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ORIGINAL ARTICLE

Anion receptor interacting with anions through hydrogen bonds and charge transfer complex

Young-Hee Kim · Sol Rhim · Jin Joo Park · Jongmin Kang

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Abstract We have designed and synthesized a new anion receptor $\mathbf{3}^{2+}$ interacting with anions through hydrogen bonds and charge transfer complex depending on concentration and basicity of anion. Therefore, anions with weak basicity such as chloride, bromide and hydrogen sulfate bound to the receptors $\mathbf{3}^{2+}$ mainly through hydrogen bonds at low concentration of anions, although charge transfer complexes were observed with large excess of these anions. Anions with strong basicity such as fluoride, acetate, benzoate and dihydrogen phosphate bound to the receptors $\mathbf{3}^{2+}$ primarily through charge transfer interactions at UV–Vis titration condition (20 μM). However, in more concentrated ^{1}H NMR titration condition (2 mM) with these anions, $\mathbf{3}^{2+}$ decomposed to unknown compound. As charge transfer complexes showed colorimetric response, they turned out to be efficient naked eye detector for anions with strong basicity such as fluoride, acetate, benzoate and dihydrogen phosphate.

Keywords Anion receptor · Charge transfer complex · Hydrogen bond · Viologen

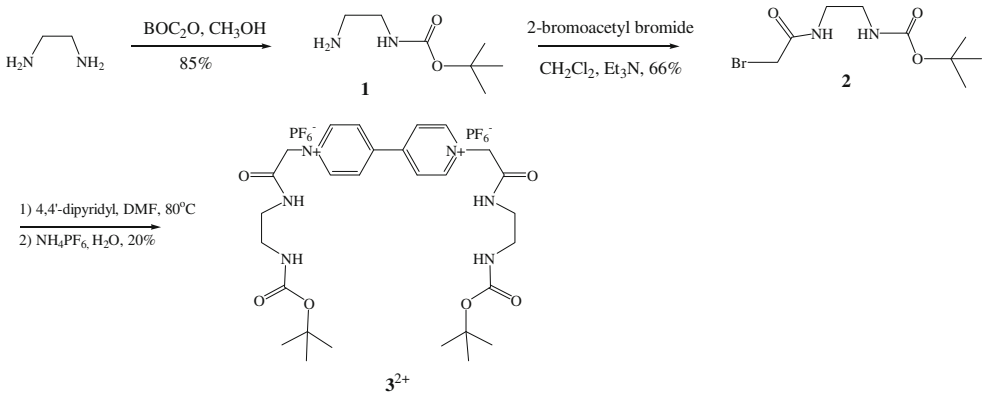
The rational design and synthesis of anion receptors have received considerable attention because anions play a major role in biological, medical, environmental, and chemical sciences [1–12]. As anions display wide range of geometries, design and synthesis of artificial receptors that exhibit high binding affinity and selectivity to a targeted anion still remain a great challenge. A wide range of artificial anion receptors have been designed to improve anion selectivities and signaling processes. Among various non-covalent interactions between anion receptor and anion, hydrogen-bonding interactions are particularly useful and effective. Receptors bearing multiple hydrogen bonding moieties have been shown to be useful to promote cooperative binding, which would result in enhanced binding affinity [13–15].

Many chemical sensors follow the approach of the covalent attachment of signaling subunits and binding sites [16, 17]. Chromogenic or fluorogenic groups that are covalently linked to the receptor moiety as signaling subunits and multiple hydrogen-bonding interactions as binding sites have been frequently utilized. Among chromogenic groups, viologens have attracted considerable interest as they can acts as both a binding and reporter group. Only a few examples have been reported utilizing a viologen moiety as a key signaling element in artificial molecular receptor despite its potential applications [18–21].

As a part of our efforts to develop more efficient anion receptors, we have designed the receptor $\mathbf{3}^{2+}$. This receptor utilized viologen as a chromogenic signaling site and amide and carbamate moiety as binding sites. The receptor $\mathbf{3}^{2+}$ has two amide groups and two carbamate groups at the end of viologen moiety. Our intention was to use viologen as a molecular scaffold to arrange hydrogen binding sites. In addition, viologen can act as a binding group as well as a reporter group. This viologen based receptor may interact with anions through hydrogen bonding, ion pairing, van der Waals interactions and ion pair charge transfer (IPCT) processes.

The synthesis of the receptor $\mathbf{3}^{2+}$ started from the reaction of ethylenediamine with di-tert-butyl dicarbonate

Y.-H. Kim · S. Rhim · J. J. Park · J. Kang (✉)
Department of Chemistry, Institute for Chemical Biology, Sejong University, Seoul 143-747, Korea
e-mail: kangjm@sejong.ac.kr



Scheme 1 The synthetic procedure for the anion receptor $\mathbf{3}^{2+}$

to give the compound **1** in 85% yields. Then the reaction of the compound **1** with 2-bromoacetyl bromide in the presence of triethylamine gave the compound **2** in 66% yields. Reaction between the compound **2** and 4,4′-dipyridyl and subsequent anion exchange reaction with ammonium hexafluorophosphate gave the receptor $\mathbf{3}^{2+}$ in 20% yields (Scheme 1).[1]

The anion binding properties of compound $\mathbf{3}^{2+}$ were investigated using UV–vis and ^{1}H NMR spectroscopy in DMSO. The receptor $\mathbf{3}^{2+}$ displayed strong absorption bands at 273 nm in DMSO. Figure 1a shows the family of spectra obtained over the course of the titration of solutions $\mathbf{3}^{2+}$ with tetrabutylammonium chloride in DMSO. Until 150 equivalents of chloride ions were added to the 20 μM solutions of $\mathbf{3}^{2+}$, λ_{max} of $\mathbf{3}^{2+}$ is moved to the longer wavelength slightly and spectra showed the clear isosbestic point at 310 nm. The presence of the sharp isosbestic point indicates that only two species were present at equilibrium over the course of the titration experiment. This result suggests that a typical hydrogen bonding complex forms between the receptor and the anion.

The formation of hydrogen bonding complex could be confirmed by a ^{1}H NMR titration. For example, in DMSO-d_6, amide N–H hydrogen and carbamate N–H hydrogen of receptor $\mathbf{3}^{2+}$ appeared at 8.70 and 6.87 ppm respectively. With addition of tetrabutylammonium chloride, amide N–H peak appearing at 8.70 ppm moved downfield until 9.10 ppm while carbamate N–H peak appearing at 6.87 ppm moved slightly until 6.95 ppm throughout titration. (Fig. 2) This result suggests that the receptor $\mathbf{3}^{2+}$ interacts with chloride through hydrogen bonds with mainly two amide hydrogens. Other two carbamate hydrogens participate in binding event only slightly. In addition, aromatic peaks appearing at 9.23 and 8.80 ppm moved downfield 9.34 and 8.87 ppm respectively, which suggest participation of aromatic hydrogens in the binding event. Participation of *o*-pyridyl CH groups of pyridinum in the viologen system is well known [22–24].

The stoichiometry between the receptor $\mathbf{3}^{2+}$ and chloride was determined by Job plot using UV–Vis spectroscopy, which showed evident 1:1 stoichiometry (Fig. 3). To calculate association constant, a Benesi-Hildebrand plot [25] by use of change at 273 nm was used in the case of UV titration. In the case of ^{1}H NMR, amide hydrogen shifting downfield was analyzed using EQNMR [26]. The association constant calculated was 6.1×10^2 from UV titration and 5.8×10^2 from ^{1}H NMR titration.

[1] Synthesis of compound **1**: To a solution of di-tert-butyl dicarbonate (1.6 g, 7.49 mmol) in methanol (5 ml) was added ethylenediamine (500 mg, 8.3 mmol) at 0 °C. The solution was stirred for an hour and the solution temperature was raised to room temperature slowly. After the solution was stirred for 4 h more, the precipitated solid was removed through filtration. Evaporation of the liquid layer and silicagel chromatography of the residue with 50% methanol in dichloromethane gave the compound **1** (1.54 g) in 88% yields. ^{1}H NMR ($CDCl_3$, 500 MHz): 5.37(s, 1H), 3.26(s, 2H), 3.03(m, 2H), 2.64 (t, $J = 6.0$, 2H), 1.30 (s, 9H)

Synthesis of compound **2**: To a solution of compound **1** (1,300 mg, 8.11 mmol) and triethylamine(1130 μl) in dichloromethane (35 ml) under nitrogen was added bromoacetyl bromide (730 μl) in dichloromethane(15 ml) at 0 °C. The solution was stirred for an hour and the solution temperature was raised to room temperature slowly. Evaporation of the liquid layer and silicagel chromatography of the residue (Hexane: Ethyl acetate = 1 : 1) gave the compound **2** (1520 mg) in 66% yields. ^{1}H NMR (DMSO-d_6, 500 MHz): 8.25(t, $J = 5.0$, 1H), 6.79 (t, $J = 5.0$,1H), 3.81 (s, 2H), 3.07 (q, $J = 6.0$, 2H), 2.96 (q, 2H, $J = 6.0$), 1.35 (s, 9H) ^{13}C NMR (DMSO-d_6, 500 MHz) 166.11, 155.64, 77.71, 29.50, 28.22, two peaks are hidden under DMSO solvent peak.

Synthesis of compound $\mathbf{3}^{2+}$: To a solution of 4,4′-dipyridyl (300 mg, 1.92 mmol) in DMF (20 ml) was added compound **2** (1,080 mg, 3.84 mmol) and refluxed overnight. The precipitated solid was filtered and washed with ether several times. Then the solid was dissolved in 30 ml water. As soon as 10 ml of 1 M NH_4PF_6 was added to the solution, the receptor $\mathbf{3}^{2+}$ was precipitated. After filtration, the solid was recrystalized with CH_3CN and dichloromethane. Filtration and drying the solid gave 320 mg (19%) of the receptor $\mathbf{3}^{2+}$. ^{1}H NMR (DMSO-d_6, 500 MHz): 9.23(d, $J = 6.5$, 4H), 8.80(d, $J = 6.5$, 4H), 8.69 (t, $J = 6.0$, 2H), 6.87 (t, $J = 6.0$, 2H), 5.49 (s, 4H), 3.19 (q, $J = 6.0$, 4H), 3.07(q, $J = 6.0$, 4H), 1.39(s, 18H) ^{13}C NMR (CD_3CN-d_3, 500 MHz) 164.64, 157.41, 151.65, 148.00, 127.74, 79.64, 63.21, 41.28, 40.30, 28.67.

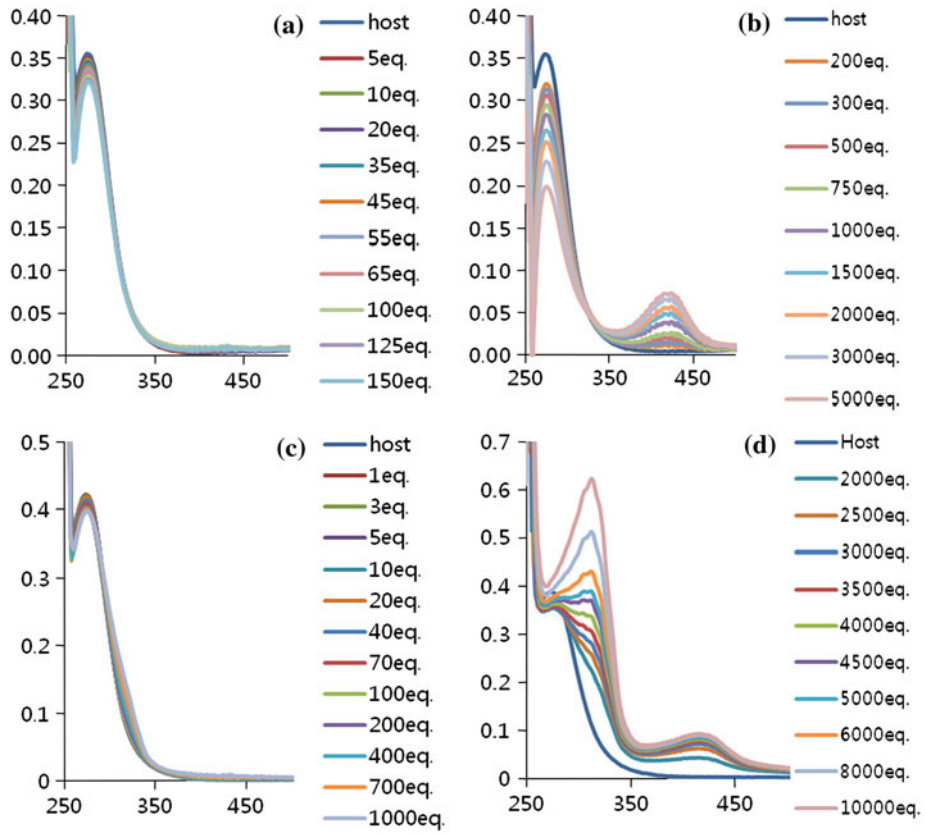


Fig. 1 Family of spectra recorded over the course of titration of 20 μM DMSO solutions of the receptors $\mathbf{3}^{2+}$ with 1–150 equivalents (**a**) 200–5,000 equivalents (**b**) tetrabutylammonium chloride solution and with 1–1,000 equivalents (**c**) 2,000–10,000 equivalents (**d**) tetrabutylammonium nitrate solution

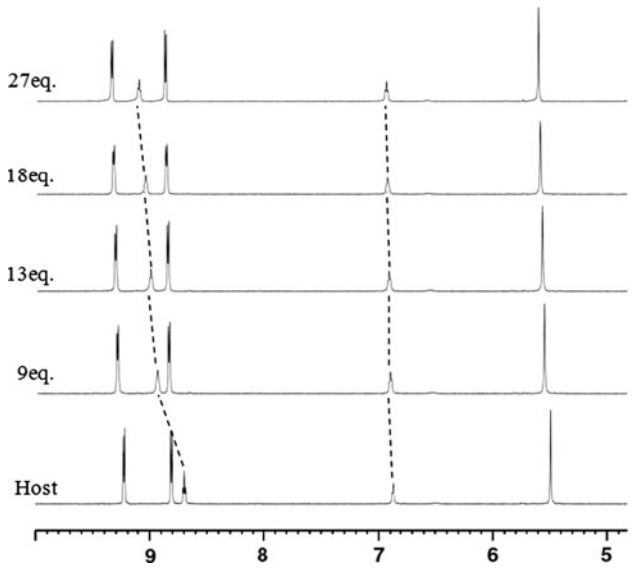


Fig. 2 ^{1}H NMR spectra of 2 mM of $\mathbf{3}^{2+}$ with increased amounts of tetrabutylammonium chloride (0–27 eq.) in DMSO-d_6

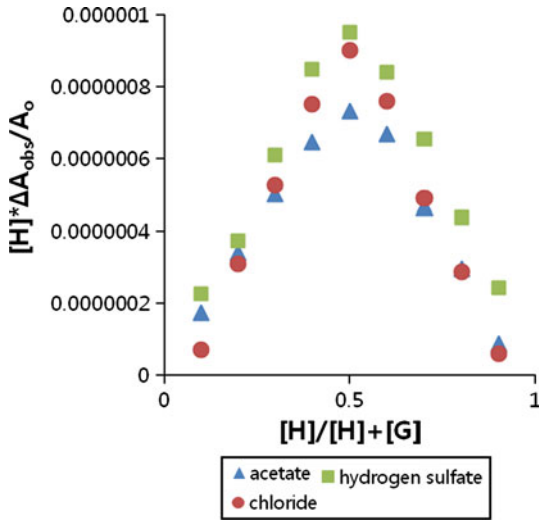


Fig. 3 The Job plots of $\mathbf{3}^{2+}$ with tetrabutylammonium chloride, tetrabutylammonium acetate and tetrabutylammonium hydrogensulfate using UV–Vis spectroscopy

When an excess of chloride ion was added, a new intense absorption band developed at 421 nm and the color of solution turned into yellow. (Fig. 1b) This absorption band is attributed to the anion-viologen charge transfer, which is well known [27–35]. Since the spectra showed the clear isosbestic points at 320 nm, we calculated association constant for the charge transfer complex using Benesi-Hildebrand plot. The association constant of yellow complex was calculated as 2.7 × 10. Similar behavior was observed with nitrate. Typical hydrogen bonding complex was observed until 1,000 equivalents of nitrate ions were added to the 20 μM solutions of $\mathbf{3}^{2+}$ (Fig. 1c). As

expected, charge transfer complex was observed with excess equivalents of nitrate ions (Fig. 1d). The association constants for the hydrogen bond complex and charge transfer complex were calculated as 5.9×10^2 and 2.3×10 respectively.

However, the addition of bromide or iodide did not induce any significant changes in the ^{1}H NMR spectrum of $\mathbf{3}^{2+}$. In UV titration of bromide and iodide, only anion-viologen charge transfer band was observed with an excess of bromide or iodide (Fig. 4). Therefore, bromide and iodide interact with the receptor $\mathbf{3}^{2+}$ only through charge transfer interactions with an excess of these anions. The association constants for the charge transfer complex for bromide and iodide were calculated as 1.3×10^2 and 4.5×10^2 respectively, which is in accordance with literature [28].

Fluoride, acetate, benzoate and dihydrogenphosphate showed different behaviors when compared with chloride, bromide, iodide and nitrate. For example, when fluoride was added to the 20 μM solutions of $\mathbf{3}^{2+}$, the color of

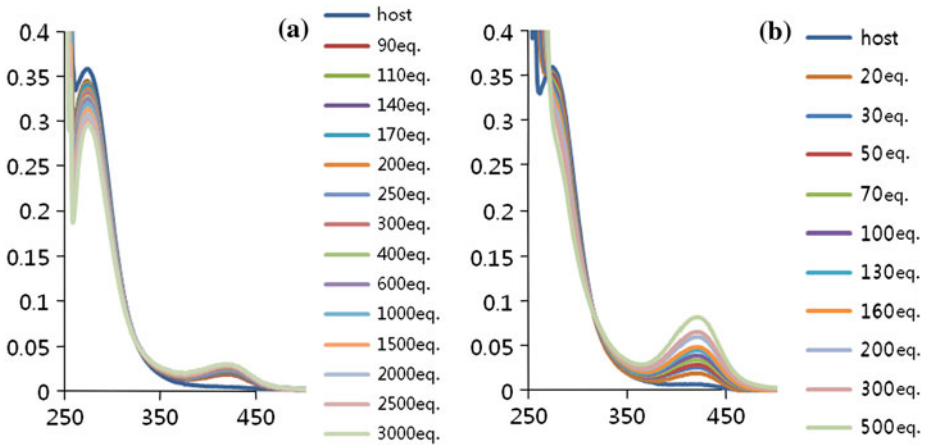


Fig. 4 Family of spectra recorded over the course of titration of 20 μM DMSO solutions of the receptors $\mathbf{3}^{2+}$ with the standard solution tetrabutylammonium bromide (**a**) and iodide (**b**)

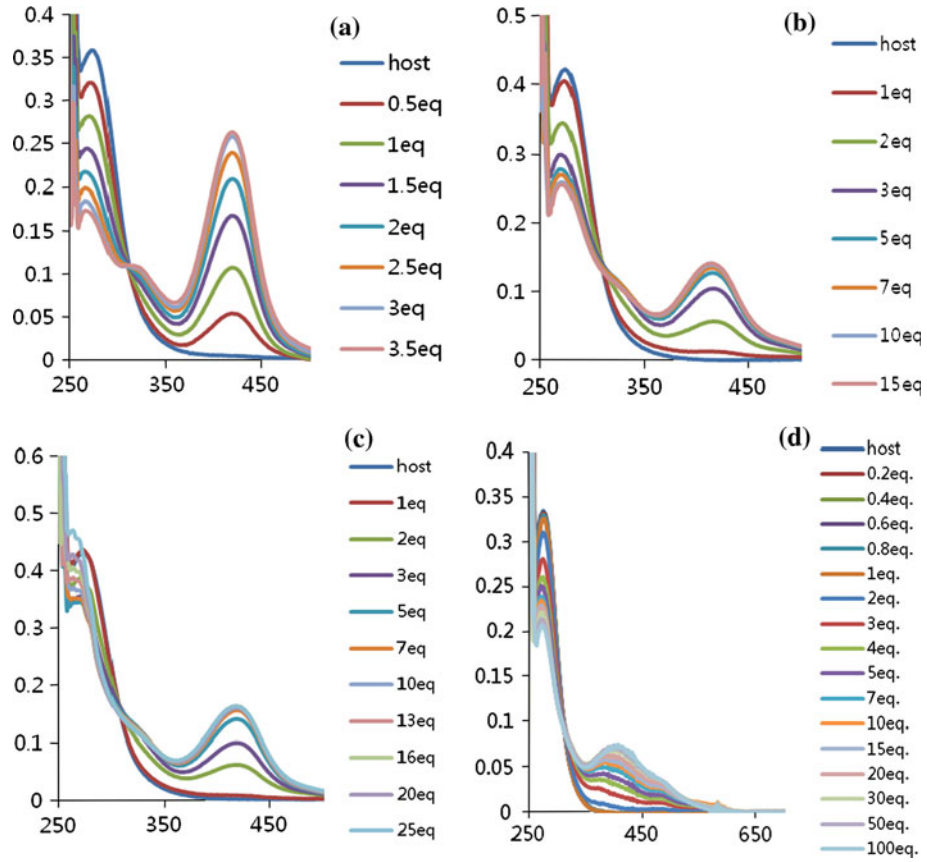


Fig. 5 Family of spectra recorded over the course of titration of 20 μM DMSO solutions of the receptors $\mathbf{3}^{2+}$ with the standard solution tetrabutylammonium fluoride (**a**), acetate (**b**) benzoate (**c**) and dihydrogen phosphate (**d**)

solution turned into purple immediately and in a few minute the purple color turned into yellow. As the color change from purple to yellow is too fast, we only recorded solution of yellow complex in UV spectrum. Therefore, only the change of λ_{max} from 273 to 421 nm was recorded (Fig. 5a). The purple complex is attributed to IPCT complex ($\mathbf{3}^{+}$) in which viologen moiety has been reduced [36, 37]. As the viologen moiety of this complex is air sensitive, it is instantly oxidized to IPCT complex ($\mathbf{3}^{2+}$) with absorption band at 421 nm. This band was assigned to the anion-viologen charge transfer.

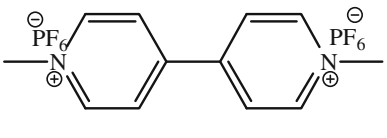
Since the spectra showed the clear isosbestic points at 308 nm, we assumed only two species were present at equilibrium and calculated association constant for the charge transfer complex using Benesi-Hildebrand plot. The association constant of yellow complex was calculated as 1.9×10^4. Almost same phenomenon was observed with the addition of acetate, benzoate, dihydrogen phosphate to the solution of $\mathbf{3}^{2+}$ (Fig. 5b–d). These anions also formed instant purple complex ($\mathbf{3}^{+}$), which also oxidized yellow complex ($\mathbf{3}^{2+}$) in a moment. While IPCT complex of acetate and benzoate with $\mathbf{3}^{2+}$ showed absorption band at 421 nm again, IPCT complex of dihydrogen phosphate with $\mathbf{3}^{2+}$ showed absorption band at 407 nm (Fig. 5d). The association constants of these anions are summarized in Table 1.

However, in ^{1}H NMR titration with fluoride, acetate, benzoate and dihydrogen phosphate new peaks began to show up upon addition of these anions, which was the evidence of decomposition. The cause of the decomposition is not clear [38]. Among the anions investigated only hydrogen sulfate did not show any evidences of charge transfer complex and only showed hydrogen bonding complex.

For comparison, we prepared methyl viologen $\mathbf{4}^{2+}$, which did not have any hydrogen bonding site. When it was titrated with fluoride or acetate in DMSO, similar phenomena were observed. For example, the color of

Table 1 The association constants (M^{-1}) of the receptors $\mathbf{3}^{2+}$ with various anions in DMSO

	K_a for hydrogen bond complex		K_a for CT complex
	UV	^{1}H NMR	UV
Cl^-	$6.1 \times 10^2 \pm 4.0 \times 10$	$5.8 \times 10^2 \pm 3.5 \times 10$	$2.7 \times 10 \pm 2.2$
Br	–	–	$1.3 \times 10^2 \pm 8.8$
I^-	–	–	$4.5 \times 10^2 \pm 2.5 \times 10$
NO_3^-	$5.9 \times 10^2 \pm 4.3 \times 10$	$8.3 \times 10^2 \pm 5.1 \times 10$	$2.3 \times 10 \pm 1.2$
HSO_4^-	$1.1 \times 10 \pm 6.8 \times 10^{-1}$	$1.5 \times 10 \pm 4.8 \times 10^{-1}$	–
F^-	–	–	$1.9 \times 10^4 \pm 1.0 \times 10^3$
$CH_3CO_2^-$	–	–	$9.8 \times 10^4 \pm 6.5 \times 10^3$
$C_6H_5CO_2^-$	–	–	$1.8 \times 10^4 \pm 1.0 \times 10^3$
$H_2PO_4^-$	–	–	$9.2 \times 10^3 \pm 6.0 \times 10^2$



$\mathbf{4}^{2+}$

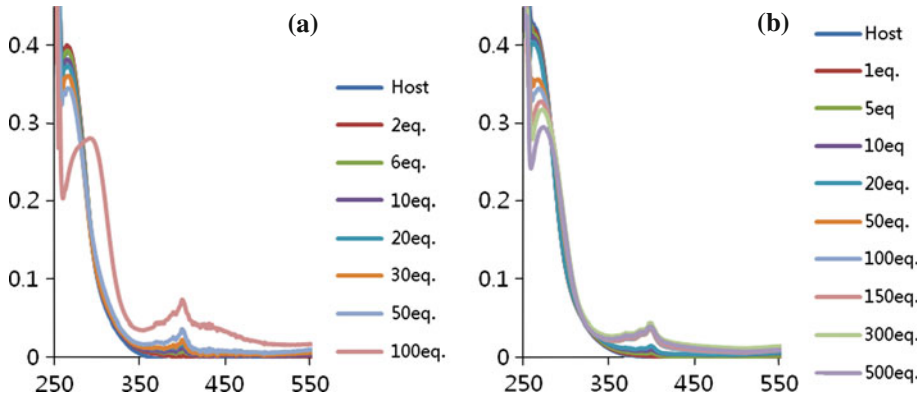


Fig. 6 Family of spectra recorded over the course of titration of 20 μM DMSO solutions of $\mathbf{4}^{2+}$ with the standard solution tetrabutylammonium fluoride (**a**) acetate (**b**)

solution turned into purple immediately and in a few minute the purple color turned into yellow. The charge transfer band was observed at 391 nm irrespective of anions (Fig. 6). However, association constants of $\mathbf{4}^{2+}$ for fluoride and acetate were much smaller than those of $\mathbf{3}^{2+}$ for the same anions. The association constants of $\mathbf{4}^{2+}$ for fluoride and acetate were calculated as 5.3×10^3 and 1.2×10^3 respectively.

In summary, the new anion receptors $\mathbf{3}^{2+}$ interacts with anions through hydrogen bonds and charge transfer complex depending concentration and basicity of anion. Anions with weak basicity such as chloride, bromide, iodide, nitrate interact with receptor $\mathbf{3}^{2+}$ mainly through hydrogen bonds while they formed IPCT complexes with $\mathbf{3}^{2+}$ when large excess of these anions were added. Only hydrogen sulfate formed hydrogen bonded complex irrespective of its concentration. However, anions with strong basicity such as fluoride, acetate, benzoate, and dihydrogen phosphate interact with receptor $\mathbf{3}^{2+}$ only through charge transfer interactions at UV–Vis titration condition (20 μM). In more concentrated ^{1}H NMR titration condition (2 mM), $\mathbf{3}^{2+}$ decomposed to unknown compound. As charge transfer complexes showed colorimetric response, they turned out to be efficient naked eye detector for anions with strong basicity such as fluoride, acetate, benzoate and dihydrogen phosphate.

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