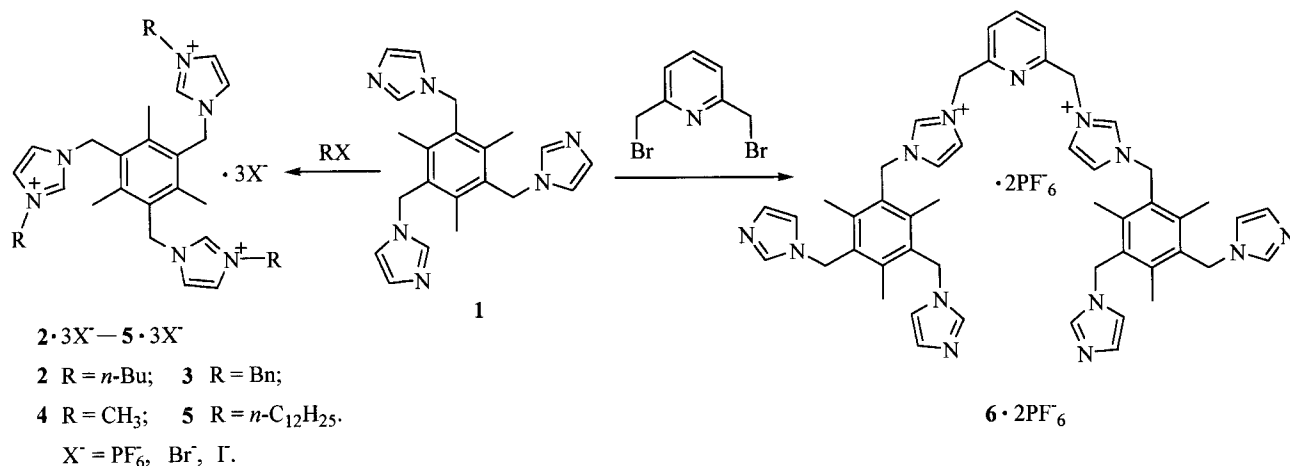
Several open chain imidazolium hosts with different shape and binding subunits were designed and synthesized. Tripodal hosts  $3 \cdot 3X^- - 5 \cdot 3X^-$  contain three imidazolium subunits as anion binding moieties and different substituents benzyl, methyl and *n*-dodecyl groups on imidazolium rings. Host  $6 \cdot 2PF_6^-$  has two imidazolium rings linked to 2,6-pyridyldimethylene group, and the four imidazolymethyl groups on the benzene ring might serve as

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## Scheme 1



cooperating groups during the host-guest binding processes.

The hosts were synthesized by the quaternization reactions of tri-imidazole intermediate **1** with different halides in dry acetonitrile under reflux (Scheme 1). Hosts  $3 \cdot 3X^- - 5 \cdot 3X^-$  were synthesized by treatment of tri-imidazole **1** with excess amount of halides. Host  $6 \cdot 2\text{PF}_6^-$  was obtained by the nucleophilic substitution of 2,6-bis(bromomethyl)pyridine with excessive tri-imidazole **1** to avoid the side reactions such as intramolecular and intermolecular cyclizations. The yields of the target compounds were from moderate to good. The hexafluorophosphate salts of the imidazolium compounds were obtained in high yields by treating the aqueous solutions of the corresponding halide salts with a saturated aqueous solution of  $\text{NH}_4\text{PF}_6$ .

The structures of the imidazolium compounds  $3 \cdot 3\text{Br}^-$ ,  $4 \cdot 3\text{I}^-$ ,  $5 \cdot 3\text{Br}^-$  and  $6 \cdot 2\text{PF}_6^-$  were determined by elemental analyses,  $^1\text{H}$  NMR, MS and IR spectra.  $^1\text{H}$  NMR spectra showed that the imidazolium ring protons H-2 was shifted more downfield about  $\delta$  1.0 as compared with the corresponding protons of the imidazole rings of their parent compound **1**, showing the strong deshielding effects of the nitrogen atoms of the imidazolium rings.

*Anion recognition of hosts  $3 \cdot nX^- - 6 \cdot nX^-$  ( $X^- = \text{PF}_6^-, \text{Br}^-, \text{I}^-$ ;  $n = 2, 3$ ) using UV spectroscopic titration*

There are many methods to characterize the host-guest interactions.<sup>6</sup> UV-vis spectroscopic titration is one

of the widely used methods for its high sensitivity to the host-guest bindings.<sup>7</sup> In this paper, the interactions between the imidazolium hosts  $3 \cdot nX^- - 6 \cdot nX^-$  ( $X^- = \text{PF}_6^-, \text{Br}^-, \text{I}^-$ ;  $n = 2, 3$ ) and anions were determined by UV spectroscopic titration.

In the UV titration experiments, addition of various concentrations of guest anions resulted in the characteristic absorptions of the imidazolium host molecules gradually decreased. When the imidazolium host (H) forms 1:1 complex with the anion (G), the equilibrium in solution is presented as Eq. (1).



The association constants of the host-guest system formed were calculated according to the Benesi-Hildebrand equation [Eq. (2)].<sup>8</sup>

$$[\text{H}]_0[\text{G}]_0/\Delta A = 1/(\Delta\epsilon K_a) + [\text{G}]_0/\Delta\epsilon \quad (2)$$

Where  $[\text{H}]_0$  and  $[\text{G}]_0$  refer to the total concentrations of the imidazolium host and anion solutions, respectively.  $\Delta\epsilon$  is the change in molar extinction coefficient between the free and complexed imidazolium, and  $\Delta A$  denotes the absorption changes of the imidazolium on addition of guest anion.

The binding constants ( $K_a$ ) and free-energy changes ( $\Delta G_0$ ) of these hosts with guest anions obtained from regression analyses for observed absorbance changes were summarized in Table 1. Benesi-Hildebrand-type analyses gave good linear relationships ( $\gamma > 0.99$ ), con-

**Table 1** Binding constants ( $K_a$ ) and free energy of complexation ( $-\Delta G^0$ ) for the 1:1 complexes between imidazoliums  $3 \cdot nX^-$ — $6 \cdot nX^-$  ( $X^- = PF_6^-, Br^-, I^-$ ;  $n = 2, 3$ ) and anions at 298.2 K

Entry	Host	Guest <sup>a</sup>	Solvent	$K_a$ (dm <sup>3</sup> /mol) <sup>b</sup>	$-\Delta G^0$ (kJ/mol)
1	$3 \cdot 3Br^-$	$HCO_3^-$	H <sub>2</sub> O	1240	17.65
2	$3 \cdot 3Br^-$	$CO_3^{2-}$	H <sub>2</sub> O	3570	20.28
3	$3 \cdot 3Br^-$	$H_2PO_4^-$	H <sub>2</sub> O	1265	17.71
4	$3 \cdot 3Br^-$	$HPO_4^{2-}$	H <sub>2</sub> O	4610	20.91
5	$4 \cdot 3I^-$	$CO_3^{2-}$	H <sub>2</sub> O	700	16.22
6	$4 \cdot 3I^-$	$PO_4^{3-}$	H <sub>2</sub> O	5465	21.33
7	$3 \cdot 3PF_6^-$	$Br^-$	acetonitrile	1670	18.39
8	$5 \cdot 3PF_6^-$	$Br^-$	acetonitrile	410	14.92
9	$6 \cdot 2PF_6^-$	$Br^-$	acetonitrile	1190	17.55
10	$6 \cdot 2PF_6^-$	$F^-$	acetonitrile	7520	22.13
11	$6 \cdot 2PF_6^-$	$Cl^-$	acetonitrile	39760	26.25
12	$6 \cdot 2PF_6^-$	$I^-$	acetonitrile	120	11.82

<sup>a</sup> Guest anions were used in the forms of Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, KH<sub>2</sub>PO<sub>4</sub>, Na<sub>2</sub>HPO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, Bu<sub>4</sub>NF, Et<sub>3</sub>NBnCl, Bu<sub>4</sub>NBr and Bu<sub>4</sub>NI, respectively; <sup>b</sup> binding constants were represented as the average of 2—3 times, and errors were  $\pm 15\%$ .

sistent with the proposition of the formation of the complexes with 1:1 binding stoichiometry in each case. For example, at the temperature of 298.2 K, the acetonitrile solution of  $6 \cdot 2PF_6^-$  with a concentration of  $4.136 \times 10^{-5}$  mol/dm<sup>3</sup> had a UV absorbance of 2.721 at the maximum absorbance wavelength of 222 nm. To 2.5 mL of this solution was added total 9  $\mu$ L of the acetonitrile solution of Et<sub>3</sub>NBnCl ( $0.1035$  mol/dm<sup>3</sup>) by each add of 1  $\mu$ L. The UV absorbance at the maximum absorbance wavelength of 222 nm consequently changed to 2.462, 2.396, 2.361, 2.334, 2.314, 2.297, 2.296, 2.289 and 2.279. According to Eq. (2), the linear regression analysis of the calculated  $[H]_0[G]_0/\Delta A$  values against  $[G]_0$  using the single factor linear least square methodology resulted in a well fit straight line (correlation coefficient  $\gamma = 0.997$ ), with the intercept value  $1/(\Delta\epsilon K_a)$  of  $2.2496 \times 10^{-9}$  mol<sup>2</sup>/dm<sup>6</sup> and the slope value  $1/\Delta\epsilon$  of  $8.9439 \times 10^{-5}$  mol/dm<sup>3</sup>. The stability constant ( $K_a$ ) and the free energy change ( $-\Delta G^0$ ) were calculated from the slope and the intercept to be 39760 dm<sup>3</sup>/mol and 26.25 kJ/mol, respectively (Entry 11).

The anion binding abilities of hosts  $3 \cdot nX^-$ — $6 \cdot nX^-$  ( $X^- = PF_6^-, Br^-, I^-$ ;  $n = 2, 3$ ) were investigated using the PF<sub>6</sub><sup>-</sup> salts and halide salts of hosts in acetonitrile and in water, respectively.

In general, when the anion recognition of the acyclic hosts that have not the hydrophobic cavities is carried out in water, the binding constants are quite small because the anions and hosts are strongly hydrated in water. How-

ever, our anion recognition experiments show that there are strong interactions between the acyclic tripodal imidazoliums  $3 \cdot 3X^-$ — $5 \cdot 3X^-$  and the anions ( $\log K_a = 2.8$ — $3.7$ ). CPK model study shows that these open-chain hosts could form proper cavities for the effective inclusion of the planar triangle anions such as  $CO_3^{2-}$  and  $HCO_3^-$  and tetrahedron anions such as  $H_2PO_4^-$ ,  $HPO_4^{2-}$  and  $PO_4^{3-}$ . The imidazoliums  $3 \cdot 3X^-$ — $5 \cdot 3X^-$  have multi-point recognition abilities to these anions because the three imidazolium groups on the arms can bind the different electronegative atoms of the anions respectively, and the cooperative effect of the groups on the hosts may increase the binding strength of the host and guest. The net charges of the anions influence the binding significantly. The binding constants of  $3 \cdot 3Br^-$  with the divalent anions are three times larger than those of the monovalent anions (Entries 1 and 2; 3 and 4), showing that in water the main force between the host and anion is the electrostatic forces. Host  $4 \cdot 3I^-$  also exhibits selective recognition to  $PO_4^{3-}$  and  $CO_3^{2-}$ , and it binds to  $PO_4^{3-}$  seven times stronger than to  $CO_3^{2-}$  (Entries 5 and 6).

In acetonitrile the interactions between halide anions and hosts are investigated. For host  $6 \cdot 2PF_6^-$ , the binding constants are followed the order  $Cl^- > F^- > Br^- > I^-$  in acetonitrile. Host  $6 \cdot 2PF_6^-$  binds  $Cl^-$  most strongly, giving the binding constant  $K_a$  as 39760 dm<sup>3</sup>/mol, and 5, 33 and 330 times larger than those of  $6 \cdot 2PF_6^-$  with  $F^-$ ,  $Br^-$  and  $I^-$ , respectively. According to the reports on that the imidazolium compounds can bind halides by

electrostatic force and hydrogen bonds in organic solutions.<sup>3,4</sup> It can be seen that the electrostatic interaction and hydrogen bonding which are originated from the positively charged imidazoliums are the essential attractive force between the hosts and anions. The preorganization effect may affect the host-guest interactions. The binding constant of tripodal host  $3 \cdot 3PF_6^-$  to  $Br^-$  is four times larger than those of  $5 \cdot 3PF_6^-$  because  $3 \cdot 3PF_6^-$  is more easily organized than the *n*-dodecyl substituted host  $5 \cdot 3PF_6^-$  for the complexing of  $Br^-$  and the long chain substituents on  $5 \cdot 3PF_6^-$  hindered the inclusion of anion.

In summary, we have developed the facile and efficient syntheses led to the imidazolium compounds that were proved to be effective hosts for anion recognition both in water and in acetonitrile. The tripodal imidazolium hosts show strong interaction with inorganic anions in water ( $\log K_a = 2.8-3.7$ ). Host  $6 \cdot 2PF_6^-$  binds  $Cl^-$  most strongly in acetonitrile, and the binding constant is 5, 33 and 330 times larger than those of  $6 \cdot 2PF_6^-$  with  $F^-$ ,  $Br^-$  and  $I^-$ , respectively. Binding experiments indicate that the electrostatic interaction, hydrogen bonding and the preorganization of binding sites of hosts play an important and essential role in the anion recognition.

## Experimental

### General methods and materials

Uncorrected melting points were taken on a micro-melting point apparatus.  $^1H$  NMR spectra were recorded on a Bruker DPX-300 instrument and chemical shifts in ppm are reported with TMS as an internal standard. ESI-MS spectra were measured on a Finnigan LCQ<sup>DECA</sup> instrument and FAB-MS spectra were measured on a VG Autospec 3000 instrument. Elemental analyses were performed on a Carlo Erba 1106 instrument. IR and UV spectra were obtained with a Nicolet FT-IR 170SX and a TU-1901 spectrophotometer, respectively.

Benzyl bromide, methyl iodide, *n*-dodecyl bromide, 1,3-dibromopropane and imidazole were redistilled or recrystallized before use. 1,3,5-Trimethyl-2,4,6-tris(*N*-imidazolylmethyl)benzene (**1**)<sup>5a</sup> and 2,6-bis(bromomethyl)pyridine<sup>9</sup> were prepared according to the literature procedures. Acetonitrile was of HPLC reagent grade. Deionized water was distilled before use. All other chemicals and reagents were obtained commercially and used

without further purification.

*General procedure for the preparation of  $3 \cdot 3X^- - 5 \cdot 3X^-$  ( $X^- = Br^-, I^-$ )*

To a stirred solution of **1** (1 mmol, 0.36 g) in 40 mL of acetonitrile at reflux, a solution of excessive halide in acetonitrile was added. The mixture was stirred for 10–30 h at the same temperature, then the solution was concentrated and filtrated. The pure product was obtained by recrystallization or column chromatography on silicon gel.

*1,3,5-Trimethyl-2,4,6-tris [*N*-(*N'*-phenylmethyl)-imidazoliummethyl]benzene tribromide salt (**3**·3Br<sup>-</sup>)*

White needle crystal was obtained by column chromatography on silicon gel using methanol as the eluent in 59% yield (0.52 g), m. p. 272–274 °C;  $^1H$  NMR ( $D_2O$ )  $\delta$ : 2.26 (s, 9H,  $CH_3$ ), 5.34 (s, 6H,  $CH_2$ ), 5.58 (s, 6H,  $CH_2$ ), 7.29–7.33 (m, 9H, 2,4,6-ArH), 7.42–7.44 (m, 6H, 3,5-ArH), 7.50 (s, 6H, 4,5-ImH), 8.74 (s, 3H, 2-ImH); IR (KBr)  $\nu$ : 3074 (w), 2976 (w), 1652, 1555, 1455 (w), 1145 (s), 721 (s)  $cm^{-1}$ ; ESI-MS  $m/z$  (%): 793 ( $M^+ - Br$ , 65), 713 ( $M^+ - 2Br$ , 5), 635 ( $M^+ - Br - benzyl - Im$ , 100), 555 ( $M^+ - 2Br - benzyl - Im$ , 75); Anal. calcd for  $C_{42}H_{45}N_6Br_3 \cdot H_2O$ : C 56.58, H 5.31, N 9.43; found C 56.65, H 5.13, N 9.73.

*1,3,5-Trimethyl-2,4,6-tris [*N*-(*N'*-methyl)imidazoliummethyl]benzene triiodide salt (**4**·3I<sup>-</sup>)* White needle crystal was obtained after recrystallization from methanol in 85% yield (0.67 g), m. p. 294 °C (dec.);  $^1H$  NMR ( $DMSO-d_6$ )  $\delta$ : 2.30 (s, 9H, Ar $CH_3$ ), 3.82 (s, 9H, Im $CH_3$ ), 5.53 (s, 6H,  $CH_2$ ), 7.64 (s, 3H, 4(5)-ImH), 7.74 (s, 3H, 5(4)-ImH), 8.82 (s, 3H, 2-ImH); IR (KBr)  $\nu$ : 3095 (s), 3032 (s), 1618 (w), 1573 (s), 1484 (w), 1454 (w), 1331, 1159 (vs), 829 (w), 748, 617 (s)  $cm^{-1}$ ; ESI-MS  $m/z$  (%): 659 ( $M^+ - I$ , 20), 577 ( $M^+ - I - Im - CH_3$ , 46), 495 ( $M^+ - I - 2Im - CH_3$ , 100); Anal. calcd for  $C_{24}H_{33}N_6I_3$ : C 36.66, H 4.23, N 10.69; found C 36.63, H 4.26, N 10.57.

*1,3,5-Trimethyl-2,4,6-tris [*N*-(*N'*-*n*-dodecyl)imidazoliummethyl]benzene tribromide salt (**5**·3Br<sup>-</sup>)*

White needle crystal was obtained by column chromatography using methanol as the eluent followed recrystallization from ethanol-ethyl acetate in 47% yield (0.54 g);  $^1H$  NMR ( $D_2O$ )  $\delta$ : 0.82–0.85 (m, 9H,  $CH_3$ ), 1.22

(s, 54H, CH<sub>2</sub>), 1.75 (s, 6H, ImCH<sub>2</sub>CH<sub>2</sub>), 2.24 (s, 9H, CH<sub>3</sub>), 4.22 (s, 6H, ImCH<sub>2</sub>), 5.54 (s, 6H, ArCH<sub>2</sub>), 7.80 (s, 3H, 4(5)-ImH), 7.86 (s, 3H, 5(4)-ImH), 9.37 (s, 3H, 2-ImH); ESI-MS *m/z* (%): 1027 (M<sup>+</sup> - Br, 82), 791 (M<sup>+</sup> - Br - C<sub>12</sub>H<sub>25</sub> - Im, 100); Anal. calcd for C<sub>57</sub>H<sub>99</sub>N<sub>6</sub>Br<sub>3</sub> · 2H<sub>2</sub>O: C 59.84, H 9.07, N 7.34; found C 59.85, H 9.15, N 7.36.

#### Procedure for the preparation of 6 · 2PF<sub>6</sub><sup>-</sup>

To a stirred solution of 1,3,5-Trimethyl-2,4,6-tris-(*N*-imidazolylmethyl)benzene (**1**) (6 mmol, 2.16 g) in 20 mL of acetonitrile at reflux, a solution of 2,6-bis-(bromomethyl)pyridine (0.5 mmol, 0.13 g) in 5 mL of acetonitrile was added dropwise in 2 h. The mixture was stirred for 1 h at reflux, then the solvent was evaporated. The crude product was purified by column chromatography on silicon gel using MeOH : NH<sub>3</sub> · H<sub>2</sub>O : saturated aqueous NH<sub>4</sub>HCO<sub>3</sub> (10:4:1, V/V/V) as the eluant. The eluant was concentrated to dryness and water was added, filtered off and the saturated aqueous NH<sub>4</sub>PF<sub>6</sub> solution was added to the filtrate. The precipitate was collected and washed several times with water to give the pure product.

2,6-Bis { *N*-[ *N'*-2,4,6-trimethyl-3,5-bis (*N*-imidazolylmethyl)phenylmethyl]imidazoliummethyl } pyridine bis (hexafluorophosphate) salt (6 · 2PF<sub>6</sub><sup>-</sup>) White powder was obtained in 50% yield (0.28 g), m. p. 218—220 °C; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ: 2.85 (d, 18H, CH<sub>3</sub>), 5.40 (s, 8H, CH<sub>2</sub>), 5.44 (s, 4H, CH<sub>2</sub>), 5.56 (s, 4H, CH<sub>2</sub>), 7.21 (s, 8H, 4,5-ImH), 7.30 (d, *J* = 7.6 Hz, 2H, 3,5-PyH), 7.68 (d, *J* = 1.7 Hz, 4H, 4,5-Im<sup>+</sup>H), 7.92 (t, 1H, 4-PyH), 8.08 (s, 4H, 2-ImH), 9.06 (s, 2H, 2-Im<sup>+</sup>H); IR (KBr) ν: 3166 (s), 1572, 1448, 1229, 1153 (s), 1090 (s), 637 (vs), 742, 558 (s) cm<sup>-1</sup>; FAB-MS *m/z* (%): 1116 (M<sup>+</sup> + 1, 6), 970 (M<sup>+</sup> - PF<sub>6</sub> + 1, 18), 824 (M<sup>+</sup> - 2PF<sub>6</sub> - 1, 1); Anal. calcd for C<sub>49</sub>H<sub>55</sub>N<sub>13</sub>P<sub>2</sub>F<sub>12</sub>: C 52.74, H 4.97, N 16.32; found C 52.29, H 4.81, N 16.46.

#### UV Spectral Measurements

The abilities of hosts 3 · *n*X<sup>-</sup> — 6 · *n*X<sup>-</sup> to bind to anions were investigated using UV spectroscopic titration method. In the UV spectral titration experiments, the cells were kept at constant temperature (298.2 ± 0.1 K)

with thermostated cell compartment. The same concentrations of guest solutions were added to the sample and reference cells, differential absorption spectra were obtained directly using the instrument. The effect of the slight volume changes on the absorption values was corrected before the regression analyses.

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