

Tris(indolyl)methene molecule as an anion receptor and colorimetric chemosensor: tunable selectivity and sensitivity for anions†‡

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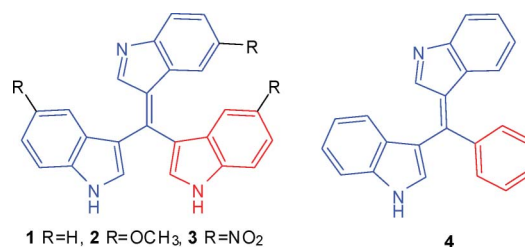
Simple tris(indolyl)methene receptors **1–3** containing conjugated bisindole skeletons have been designed and synthesized. The anion binding and sensing properties have been studied using UV-vis spectroscopy and ¹H NMR titration technique. Compared with 3,3'-bis-indolyl phenylmethene (**4**), tris(indolyl)methene receptors could highly selectively detect F⁻ based on two stages of proton transfer, along with stepwise drastic color changes. The introduction of the electron withdrawing or donating groups into indole unit, which tunes the acidities of the hydrogen bond sites, partially enhanced or inhibited the occurrence of the deprotonation of receptor and has a positive effect on the selectivity and sensitivity of such “proton-transfer” chemosensors for anions.

Introduction

The search for new host molecules for anion recognition and sensing through hydrogen bonding interaction has been an active research area,¹ due to the importance of anions in a wide range of medicinal, environmental and biological processes.² One of the most attractive approaches in this field involves the construction of colorimetric chemosensors since naked eye detection can offer qualitative and quantitative information.³ Most of the known colorimetric chemosensors are based on the synthetic receptors generally containing some combination of anion binding unit and signal-reporting group (chromophore), either covalently attached or intermolecularly linked.⁴ Recently, indole-based receptors have attracted considerable attention.⁵ The acidity of the pyrrole NH group is expected to be enhanced by conjugation with benzene,⁶ which would lead to higher binding affinity for anions.

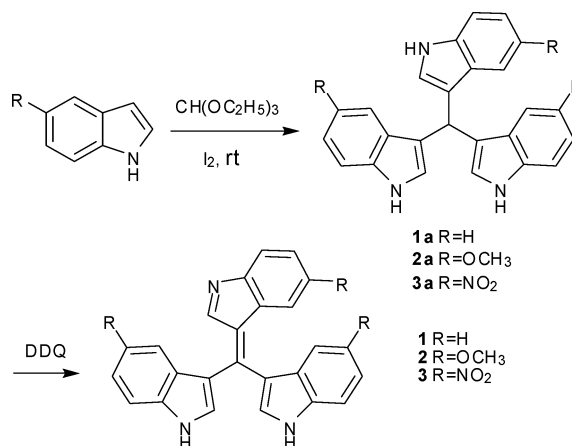
Previously, we presented a simple chemosensor **4** utilizing bis(3-indolyl)methene (BIM) skeleton as building block, which allows for the colorimetric detection of F⁻ and AcO⁻ in organic aprotic solution based on the proton transfer signaling mode.⁷ The large conjugated bis(3-indolyl)methene skeleton could not only act as a color-reporting group, but also provide as an acidic H-bond donor moiety and a basic H-bond acceptor moiety for anion binding. In addition, the bis(indolyl)methene skeleton has also been demonstrated to be an efficient chromogenic and fluorescent moiety for metal ion sensing by Kim and coworkers.⁸ However, this system is proved to be inefficient in discriminating between F⁻

and AcO⁻ at high analyte concentration. As an extension of our work, we have designed tris(3-indolyl)methene compounds **1–3**, by modifying the BIM skeleton to control the acidity and steric array of the H-bond sites, thus to tune the selectivity and sensitivity of such “proton-transfer” chemosensors for anions. Herein, we wish to report the synthesis of the chemosensors, and demonstrate their particular abilities in anion recognition and sensing.



Results and discussion

The synthesis of compounds **1–3** was shown in Scheme 1. Compounds **1a–3a** were synthesized easily using iodine as the catalyst according to the procedure describing in the previous literatures in 85%, 81%, and 80% yield, respectively.⁹ Compounds



Scheme 1 Synthesis of compounds **1–3**.

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1–3 were formed by treating the precursor **1a–3a** with DDQ in acetonitrile or acetone in about 25%, 36%, and 40% yield, respectively.

Comparing with bis(indolyl)methene **4**, compound **1** substitutes a larger indolyl group for the phenyl group. Structurally, compound **1** could be deemed as the combination of two BIM skeletons, possessing two H-bond donor sites, which may lead to double deprotonation process in a certain condition. This speculation was validated by the observation that the color changes drastically upon addition of F^- (Fig. 1). Furthermore, substitution of a larger group results in deleterious effects on coplanarity of three aromatic rings, which disfavors the propagation of electron onto the π -conjugated skeleton. The selectivity and sensitivity of such conjugated bisindole-based chemosensor for anions may be tuned by modifying the skeleton.

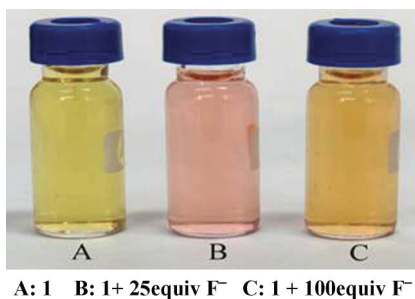


Fig. 1 Color changes of **1** (2.5×10^{-5} M in CH_3CN) upon addition of 0, 25, 100 equiv of F^- .

The interaction of compound **1** with F^- was studied in detail using UV-vis spectroscopic technique and interesting spectral behaviors were observed, as shown in Fig. 2. Compound **1** was characterized by a strong band ($\lambda = 457$ nm, $\epsilon_{max} = 2 \times 10^4$ dm³ mol⁻¹ cm⁻¹) which is assigned to π - π^* transitions of conjugated bisindole skeleton. In the presence of 0–1 equiv of F^- , the absorption at 457 nm of **1** decreases and undergoes a moderate blue-shift to 437 nm, presumably due to the formation of the H-bond complex with F^- and the distortion of the planarity of the conjugated system. With adding excessive amount of F^- , two stages of distinct changes in color and spectra were observed. In the presence of 1–30 equiv of F^- , the solution color gradually turned from yellow to light-pink. Correspondingly, the intensity of the band at 437 nm reduced gradually and a new intense

absorption band centered at 513 nm evolved until reaching its maximum upon the addition of 30 equiv of F^- , accompanied by one clearly isosbestic point at 467 nm. We attributed these spectral changes to the deprotonation of one NH moiety, due to the high stability of complex $[HF_2]^-$.¹⁰ It is the mono-deprotonation that is responsible for the first pronounced color change. A red-shift with a similar great extent (from 423 to 517 nm) has been observed on the interaction of bis(indolyl)methene compound **4** with F^- .⁷ On addition of a further excess of F^- , the band at 513 nm gradually decreased and a new blue-shift band at 477 nm evolved, while the color of the solution turned from light-pink to orange. We ascribed this new band to the double deprotonated form of compound **1**. Perhaps due to the weak ability of electron acceptor in decentralizing the increased electron density of the conjugated system, compound **1** was forced to undergo a conformational change, in which three aromatic rings were less coplanar in the form of $[L]^{2-}$ than that of $[HL]^-$, leading to a moderate blue-shift in the absorption band.

Titration with the strong base $[Me_3N]OH$, which definitely leads to deprotonation, also induced the same color and spectral changes of **1** as those observed with F^- anions (Fig. S1, ESI[†]). Furthermore, the F^- -induced two-step changes in color and spectra are reversible, progressive additions of protic solvent (such as methanol or water) result in turning the orange solution to light-pink, then to yellow. Correspondingly, the absorption band recovers from 477 nm to 513 nm, then finally to 449 nm (see Fig. S2, ESI[†]). This phenomenon may be due to that protic solvents could compete for F^- with the NH moieties, disfavoring the formation of $[L]^{2-}$ and $[HL]^-$.

Previous study showed that the deprotonation of compound **4** was also induced by adding large excess of AcO^- (up to 100 equiv), and the color and spectral changes were similar to the case of F^- .⁷ Different from **4**, compound **1** has advantage in discriminating AcO^- and F^- at high concentration, partly due to the weakening of the acidity of the indole NH groups of **1** through structural modification. Upon addition of large amount of AcO^- , the absorption band at 437 nm decreased and underwent a moderate red-shift, while a less strong shoulder peak at 513 nm appeared and only increased to a certain extent (Fig. 3a), which could not induce obvious color change. The result suggested that the basicity of AcO^- is insufficient to induce complete deprotonation of compound **1**, and the system should be in an incipient state of mono-deprotonation of **1**.

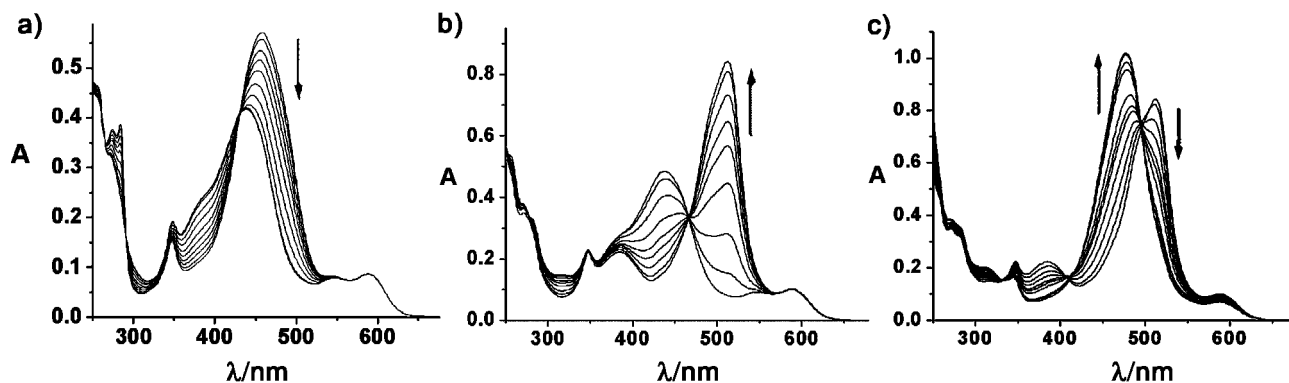


Fig. 2 The changes in UV-vis spectra of **1** recorded in CH_3CN (2.5×10^{-5} M) after addition of: (a) 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 equiv of F^- ; (b) 1, 2, 3, 5, 7, 9, 15, 20, 30 equiv of F^- ; (c) 30, 40, 50, 60, 70, 80, 100, 125, 150, 175, 200 equiv of F^- .

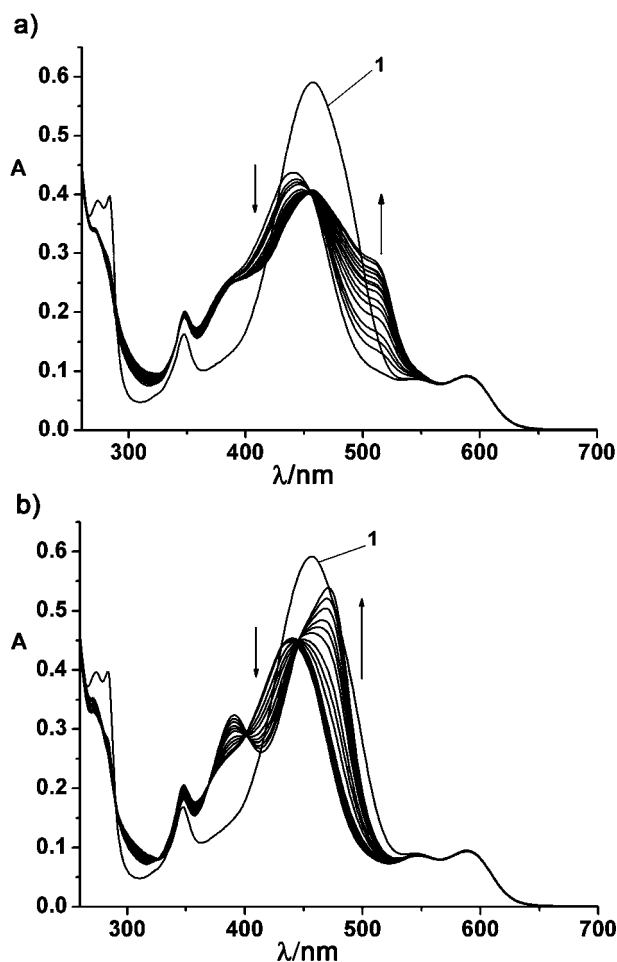


Fig. 3 The changes in UV-vis spectra of **1** recorded in CH_3CN (2.5×10^{-5} M) after addition of (a) 0, 10, 20, 30, 40, 50, 60, 70, 80, 100, 120, 140, 160, 180, 200 equiv of AcO^- ; (b) 0, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 75, 100, 200 equiv of H_2PO_4^- .

Additionally, the absorption spectral changes of **1** on addition of H_2PO_4^- are shown in Fig. 3b. Upon addition of excessive amount of H_2PO_4^- to the CH_3CN solution of **1**, a red-shifted absorption band appeared at 471 nm rather than 513 nm, which is similar to that witnessed in the process of F^- -induced double deprotonation, along with isosbestic points at 370 nm, 401 nm and 446 nm. The results led us to suggest that H_2PO_4^- , with bulky size, could interact with two NH sites of **1** to form multiple hydrogen bonds complex by 1 : 1 binding model, which may be in an incipient state of the double deprotonation of **1**, and the weak basicity of H_2PO_4^- suppresses the deprotonation process.

The anion binding ability of **1** with other anions (Cl^- , Br^- , I^- , ClO_4^- and HSO_4^- added as their tetrabutylammonium salts) were also evaluated through UV-vis method (Fig. S3, ESI ‡). No significant spectral and color changes were observed, even in large excess amount because of the weak coordination interaction. Furthermore, compound **1** is inefficient in detecting HSO_4^- through protonation mode in aqueous system compared with compound **4** (Fig. S4, ESI ‡),⁷ presumably due to the weakening of the basicity of the H-bond acceptor by steric modification.

As a new kind of chromogenic molecules based on BIM skeleton, tris(indolyl)methene **1** could highly selectively sense F^-

by two stages of proton transfer, with the limit of detection (LOD) of 9.28 ppm for F^- , 459 ppm for AcO^- , and 558 ppm for H_2PO_4^- , respectively,¹¹ which further shows that **1** could obviously distinguish F^- from other anions through spectral behaviors. Similar anion binding and sensing properties were also observed in the more polar DMSO (Fig. S5, ESI ‡).

The interaction of **1** and F^- was also monitored using ^1H NMR titration in $\text{DMSO}-d_6$ (solubility problems prevented the studies in CD_3CN solution), as shown in Fig. 4. The shift at 13.3 ppm that pertains to the NH groups disappeared and the aromatic proton signals underwent continuous upfield shifts along with the stepwise deprotonation. Such effect can be due to the negative electron transfer onto the π -conjugated framework, acting as a shielding effect and cause an upfield shift.¹² During the titration experiment, it is found that there exist two titration pause, which may relate to the two states of proton transfer. In addition, a signal of $[\text{HF}_2]^-$ at 16.1 ppm was obtained during the titration process of compound **2** with F^- (Fig. S6, ESI ‡), which indicated the deprotonation of receptor and the formation of $[\text{HF}_2]^-$ species.^{3c,10,13}

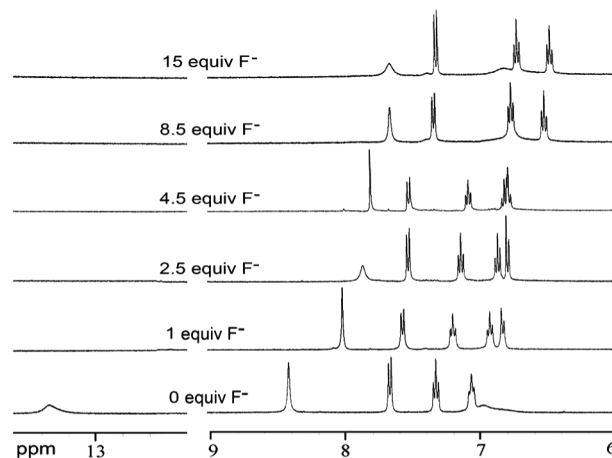


Fig. 4 ^1H NMR spectra of **1** (1.0×10^{-2} M) in $\text{DMSO}-d_6$ upon addition of various quantities of tetrabutylammonium fluoride.

Similar to the case of **1**, compound **2**, bearing electron-donating methoxy groups on indole units, also exhibited selective binding towards F^- over other anions tested (Fig. S7, ESI ‡). However, the introduction of methoxy groups into tris(indolyl)methene skeleton, which leads to the decreased acidity of the indole NH proton, decreased the affinity of compound **2** towards anions. Compared with compound **1**, the F^- -induced reversible deprotonation of compound **2** occurred at high F^- concentration, and the absorption bands related to the mono- and double-deprotonation forms were centered at 509 nm and 483 nm (Fig. S8, ESI ‡), respectively, two distinct drastic color changes from orange solution to light-pink, then to yellow were also observed in this process. As for AcO^- or H_2PO_4^- , the titration spectra of compound **2** showed only a slight red-shift at high anion concentration (up to 200 equiv) (Fig. S9 and S10, ESI ‡), which indicated that the H-bond interaction of **2** with AcO^- or H_2PO_4^- was obviously weakened.

On the other hand, the anion binding and sensing properties of compound **3** were observed using UV-vis spectroscopy technique. The introduction of electron-withdrawing nitro groups into

tris(indolyl)methene skeleton, which leads to the increase in the acidity of the indole NH proton, has a positive effect on the affinity and selectivity of compound **3** towards anions. As shown in Fig. 5, compound **3** exhibited selective binding and colorimetric sensing towards F^- , AcO^- and $H_2PO_4^-$ over other anions tested. The addition of 2 equiv of F^- induced the fully mono-deprotonation process, and further double deprotonation evolved until reaching equilibrium when 20 equiv of F^- was added. The absorption bands related to the mono- and double-deprotonation forms were centered at 546 nm and 523 nm (Fig. S11, ESI ‡), respectively.

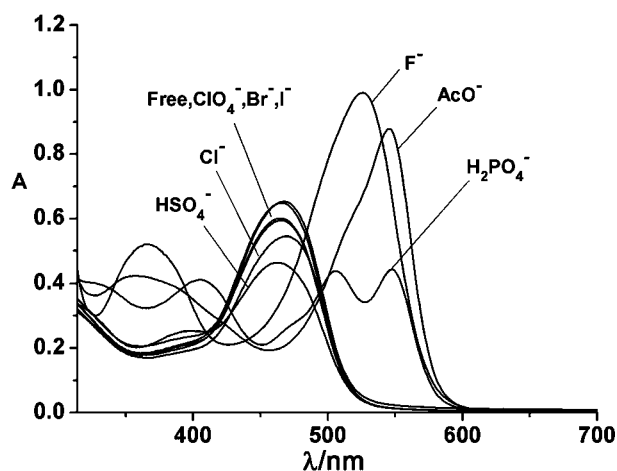


Fig. 5 UV-vis spectra of **3** recorded in CH_3CN (2.5×10^{-5} M) after addition of 25 equiv of various anions (none, F^- , AcO^- , Cl^- , Br^- , I^- , HSO_4^- , ClO_4^- , $H_2PO_4^-$).

Due to the increase in the acidity of indole NHs, the AcO^- -induced mono-deprotonation of compound **3** was observed (Fig. 6a). The new absorption bands at 546 nm, completely similar to the mono-deprotonation induced by F^- , continuously increases in intensity, reaching a maximum upon addition of 10 equiv of this anion. However, no further double deprotonation occurred even in the presence of large excess of AcO^- (1000 equiv), due to the basicity of AcO^- . Fig. 6b shows the results of absorption titration of **3** with $H_2PO_4^-$. Addition of $H_2PO_4^-$ leads to decrease in the 458 nm absorption band, along with mild increase in the 546 nm and 503 nm bands with the effect that the solution changed color from yellow to pink. The spectral change almost stops upon addition of 10 equiv of $H_2PO_4^-$. The results indicate that the deprotonation of **3** by $H_2PO_4^-$ anion is incomplete and the interaction may involve multiple hydrogen-bonded complex.

The above results show significant differences in anion binding and optical properties among receptors **1**, **2**, and **3** although only slight structural modification was made by introducing electron-donating methoxy groups and electron-withdrawing nitro groups, which tuned the binding abilities and optical responses of tris(indolyl)methene skeleton towards F^- , AcO^- , and $H_2PO_4^-$ anions. On the other hand, the definite stoichiometric ratio between receptors **1–3** and AcO^- or $H_2PO_4^-$ was determined to be 1:1 by Job's-plot experiments, the equilibrium constants of receptors **1–3** with three basic anions were evaluated through nonlinear least squares fitting by origin software,¹⁴ and summarized in Table 1.

A further insight into Table 1 reveals that receptor **3** shows much higher binding affinity for F^- , AcO^- , and $H_2PO_4^-$ than receptors **1**

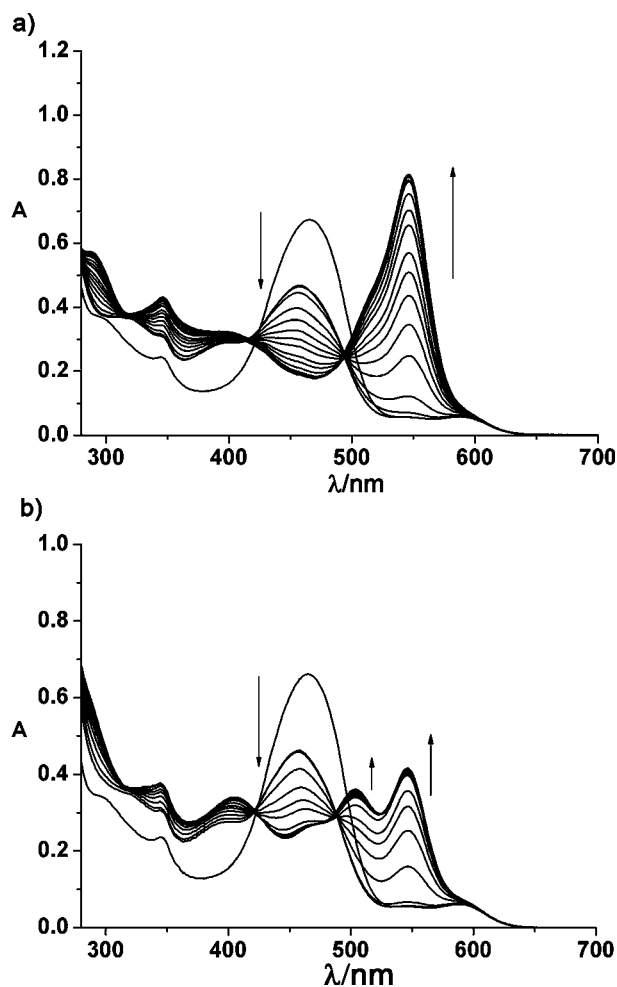


Fig. 6 The changes in UV-vis spectra of **3** recorded in CH_3CN (2.5×10^{-5} M) after addition of (a) 0, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, 2, 4, 6, 8, 10, 15, 20, 50, 100 equiv of AcO^- ; (b) 0, 1, 2, 4, 6, 8, 10, 15, 20, 30, 40, 60, 80, 100 equiv of $H_2PO_4^-$.

Table 1 Equilibrium constants for the interaction of receptors **1–3** with F^- , AcO^- and $H_2PO_4^-$ at 25 °C

Anion	Receptor		
	1	2	3
F^-	$6.68 \times 10^3 \pm 697^b$ $1.79 \times 10^3 \pm 47^c$	$5.69 \times 10^3 \pm 437^b$ $1.34 \times 10^3 \pm 36^c$	$> 10^7^b$ $2.68 \times 10^4 \pm 3158^c$
AcO^-	$3.98 \times 10^2 \pm 14^a$	$2.91 \times 10^2 \pm 8^a$	$1.49 \times 10^5 \pm 5310^b$
$H_2PO_4^-$	$1.18 \times 10^3 \pm 59^a$	$3.19 \times 10^2 \pm 7^a$	$8.42 \times 10^3 \pm 1744^b$

^a The association constant. ^b The mono-deprotonated dissociation constant. ^c The double-deprotonated dissociation constant.

and **2**, due to the increasing in the acidity of indole NHs caused by the electron withdrawing nitro group. Receptors **1–3** all show the double deprotonation by F^- , and the first dissociation constants are bigger than the second dissociation constants, which was probably due to decreasing the NH proton acidity after mono-deprotonation. Based on hydrogen bond interaction, receptors **1** and **2** give much higher binding affinity for $H_2PO_4^-$ than for AcO^- . This selectivity will be attributed to the fitness of size and

shape of dihydrogen phosphate anion towards binding sites of tris(indolyl)methene by multiple hydrogen bonds.^{5g,15}

Conclusion

To sum up, tris(indolyl)methene, a new kind of unexplored chromogenic molecules based on BIM skeleton, proved an excellent chemosensor for F⁻ by two stages of proton transfer, and could also distinguish AcO⁻ and H₂PO₄⁻ through spectral behaviors. The introduction of the electron donating group into the tris(indolyl)methane skeleton decrease the binding ability of the hydrogen bond site, which partially inhibit the occurrence of the deprotonation, and improve the selectivity. In contrast, the introduction of the electron withdrawing group increases notably the proton acidity of the hydrogen bond donor moiety, and promotes the occurrence of the reversible deprotonation, while improving anion affinity and response sensitivity of the receptor, and reduced the anion selectivity. Consequently, as a promising building block, the BIM skeleton seems to be general for developing more anion receptors and sensors through some modification.

Experimental section

Tris(1*H*-indol-3-yl)methane (1a)

Compound **1a** was prepared according to the literature method.^{9a} Iodine (0.02 g, 0.1 mmol) was added to a mixture of the indole (0.23 g, 2 mmol) and orthoformate (0.10 g, 0.66 mmol) in acetonitrile (4 mL), and the reaction was stirred at room temperature for 5 min. the solvent was removed under reduced pressure, and the residue was directly purified by column chromatography and eluted with n-hexane–EtOAc (v/v, 3:1) to afford the product (white solid). Yield 85%, mp: 238–240 °C. IR (KBr) 3399, 3046, 1605, 1448, 1417, 1331, 1088, 744 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 10.70 (s, 3H, NH), 7.39 (d, 3H), 7.32 (d, 3H), 7.01 (t, 3H), 6.92 (d, 3H), 6.84 (t, 3H), 6.04 (s, 1H, Ar3CH). MS (ESI) *m/z*: 359.9 ([M – H]⁻).

Tris(5-methoxy-1*H*-indol-3-yl)methane (2a)

Compound **2a** was prepared in a similar manner to compound **1a**. the reaction was stirred at room temperature for 20 min, and purification by silica column chromatograph and eluted with n-hexane–EtOAc (v/v, 3:2) to afford the product (white solide). Yield 81%, mp: 218–220 °C. IR (KBr) 3404, 3048, 2991, 2937, 2830, 1621, 1582, 1483, 1436, 1219, 1168, 1042, 800 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) (ppm): 10.56 (s, 3H, NH), 7.22 (d, 3H), 6.94 (s, 3H), 6.85 (d, 3H), 6.67 (dd, 3H), 5.91 (s, 1H, Ar3CH), 3.58 (s, 9H). MS (ESI) *m/z*: 452.0 ([M+H]⁺).

Tris(5-nitro-1*H*-indol-3-yl)methane (3a)

Compound **3a** was prepared according to the literature method.^{9b} Iodine (0.02 g, 0.1 mmol) was added to a mixture of the 5-nitroindole (0.32 g, 2 mmol) and orthoformate (0.10 g, 0.66 mmol) in a closed vessel, and the reaction was stirred at room temperature for 20 min. and then the residue was directly purified by column chromatography and eluted with petroleum ether (b.p. 60–90 °C)/EtOAc (v/v, 1:2) to afford the product (yellow solide).

Yield 80%, mp: >300 °C. IR (KBr) 3360, 1621, 1511, 1472, 1323, 1213, 1080, 743 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) (ppm): 11.67 (s, 3H, NH), 8.45 (d, 3H), 7.99 (dd, 3H), 7.57 (d, 3H), 7.28 (s, 3H), 6.61 (s, 1H, Ar3CH). MS (ESI) *m/z*: 495.7 ([M – H]⁻).

3,3'-((3*H*-Indol-3-ylidene)methylene)bis(1*H*-indole) (1)

Compound **1a** (0.36 g, 1 mmol) was dissolved in acetonitrile (25 mL), DDQ (0.34 g, 1.5 mmol) solution of acetonitrile was dropwise and slowly added to the solution. This reaction was allowed for 1 h and gave a dark red precipitate, which was filtered, washed with CH₃CN, and recrystallized from ethanol. Yield 25%, mp: >300 °C. IR (KBr) 3375, 3117, 2983, 2215, 1699, 1620, 1566, 1476, 1409, 1307, 1213, 1127, 1009, 831, 743 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) (ppm): 8.41 (s, 3H), 7.69 (d, 3H), 7.34 (t, 3H), 7.07 (t, 3H), 6.94 (s, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ: 160.36, 143.53, 138.79, 130.02, 124.64, 124.46, 123.52, 123.08, 120.80, 120.56, 118.09, 115.38, 113.99, 113.76. HRMS (ESI) *m/z* ([M+H]⁺) calcd for C₂₅H₁₇N₃: 360.1495; found, 360.1490.

3,3'-((5-Methoxy-3*H*-indol-3-ylidene)methylene)bis(5-methoxy-1*H*-indole) (2)

Compound **2a** (0.45 g, 1 mmol) was dissolved in acetonitrile (25 mL), DDQ (0.34 g, 1.5 mmol) solution of acetonitrile was dropwise and slowly added to the solution. This reaction was allowed for 1 h and gave a dark red precipitate, and then the precipitate was directly purified by column chromatography and eluted with EtOAc–methanol (v/v 3:1) to afford the product. Yield 36%, mp: >300 °C. IR (KBr) 3362, 3135, 2974, 2892, 2210, 1623, 1593, 1461, 1212, 1050, 793 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.34 (s, 3H), 7.60 (d, 3H), 6.99 (dd, 3H), 6.38 (s, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ: 159.24, 155.94, 142.15, 141.94, 133.30, 127.15, 126.91, 118.09, 114.43, 113.59, 103.80, 54.94 HRMS (ESI) *m/z* (M+H⁺) calcd for C₂₈H₂₃N₃O₃: 450.1812; found, 450.1806.

3,3'-((5-Nitro-3*H*-indol-3-ylidene)methylene)bis(5-nitro-1*H*-indole) (3)

Compound **3a** (0.5 g, 1 mmol) was dissolved in acetone (25 mL), DDQ (0.34 g, 1.5 mmol) solution of acetone was dropwise and slowly added to the solution. This reaction was allowed for 6 h and gave a dark brown precipitate, which was filtered, washed with acetone. Yield 40%. mp: >300 °C. IR (KBr) 3378, 3099, 2871, 2210, 1703, 1526, 1453, 1343, 1211, 1130, 1057, 829, 740 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ: 8.91 (s, 3H), 8.28 (dd, 3H), 8.00 (d, 3H), 7.83 (s, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ: 174.25, 171.97, 171.02, 160.48, 144.59, 143.57, 142.29, 136.17, 126.09, 120.23, 117.97, 117.03, 114.99. HRMS (ESI) *m/z* ([M+H]⁺) calcd for C₂₅H₁₄N₆O₆: 495.1048; found, 495.1053.

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Notes and references

- (a) R. Martínez-Mañez and F. Sancenón, *Chem. Rev.*, 2003, **103**, 4419; (b) C. Caltagirone and P. A. Gale, *Chem. Soc. Rev.*, 2009, **38**, 520; (c) S. L. Wiskur, H. Ait-Haddou, J. J. Lavigne and E. V. Anslyn, *Acc. Chem. Res.*, 2001, **34**, 963; (d) V. Amendola and L. Fabbri, *Chem. Commun.*, 2009, 513.
- (a) P. A. Gale and R. Quesada, *Coord. Chem. Rev.*, 2006, **250**, 3219; (b) T. Gunnlaugsson, M. Glynn, G. M. Tocci, P. E. Kruger and F. M. Pfeffer, *Coord. Chem. Rev.*, 2006, **250**, 3094; (c) E. A. Katayev, Y. A. Ustynyuk and J. L. Sessler, *Coord. Chem. Rev.*, 2006, **250**, 3004.
- (a) H. D. P. Ali, P. E. Kruger and T. Gunnlaugsson, *New J. Chem.*, 2008, **32**, 1153; (b) Z. H. Lin, S. J. Ou, C. Y. Duan, R. G. Zhang and Z. P. Bai, *Chem. Commun.*, 2006, 624; (c) S. Z. Hu, Y. Guo, J. Xu and S. J. Shao, *Org. Biomol. Chem.*, 2008, **6**, 2071; (d) M. V. Lopez, M. R. Bermejo, M. E. Vazquez, A. Taglietti, G. Zaragoza, R. Pedrido and M. Martinez-Calvo, *Org. Biomol. Chem.*, 2010, **8**, 357.
- (a) H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2001, **40**, 154; (b) J. W. Steed, *Chem. Soc. Rev.*, 2009, **38**, 506; (c) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515; (d) E. Veale, G. Tocci, F. Pfeffer, P. Kruger and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2009, **7**, 3447.
- (a) P. A. Gale, *Chem. Commun.*, 2008, 4525; (b) J. R. Hiscock, C. Caltagirone, M. E. Light, M. B. Hursthouse and P. A. Gale, *Org. Biomol. Chem.*, 2009, **7**, 1781; (c) A. Brown, K. M. Mullen, J. Ryu, M. J. Chmielewski, S. r. M. Santos, V. Felix, A. L. Thompson, J. E. Warren, S. I. Pascu and P. D. Beer, *J. Am. Chem. Soc.*, 2009, **131**, 4937; (d) D. Makuc, M. Lenarcic, G. W. Bates, P. A. Gale and J. Plavec, *Org. Biomol. Chem.*, 2009, **7**, 3505; (e) C. Caltagirone, J. R. Hiscock, M. B. Hursthouse, M. E. Light and P. A. Gale, *Chem.–Eur. J.*, 2008, **14**, 10236; (f) C. Caltagirone, P. A. Gale, J. R. Hiscock, S. J. Brooks, M. B. Hursthouse and M. E. Light, *Chem. Commun.*, 2008, 3007; (g) J. L. Sessler, D.-G. Cho and V. Lynch, *J. Am. Chem. Soc.*, 2006, **128**, 16518; (h) P. Dydio, T. Zielinski and J. Jurczak, *Chem. Commun.*, 2009, 4560; (i) Y. Shiraiishi, H. Maehara and T. Hirai, *Org. Biomol. Chem.*, 2009, **7**, 2072.
- (a) F. G. Bordwell, X. Zhang and J. P. Cheng, *J. Org. Chem.*, 1991, **56**, 3216; (b) F. G. Bordwell, *Acc. Chem. Res.*, 1988, **21**, 456; (c) F. G. Bordwell, G. E. Drucker and H. E. Fried, *J. Org. Chem.*, 1981, **46**, 632.
- X. M. He, S. Z. Hu, K. Liu, Y. Guo, J. Xu and S. J. Shao, *Org. Lett.*, 2006, **8**, 333.
- J. W. Lee, S. Y. Park, B. K. Cho and J. S. Kim, *Tetrahedron Lett.*, 2007, **48**, 2541.
- (a) Z.-H. Zhang and J. Lin, *Synth. Commun.*, 2007, **37**, 209; (b) X.-F. Zeng, S.-J. Ji and X.-M. Su, *Chin. J. Chem.*, 2008, **26**, 413; (c) R. Nagarajan and P. T. Perumal, *Chem. Lett.*, 2004, **33**, 288.
- S. O. Kang, D. Powell, V. W. Day and K. Bowman-James, *Angew. Chem., Int. Ed.*, 2006, **45**, 1921.
- The limit of detections (LOD) of **1** for F⁻, AcO⁻, H₂PO₄⁻ were determined according to the equation LOD = 3 × δ_{black} / m (where δ_{black} is the standard deviation of the black and m is the slope of the calibration plot). See: (a) H.-T. Niu, D. Su, X. Jiang, W. Yang, Z. Yin, J. He and J.-P. Cheng, *Org. Biomol. Chem.*, 2008, **6**, 3038–3040.
- (a) D. E. Gomez, L. Fabbri, M. Licchelli and E. Monzani, *Org. Biomol. Chem.*, 2005, **3**, 1495–1500; (b) D. Esteban-Gomez, L. Fabbri and M. Licchelli, *J. Org. Chem.*, 2005, **70**, 5717–5720; (c) R. M. Duke, J. E. O'Brien, T. McCabe and T. Gunnlaugsson, *Org. Biomol. Chem.*, 2008, **6**, 4089–4092; (d) C. Caltagirone, G. W. Bates, P. A. Gale and M. E. Light, *Chem. Commun.*, 2008, 61–63; (e) F. M. Pfeffer, K. F. Lim and K. J. Sedgwick, *Org. Biomol. Chem.*, 2007, **5**, 1795–1799.
- (a) P. Bose and P. Ghosh, *Chem. Commun.*, 2010, **46**, 2962; (b) X. J. Peng, Y. K. Wu, J. L. Fan, M. Z. Tian and K. L. Han, *J. Org. Chem.*, 2005, **70**, 10524; (c) Y.-M. Zhang, Q. Lin, T.-B. Wei, X.-P. Qin and Y. Li, *Chem. Commun.*, 2009, 6074; (d) T. Gunnlaugsson, P. E. Kruger, T. C. Lee, R. Parkesh, F. M. Pfeffer and G. M. Hussey, *Tetrahedron Lett.*, 2003, **44**, 6575.
- The stoichiometry ratio of the complexes and the fitting method for equilibrium constants see Supporting Information. The related examples, See: (a) B. Valeur, J. Pouget, J. Bourson, M. Kaschke and N. P. Ernsting, *J. Phys. Chem.*, 1992, **96**, 6545; (b) V. Amendola, D. Esteban-Gomez, L. Fabbri and M. Licchelli, *Acc. Chem. Res.*, 2006, **39**, 343–353.
- (a) Grigory V. Zyryanov, Manuel A. Palacios and P. Anzenbacher, Jr., *Angew. Chem., Int. Ed.*, 2007, **46**, 7849–7852; (b) T. Sakamoto, A. Ojida and I. Hamachi, *Chem. Commun.*, 2009, 141–152; (c) H. F. M. Nelissen and D. K. Smith, *Chem. Commun.*, 2007, 3039–304; (d) Y. M. Sun, C. Zhong, R. Gong and E. Q. Fu, *Org. Biomol. Chem.*, 2008, **6**, 3044–3047; (e) H. Shao, H. Lin and H. K. Lin, *Spectrochim. Acta, Part A*, 2008, **70**, 682–685; (f) J. Shao, H. Lin and H. K. Lin, *Dyes Pigm.*, 2009, **80**, 259–263; (g) C. Olivier, Z. Grote, E. Solari, R. Scopelliti and K. Severin, *Chem. Commun.*, 2007, 4000–4002.