Anion Binding and Sensing Properties of Bis(3-indolyl)methene Derivatives Based on Proton Transfer Process

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Received October 25, 2010: Revised December 16, 2010: Accepted December 21, 2010

Abstract: A series of the bis(3-indolyl)methene derivatives were synthesized and their anion binding and sensing properties in CH_3CN or mixed CH_3CN/H_2O solution have been investigated in detail by UV-vis spectroscopic techniques. The deprotonation/protonation of the bis(3-indolyl)methene receptor is responsible for the dramatic color and spectral changes. The introduction of the electron-donating or withdrawing group into different moiety of the bis(3-indolyl)methene skeleton, which tunes the acidity of the H-bond donor moiety or the basicity of the H-bond acceptor moiety, has a positive effect on the selectivity and sensitivity of such "proton-transfer" chemosensors for anions.

Keywords: Anion recognition, bis(3-indolyl)methene, colorimetric chemosensor, hydrogen bond, proton transfer, tunable selectivity and sensitivity.

1. INTRODUCTION

Anion recognition and sensing is an important research area in supramolecular chemistry, mainly because of the understanding that anions play key roles in biology, medicine, catalysis and environmental sciences [1]. The development of the electroneutral receptors and chemosensors for anions continues to provide a challenge for supramolecular chemists and has been attracting much attention in recent years [2]. More and more efforts have been devoted to develop novel receptors for anion recognition and sensing [3]. Most of the known colorimetric chemosensors are based on the synthetic receptors generally consisting of two parts: binding site and signal-reporting group (chromophore), either covalently attached or intermolecularly linked. Generally, the binding sites are the H-bond donor groups which in most cases contain the NH fragment of the carboxyamides, sulfonamides, urea, thiourea and pyrroles [4]. In the last years, indoles, as an important class of hydrogen bond donor-based building blocks, have been designed for a variety of anion receptors and sensors due to the high binding affinity and selectivity for specific anionic guests [5].

Previously, we reported the bis(3-indolyl)methene compound **1a** that can be used as anion receptor for the colorimetric detection of either F^- and AcO^- in organic aprotic solution or HSO_4^- in water-containing medium through the reversible proton transfer signaling mode [6]. The conjugated bis(3-indolyl)methene skeleton can not only act as a color-reporting group but also provide an acidic H-bond donor moiety and a basic H-bond acceptor moiety for anion binding. In an effort to further investigate its potential ability for anion binding and sensing, a series of the bis(3-indolyl)methene derivatives were designed by introducing the electron-withdrawing nitro group or electron-donating methoxy group into the different moiety of the bis(indolyl)methene skeleton, which can tune the acidity of the H-bond donor moiety or the basicity of the H-bond acceptor moiety. Here in, the anion recognition and sensing behaviors of the derivatives were evaluated in detail using the UV-vis spectroscopic techniques.

2. RESULTS AND DISCUSSION

The *meso*-phenyl bis(3-indolyl)methene derivatives were successfully synthesized by treating the bis(3-indolyl) methane precursors with DDQ in CH_3CN, as shown in Scheme **1**. According to a literature method [7], the bis(3-indolyl)methane compounds were prepared by the condensation of indole derivatives with corresponding benzaldehyde in CH_3OH.

The bis(3-indolyl)methene derivatives usually display the characteristic absorption band at 424-438 nm regions, which is assigned to the π-π^* transition of the conjugated bisindole skeleton and make the color of the solution yellow. As for receptors **1a**, **1c** and **1e**, the weak shoulder peaks at 500 nm and 590 nm (Fig. **S1**), which disappeared when adding a small quantity of polar protic solvent such as CH_3OH or H_2O to the solution, can be presumably attributed to its intermolecular hydrogen bond interaction.

The anion binding and sensing properties of receptors **1b** and **1c**, containing a nitro group or methoxy group in the *meso*-phenyl ring of bis(3-indolyl)methene skeleton, were first studied by UV-vis spectroscopic measurements. Similar to the case of receptor **1a** [6], receptor **1b** or **1c** was found to exhibit highly selective binding properties towards fluoride

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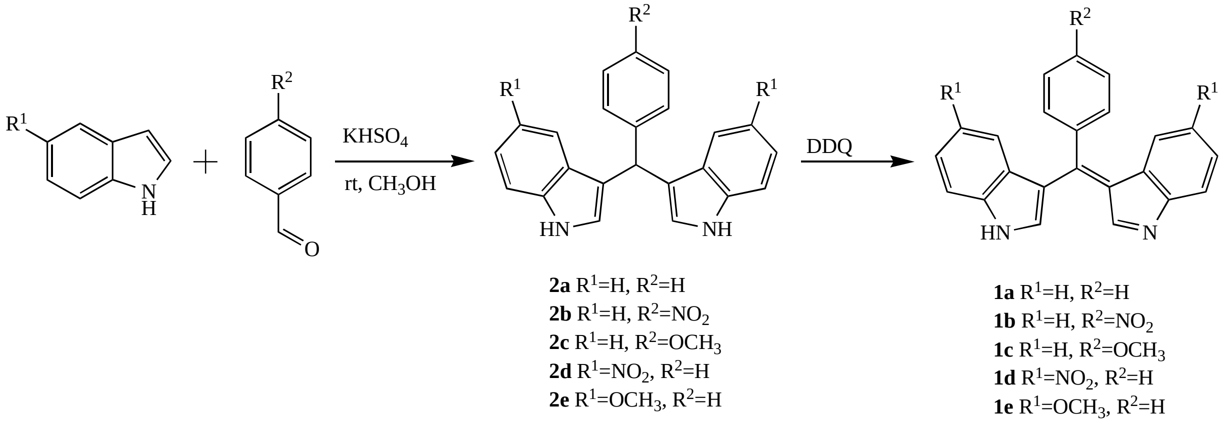

Scheme 1. The synthesis of compounds **1** and **2**.

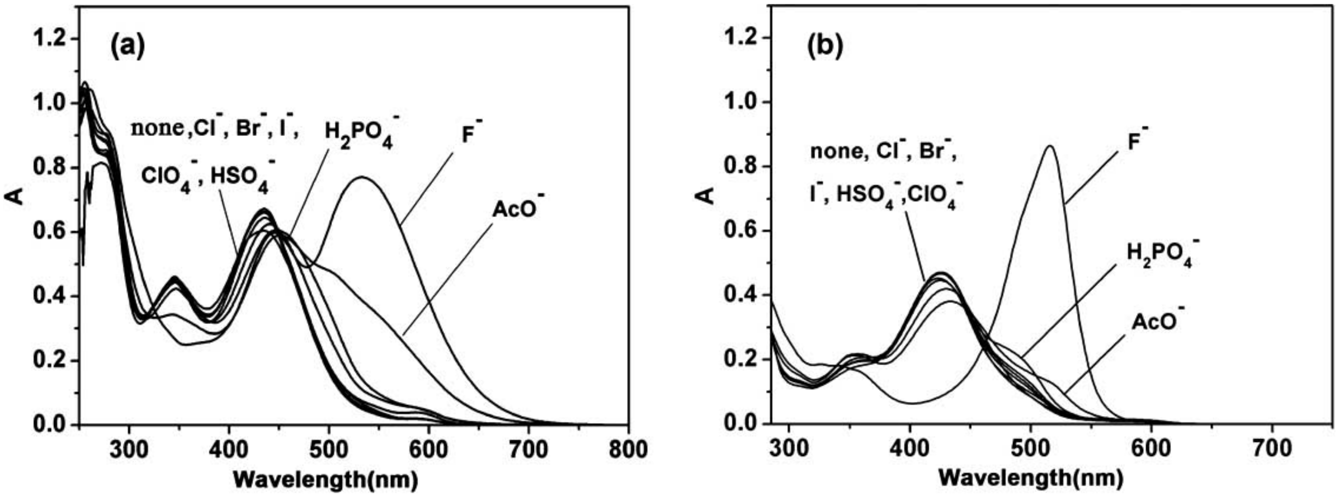

Fig. (1). Changes in UV–vis spectra of **1b** (**a**) and **1c** (**b**) (5×10^{-5} M) recorded in CH_3CN after addition of 25 equiv of various anions (F^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, Cl^-, Br^-, and I^-, as their Bu_4N^+ salts).

anions in CH_3CN, as revealed by the marked F^--induced changes in the absorption spectra (Fig. **1**). The new absorption band indicative of the deprotonated form of receptor **1b** or **1c** appeared at 531 nm and 515 nm, respectively, while the solution color all turned from yellow to red. Careful evaluation of titration experiments carried out by F^- anion revealed the process from H-bond interaction to deprotonation (Fig. **S2**, **S3**). Similar, but less remarkable spectral changes could be also observed in the presence of a large excess of AcO^- (Fig. **S4**, **S5**), ascribed to the incomplete deprotonation of receptor **1b** or **1c**. As for $H_2PO_4^-$, only a slight red shift of the band at about 430 nm, due to the formation of a hydrogen-bonded complex, was observed. However, the other anions tested induced the negligible responses. The above results showed that the introduction of electron-withdrawing or electron-donating group into the *meso*-phenyl of bis(3-indolyl)methene **1a** has no significant effect on its selectivity and affinity towards anions in CH_3CN (see Table **1**).

On the other hand, in mixed CH_3CN/H_2O (4:1, v/v) solution, receptors **1b** and **1c** also showed the same sensing properties for HSO_4^- over other anions tested as that of receptor **1a** [6], and the new absorption band pertained to the protonated form of receptor **1b** or **1c** appeared at 517 nm and 488 nm, respectively (Fig. **2**), with the effect that the solution instantaneously changed color from yellow to pink. Moreover, receptor **1c** was found to display a similar, but less remarkable spectral and color change upon addition of $H_2PO_4^-$, which indicated that the introduction of methoxy group into *meso*-phenyl ring of bis(3-indolyl)methene skeleton increased the basicity of the H-bond acceptor site of receptor **1c** to a certain extent.

As expected, the increased affinity and sensitivity towards anions has been achieved by the introduction of electron-withdrawing substituents into the indole ring of the bis(3-indolyl)methene skeleton. Due to the increase in the acidity of indole NH caused by the nitro group, receptor **1d** exhibited selective binding and colorimetric sensing towards F^-, AcO^- and $H_2PO_4^-$ over other anions tested, and AcO^- and $H_2PO_4^-$ induced the same spectral and color changes as F^- did (Fig. **3a**, **S6**). Compared with receptor **1a** whose equilibrium constant was determined in CH_3CN, receptor **1d** gives much higher binding affinity for these anions (see Table **1**).

As shown in (Fig. **3**), upon addition of F^- from 0 to 0.5 equiv, the absorption band at 438 nm of receptor **1d** slightly increased and shifted to 434 nm, which is assigned to the formation of the initial H-bond complex. With further

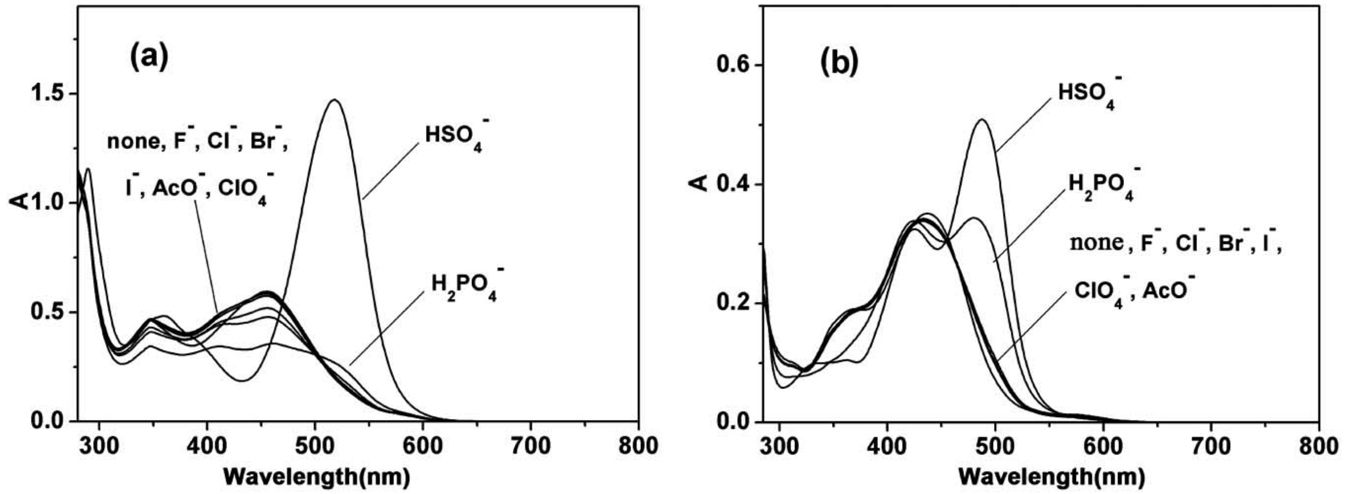

Fig. (2). Changes in UV–vis spectra of **1b** (**a**) and **1c** (**b**) (5×10^{-5} M) recorded in CH_3CN/H_2O (4:1, v/v) after addition of 25 equiv of various anions.

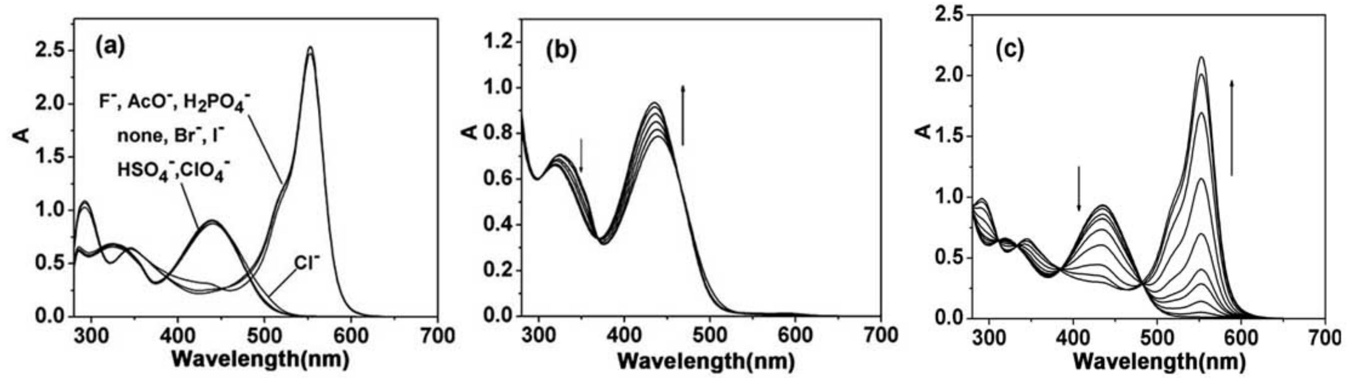

Fig. (3). Changes in UV–vis spectra of **1d** recorded in CH_3CN (5×10^{-5} M) after addition of (**a**) 25 equiv of various anions; (**b**) 0, 0.1, 0.2, 0.3, 0.4, 0.5 equiv of F^-; (**c**) 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.5, 2, 2.5, 3 equiv of F^-.

increasing in F^- concentration, the band at 434 nm decreased gradually along with a new red-shifted band at 552 nm evolving and reaching a maximum upon addition of 3 equiv of F^- (Fig. **3c**), which is ascribed to the internal charge transfer (ICT) process of the deprotonated bis(3-indolyl)methene skeleton. The same deprotonation process of receptor **1d** was also induced by addition of over 0.5 equiv of AcO^- or 1 equiv of $H_2PO_4^-$ anions (Fig. **S7**, **S8**). Moreover, a slight decrease in intensity of the absorption band at 438 nm of receptor **1d** along with a slight red shift was observed after adding an excess of Cl^- (Fig. **S9**), which corresponded to the formation of a hydrogen-bonded complex as a result of the increased acidity of indole NH. The above results show significant differences in anion binding and colorimetric sensing properties between receptor **1d** and receptor **1a** or **1b**. The electron-withdrawing nitro group on indole ring can notably enhance the proton acidity of the indole NH and promote the occurrence of the deprotonation, therefore, the increased affinity and sensitivity towards anions could be expected, but the anion selectivity decreased. On the other hand, the introduction of nitro group into indole unit can decrease the electron density of indole N of the H-bond acceptor site, and in consequence, the sensing sensitivity of receptor **1d** towards H^+ may be decreased in water-containing system. Compared with that of receptor **1a**, a less remarkable spectral change was observed upon addition of HSO_4^- to the CH_3CN/H_2O solution of receptor **1d** (Fig. **S10**), giving a faint color change from yellow to baby pink.

In order to improve the protonation of bis(3-indolyl)methene receptor in water-containing system, the basicity of H-bond acceptor site can be increased. It has been achieved by the introduction of electon-donating substituents into bis(3-indolyl)methene skeleton. The methoxy-bearing derivatives **1c** and **1e** displayed the increased affinity and sensitivity for HSO_4^- and $H_2PO_4^-$ in CH_3CN/H_2O. Compared with receptor **1c** which showed a moderate sensing sensitivity for $H_2PO_4^-$ (Fig. **2b**), receptor **1e** exhibited the almost same spectral and color response for $H_2PO_4^-$ as that for HSO_4^- (Fig. **4a**), due to the distinctly increased basicity of H-bond acceptor site caused by methoxy group in indole ring. On stepwise addition of HSO_4^-, the clear spectral evolution was observed (Fig. **4b**), the absorption band at 434 nm decreased and a new strong absorption band at 498 nm, due to the protonated receptor $[H_2L]^+$, increased gradually and reached its limiting value after addition of about 5 equiv of HSO_4^-. Moreover, the titration process of the HSO_4^- was carried out in mixed CH_3CN/H_2O (1:1, v/v) solution (Fig.

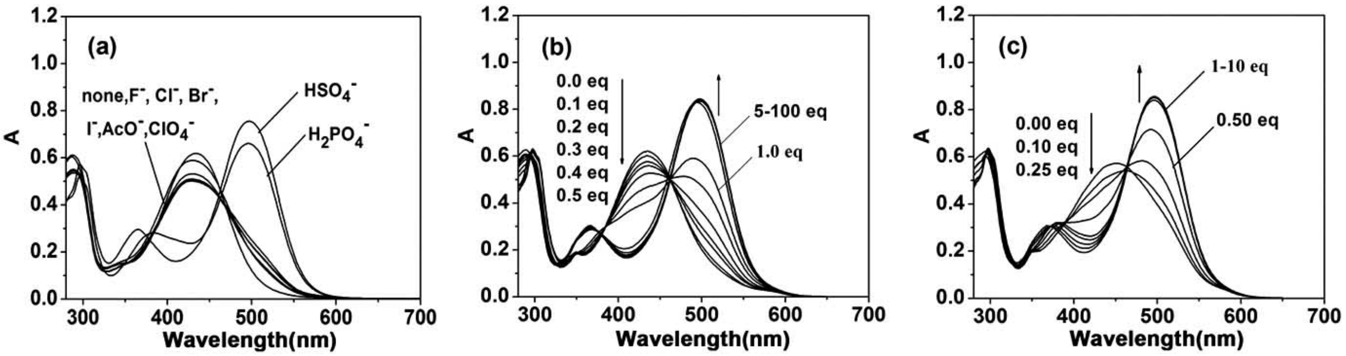

Fig. (4). Changes in UV–vis spectra of **1e** (5×10^{-5} M) after addition of: (**a**) 25 equiv of various anions in CH_3CN/H_2O (4:1, v/v); (**b**) 0-100 equiv of HSO_4^- in CH_3CN/H_2O (4:1, v/v); and (**c**) 0-10 equiv of HSO_4^- in CH_3CN/H_2O (1:1, v/v).

4c), the spectral changes reached its limiting value after addition of about 1 equiv of HSO_4^-. Thus it can be seen that the higher the water content, the more sensitivity, which is related to the ionization degree of the HSO_4^-.

On the other hand, in CH_3CN solution, receptor **1e** displayed selective recognition and colorimetric sensing of F^- over other anions tested (Fig. **S11**), which was completely similar to the case of receptor **1a**. The result indicated that the introduction of electron-donating methoxy groups into indole rings of bis(3-indolyl)methene **1a** has no significant effect on its selectivity and affinity towards anions in CH_3CN.

The deprotonation/protonation of the bis(3-indolyl) methene receptors **1b**-**1e** is also reversible, as described in the case of receptor **1a** [6]. The interaction of receptors **1a**-**1e** with anions in CH_3CN involves the mixed process: initial hydrogen-bonded complex formation at low anion-receptor ratios, then followed by the deprotonation of the indole NH proton in presence of an excess of F^- or AcO^-. The two processes can be described by the following equilibrium (1) and (2) [4a, 8]:

$$LH + X^- \overset{K_a}{\rightleftharpoons} [LH\cdots X]^- \qquad (1)$$

$$[LH\cdots X]^- + X^- \overset{K_d}{\rightleftharpoons} L^- + [HX_2]^- \qquad (2)$$

The equilibrium constants (where K_a and K_d are the association constant and disassociation constant, respectively) of the receptors **1a**-**1e** with anions were evaluated through nonlinear least squares fitting by origin software according to 1:1 stoichiometry [9], and the results are summarized in Table **1**.

A further insight into Table **1** reveals that the highest affinity of receptor **1d** is displayed for F^-, AcO^-, $H_2PO_4^-$ and Cl^-, due to the increase in the acidity of the indole NH proton caused by the electron-withdrawing nitro group on the indole moiety. In addition, the order of the affinity of receptors **1a**-**1e** towards anions is: $F^- > AcO^- > H_2PO_4^- > Cl^- >> Br^-, I^-, HSO_4^-$, and ClO_4^-, which is consistent with their basicity in CH_3CN.

3. EXPERIMENTAL SECTION

General

^{1}H NMR spectra were recorded on a Bruker AV400 instrument at 400 MHz with TMS as an internal standard. ESI-MS measurements were carried out using a Waters ZQ4000 mass spectrometer. IR spectra were measured using a Thermo Nicolet NEXUS TM spectrometer as KBr disks. Melting points were detected on a PHMK 05 micro melting point apparatus and are uncorrected. UV-vis spectra were performed on a PerkinElmer Lamda 35 spectrophotometer

Table 1. Equilibrium Constants [K(M^{-1})] for the Compounds 1a-1e with Various Anions in CH_3CN at 25 °C

Anions	Receptors				
	1a	**1b**	**1c**	**1d**	**1e**
F^-/K_d	$3.40\times10^3\pm180$	$3.04\times10^3\pm296$	$3.80\times10^3\pm567$	$(2.30\pm0.5)\times10^4$	$2.81\times10^3\pm347$
AcO^-/K_d	$7.56\times10^2\pm29$	$1.75\times10^3\pm68$	$5.65\times10^2\pm18$	$(1.43\pm0.5)\times10^4$	$6.14\times10^2\pm25$
$H_2PO_4^-/K_a$	$5.47\times10^2\pm24$	$6.86\times10^2\pm46$	$4.28\times10^2\pm26$	$(8.44\pm1.5)\times10^3$ [b]	$5.31\times10^2\pm17$
Cl^-/K_a	- [a]	-	-	$5.70\times10^2\pm26$	-
Br^-/K_a	-	-	-	-	-
I^-/K_a	-	-	-	-	-
HSO_4^-/K_a	-	-	-	-	-
ClO_4^-/K_a	-	-	-	-	-

[a] the spectral change is little and the affinity constant cannot be determined. [b] The dissociation constant K_d.

(1-cm quartz cell) at room temperature. The tetra-n-butylammonium fluoride was purchased from Fluka, the other tetra-n-butylammonium (Bu_4N^+) salts of different anions were purchased from Alfa Aesar. CH_3CN was used the chromatographically pure.

Experimental Procedure for compounds 2a-2e

Typical to **2a**. $KHSO_4$ (0.17g, 1.25 mmol) was added to a mixture of indole (0.30g, 2.5 mmol) and benzaldehyde (0.13g, 1.25 mmol) in dry methanol (10 mL), and the reaction was stirred for 2 h at room temperature. Then water (10 mL) was added to quench the reaction, and the aqueous phase was extracted with CH_2Cl_2 (3×10 mL). The organic phase was dried with anhydrous $MgSO_4$, and purified by column chromatography and eluted with ethyl acetate and petroleum ether mixture to afford the product **2a** (white solid). Similarly, the compounds **2b**, **2c** and **2e** were synthesized following the above procedure. As for the compound **2d** was prepared under inert atmosphere refluxing for 12h, then the reaction mixture was cooled to room temperature. Precipitate formed was filtered and washed with CH_3OH, then recrystallization with acetone/H_2O.

Compound 2a

Yield=90%. Mp: 128-130 ºC. IR (KBr) 3407, 3054, 1597, 1458, 1417, 1331, 1213, 1088, 1009, 743 cm^{-1}. ^1H NMR (400MHz, DMSO–d_6), (ppm): 10.82 (s, 2H), 7.35 (t, 4H), 7.26 (t, 4H), 7.16 (t, 1H), 7.03 (t, 2H), 6.85 (t, 2H), 6.82 (s, 2H), 5.83 (s, 1H, Ar–CH). MS(ESI): *m/z* 340.1 ($[M+NH_4]^+$).

Compound 2b

Yield=88%. Mp: 232–233 ºC. IR (KBr) 3462, 3423, 3383, 3054, 1589, 1503, 1448, 1338, 1221, 1096, 1009, 743 cm^{-1}. ^1H NMR (400MHz, DMSO–d_6), (ppm): 10.92 (s, 2H), 8.15 (d, 2H), 7.61 (d, 2H), 7.37(d, 2H), 7.29 (d, 2H), 7.06 (t, 2H), 6.90 (s, 2H), 6.89 (t, 2H), 6.03 (s, 1H, Ar–CH). MS(ESI): *m/z* 390.2 ($[M+Na]^+$).

Compound 2c

Yield=40%. Mp: 187-189 ºC.IR (KBr) 3394, 3054, 2946, 2831, 1610, 1509, 1454, 1418, 1335, 1245, 1171, 1093, 1009, 784, 741 cm^{-1} ^1H NMR (400MHz, $CDCl_3$),, (ppm): 7.88 (brs, 2H), 7.35 (m, 4H), 7.24 (s, 2H), 7.15 (t, 2H), 6.99 (t, 2H), 6.80 (d, 2H), 6.63 (d, 2H), 5.82 (s, 1H), 3.76 (s, 3H). MS(ESI): *m/z* 352.1 ($[M+H]^+$).

Compound 2d

Yield=65%. Mp: >300 ºC IR (KBr) 3303, 3026, 2856, 1625, 1509, 1476, 1319, 1091, 740 cm^{-1}. ^1H NMR (400MHz, DMSO–d_6), (ppm): 11.66 (s, 2H), 8.30 (d, 2H), 7.95 (dd, 2H), 7.53 (d, 2H), 7.39 (d, 1H), 7.31 (t, 2H), 7.21 (t, 2H), 7.12 (s, 2H), 6.19 (s, 1H, Ar–CH). HRMS (ESI) *m/z* ($[M+NH_4]^+$) calcd for $C_{23}H_{16}N_4O_4$: 430.1510; found, 430.1509.

Compound 2e

Yield=89%. Mp: 215-217 ºC. IR (KBr) 3389, 3310, 2934, 2824, 1623, 1577, 1482, 1443, 1280, 1208, 1168, 1019, 925, 807, 721. ^1H NMR (400MHz, DMSO–d_6), (ppm): 10.66(s, 2H), 7.35(d, 2H), 7.27(d, 2H), 7.22(d, 2H), 7.16(t, 1H), 6.81(d, 2H), 6.72(d, 2H), 6.68(dd, 2H), 5.73(s, 1H), 3.58(s, 6H). MS(ESI): *m/z* 381.4 ($[M-H]^-$).

Experimental Procedure for Compounds 1a-1e

Typical to **1a**. Compound **2a** (0.17 g, 0.5 mmol) was dissolved in acetonitrile (8 mL), DDQ (0.14 g, 0.6 mmol) solution of acetonitrile was dropwise and slowly added to the solution. This reaction was allowed for 30 min and given the dark red precipitate, which was filtered, washed with CH_3CN, and recrystallized from mixed ethanol/water solution. Similarly, the compounds **1b, 1c** and **1e** were synthesized following the above procedure, as for the compound **1d** was prepared in acetone solvent.

Compound 1a

Yield=37%. Mp: 242-243 ºC. IR (KBr) 3384, 3108, 3058, 2792, 2546, 2201, 1956, 1583, 1520, 1481, 1409, 1240, 1176, 1122, 996, 833, 747. ^1H NMR (400MHz, DMSO–d_6), (ppm): 8.33 (s, 2H), 7.74 (t, 1H), 7.60 (m, 6H), 7.27 (t, 2H), 7.00 (t, 2H), 6.65 (d, 2H). HRMS (ESI) *m/z* ($[M+H]^+$) calcd for $C_{23}H_{16}N_2$: 321.1386; found, 321.1383.

Compound 1b

Yield=25%. Mp > 300 ºC. IR (KBr) 3384, 3236, 3110, 3069, 2974, 2925, 2593, 2201, 1942, 1582, 1523, 1478, 1408, 1347, 1239, 1172, 1116, 998, 823, 760. ^1H NMR (400MHz, DMSO–d_6), (ppm): 10.92 (s, 1H), 8.43 (d, 2H), 8.31 (d, 2H), 7.82 (d, 2H), 7.60 (d,2H), 7.28 (t, 2H), 7.00 (t, 2H), 6.67 (d, 2H). MS(ESI): *m/z* 366.2 ($[M+H]^+$).

Compound 1c

Yield=45%. Mp: 232-234 ºC. IR (KBr) 3416, 3110, 2540, 2199, 1604, 1508, 1479, 1408, 1370, 1173, 1122, 1025, 996, 891, 810, 753. ^1H NMR (400MHz, DMSO–d_6), (ppm): 8.27 (s, 2H), 7.61 (d, 2H), 7.55 (d, 2H), 7.28 (t, 2H), 7.18 (d, 2H), 7.06 (t, 2H), 6.80 (d, 2H), 3.92 (s, 3H). MS(ESI): *m/z* 351.3 ($[M+H]^+$).

Compound 1d

Yield=35%. Mp > 300 ºC. IR (KBr) 3097, 3049, 2552, 2205, 1966, 1623, 1588, 1536, 1475, 1444, 1398, 1336, 1272, 1241, 1174, 1105, 994, 888, 829, 760. ^1H NMR (400MHz, DMSO–d_6), (ppm): 8.34(d,1H), 7.98(d,2H), 7.56(d,2H), 7.47(d,2H), 7.37(t,2H), 7.29(t,2H), 6.94(s,2H). HRMS (ESI) *m/z* ($[M+H]^+$) calcd for $C_{23}H_{14}N_4O_4$: 411.1088; found, 411.1081.

Compound 1e

Yield=32%. Mp: 239-241 ºC. IR (KBr) 3423, 3104, 3049, 2986, 2929, 2827, 2546, 2198, 1968, 1591, 1525, 1459, 1404, 1365, 1334, 1285, 1223, 1181, 1112, 1031, 993, 835, 754. ^1H NMR (400MHz, DMSO–d_6), (ppm): 8.34(s, 2H), 7.77(t, 1H), 7.66(t, 2H), 7.58(d, 2H), 7.52(d, 2H), 6.92(dd, 2H), 6.06(s, 2H), 3.41(s, 6H). HRMS (ESI) *m/z* ($[M+H]^+$) calcd for $C_{25}H_{20}N_2O_2$: 381.1598; found, 381.1594.

CONCLUSION

In this work, several of nitro- or methoxy-substituted bis(3-indolyl)methene derivatives were synthesized, and the derivatives show significant differences in anion binding and colorimetric sensing properties. The electron-withdrawing or electron-donating group at the para position of *meso*-phenyl ring have no significant effect on its selectivity and affinity towards anions in CH_3CN. However, the presence of electron-withdrawing nitro groups in indole rings of the bis(3-indolyl)methene skeleton can notably enhance the anion binding affinity and sensing sensitivity due to the increased acidity of the H-bond donor moiety, and the nitro-bearing receptor displays indistinguishable spectra and color response towards F^-, AcO^- and $H_2PO_4^-$ in CH_3CN. Moreover, the introduction of electron-donating methoxy groups into bis(3-indolyl)methene skeleton can increase the basicity of H-bond acceptor moiety and enhanced the sensitivity for H^+ in water-containing system. The anion-induced deprotonation/protonation of the H-bond donor/acceptor moiety modulates the internal charge transfer state of the bis(3-indolyl)methene skeleton and gives rise to the dramatic color and spectral changes.

ACKNOWLEDGEMENT

This work was supported by the National Natural Science Foundation of China (Grant No. 20672121).

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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