Synthesis and characterization of indolocarbazole-quinoxalines with flat rigid structure for sensing fluoride and acetate anions†

Ting Wang, Yu Bai, Liang Ma and Xiu-Ping Yan*

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A new series of indolocarbazole-quinoxalines (ICQ, receptors **6** and **7**) are prepared and characterized for effective fluoride and acetate anion sensing. The new indole-based system has a highly flat rigid structure with a large π system, and exhibits high binding affinity and sensitivity for acetate and fluoride anions. Receptors **6** and **7** give abundant and unique spectral features in dimethyl sulfoxide (DMSO). Both fluoride and acetate anions cause a bathochromic shift of the absorption peaks of receptor **7** in DMSO, whereas only fluoride anion results in a remarkable shift of the absorption peak of receptor **6** in DMSO. Receptors **6** and **7** can also operate as efficient colorimetric sensors for naked-eye detection of fluoride and acetate anions, and their combined use also offers a simple way for distinguishing these two anions by the naked-eye. The analysis of a Job's plot for the binding of receptor **7** and F^-, single crystal structures of **7**·TBACl and **7**·$TBACH_3COO$ confirm 1 : 1 binding stoichiometry. Notably, the ICQ system offers novel and excellent receptors for acetate anion both in solution and in crystalline solid through the formation of two hydrogen bonds.

Introduction

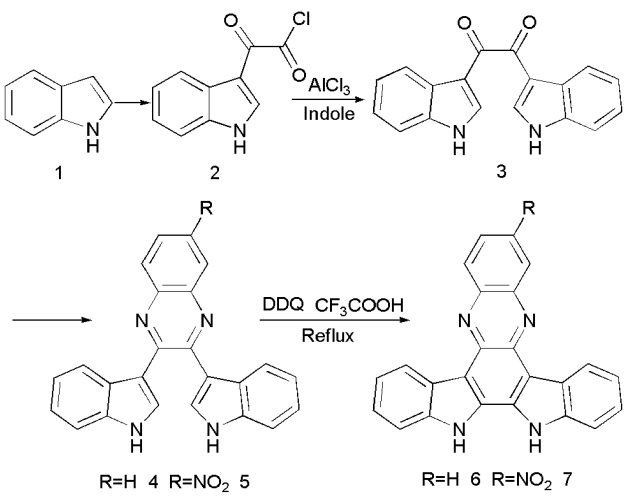
Anions play a fundamental and important role in a wide range of chemical, biological, medical and environmental processes. Increasing efforts have been made to employ a variety of motifs to design efficient anion sensors, including those based on amide, phenol, urea and pyrrole units.[1,2] As an example, the urea, thiourea and guanidinium motifs have been demonstrated to be good hydrogen bond donors and excellent receptors for carboxylates such as the acetate anion, a particularly common and important functional group in biological and synthetic organic molecules, and have attracted immense attention.[3] The rational design of efficient receptors for the Y-shaped acetate anion using other novel motifs compared with those motifs used widely is relatively difficult.

Recently, several groups[4–10] have prepared a few indole-based receptors such as indolocarbazoles and diindolylquinoxalines (DIQ, receptors **4** and **5**) as potential hydrogen bond donors for anions, and demonstrated their promising prospects for binding anions. However, to the best of our knowledge, few indole-based receptors for the acetate anion, especially structurally characterized receptor–acetate complexes with rational designs, have been reported so far.

Herein, we report a new series of indolocarbazole-quinoxalines (ICQ, receptors **6** and **7**) for effective acetate and fluoride anion sensing. The new indole-based system prepared has a highly flat rigid structure with a large π system, and exhibits high binding affinity and sensitivity for acetate and fluoride anions. Receptors **6** and **7** can operate as efficient colorimetric sensors for naked-eye detection of acetate and fluoride anions, and their combined use also offers a simple way for distinguishing these two anions by the naked-eye. Notably, the ICQ system offers novel and excellent receptors for acetate anions both in solution and in crystalline solid through the formation of two hydrogen bonds.

Results and discussion

Receptors **6** and **7** relying on an α,α′-connection of two indole motifs of DIQ were synthesized according to Scheme 1. 2,3-Diindol-3′-yl diketone (**3**) was prepared from indole (**1**) and 2-(3-indolyl)-2-oxoacetyl chloride (**2**) in a mixture of dichloroethane and heptane in the presence of $AlCl_3$ but without the need for an indole Grignard agent.[11] The synthesis of DIQ (**4** and **5**) was adapted from previously reported procedures.[7,12] Intramolecular crossed-dimerization of the two indole motifs was achieved



Scheme 1 Synthesis of receptors **6** and **7**.

Research Center for Analytical Sciences, College of Chemistry, Nankai University, 94 Weijin Road, Tianjin, 300071, China. E-mail: xpyan@nankai.edu.cn; Fax: (+86)22-23506075

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through acid-promoted dimerization.[13] With the aid of dichlorodicyanoquinone (DDQ), DIQ in boiling trifluoroacetic acid turned into final receptors **6** and **7** in quantitative yields. The product was recrystallized for further investigation.

Receptors **6** and **7** give five UV–vis absorption peaks with a big molar absorption coefficient in dimethyl sulfoxide (DMSO) (Fig. 1 and 2). The UV–vis absorption titration shows the spectral change of receptors **6** and **7** upon addition of anions. Addition of CH_3COO^- and F^- to receptor **7** in DMSO caused a bathochromic shift of the absorption peaks from 372 nm to 390 nm ($\Delta\lambda_{max}$ = 18 nm) for acetate anion, to 404 nm ($\Delta\lambda_{max}$ = 32 nm) for fluoride anion and from 451 nm to 560 nm ($\Delta\lambda_{max}$ = 109 nm) for both anions (Fig. 1). Notably, complex formation can be visually perceived through a distinct color change from bright yellow to gray. However, only F^- resulted in a remarkable decrease of the absorption peak at 420 nm and a new absorption peak at 460 nm for receptor **6** in DMSO, and also a clear color change from yellow to orange. Interestingly, addition of CH_3COO^- and F^- to receptor **6** in a less polar solvent, acetonitrile, slightly changed the absorption peaks ($\Delta\lambda_{max}$ = 7 nm) (Fig. 2). The corresponding color change is difficult to discriminate by the naked eye. The phenomena are attributed to a solvent effect which plays a crucial role in controlling anion binding strength and selectivity.[1b] The color changes of receptors **6** and **7** upon addition of various anions indicate that the combined use of these receptors can provide an easy way to distinguish acetate and fluoride anions by the naked eye on the basis of the different color changes of receptors **6** and **7** (Fig. 3).

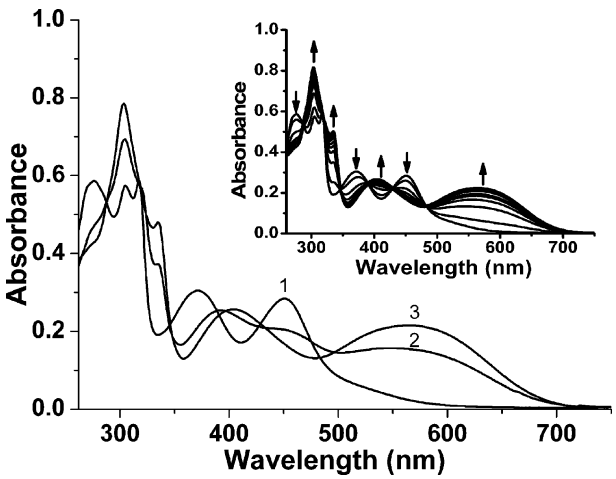


Fig. 1 UV–vis spectral changes of receptor **7** (1.5×10^{-5} M) observed upon addition of fluoride anion (10 equiv.). (Inset) The titration with F^- in DMSO (0 to 28 equiv.). 1: Receptor **7** in DMSO. 2: Receptor **7** + 10 equiv. CH_3COO^- in DMSO. 3: Receptor **7** + 10 equiv. F^- in DMSO.

In contrast, receptors **4** and **5** give less UV–vis absorption peaks with a smaller molar absorption coefficient in DMSO. Addition of fluoride and acetate anions to receptors **4** and **5** in DMSO did not cause significant changes of their spectra and color (Figure S1, Supporting Information). However, fluoride and acetate anions resulted in remarkable spectral and color changes of receptors **6** and **7** in DMSO as these receptors possess a large π system of the flat rigid structure and offer high binding affinity for the anions in DMSO. The above results show significant differences in binding and optical properties between receptors **4** & **5** and receptors **6**

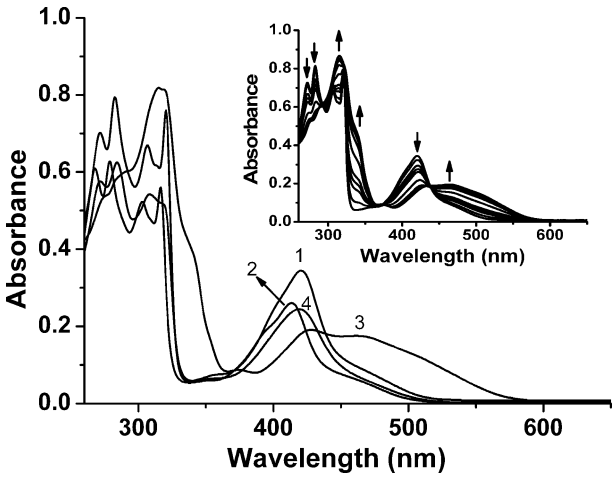


Fig. 2 UV–vis spectral changes of receptor **6** (1.5×10^{-5} M) observed upon addition of fluoride and acetate anions (10 equiv.). (Inset) The titration with F^- in DMSO (0 to 28 equiv.). 1: Receptor **6** in DMSO. 2: Receptor **6** in acetonitrile. 3: Receptor **6** + 10 equiv. F^- in DMSO. 4: Receptor **6** + 10 equiv. F^- in acetonitrile.

Fig. 3 Color changes of receptors **6** and **7** upon addition of anions. [**6**] = [**7**] = 3×10^{-5} M in DMSO; **6** + 10 equiv. anion (top), **7** + 5 equiv. anion (bottom). From left to right: none, F^-, Cl^-, Br^-, I^-, HSO_4^-, $H_2PO_4^-$, NO_3^-, CH_3COO^-.

& **7** although only slight structural modification was made from receptors **4** and **5** to receptors **6** and **7** through the α,α′-connecting of two indole motifs in receptors **4** and **5**.

Association constants determined from the UV–vis absorption titration or fluorescence titration are summarized in Table 1. The titration curves with F^-, Cl^- and $H_2PO_4^-$ (Figures S2 and

Table 1 Association constants (K_a/M^{-1})of some indole-based receptors with various anions at room temperature

	4[a]	**5**[a]	**6**[b]	**7**[b]
F^-	2100	—	15531	152535
Cl^-	170	470	514	821
Br^-	—	—	<100[c]	<100[c]
I^-	—	—	<100[c]	<100[c]
$H_2PO_4^-$	6800	20000	9933	78845
HSO_4^-	80	250	<100[c]	<100[c]
NO_3^-	—	—	<100[c]	<100[c]
CH_3COO^-	—	—	20602[d]	24452[d]

[a] Values from Ref. 7 and determined in dichloromethane. [b] Determined by UV–vis spectroscopic titration in DMSO with errors ranging from 3% (**6** + CH_3COO^-) to 14% (**7** + F^-). Anions were used in the form of their tetrabutylammonium (TBA) salts. [c] Estimated, clear binding profiles were not observed. [d] Determined by the fluorescence titration.

S3, Supporting Information) reveal several isosbestic points as expected for a 1 : 1 binding stoichiometry. A Job's plot for the binding of receptor **7** with F^- (Figure S4, Supporting Information) and the single crystal X-ray diffraction analysis of the complex formed between receptor **7** and TBACl (Fig. 4)[14] confirm their 1 : 1 binding stoichiometry. In the single crystal structure of the **7**·TBACl complex the chloride anion is located between the middle of two indole NH groups in the same plane and stabilized by two hydrogen bonds with N–H $\cdots$ Cl distances of 2.262 Å and 2.307 Å, respectively. Furthermore, the planes of the receptor molecule are partly overlapped as consequence of π–π interactions with a distance of 3.41 Å.

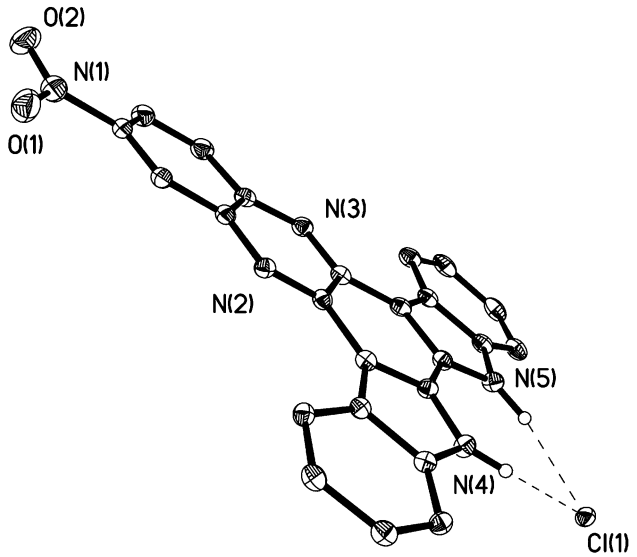


Fig. 4 Single-crystal X-ray diffraction structure of **7**·TBACl. Thermal ellipsoids are scaled to the 30% probability level. The TBA counter-ions and most hydrogen atoms have been omitted for clarity. Dashed lines indicate the hydrogen-bond interactions.

A further insight into Table 1 reveals that the highest affinity of receptor **6** is displayed for CH_3COO^- and F^-, receptor **7** for F^-, followed by $H_2PO_4^- >> Cl^- > HSO_4^- \sim NO_3^-$. Due to the increase in the acidity of indole NHs caused by the electron withdrawing nitro group, nitro-bearing receptor **7** shows much higher binding affinity than receptor **6**. Compared with receptors **4** and **5** whose binding constants were determined in dichloromethane, receptors **6** and **7** give much higher binding affinity for the anions even in the more polar solvent DMSO. We ascribe such character to the flat rigid structure formed by the α,α′-connection of the two indole motifs. The larger π system (receptors **6** and **7** *cf.* receptors **4** and **5**) along with the electron withdrawing of the nitro group (receptor **7** *cf.* receptor **5**) increases the acidity of indole NHs, making receptors **6** and **7** bind electron-rich anions more favorably than receptors **4** and **5**. On the other hand, the rigid plane without any flexible bonds of receptors **6** and **7** gives a fixed cavity for binding anions without bond rotation.

However, receptors **4** and **5** based on β-connectivity linking the two indole motifs to the quinoxaline core provide a more open and less rigid cavity to favor binding the relatively large dihydrogen phosphate anion. Receptors **6** and **7**, further modified through the α,α′-connection of two indole motifs in receptors **4** and **5**, possess rigid structure and also offer considerable selectivity for special anions with suitable size, shape and basicity. For instance, receptor **7** shows high selectivity for fluoride anion ($K_a(F)/K_a(Cl) = 185$, $K_a(F)/K_a(HSO_4) > 1500$, $K_a(F)/K_a(NO_3) > 1500$).

The flat rigid structure with a large π system also gives the ability of ICQ to operate as a fluorescent sensor for anions. Significant quenching of emission with no change in the structure of the emission bands of receptor **6** was observed upon addition of CH_3COO^- (Fig. 5). A similar result was also observed for F^- and $H_2PO_4^-$. The quenching of emission by these anions indicates that the receptor–anion complexes participate in photoinduced electron transfer (PET) quenching phenomena.[3h] Significant fluorescence quenching also occurred upon addition of these anions to receptor **7**. A typical such change for CH_3COO^- is shown in Figure S6 (Supporting Information).

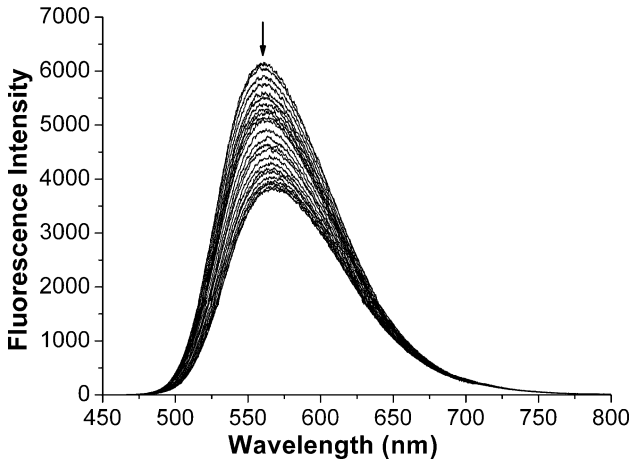


Fig. 5 Fluorescence quenching of receptor **6** (1.5×10^{-5} M) upon titration with CH_3COO^- in DMSO.

It is worth mentioning that the shape of the indole NH groups of the flat molecule is similar to that of urea and thiourea. Therefore, the ICQ system is a particularly excellent receptor for Y-shaped anions such as carboxylates through the formation of two hydrogen bonds for 1 : 1 binding stoichiometry like urea binding these anions.[3e] The proposed conformation (Scheme 2) is confirmed by single crystal X-ray diffraction analysis of the complex formed between receptor **7** and $TBACH_3COO$ (Fig. 6).[15] The N–H $\cdots$ O distances of the two hydrogen bonds between the O (acetate anion) and the NH (receptor **7**) (1.799 Å and 1.828 Å) are similar to those between the O (acetate anion) and the NH (urea) (1.797 Å and 1.852 Å).[3f] ^{1}H NMR titration in DMSO-d_6 shows that the addition of acetate anion resulted in a significant downfield shift and disappearance of the two split indole NHs as a result of the formation of two hydrogen bonds (Figure S7, Supporting Information).

Conclusions

We have successfully developed a novel series of indole-based receptors **6** and **7** that are particularly efficient for sensing acetate and fluoride anions. Combined use of receptors **6** and **7** on the basis of their color change upon addition of acetate and fluoride anions also offers a simple way for distinguishing these two anions by the naked-eye. This new ICQ system with a large π system gives

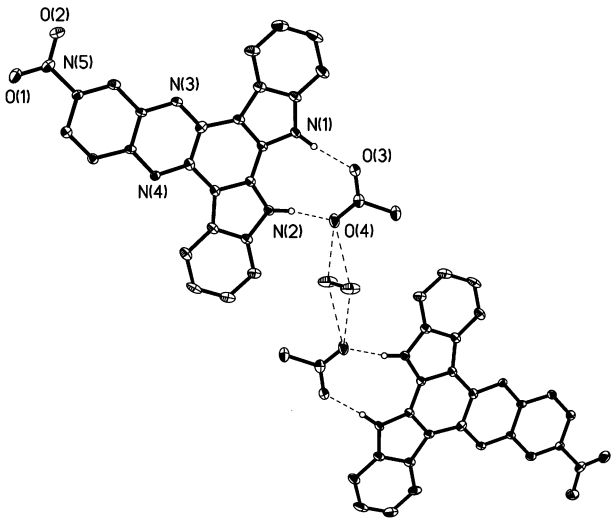
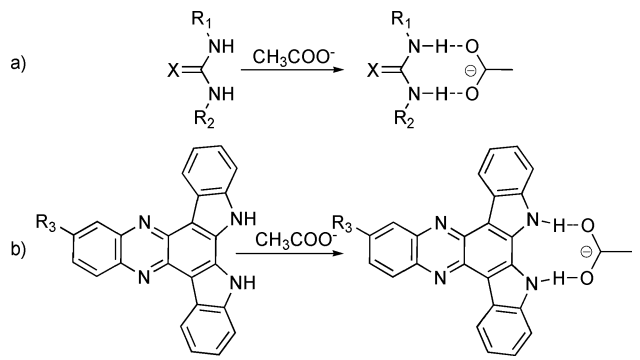


Fig. 6 Single-crystal X-ray diffraction structure of **7**·TBACH$_3$COO·CHCl$_3$·1/2H$_2$O. Thermal ellipsoids are scaled to the 30% probability level. The TBA counter-ions, most hydrogen atoms and solvent molecule (CHCl$_3$) have been omitted for clarity. Dashed lines indicate the hydrogen-bond interactions. The water molecule is disordered over two positions.



Scheme 2 a) The formation of two hydrogen bonds between acetate anion and the urea (X = O) or thiourea (X = S) receptor. R_1 and R_2 are functional groups. b) Proposed conformation of ICQ system (R_3 = H, receptor **6**; R_3 = NO_2, receptor **7**) Binding with acetate anion through the formation of two hydrogen bonds for 1 : 1 binding stoichiometry.

a unique spectral feature, being promising as the basis for new dyes or electron-donor–receptor materials.

Experimental

General

All reagents used were of at least analytical grade. All solvents were purified by standard procedures. Tetra-*n*-butylammonium fluoride trihydrate, tetra-*n*-butylammonium iodide, tetra-*n*-butylammonium nitrate, tetra-*n*-butylammonium hydrogen sulfate, tetra-*n*-butylammonium acetate, tetra-*n*-butylammonium dihydrogenphosphate were purchased from Alfa Aesar China (Tianjin) LTD, tetra-*n*-butylammonium chloride and tetra-*n*-butylammonium bromide were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China) and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian UNITY PLUS-400 and a Bruker Avance 300, respectively. High resolution mass spectra (HRMS) were determined on an IonSpec 7.0T FT-ICR mass spectrometer. UV–vis absorption spectra were measured with a Shimadzu UV-3600 UV-Vis spectrophotometer. Fluorescence spectra were recorded at room temperature on a Hitachi FL-4500 fluorescence spectrometer.

Synthesis of receptor 6

2,3-Di(1*H*-indol-3-yl)quinoxaline (**4**, 302 mg, 0.84 mmol) and dichlorodicyanoquinone (DDQ, 230 mg, 1.01 mmol) were dissolved in neat trifluoroacetic acid (30 mL) and the resultant solution was heated at reflux for 4 hours until the reaction was complete (TLC). The residual trifluoroacetic acid was then removed by vacuum distillation. The semi-solid was washed with brine, saturated aq. $NaHCO_3$ and brine. The product was recrystallized from ethyl acetate to give **6** (101 mg, 34%) as orange–red needle-shaped crystals. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS,) δ = 7.45–7.52 (m, 4H; ArH), 7.88–7.93 (m, 4H; ArH), 8.41 (dd, J = 3.43 Hz, 6.46 Hz, 2H; ArH), 9.11 (dd, J = 1.83 Hz, 6.67 Hz, 2H; ArH), 12.00 (s, 2H; NH); ^{13}C-NMR (75 MHz, DMSO-d_6, 298 K, TMS) δ = 112.0, 112.5, 121.3, 122.4, 124.2, 124.8, 128.3, 128.8, 129.9, 137.9,139.7, 140.2; HRMS (ESI) $C_{24}H_{15}N_4$: calcd. 359.1297; found m/z 359.1282 [M + H$^+$]; UV–Vis (dimethyl sulfoxide): $\lambda_{max}(\varepsilon)$ = 272 (47017), 283 (52917), 307 (44417), 320 (50050), 420 (22900).

Synthesis of receptor 7

2,3-Di(1*H*-indol-3-yl)-6-nitroquinoxaline (**5**, 300 mg, 0.74 mmol) and dichlorodicyanoquinone (DDQ, 201 mg, 0.89 mmol) were dissolved in neat trifluoroacetic acid (30 mL) and the resultant solution was heated at reflux for 4 hours until the reaction was complete (TLC). The residual trifluoroacetic acid was then removed by vacuum distillation. The semi-solid was washed with brine, saturated aq. $NaHCO_3$ and brine. The product was recrystallized from *N*,*N*-dimethylformamide to give **7** (150 mg, 50%) as red needle-shaped crystals. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K, TMS) δ = 7.40–7.50 (m, 4H; ArH), 7.84 (t, J = 8.41 Hz, 8.41 Hz, 2H; ArH), 8.36 (d, J = 9.19 Hz, 1H; ArH), 8.43 (dd, J = 2.05 Hz, 9.14 Hz, 1H; ArH), 8.93 (t, J = 8.60 Hz, 8.60 Hz, 2H; ArH), 9.00 (d, J = 1.88 Hz, 1H; ArH), 11.98 (s, 1H; NH), 12.05 (s, 1H; NH); HRMS (ESI) $C_{24}H_{14}N_5O_2$: calcd. 404.1147; found m/z 404.1138 [M + H$^+$]; UV–Vis (dimethyl sulfoxide): $\lambda_{max}(\varepsilon)$ = 275 (39714), 305 (38733), 318 (39152), 371 (20390), 451 (21800). The structure was also confirmed by the single crystal X-ray diffraction analysis.

X-Ray crystallography

Single crystals of **7**·TBACl and **7**·TBACH$_3$COO were obtained by slow diffusion of *n*-hexane into a chloroform solution of receptor **7** and the corresponding anion at room temperature. The X-ray single crystal diffraction data for **7**·TBACl and **7**·TBACH$_3$COO·CHCl$_3$·1/2H$_2$O were collected on a Rigaku MicroMAX007 with Mo-Kα radiation (λ = 0.71073 Å) at 113 K ± 2 K in the ω–2θ scanning mode. The structures were solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on F^2.[16,17] Anisotropic thermal parameters were assigned to all non-hydrogen atoms.

The organic hydrogen atoms were generated geometrically. Details of crystal data, data collections, and structure refinements are summarized in Tables S1 and S2 in the Supporting Information.

Acknowledgements

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14 Crystal data for **7**·TBACl: $C_{40}H_{49}ClN_6O_2$, triclinic, space group $P\bar{1}$, $a = 10.0553(19)$ Å, $\alpha = 64.024(7)°$, $b = 13.715(2)$ Å, $\beta = 80.245(12)°$, $c = 15.384(3)$ Å, $\gamma = 70.714(10)°$, $V = 1799.5(6)$ Å^3, $Z = 2$; $M_r = 681.30$, $\rho_{calcd} = 1.257$ Mg m^{-3}, μ(Mo-Kα) = 0.150 mm^{-1}, final $R1 = 0.0609$ for 6329 reflection of $I > 2\sigma(I)$, $R1 = 0.0756$, $wR2 = 0.1702$ for all 18561 reflections. CCDC-657906†.

15 Crystal data for **7**·TBACH$_3$COO·CHCl$_3$·1/2H$_2$O: $C_{43}H_{54}Cl_3N_6O_{4.5}$, triclinic, space group $P\bar{1}$, $a = 12.077(2)$ Å, $\alpha = 108.73(3)°$, $b = 13.878(3)$ Å, $\beta = 107.18(3)°$, $c = 14.279(3)$ Å, $\gamma = 95.52(3)°$, $V = 2116.4(7)$ Å^3, $Z = 2$, $M_r = 833.27$, $\rho_{calcd} = 1.308$ Mg m^{-3}, μ(Mo-Kα) = 0.267 mm^{-1}, final $R1 = 0.0537$ for 7406 reflection of $I > 2\sigma(I)$, $R1 = 0.0658$, $wR2 = 0.1181$ for all 13051 reflections. CCDC-657907†.

16 G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997.

17 G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.