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Nitro-substituted 3,3′-bis(indolyl)methane derivatives as anion receptors: Electron-withdrawing effect and tunability of anion binding properties

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ABSTRACT

A series of nitro-substituted 3,3′-bis-indolyl phenylmethane derivatives were synthesized and their anion binding properties were investigated in detail. The introduction of the electron-withdrawing nitro group into indole unit and/or *meso*-phenyl ring, which leads to the increased acidity of indole NH and *meso*-position CH proton, has a positive effect on anion binding. The nitro-substituted bis(indolyl)methane receptors exhibited selective colorimetric sensing of F^- anion, as revealed by the notable color and spectral changes, rationally due to the deprotonation of the indole NH of the receptor. Meanwhile, the additive introduction of the nitro substituents on the *meso*-phenyl ring of bis(indolyl)methane can lead to the deprotonation of the *meso*-position CH and further induce an irreversible oxidation process obtaining bis(indolyl)methene product in the F^- anion sensing system.

1. Introduction

The binding and detection of anionic substrates by artificial receptors is currently an area of significant interest because they play a fundamental and important role in chemical and biological processes [1–5]. The neutral anion receptors containing urea [6–10], thiourea [11–14], amide [15–17], phenol [18–20], pyrrole moieties [21–23] and so on, which can provide one or more hydrogen bond donor sites for selective binding anions, have been widely reported. In the last years, indoles, as an important class of building blocks based on hydrogen bond donor, have been integrated into a variety of anion receptor and sensor frameworks as either functionalized indoles, biindoles or indolocarbazoles [24–33], which exhibit high binding affinities and selectivities for specific anionic guests [34–36].

The conjugated bis(indolyl)methene receptor for the colorimetric detection of either F^- in aprotic solvent or HSO_4^- in water-containing medium was previously used in our lab [37], and the reversible deprotonation/protonation of receptor induced the changes in color and absorption spectra. Practically, the precursor bis(indolyl)methanes, containing 2- and 3-linked indole groups, can also act as molecular receptors for selective binding anions through hydrogen bond interactions, which have been studied by Ito and coworkers using ^1H NMR titration techniques [38]. Generally, under the spectrophotometric titration concentration condition, the simple 3,3′-bis(indolyl)methane receptors were shown to bind anions, including more basic F^-, AcO^-, $H_2PO_4^-$ anions with very weak responses in the absorption spectra, which indicated the lower affinity of the indole NH as the hydrogen bond donor for anions. Thus improving anion binding and sensing ability of bis(indolyl)methane-based receptor is strongly desired. A simple and familiar approach is to introduce the electron-withdrawing group into the 3,3′-bis(indolyl)methane skeleton, which leads to an increased acidity of indole NH or *meso*-position CH. As a result, we found that the introduction of the nitro group has a positive effect on anion binding behavior of 3,3′-bis(indolyl)methane, and the nitro derivatives were found to exhibit selective colorimetric sensing of F^- anion, due to deprotonation of the indole NH and/or *meso*-position CH, as well as the formation of bis(indolyl)thene product. Herein, we would like to present our studies on the anion binding properties of the nitro-substituted 3,3′-bis(indolyl)methane receptors.

2. Experimental

2.1. Materials and methods

All reagents for synthesis were obtained commercially and used without further purification. The tetra-n-butylammonium fluo-

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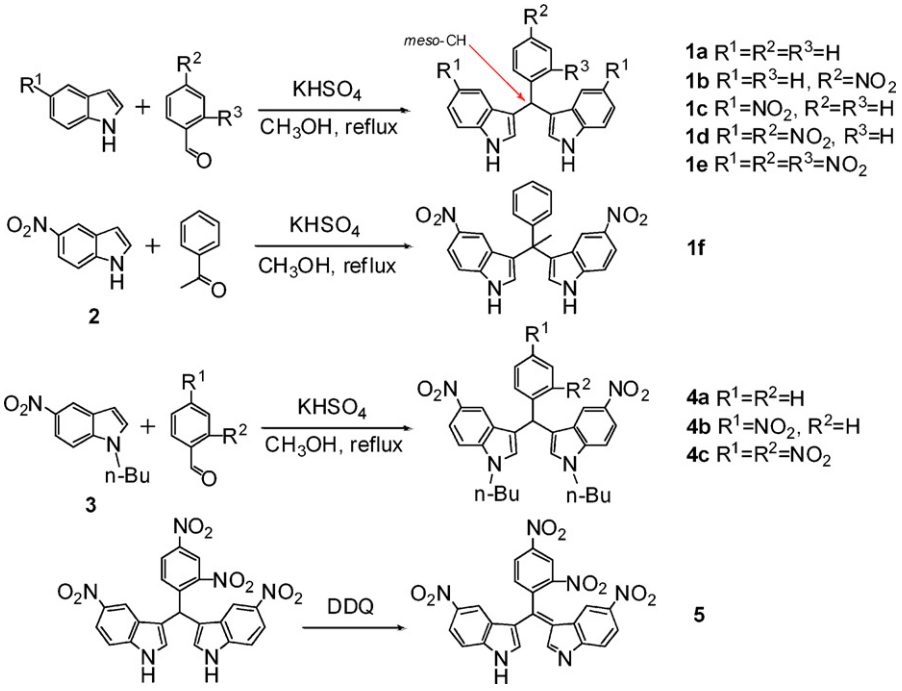


Scheme 1. Synthesis and molecular structures of compounds **1**–**5**.

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

2.2. General experimental procedure for the synthesis of the receptors *1–5*

2.2.1. Synthesis of the 3,3′-bis(indolyl)methane compounds *1a–1f*

Typical to **1a**, compounds **1a** were prepared according to a literature method [39–41]. $KHSO_4$ (0.17 g, 1.25 mmol) was added to a mixture of indole (0.30 g, 2.5 mmol) and benzaldehyde (0.13 g, 1.25 mmol) in dry methanol (10 mL), and the reaction was stirred at room temperature for 2 h. 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 (white solid). Similarly, the compounds **1b** were synthesized following the above procedure [40]. The compounds **1c**–**1f** were prepared under inert atmosphere refluxing for 12 h, and then the reaction mixture was cooled to room temperature. Precipitate formed was filtered and washed with CH_3OH, then recrystallization with acetone/H_2O. Moreover, the compound **1e** was obtained by the silica column chromatograph (EtOAc/petroleum ether (bp 60–90 °C), 2:1 v/v) (see Scheme 1).

*2.2.1.1. Compound **1a**.* Yield = 90%. mp: 128–130 °C. IR (KBr) 3407, 3054, 1597, 1458, 1417, 1331, 1213, 1088, 1009, 743 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 10.82 (s, 2H), 7.35 (dd, 4H, J = 5.6, 7.6), 7.26 (td, 4H, J = 8, 8), 7.16 (t, 1H, J = 7.2), 7.03 (t, 2H, J = 7.2), 6.85 (t, 2H, J = 7.2), 6.82 (s, 2H), 5.83 (s, 1H, Ar–CH). MS(ESI): m/z 340.1 ($[M + NH_4]^+$).

*2.2.1.2. Compound **1b**.* Yield = 88%. mp: 232–233 °C. IR (KBr) 3462, 3423, 3383, 3054, 1589, 1503, 1448, 1338, 1221, 1096, 1009, 743 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 10.92 (s, 2H), 8.15 (d, 2H, J = 8.8), 7.61 (d, 2H, J = 8.8), 7.37(d, 2H, J = 8.4), 7.29 (d, 2H, J = 8), 7.06 (t, 2H, J = 7.2), 6.90 (s, 2H), 6.89 (t, 2H, J = 7.6), 6.03 (s, 1H, Ar–CH). MS(ESI): m/z 390.2 ($[M + Na]^+$).

*2.2.1.3. Compound **1c**.* Yield = 65%. mp: >300 °C. IR (KBr) 3303, 3026, 2856, 1625, 1509, 1476, 1319, 1091, 740 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 11.66 (s, 2H), 8.30 (d, 2H, J = 2.4), 7.95 (dd, 2H, J = 2.4, 2), 7.53 (d, 2H, J = 9.2), 7.39 (d, 1H, J = 7.2), 7.31 (t, 2H, J = 7.6), 7.21 (t, 2H, J = 7.6), 7.12 (s, 2H), 6.19 (s, 1H, Ar–CH). ^{13}C NMR δ: 143.80, 140.25, 139.85, 128.54, 127.66, 126.48, 125.80, 120.56, 116.71, 112.15, 38.51. HRMS (ESI) m/z ($[M + NH_4]^+$) calcd. for $C_{23}H_{16}N_4O_4$: 430.1510; found, 430.1509.

*2.2.1.4. Compound **1d**.* Yield = 45%. mp: 287–289 °C. IR (KBr) 3292, 3101, 2846, 1629, 1513, 1480, 1327, 1092, 740 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 11.78(s, 2H), 8.38 (d, 2H, J = 2), 8.20 (d, 2H, J = 8.8), 7.99 (dd, 2H, J = 2, 2.4), 7.66 (d, 2H, J = 8.8), 7.56 (d, 2H, J = 8.8), 7.22 (s, 2H), 6.48 (s, 1H, Ar–CH). MS(ESI): m/z 456.5 ($[M–H]^-$).

*2.2.1.5. Compound **1e**.* Yield = 62%. mp: 191–192 °C. IR (KBr) 3403, 3093, 1629, 1522, 1475, 1335, 1091, 736 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 11.84 (s, 2H), 8.80 (d, 1H, J = 2.4), 8.41 (dd, 1H, J = 2.4, 2.4), 8.34 (d, 2H, J = 2), 8.00 (dd, 2H, J = 2.4, 2.4), 7.57 (d, 3H, J = 9.2), 7.19 (s, 2H), 6.78 (s, 1H, Ar–CH). ^{13}C NMR δ: 148.77, 146.36, 143.40, 140.55, 139.82, 139.65, 131.98, 128.60, 128.43, 127.36, 125.38, 120.14, 117.54, 116.99, 115.88, 112.32, 34.18. HRMS (ESI) m/z ($[M + NH_4]^+$) calcd. for $C_{23}H_{14}N_6O_8$: 520.1211; found, 520.1216.

*2.2.1.6. Compound **1f**.* Yield = 42%. mp: 292–293 °C. IR (KBr) 3326, 2988, 2949, 1623, 1513, 1466, 1318, 1066, 744 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 11.73(s, 2H), 7.93 (dd, 2H, J = 2.4, 2), 7.89 (s, 2H), 7.56 (d, 2H, J = 9.2), 7.33 (d, 4H, J = 4.4), 7.26 (m, 1H), 7.18 (s, 2H), 2.31(s, 3H). ^{13}C NMR δ: 146.92, 140.29, 139.87, 128.09, 127.42, 126.32, 125.10, 124.85, 117.33, 116.27, 112.30, 42.99, 29.81. HRMS (ESI) m/z ($[M+Na]^+$) calcd. for $C_{24}H_{18}N_4O_4$: 449.1220; found, 449.1213.

*2.2.2. Synthesis of the 3,3′-bis(indolyl)methane compounds **4a**–**4c***

Compound **3** was synthesized according to the literature method [42,43], which was used directly in next step.

Typical to **4a**, N-(n-butyl)-5-nitroindole (0.44 g, 2 mmol) was dissolved in 10 mL CH_3OH. To this solution was added phenzaldehyde (0.10 g, 1 mmol), then $KHSO_4$ (0.14 g, 1 mmol) was added and stirred under inert atmosphere refluxing for 12 h. Then the reaction mixture was cooled to room temperature. Precipitate formed was filtered and washed with CH_3OH, then recrystallized from acetone/H_2O and gained 0.26 g. Similarly, the compounds **4b** were synthesized following the above procedure. The compound **4c** was obtained by the silica column chromatograph (EtOAc–petroleum ether (bp 60–90 °C), 1:3, v/v) (see Scheme 1).

*2.2.2.1. Compound **4a**.* Yield = 49%. mp: 148–150 °C. IR (KBr) 3406, 3120, 3061, 2951, 2929, 2871, 1608, 1579, 1512, 1483, 1446, 1402, 1329, 1102, 1058, 896, 742 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 8.31 (s, 2H), 8.00 (dd, 2H, J = 2.4, 2.4), 7.67 (d, 2H, J = 9.2), 7.42 (d, 2H, J = 7.2), 7.35 (t, 2H, J = 7.6), 7.25 (t, 1H, J = 7.2), 7.19 (s, 2H), 6.21 (s, 1H, Ar-CH), 4.20 (m, 4H), 1.68 (m, 4H), 1.17 (m, 4H), 0.82 (t, 6H, J = 7.2). ^{13}C NMR δ: 143.29, 140.13, 139.24, 130.82, 128.50, 128.15, 126.48, 125.98, 119.90, 116.52, 110.54, 45.59, 38.49, 31.82, 19.32, 13.39. HRMS (ESI) m/z ($[M+NH_4]^+$) calcd. for $C_{31}H_{32}N_4O_4$: 542.2762; found, 542.2758.

*2.2.2.2. Compound **4b**.* Yield = 55%. mp: 181–182 °C. IR (KBr) 3435, 3106, 3066, 2957, 2917, 2863, 1615, 1513, 1482, 1450, 1324, 1191, 1098, 1058, 902, 807, 736 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 8.34 (d, 2H, J = 2), 8.22 (d, 2H, J = 8.8), 8.00 (dd, 2H, J = 2.4, 2.4), 7.69 (d, 2H, J = 9.2), 7.65 (d, 2H, J = 8.8), 7.25 (s, 2H), 6.46 (s, 1H, Ar–CH), 4.19 (m, 4H), 1.68 (m, 4H), 1.15 (m, 4H), 0.80 (t, 6H, J = 7.2). ^{13}C NMR δ: 151.28, 146.20, 140.28, 139.21, 131.17, 129.40, 125.80, 123.84, 118.64, 116.69, 116.31, 110.67, 45.66, 38.02, 31.79, 19.31, 13.38. HRMS (ESI) m/z ($[M+NH_4]^+$) calcd. for $C_{31}H_{31}N_5O_6$: 587.2613; found, 587.2609.

*2.2.2.3. Compound **4c**.* Yield = 60%. mp: 172–174 °C. IR (KBr) 3439, 3097, 2962, 2930, 2874, 1600, 1509, 1330, 1102, 739 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6), (ppm): 8.81 (d, 1H, J = 2.4), 8.46 (dd, 1H, J = 2.4, 2.4), 8.30 (d, 2H, J = 2), 8.01 (dd, 2H, J = 2, 2.4), 7.70 (d, 2H, J = 8.8), 7.57 (d, 1H, J = 8.8), 7.26 (s, 2H), 6.79 (s, 1H, Ar–CH), 4.19 (m, 4H), 1.68 (m, 4H), 1.15 (m, 4H), 0.80 (t, 6H, J = 7.2). ^{13}C NMR δ: 148.88, 146.49, 143.02, 140.52, 139.36, 131.99, 127.49, 125.67, 120.24, 116.88, 110.86, 45.74, 34.39, 31.76, 19.29, 13.42. HRMS (ESI) m/z ($[M+NH_4]^+$) calcd. for $C_{31}H_{30}N_6O_8$: 632.2463; found, 632.2459.

*2.2.3. Synthesis of the 3,3′-bis(indolyl)methene compound **5***

Compound **1e** (0.25 g, 0.5 mmol) was dissolved in acetone (10 mL), a solution of DDQ (0.11 g, 0.5 mmol) in acetone was dropwise and slowly added to the solution. This reaction was allowed for 3 h and gave a dark red precipitate, which was filtered, washed with acetone and gained 0.12 g.

Yield = 48%. mp: (>300 °C). IR (KBr): 3416, 3098, 2217, 1534, 1439, 1395, 1343, 1270, 1189, 1108, 1050, 830, 734 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ: 11.82 (s, 1H, NH), 8.63 (s, 1H), 8.37 (d, 2H, J = 2), 8.31 (dd, 1H, J = 2, 2), 8.01 (dd, 2H, J = 2, 2), 7.59 (d, 3H, J = 8.8), 7.04 (s, 2H). ^{13}C NMR δ: 179.98, 172.00, 150.64, 149.26, 146.82, 144.03, 140.47, 139.94, 136.67, 133.59, 131.51, 129.03, 128.80, 124.93, 121.90, 119.24, 117.90, 116.78, 113.59, 112.31, 101.65. HRMS (ESI) m/z ($[M+H]^+$) calcd. for $C_{23}H_{12}N_6O_8$: 501.0789; found, 501.0797.

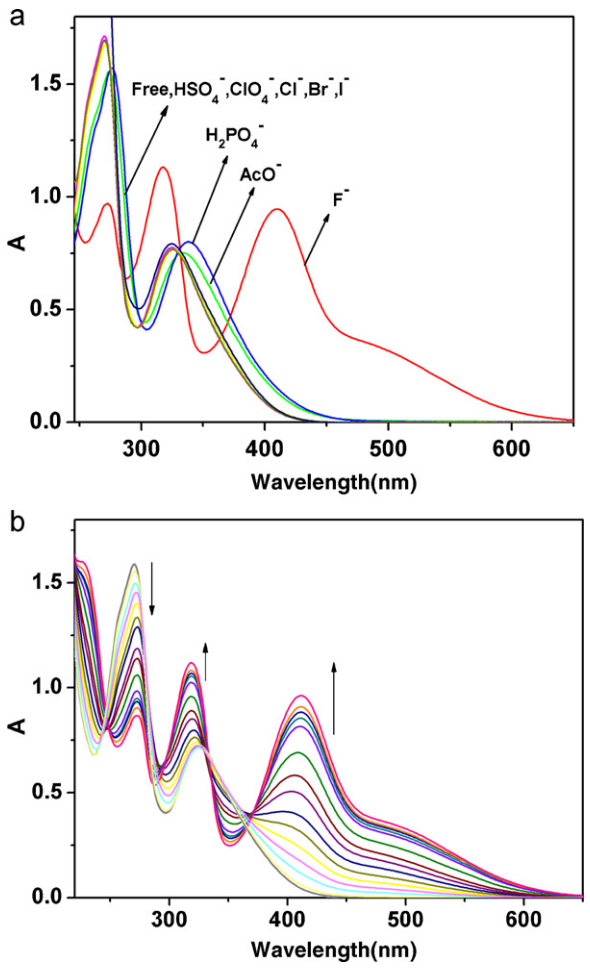


Fig. 1. Changes in UV–vis spectra of **1c** recorded in CH_3CN (5×10^{-5} M) after addition of (a) 100 equiv of various anions and (b) 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 25, 30, 40, 60, 80 and 100 equiv of F^-.

3. Results and discussion

The anion binding and sensing properties of these bis(indolyl)methanes have been studied by using UV–vis spectroscopic techniques. As above-mentioned, in the presence of 100 equiv of various anions tested (F^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, Cl^-, Br^-, and I^-, as their tetrabutylammonium salts) in CH_3CN, the simple model compound **1a** showed negligible responses in the absorption spectra. Similar results were also observed in the case of compound **1b** (see Fig. S1), which indicates that only introduction of a nitro group into the *meso*-phenyl ring of the 3,3′-bis(indolyl)methane **1a** failed to improve the affinity of indole NH as hydrogen bond donor sites for anions.

Differently, the introduction of the electron-withdrawing nitro group into indole unit of the 3,3′-bis(indolyl)methane has a positive effect on anion binding. The UV–vis spectrum of receptor **1c** in CH_3CN (5×10^{-5} M) exhibits two strong absorption bands at 270 nm and 325 nm, which are assigned to π–π^* transitions of the nitroindole moiety. The results of titration experiments carried out by using the above-mentioned set of anions, as shown in Fig. 1a, indicated that only F^- anion gave rise to a remarkable spectral

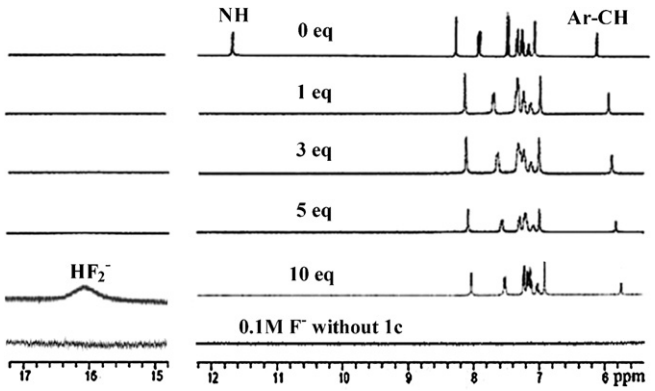


Fig. 2. Partial ^{1}H NMR titration spectra of **1c** (10^{-2} M) with F^- from 0 to 10 equiv and F^- alone (bottom) (DMSO-d_6 400 MHz).

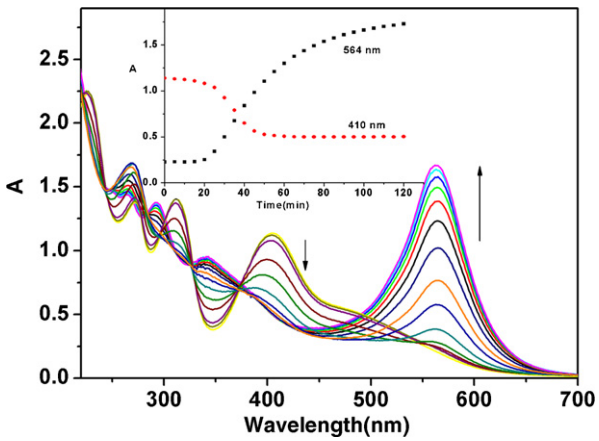


Fig. 3. Spectral changes of the interaction system of **1e** (5×10^{-5} M) and 100 equiv of F^- during 20–120 min. Inset: the spectral intensity changes observed at 410 nm and 564 nm.

change with the effect that the solution instantaneously changed color from colorless to orange-yellow (Fig. S2), which allow the potential for "naked eye" detection. As for AcO^- and $H_2PO_4^-$, only slight bathochromic shifts of the band at 325 nm were observed as a result of the formation of hydrogen-bonding complex, and the other anions tested induced the negligible responses. On stepwise addition of F^- anion to the solution of **1c**, the clear spectral evolution was observed (Fig. 1b). With increasing concentration of F^-, the absorption band at 270 nm decreased and the absorption band at 325 nm increased gradually along with a slight blue shift, at the same time, a new strong absorption band at 410 nm and less strong shoulder peak at 500 nm continuously increases in intensity, which was responsible for the solution color change.

Titration with the strong base $[Me_4N]OH$ (tetramethylammonium hydroxide), which definitely leads to deprotonation, also induced the same color and spectral changes of **1c** as those observed with F^- anions (Fig. S3). The new absorption band that develops at 410 nm pertains to the negative charge delocalization of the deprotonated nitroindole moiety, which was also further confirmed by Bronsted acid-base reaction of compound **2** (5-nitroindole) with $[Me_4N]OH$ (Fig. S4), whereas, no obvious shoulder peak at 500 nm was observed in the case of compound **2**. On the other hand, the interaction of compound **1f** and F^- showed a completely similar color and spectral changes process to the case of **1c** (Fig. S5). The control experiment result suggests that the formation of the absorption between 450 and 600 nm region does not result from either the deprotonation of the *meso*-position CH of **1c** or further partial oxidation of **1c** to respective bis(indolyl)methene.

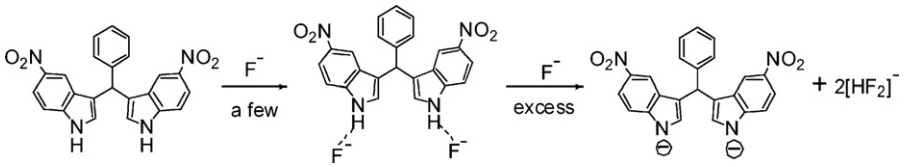
The interaction of receptor **1c** with F^- was carried out by using ^{1}H NMR titration experiments in DMSO-d_6, and the results of the stepwise addition of F^- anion to a solution of receptor **1c** were shown in Fig. 2. The signal of indole NH proton, which in the free receptor appears at δ 11.64 ppm, disappeared on addition of 1 equiv of F^-. The signal of $[HF_2]^-$ at 16.1 ppm was obtained after addition of 10 equiv of F^-, which was consistent with the other group reported [44–47]. The observations reveal that F^- anion induced the deprotonation of the indole NH proton, which increases the electron density of the indole unit, thus causing a shielding effect. Correspondingly, the proton signals of indole ring and *meso*-position CH underwent slight upfield shifts with increasing the concentration of F^-. However, the NMR titration experiments mainly reveal the interaction of the host/guest under the high concentration condition, and merely act as aids in proof to explain the phenomenon of the UV–vis spectra [12].

Above results suggested that the interaction between receptor **1c** and F^- anion involves mixed processes: initial hydrogen-bonded complex formation at low anion-to-receptor ratios, this then being followed by the deprotonation of the indole NH of receptor **1c** in the presence of an excess of fluoride anion, the above two processes can be shown in Scheme 2. Further experiment indicated that the F^--induced deprotonation process of **1c** is fully reversible, as indicated by the fact that on progressive addition of water (Fig. S6), the orange-yellow CH_3CN solution turns colorless and the absorption spectra almost exactly coincided with the spectrum of receptor **1c**.

Next, the anion binding and sensing properties of nitro-substituted 3,3′-bis(indolyl)methane derivatives **1d** and **1e**, bearing mono- or di-nitro substituents on the *meso*-phenyl ring, were studied. The receptors also exhibited selective binding towards F^- over other anions tested in CH_3CN and DMSO. The spectral and color changes from colorless to orange-yellow are completely similar to the case of receptor **1c** (Figs. S7 and S8), meanwhile, the processes can be fully reversed by addition of water. Nevertheless, it is noteworthy that the sensing system of **1d** or **1e** is unstable, as revealed by the succeeding changes in color and absorption spectra. Fig. 3 showed dynamic spectral changes of the sensing system of **1e** with the time, the absorption band at 410 nm and the shoulder peak at 500 nm began to decrease after standing about 25 min, while a new absorption band appeared at 564 nm along with the increase in intensity, and this process reached the stable state within 120 min, with the effect that the solution changed color from orange-yellow to purple-red. A similar, but slower process could also be observed in the sensing system of **1d**.

The reversibility of the process was examined by adding an excess of water to the system of **1e**, in result, the absorption spectrum cannot revert to the original spectrum of **1e** (Fig. 4). Interestingly, the formed spectral profile with a strong absorption band at 455 nm mainly coincided with that of the bis(indolyl)methene compound **5**, an oxidation product of **1e**. Control experiment showed that addition of F^- to compound **5** in CH_3CN caused the same absorption band at 564 nm, due to the deprotonation of **5**, and the deprotonation process is also fully reversible. The results indicated that, in the sensing system of **1e**, a further irreversible oxidation process occurred, which resulted in the formation of corresponding bis(indolyl)methene product.

As control experiments, the interaction of the compound **4a–c** with various anions was also studied by using UV–vis spectroscopic techniques. Addition of 100 equiv of the above-mentioned set of anions to the solution of **4a–c** (5×10^{-5} M) in CH_3CN, compound **4a** could not give any response in absorption spectra and compound **4b** has a low energy spectra change at 500 nm only to F^- (Fig. S9). Nevertheless, compound **4c** showed the appearance of a new and strong absorption band at 500 nm in the presence of F^- (Fig. 5), which should be assigned to n–π^* electron transitions of 3,3′-bis(indolyl)methane skeleton as a result of the formation of the



Scheme 2. The probable deprotonation process of receptor **1c** with F^-.

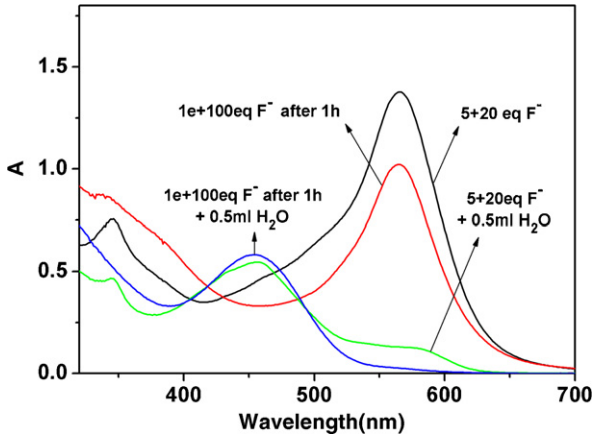


Fig. 4. UV–vis spectra of **1e** and **5** recorded in CH_3CN (5×10^{-5} M) induced by addition of F^- and 0.5 mL H_2O.

meso-position carbanion induced by F^-, and the solution instantaneously changed color from colorless to purple-red. Compared to compounds **4a** and **4b**, the acidity of the *meso*-position CH proton of compound **4c**, with dinitro substituents on the *meso*-phenyl ring, is markedly enhanced and the *meso*-position CH proton is easy to be deprotonated by F^-, which can act as the binding site of chemosensor for selective sensing of F^- by the single CH proton based on proton transfer process.

The observation on control experiments of compounds **4a–c** suggested that the introduction of the electron-withdrawing nitro groups into the *meso*-phenyl ring can effectively enhance the acidity of the *meso*-position CH proton of the 3,3′-bis(indolyl)methane. Compared with receptor **1c**, in the F^- sensing system of receptor **1e** and **1d**, the *meso*-position CH proton acidity of the receptor can be further increased, which potentially resulted in a further free radical oxidation process induced by the traces of oxygen [48].

The equilibrium constants (or proton-dissociation constants) of receptors **1c–e** with F^- were evaluated using the Benesi–Hildebrand equation by origin software [49]. The plot of

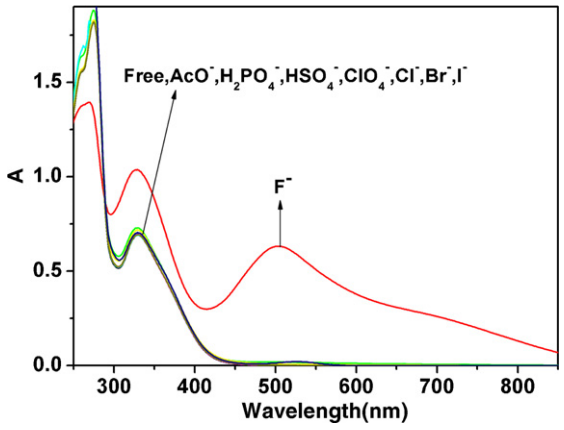


Fig. 5. Changes in UV–vis spectra of **4c** recorded in CH_3CN (5×10^{-5} M) after addition of 100 equiv of various anions.

$1/(A - A_0)$ against $1/[F^-]^2$ shows a liner relationship (Fig. S10), indicating that the stoichiometric ratio of the host/guest is 1:2, which confirmed the speculation of Scheme 2. The equilibrium constants of receptors with F^- were calculated to be $4.85 \times 10^5\ M^{-2}$ for **1c**, $9.94 \times 10^5\ M^{-2}$ for **1d**, $1.32 \times 10^6\ M^{-2}$ for **1e**, respectively. The results shows that the introduction of nitro group into *meso*-phenyl enhance the affinity of the receptors for F^-.

4. Conclusions

We herein described the anions binding properties of a series of nitro-substituted 3,3′-bis(indolyl)methane derivatives. By introducing the electron-withdrawing nitro group into the indole units and *meso*-phenyl ring of 3,3′-bis(indolyl)methane skeleton that recognizes anions through hydrogen bonding, we have realized a complete selectivity in colorimetric sensing of F^- anion in comparison with other anions tested. The sensing selectivity is mainly attributed to the deprotonation of the indole NH units. The nitro substituents on the *meso*-phenyl ring of bis(indolyl)methane enhanced the *meso*-position CH proton acidity of the receptor, which maybe induced an irreversible oxidation process obtaining bis(indolyl)methene product in the F^- anion sensing system.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.12.004.

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