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PAPER

Highly selective colorimetric sensing of cyanide based on formation of dipyrrin adducts†

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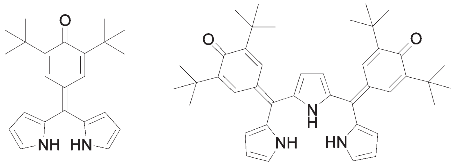
Cyanide sensing has attracted increasing interest due to its toxicity and wide use in industrial activities. Herein, we developed three colorimetric cyanide sensors by the modification of the α-position of a dipyrrin chromophore with various carbonyl groups, namely, C_6F_5CO, C_6H_5CO and CHO for **1**, **2** and **3**, respectively. In dichloromethane, these sensors respond to both CN^- and F^- with distinct colour changes. UV-Vis, ^1H NMR and HRMS measurements imply a two-process interaction between the sensors and CN^-. Initially, CN^- forms a hydrogen bond with the NH moiety, and then it attacks the carbonyl group of the sensors *via* a nucleophilic addition reaction. In contrast, in aqueous systems, only cyanide induced vivid solution colour changes from light yellow to pink *via* nucleophilic addition reactions. The CN^- detection limits reach a micromolar level of 3.6×10^{-6} M, 4.2×10^{-6} M and 7.1×10^{-6} M for **1**, **2** and **3**, respectively. In view of the easy synthesis and the highly selective recognition of CN^- with vivid colour changes, **1–3** may be developed as a novel and promising prototype of selective and sensitive colorimetric cyanide sensors.

Introduction

Development of anion sensors is of great interest in supramolecular chemistry due to their chemical and biological importance.[1] Among various anions, cyanide is known to be extremely toxic to living organisms.[2] It has been reported that 0.5–3.5 mg of cyanide in per kg of body weight is lethal for human beings.[3] Nevertheless, cyanide is still widely used in gold mining, electroplating, plastics production, and other industrial activities,[4] therefore, accidental release of cyanide into the environment happens occasionally. Thus, cyanide sensing has attracted increasing interest from the areas of chemical and environmental sciences. Recently, some cyanide sensors have been reported for applications in aqueous solutions and biological systems.[5]

Among various sensing strategies, optical sensors that are based on colour or fluorescence changes have been greatly developed in the past decade due to their convenient synthesis and rapid implementation.[6] In particular, colorimetric sensors that can selectively recognize anion species through visible colour changes are widely used owing to their convenient utilization, low cost and no equipment requirements.[7] In spite of this, the number of colorimetric cyanide sensors is still rather limited compared with those for many other anions.[8] Furthermore, many of the reported cyanide sensors cannot be applied in aqueous media or suffer from disturbance by anions such as F^- and AcO^-. Therefore, it is desirable to develop more practical sensors that show high selectivity and sensitivity to CN^- in aqueous systems.

Dipyrrins, well known for their boron complexes as BODIPY dyes,[9] are dipyrrolic compounds which were first popularized by Fischer and Orth.[10] Research on dipyrrins mainly focuses on their metal and boron complexes due to their interesting luminescent and coordination properties,[9,11] whereas the use of dipyrrins as cation or anion sensors has not attracted much attention.[11b] In this respect, we designed and synthesized di- and tripyrrins that selectively bind Zn^{2+} in both DMF and aqueous solutions with a "turn on" type fluorescence and tunable emission colours.[12] On the other hand, the NH moiety in dipyrrins may be utilized to bind anions.[13] In this respect, we have reported two acyclic oligopyrrole–hemiquinone compounds (Scheme 1) for selective binding of fluoride anions.[14]



Scheme 1 Chemical structures of the oligopyrrole–hemiquinone compounds utilized for fluoride sensing.

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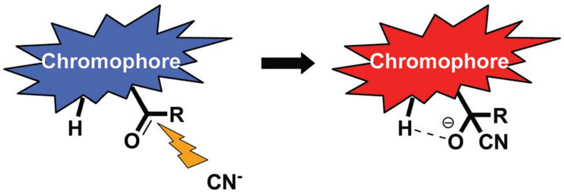
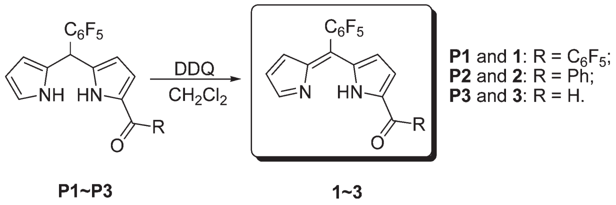
† Electronic supplementary information (ESI) available: Characterization spectra of sensor **1**; Figures and photographs showing the sensing behavior of **1**–**3**; Fig. S1–S16. See DOI: 10.1039/c2ob25297j



Scheme 2 Stabilization of the cyanide adduct *via* hydrogen bonding.



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

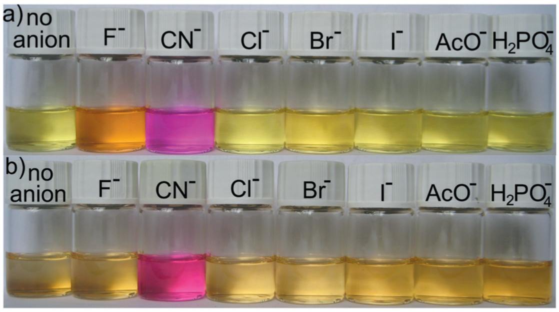


Fig. 1 A photograph showing the colour change of **1** (20 μM) upon addition of 800 μM of various anions: (a) in CH_2Cl_2, (b) in DMSO–H_2O, 4 : 1, v/v.

Based on this background and in view of the bright colours of dipyrrins, we continued to check the possibility of developing colorimetric CN^- sensors based on dipyrrin compounds. One of the effective strategies for the design of CN^- sensors is the combination of a hydrogen bonding donor with an electron-withdrawing group, such as a carbonyl group.[8*h*,*u*,15] In such a way, CN^- may attack the carbon atom to afford a cyanohydrin containing intermediate, which may be stabilized by the hydrogen bonding as indicated in Scheme 2.[15] Fortunately, it is convenient to synthesize carbonyl-substituted dipyrrins, which meet the structural requirements for CN^- sensing. Thus, compounds **1–3** (Scheme 3) were synthesized and utilized for colorimetric CN^- sensing.

In compound **1**, a strongly electron-withdrawing C_6F_5 group was incorporated with the purpose of enhancing the electron-deficient character of the carbonyl C atom, thus promoting the interaction with CN^-, and improving the sensing sensitivity.

Results and discussion

Synthesis of cyanide sensors 1–3

Compounds **1–3** were conveniently synthesized by the oxidation of the corresponding dipyrromethanes with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) in moderate to high yields and were fully characterized by ^1H NMR, ^{13}C NMR and HRMS (Scheme 3, Fig. S1–S3†); **2** and **3** have been communicated in our previous report.[12] Starting from commercially available materials, only three steps were involved to synthesize sensors **1–3** with moderate to high yields.

Naked eye detection of CN^-

For the sake of brevity, we take compound **1** as an example. Initially, we checked the colour changes of **1** in dichloromethane upon addition of various anions. As shown in Fig. 1a, fluoride induced a colour change from light yellow to orange, and cyanide induced a vivid colour change to pink. In contrast, other anions caused only negligible colour changes. Based on these observations, the colour changes can be employed to distinguish fluoride and cyanide from other anions by the naked eye. On the other hand, in a water-containing solvent such as DMSO–H_2O (4 : 1), the addition of F^- did not induce any noticeable colour change. Only the addition of cyanide induced a vivid colour change from light yellow to pink (Fig. 1b). Hence, **1** shows a highly selective sensing of CN^- in aqueous solution. Similar results were observed for **2** and **3** (Fig. S4–S5†). Inspired by these rough observations, we continued to investigate the CN^- sensing behavior in detail.

UV-Vis absorption measurements

UV-Vis titration experiments were first carried out in dichloromethane. Upon addition of CN^- to a CH_2Cl_2 solution of sensor **1**, two successive processes were observed. When 0–28 μM CN^- was added (Fig. 2a), the peak at 419 nm gradually decreased, and meanwhile a new peak centered at 498 nm gradually developed. In addition the solution colour changed to orange, which is similar to that observed for the addition of F^-. This process can be ascribed to the occurrence of hydrogen bonding between CN^- and the N–H moiety of the sensor.[8*v*] When more equivalents of cyanide were added, the peak at 498 nm gradually decreased and a new peak developed at about 547 nm with an isosbestic point observed at 518 nm (Fig. 2b), indicative of another interaction process. UV-Vis spectral changes of sensors **2** and **3** in CH_2Cl_2 upon addition of CN^- exhibited two processes similar to those observed for sensor **1**. For sensor **2**, the addition of 0–80 μM of CN^- resulted in significant absorbance changes, and further addition of 100–400 μM of CN^- leads to the development of a new absorption peak at about 544 nm (Fig. 3), while the addition of 100–420 μM of CN^- to **3** leads to disappearance of the peak at 504 nm, and development of a new broad peak at 534 nm (Fig. 4). More equivalents of CN^- were needed to complete the interaction processes of **2** and **3** compared to those of sensor **1**, indicating that the interactions for sensors **2** and **3** are weaker as compared with **1**. The difference may result from the presence of an electron withdrawing pentafluorobenzoyl group in compound **1**, which enhances its anion affinity.

It is well known that CN^- may attack the carbon atom of a carbonyl group and this nucleophilic reaction has been extensively utilized to design CN^- sensors.[15,16] Considering the fact

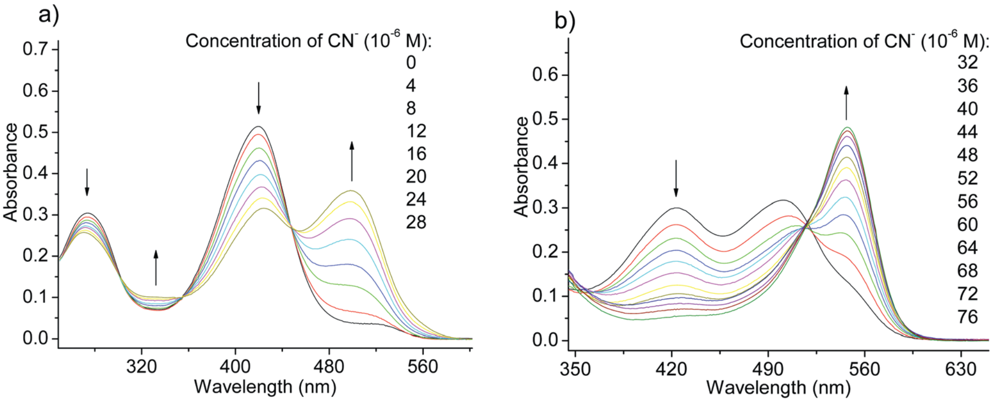


Fig. 2 UV-Vis spectral changes of **1** (20 μM) observed upon the addition of CN^- (TBA salt) in CH_2Cl_2: (a) 0–28 μM; (b) 32–76 μM.

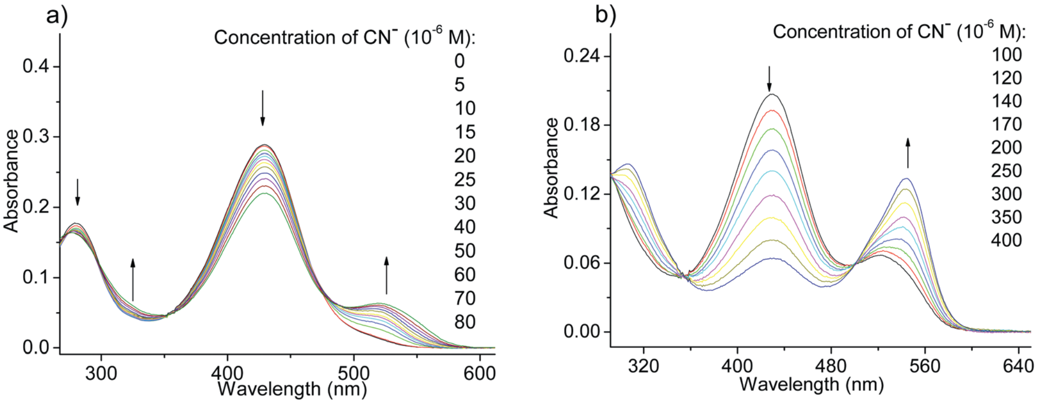


Fig. 3 UV-Vis spectral changes of **2** (10 μM) observed upon the addition of CN^- (TBA salt) in CH_2Cl_2: (a) 0–80 μM; (b) 100–400 μM.

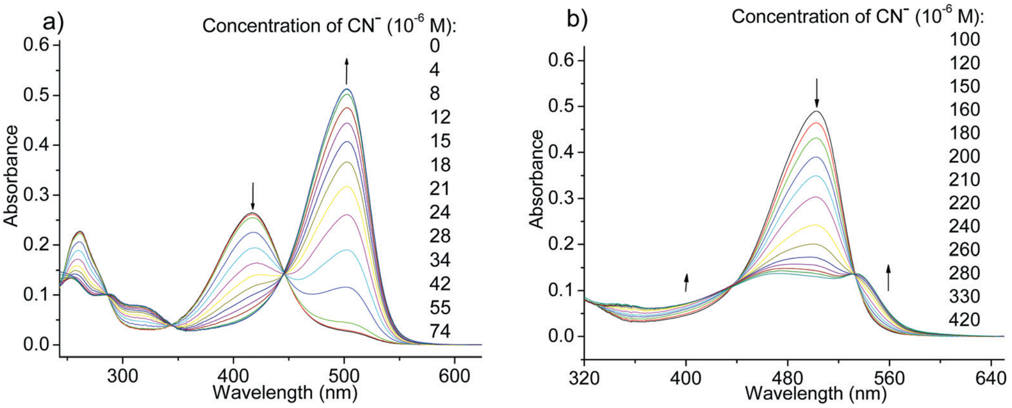
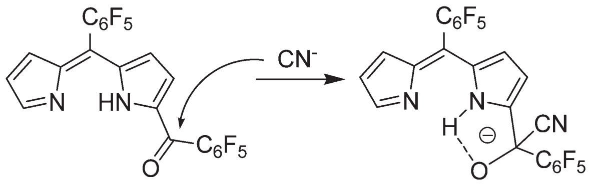


Fig. 4 UV-Vis spectral changes of **3** (12 μM) observed upon the addition of CN^- (TBA salt) in CH_2Cl_2: (a) 0–74 μM; (b) 100–420 μM.

that each of the sensors has a carbonyl group at the α-position of the pyrrolic unit, we presume that the second process observed in UV-Vis titration measurements corresponds to the occurrence of a nucleophilic reaction at the carbonyl carbon atom to afford a dipyrrin adduct, which may be stabilized by the formation of an intramolecular hydrogen bond with the NH moiety of the pyrrolic unit (Scheme 4). CN^- sensors involving similar nucleophilic reactions and the stabilization of resulting adduct by $O^- \cdots H$ hydrogen bonds have also been reported.[8n,15] The presence of the dipyrrin–CN^- adduct is evidenced by the HRMS spectra of the cyanide adduct of **3**, in which a peak corresponding to $[\mathbf{3} + CN]^-$ was observed at an *m*/*z* value of 364.0511 (Fig. S6†).

For many practical purposes, the detection limit is one of the most important parameters in anion sensing. Based on the UV-Vis measurements, the detection limits[17] of sensors **1–3** towards CN^- are determined to be 3.6×10^{-6} M, 4.2×10^{-6} M and 7.1×10^{-6} M respectively (Fig. 5, S7–S8†). Among these sensors, **1** shows the best detection limit, indicative of the strongest interaction with CN^-, which may be ascribed to the presence of an electron-withdrawing C_6F_5 group in the molecule of



Scheme 4 A nucleophilic mechanism proposed for cyanide sensing by **1**.

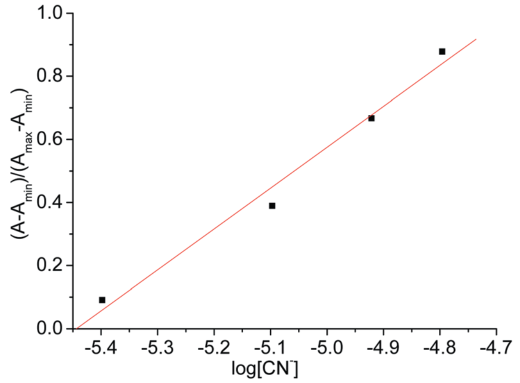


Fig. 5 A plot of $(A - A_{min})/(A_{max} - A_{min})$ *vs.* log([CN$^-$]); the calculated detection limit of sensor **1** is 3.6×10^{-6} M according to the literature method.[17] A is the absorbance at 498 nm. The linear regression affords an R value of 0.991.

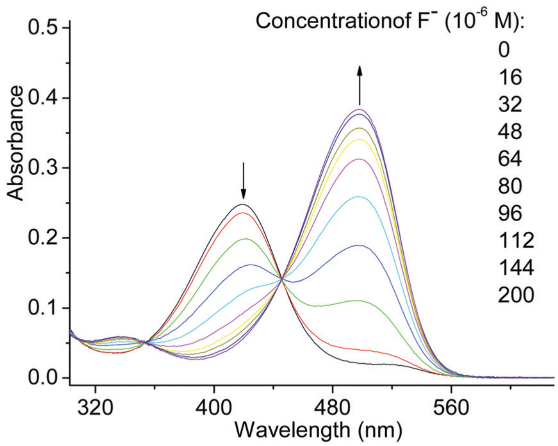


Fig. 6 UV-Vis spectral changes of **1** (20 μM) observed upon the addition of 0–200 μM F$^-$ (TBA salt) in CH_2Cl_2.

1. These detection limit values lie below the safety limit of 7.8 μM set by the US Environmental Protection Agency,[18] indicating that these sensors may be sensitive enough for potential applications.

In contrast to the two processes observed upon addition of cyanide, addition of fluoride to a CH_2Cl_2 solution of **1** induced simple UV-Vis spectral changes (Fig. 6), with the peak at 419 nm gradually decreased and a new peak developed at 498 nm. Three isosbestic points were observed at 306, 353 and 446 nm, indicative of a clean conversion throughout the titration process. The spectral changes can be ascribed to an internal charge transfer (ICT) process originating from the hydrogen bonding interaction between F$^-$ and the N–H moiety of sensor **1**.[14]

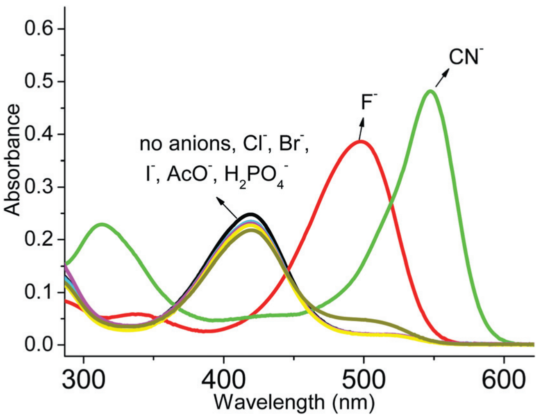


Fig. 7 UV-Vis spectral changes of **1** (20 μM) observed upon the addition of various anions (TBA salts, 76 μM for CN$^-$, 200 μM for F$^-$, 4000 μM for Cl$^-$, Br$^-$, I$^-$, AcO$^-$, and $H_2PO_4^-$) in CH_2Cl_2.

Compared with the pronounced UV-Vis spectral changes caused by CN$^-$ and F$^-$, the addition of Cl$^-$, Br$^-$, I$^-$, AcO$^-$ and $H_2PO_4^-$ did not induce obvious changes in the colour and the UV-Vis spectrum of sensor **1** (Fig. 7). These results indicate that in CH_2Cl_2, sensor **1** can be used for selective sensing of CN$^-$ and F$^-$ based on the distinct colour changes.

For sensors **2** and **3**, the addition of F$^-$ leads to similar UV-Vis spectral changes (Fig. S9–S10†), but more equivalents of F$^-$ are required due to the lack of an electron withdrawing group at the α-position. Similar to that observed for **1**, even excess of Cl$^-$, Br$^-$, I$^-$, AcO$^-$ and $H_2PO_4^-$ cannot induce obvious changes in the UV-Vis spectra of sensors **2** and **3** (Fig. S11–S12†), indicating that sensors **2** and **3** can also be used for selective sensing of CN$^-$ and F$^-$ in CH_2Cl_2.

^{1}H NMR titration study

Further insights into the proposed sensing mechanism were investigated by ^{1}H NMR titration measurements. For sensor **1**, the pyrrolic NH peak has a large chemical shift value of 13.01 ppm, indicating the presence of an intramolecular N–H···N hydrogen bond. With the addition of 12 mM of CN$^-$, the NH peak is weakened with new peaks developing at 6.18, 6.13 and 6.07 ppm (Fig. 8), indicative of the generation of a cyanide adduct, which is accompanied by interruption of the original intramolecular hydrogen bonding and the formation of a new H-bond between CN$^-$ and the NH group.[8*h*,*n*,15] With the addition of 40 mM of CN$^-$, the pyrrolic α proton at 8.24 ppm is shifted to 6.73, and the peaks for β-pyrrolic protons are also shifted upfield, which may result from the shielding effect of the more electron-rich cyanohydrin group as compared with the original carbonyl group.

For sensor **2**, a decrease of the NH signal was also observed upon adding 12 mM of CN$^-$, and phenyl and pyrrolic protons of **2** also showed an upfield shift to δ 7.83, 7.54, 7.47, 6.75, 6.13, 6.04, 5.99 ppm upon adding more equiv. of CN$^-$ (Fig. S13†). Similar results were also observed during the ^{1}H NMR titration of **3** with CN$^-$ (Fig. S14†). The two interaction processes

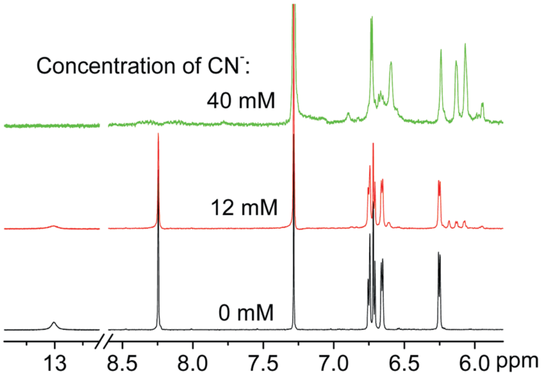


Fig. 8 Plots of ^1H NMR spectra of **1** (20 mM) on addition of CN^- in $CDCl_3$.

observed in the ^1H NMR titration experiments are consistent with those obtained from UV-Vis absorption measurements, and these results support the proposed "nucleophilic addition" mechanism.

Highly selective sensing of CN^- in aqueous solutions

For many practical purposes, it is important to detect CN^- in aqueous systems. To examine the practicability of these sensors, we checked the sensing behavior in DMSO–H_2O (4 : 1, v/v). To our delight, sensors **1–3** can selectively sense CN^- in the aqueous media. With the addition of CN^- to an aqueous solution of sensor **1**, the colour changed from light yellow to pink (Fig. 1b) and a new absorption peak developed at 545 nm (Fig. 9a). In contrast, other anions, such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ cannot induce obvious colour or UV-Vis absorption changes even with a large excess (Fig. 9a), which may be ascribed to the suppression of hydrogen bonding interactions in the aqueous solution. It is well known that cyanide sensing may be detrimentally interfered with by some other anions, especially F^- and AcO^-. Thus, we continued to perform competition experiments to further elucidate the selectivity of the sensors. When various anions (F^-, Cl^-, Br^-, I^-, AcO^- and $H_2PO_4^-$) were added at 4000 μM to the solutions of **1**, no obvious absorption changes were observed, but when 400 μM CN^- was added, the solution colours vividly changed from light yellow to pink and a new peak developed at about 545 nm (Fig. 9b). From these results, we can conclude that in the solutions of these sensors, the addition of competing anions did not interfere significantly with CN^- sensing. Similarly, selective sensing of CN^- was also observed for sensors **2** and **3**. Corresponding spectra are shown in the ESI (Fig. S15–16†). Accordingly, sensors **1–3** can be established as a novel and promising type of highly selective colorimetric cyanide sensor in aqueous media.

Conclusions

In conclusion, we synthesized three dipyrrin compounds **1–3**. Each of the molecules has a carbonyl group attached to the α-position of the pyrrolic unit. Upon addition of F^- to dichloromethane solutions of **1–3**, the solution colours changed from light yellow to orange, and the addition of CN^- induced a vivid colour change to pink. In contrast, the addition of Cl^-, Br^-, I^-, AcO^- and $H_2PO_4^-$ did not induce obvious colour changes. Hence, **1–3** can be utilized to selectively sense F^- and CN^- based on distinct colour changes. The detection limits of sensing CN^- are 3.6 μM, 4.2 μM and 7.1 μM for **1**, **2**, and **3**, respectively. However in aqueous solution, due to the competition effect of H_2O, the hydrogen bonding interactions are suppressed and sensors **1–3** no longer respond to F^-. Fortunately, CN^- may attack the carbonyl group of these dipyrrins to afford an adduct, which is accompanied by vivid colour changes, and this provides a convenient approach for sensing CN^- in aqueous solutions. These results indicate that the incorporation of a carbonyl group into the α-position of a dipyrrin unit is an effective strategy for designing CN^- sensors which can be utilized in both organic solvent and aqueous systems, and the detection limit can be easily modulated by the substituent attached to the carbonyl group. In view of the easy synthesis and the highly selective recognition of CN^- with vivid colour changes, **1–3** may be developed as a novel and promising prototype of selective and sensitive colorimetric cyanide sensors.

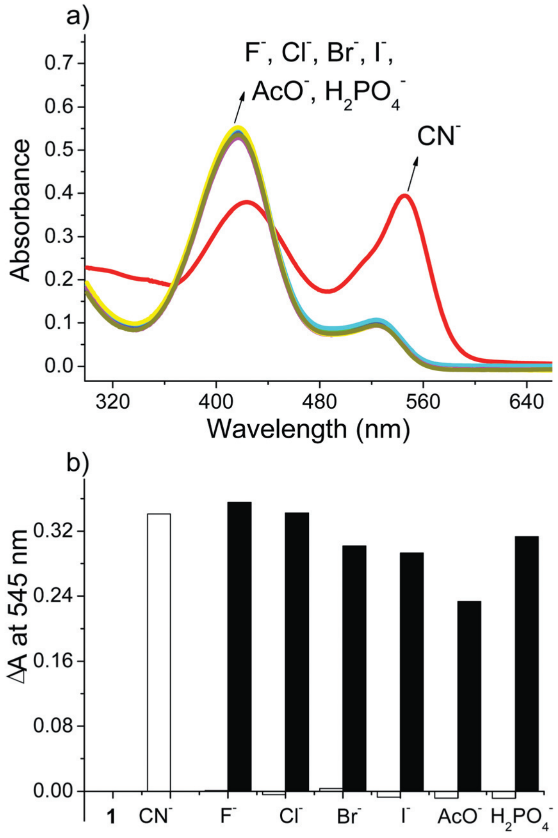


Fig. 9 Changes in the UV-Vis absorption spectrum of **1** (20 μM) in the presence of the TBA salts of various anions (400 μM for CN^-, 4000 μM for F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$) in DMSO–H_2O, 4 : 1, v/v: (a) in the presence of various anions. (b) White bars represent the addition of anions. Black bars represent the addition of 4000 μM of indicated anions, followed by 400 μM of CN^- anions.

Experimental

General

Commercial available solvents and reagents were used as received. Water was used after redistillation. Deuterated solvents for NMR measurements were available from Aldrich. UV-Vis absorption spectra were recorded on a Varian Cary 100 spectrophotometer, with a quartz cuvette (path length = 1 cm). ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker AM 400 spectrometer with tetramethylsilane (TMS) as the internal standard. HRMS were performed using a Waters LCT Premier XE spectrometer. Column chromatography was carried out in air using silica gel (200–300 mesh) purchased from Qingdao Haiyang Chemical Co., Ltd (China). Reactions were monitored by thin-layer chromatography. **P1**, **P2** and **P3** were prepared from the reaction of pyrrole with corresponding aldehydes according to reported methods.[19] The preparation of **2** and **3** were communicated in our previous work.[12]

UV-Vis absorption spectra measurements

The absorption spectra of **1** (20 μM) were measured at 25 °C in dichloromethane and aqueous solution (DMSO–H_2O, 4 : 1, v/v). The absorption spectra of **2** (10 μM) and **3** (12 μM) were measured under the same conditions. Tested anions such as F^-, CN^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ were added as TBA salts dissolved in dichloromethane.

^{1}H NMR titration details

^{1}H NMR titrations of **1–3** with anions were performed in $CDCl_3$, with 0.01 mmol of each sensor dissolved in 0.5 mL of $CDCl_3$. Tetrabutylammonium cyanide was dissolved in $CDCl_3$, and added to the NMR tube *via* a syringe.

Synthesis of 1

P1 (253 mg, 0.5 mmol) was dissolved in 125 mL of CH_2Cl_2, then DDQ (170 mg, 0.75 mmol) was added. The mixture was stirred at room temperature for 2 h and then purified by a silica gel column (eluent: CH_2Cl_2–PE = 1 : 2) to afford the crude product **1** which was recrystallized from CH_2Cl_2 and *n*-hexane (121 mg, yield: 48%). Mp: 108–109 °C. UV-Vis (CH_2Cl_2) λ_{max} (nm): 273, 419. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ = 12.99 (s, 1H, pyrrolic-NH), 8.22 (s, 1H, pyrrolic-αH), 6.74 (d, J = 4.8 Hz, 1H, pyrrolic-βH), 6.70 (d, J = 4.8 Hz, 1H, pyrrolic-βH), 6.64 (d, J = 4.4 Hz, 1H, pyrrolic-βH), 6.24 (d, J = 4.0 Hz, 1H, pyrrolic-βH). ^{13}C NMR ($CDCl_3$, Bruker 100 MHz, 298 K): δ 173.4, 165.0, 154.4, 137.4, 137.1, 134.0, 129.3, 121.7, 120.2, 119.3. HRMS: obsd 505.0392, calcd for $C_{22}H_7N_2OF_{10}$ ([M + H]$^+$): 505.0399. Anal. Calcd for $C_{22}H_6N_2OF_{10}\cdot 0.2C_6H_{14}$ (%): C, 53.43, H, 1.70, N, 5.37. Found: C, 53.31, H, 1.96, N, 5.27%.

Synthesis of 2

P2 (500 mg, 1.2 mmol) was dissolved in 300 mL of CH_2Cl_2, then DDQ (409 mg, 1.8 mmol) was added. The mixture was stirred at room temperature for 1 h and then purified by a silica gel column (eluent: CH_2Cl_2) to afford the crude product 2 which was recrystallized from CH_2Cl_2 and *n*-hexane (205 mg, yield: 41.2%). Mp: 92–94 °C. UV-Vis (CH_2Cl_2) λ_{max} (nm): 280, 429. ^{1}H NMR ($CDCl_3$, Bruker 400 MHz, 298 K): δ 12.89 (s, 1H, pyrrolic-NH), 8.16 (s, 1H, pyrrolic), 7.93 (t, 2H, Ph-H), 7.59 (t, 1H, Ph-H), 7.5 (t, 2H, Ph-H), 6.8 (d, 1H, J = 4.0 Hz, pyrrolic), 6.71 (d, 1H, J = 4.4 Hz, pyrrolic), 6.64 (d, 1H, J = 4.8 Hz, pyrrolic), 6.27 (d, 1H, J = 4.0 Hz, pyrrolic). ^{13}C NMR ($CDCl_3$, Bruker 100 MHz, 298 K): δ 185.10, 163.39, 152.76, 138.49, 137.88, 135.28, 133.44, 132.38, 129.08, 128.47, 128.13, 122.36, 119.63, 119.23. HRMS: obsd 415.0874, calcd for $C_{22}H_{12}F_5N_2O$ ([M + H]$^+$): 415.0870. Anal. Calcd for $C_{22}H_{11}N_2OF_5$ (%): C, 63.77, H, 2.68, N, 6.76. Found: C, 63.56, H, 2.67, N, 6.77%.

Synthesis of 3

P3 (340 mg, 1 mmol) was dissolved in 250 mL of CH_2Cl_2, then DDQ (340 mg, 1.5 mmol) was added. The mixture was stirred at room temperature for 30 min and then purified by a silica gel column (eluent: CH_2Cl_2–PE = 1 : 1) to afford the crude product 3 which was recrystallized from CH_2Cl_2 and *n*-hexane (251 mg, yield: 74.2%). Mp: 118–119 °C. UV-Vis (CH_2Cl_2) λ_{max} (nm): 261, 417. ^{1}H NMR ($CDCl_3$, Bruker 400 MHz, 298 K): δ 12.76 (b, 1H, pyrrolic-NH), 9.72 (s, 1H, CHO-H), 8.16 (s, 1H, pyrrolic-αH), 6.90 (d, 1H, J = 4.4 Hz, pyrrolic), 6.71 (d, 1H, J = 4.8 Hz, pyrrolic), 6.65 (d, 1H, J = 4.8 Hz, pyrrolic), 6.26 (d, 1H, J = 4.0 Hz, pyrrolic). ^{13}C NMR ($CDCl_3$, Bruker 100 MHz, 298 K): δ 180.49, 163.74, 153.16, 139.27, 136.07, 133.60, 128.51, 119.91, 119.65. HRMS: obsd 339.0562, calcd for $C_{16}H_8F_5N_2O$ ([M + H]$^+$): 339.0557. Anal. Calcd for $C_{16}H_7N_2OF_5$ (%): C, 56.82, H, 2.09, N, 8.28. Found: C, 56.72, H, 2.19, N, 8.18%.

Acknowledgements

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