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A cyanide-selective colorimetric "naked-eye" and fluorescent chemosensor based on diketopyrrolopyrrole-hydrazone conjugate and its use for the design of molecular-scale logic device

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Abstract

A novel diketopyrrolopyrrole (DPP)-hydrazone based receptor **1** was designed and synthesized as a selective fluorescent and colorimetric chemosensor for cyanide without interference from other common anions including fluoride and acetate. The spectral responses of **1** to cyanide were studied: an approximately 130 nm red shift in absorption spectra (from $\lambda_{max\text{-}ab}$ = 516 nm to $\lambda_{max\text{-}ab}$ = 646 nm and the color change from pink to indigo) and "turn-off" emission response was observed. The experimental results revealed that the formation of anionic species from deprotonation of the hydrazone N-H moiety by cyanide was responsible for the spectral changes. Density function theory calculations were conducted to rationalize the optical response of the receptor **1**. In the presence of cyanide, receptor **1** could act as an "Off-On" fluorescent probe for trifluoroacetic acid (TFA) based on the reversible protonation process, which may be represented by a complementary "IMPLICATION/INHIBIT" logic gate at molecular level employing CN^--TFA as the chemical inputs. The detection limit was 0.23 μM using the fluorescence spectra changes, which was far lower than the WHO guideline of 1.9 μM.

Keywords: Colorimetric; Chemosensor; Diketopyrrolopyrrole (DPP); Anions sensing; Fluorescence; Logic gates

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1 Introduction

The recognition and detection of anions is extremely necessary because anions play so many positive and negative effects in the lives. Cyanide is well known as one of the most toxic species and is extremely harmful to mammals. Any accidental release of cyanide to the environment causes serious problems.[1] Therefore, the maximum permissive level of cyanide in drinking water is set at 1.9 μM by the World Health Organization (WHO). Nevertheless, cyanide salts are still widely used as industrial materials in gold mining, electroplating, plastics production and other fields. Widespread applications of cyanide raises a number of environmental concerns and these issues necessitate the development of sensor molecules that can adequately detect this anion in a variety of settings. So, it is highly desirable to develop sensitive, selective and quick detection methods for toxic cyanide anions.

On the other hand, in biological and environmental systems, anion-receptor interactions commonly occur in aqueous media. Therefore, much attention has been paid to develop anion sensors that work in the aqueous phase. However, examples of chromogenic sensor molecules that are capable of recognizing cyanide ions in aqueous environments are much fewer compared to those that display sensing features in nonaqueous solutions.[2] High solvation energy of the cyanide ion in aqueous environments is known to affect adversely the hydrogen-bonded adduct formation between the receptor unit and the CN^-.[3] The recognition and separation of the CN^- anion from an aqueous media is a challenging task. An alternate approach, adopted by many researchers, for recognition of CN^- in aqueous solution is based on

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chemodosimetric methodology. This involves coordination of free cyanide ion to a transition metal ion or unsaturated boron center,[4] or to an electrophilic carbonyl functionality.[5] However, such examples have certain limitations such as delayed response, lack of reversibility or use of elevated reaction temperature. The few reports that describe the recognition of CN^- in aqueous solution in the presence of F^-, AcO^-, $H_2PO_4^-$, and SO_4^{2-}, utilizing the hydrogen bond motif, suffer from lack of selectivity due to its poor ability to form hydrogen bonds with receptors.[6-18] Furthermore, most of these sensors are normally irreversible and one time use for sensing cyanide ion. A hydrazone (-CH=N-NH-) contained hydrogen donor moiety of N-H, which had the tendency for binding of anions was used as binding site with cyanide.[19-23] Recently, a Schiff-base based on 5-(4-nitrophenyl)-2-furan and naphtho[2,1-b]furan-2-carbohydrazide was reported for the selective detection of cyanide in aqueous medium *via* deprotonating between the hydrazide moiety of probe and cyanide.[24] However, this probe showed low detection limit due to low activity of hydrazide.

1,4-Diketo-3,6-diphenylpyrrolo[3,4-c]pyrrole (DPP) and its derivatives[25] represent a class of brilliant red and strongly fluorescent high-performance pigments and have exceptional light, weather and heat stability and high light fastness. In view of this and as a longstanding interested in molecular recognition of our group based on DPP,[26] herein, we report a simple, easy to prepare yet highly selective cyanide receptor **1** (Scheme 1) for the rapid detection and colorimetric sensing of cyanide from aqueous media. The N-H protons on hydrazone become appreciably activiated

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due to presence of the strong electron-withdrawing effect of 2,4-dinitrophenyl, C=N and DPP moieties. There was a deprotonation process between the probe molecule and cyanide, which increased the ability of intramolecular charge transfer which enlarge the conjugate system of the probe and then gave rise to large changes in the absorption spectra (from $\lambda_{max\text{-}ab}$ = 516 nm to $\lambda_{max\text{-}ab}$ = 646 nm and the color change from pink to indigo) and "turn-off" emission response at 601 nm with 92% fluorescence quenching. To the best of our knowledge, it was the first sensor for cyanide ever reported with a 130 nm red shift response, which could gave a colorimetric and "on-off" fluorescence response instantly. Notably, this probe serves as a recyclable component in sensing materials by adding of trifluoroacetic acid (TFA). After the addition of TFA, **1**-CN shows an immediate visible change in color from indigo to pink within a short time of 5 s, and the fluorescence recovered at the same time. A complementary "IMPLICATION/INHIBIT" logic gate at molecular level employing CN^--TFA as the chemical inputs can be achieved.

2. Experimental

2.1. Chemicals and instruments

Nuclear magnetic resonance spectra were recorded on Bruker Avance III 400 MHz and chemical shifts are expressed in ppm using TMS as an internal standard. The UV-vis absorption spectra were recorded using a Helios Alpha UV-vis scanning spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 FL spectrophotometer with quartz cuvette (path length = 1cm).

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2,5-Dioctyl-3,6-bis(4'-formylphenyl)pyrrolo[3,4-c]pyrrole-1,4-dione (compound **5**) was synthesized according to our published literature.[27]

The aqueous solutions of anions (F^-, CN^-, Cl^-, Br^-, I^-, AcO^-, HPO_4^{2-}, $H_2PO_4^-$, NO_3^-, SCN^-, CO_3^{2-}, PO_4^{3-}, S^{2-}) were prepared from their tetrabutylammonium or sodium salts with distilled water. **1** was dissolved in THF at room temperature to afford the stock solution (10^{-3} M). Test solutions were prepared by placing 1 mL of **1** stock solution into a 100 mL volumetric flask, adding an appropriate aliquot of each anion stock and 7 mL distilled water, and diluting the solution to 100 mL with THF. The resulting solution was shaken well before recording the absorption and emission spectra.

2.2. Computational methods

The ground-state geometry optimization of **1** and its receptor-additive form (**1**-2CN^-) were performed on density functional theory (DFT) with the B3LYP/6-31G(d) level of the Gaussian 03 program. The UV-vis absorptions of receptor **1** and its deprotonated species were calculated with the B3LYP/6-31G(d) level of the Gaussian 03 program based on the optimized ground-state geometry.

*2.3. Synthesis of receptor **1***

113.6 mg (0.2 mmol) coumpond **5** and 198.2 mg (1 mmol) 2,4-dinitrophenylhydrazine were dissolved in 50 mL ethanol and six drops acetic acid was added to start the reaction, then the resulting solution was heated and refluxed for 4 h. Dark red

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precipitate was filtered and washed twice with hot ethanol (2 × 10 mL). Finally, 166.3 mg dark red solid in 87.4% yield was obtained. m.p. 281 °C-282 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm):11.40 (s, 2H), 9.15 (s, 2H), 8.38 (d, 2H, *J*=8 Hz), 8.17 (s, 2H), 8.11 (d, 2H, *J*=8 Hz), 7.93 (s, 8H), 3.79 (t, 4H，*J*= 8 Hz), 1.57-0.77 (m, 30H). ^{13}C NMR (100 MHz, δ, ppm): 160.05, 143.91, 138.35, 134.65, 131.05, 128.67, 123.84, 122.11, 115.59, 108.47, 43.02, 32.81, 30.59, 28.92, 24.93, 14.53. HRMS-ESI: *m/z* calcd (%) for $C_{48}H_{52}N_{10}O_{10}$: 928.3868 $[M+Na]^+$; Found: 951.3760.

3. Results and discussions

*3.1. Design and Synthesis of receptor **1***

Although several literatures utilized hydrogen bonding approach based on DPP for detection of fluoride ion in organic solvents,[28-30] however, a cyanide receptor based on DPP that operates in aqueous solvent mixture has never been reported. The problems are mainly related to poor interaction between the receptor and cyanide anion due to its higher Gibbs energy of hydration. With this in mind, we decided to introduce electron withdrawing 2,4-dinitrophenyl and Schiff base groups, as well as electron-deficient DPP moiety to enhance activity of N-H based on receptor **1**. Thus, it is anticipated that receptor **1** should be highly reactive and selective to CN^- from aqueous media.

A convenient synthetic route to receptor **1** was developed as shown in Scheme 1. 2,5-Dioctyl-3,6-bis(4'-formylphenyl)pyrrolo[3,4-c]pyrrole-1,4-dione (compound **5**) was prepared from *p*-cyanobenzaldehyde as a starting material in four steps. Receptor

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1 was obtained by a straightforward condensation reaction of compound **5** with 2,4-dinitrophenylhydrazine in 87.4% yield as a dark red solid. The ^{1}H NMR spectrum of receptor **1** showed the distinctive signals at 11.4 ppm corresponding to the resonance of hydrazone N-H adjacent to C=N bond (-CH=N-NH-). The ^{1}H NMR, ^{13}C NMR and HRMS spectra of receptor **1** are shown in Figs. S1-S3.

*3.2 Spectroscopic responses of **1** to anions*

A hydrazone (-CH=N-NH) had the tendency for binding of anions, and DPP moiety was an efficient fluorophore. Therefore, the combination of the hydrazone and DPP in a single molecular framework was very useful to create a probe by following the changes in the spectral properties.

The anion binding abilities of the receptor **1** with F^-, CN^-, Cl^-, Br^-, I^-, AcO^-, HPO_4^{2-}, $H_2PO_4^-$, NO_3^-, SCN^-, CO_3^{2-}, PO_4^{3-}, S^{2-} in aqueous media were studied through UV-vis, fluorescence spectra and naked eye color changes. The anions tested were used as their tetrabutylammonium or sodium salts in distilled water while receptor **1** was taken as its 1.0×10^{-5} M THF/H_2O (93/7, v/v) solution.

Receptor **1** showed two major absorption peaks at 396 nm and 516 nm. Upon addition of 6 equiv of various anions (F^-, CN^-, Cl^-, Br^-, I^-, AcO^-, HPO_4^{2-}, $H_2PO_4^-$, NO_3^-, SCN^-, CO_3^{2-}, PO_4^{2-}, S^{2-}) to **1**, there were no significant UV-vis spectral change in the nature of the spectra except for CN^-, as shown in Fig. 1a. It was interesting to observe that upon interaction of **1** with CN^-, two new absorbance peaks emerged at 462 and 646 nm. Meanwhile, the absorbance peaks at 396 and 516 nm disappeared.

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DOI: 10.1039/C6RA21669B

However, addition of AcO^- and F^- only gave minor response to **1**.

The difference in **1** response to anions could thus be used to develop a colorimetric assay. The color change from pink to indigo occurred very rapidly (within 10 seconds), which was sufficiently distinct to be discriminated from other anions through naked eye itself. The corresponding naked eye changes were present in Fig. 1b.

A titration of **1** with CN^- indicated that there was a gradual increase in the absorbance at 462 and 646 nm upon increment of the CN^- concentration, as shown in Fig. 2. At the same time, the absorbance peaks at 396 and 516 nm disappeared. Two clear isosbestic points at 315 and 439 nm were observed during the titration process, indicating formation of intermediates species with the receptor **1**. The absorption at 646 nm began to increase significantly and reached the limit value after 6 equiv of CN^- were added, indicating that a CN^--induced deprotonation of hydrazone N-H had occurred. This was confirmed by adding OH^- (as Bu_4NOH) to the solution of receptor **1**, which gave similar UV-vis spectral changes (Fig. S4) to those observed with CN^- ion.

Receptor **1** was strongly fluorescent with maximum emission band at 601 nm upon excitation at 516 nm. Upon addition of 5 equiv. CN^- to the solution, the fluorescence quenching of 92% was observed and the emission peak underwent a minor blue shift from 601 nm to 593 nm, suggesting that the new species is much less luminescent than the original one (Fig. 3). This may be ascribed to the N-H···CN hydrogen bonding, which enhanced the electron-donating ability of N atom and facilitated the intramolecular photoinduced electron transfer, resulting in fluorescence turn-off. But

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addition of Cl^-, Br^-, I^-, HPO_4^{2-}, $H_2PO_4^-$, NO_3^-, SCN^-, CO_3^{2-}, PO_4^{2-}, S^{2-}resulted in insignificant changes in the fluorescent spectra (Fig. 4a). In the case of AcO^- and F^- anions, fluorescence quenching rates of 15% and 18% were obtained, respectively. However, these changes were smaller in magnitude when compared to CN^-. Thus, the significant change of **1** with a clear emission color change from red fluorescent solution to nonfluorescent solution in presence of CN^- was present, an agreement with the appearance of fluorescence quenching of 92% in the corresponding fluorescence spectra. In the presence of the other anions, no changes in fluorescence were observed. The corresponding naked eye fluorescence changes were present in Fig. 4b. All these findings suggested that **1** allowed selective and sensitive CN^- detection over other anions by both colorimetric and fluorometric analyses.

It is well known that cyanide ions have high solvation energy in water (ΔGh = −295 kJ/mol). However, **1** had no interaction with other anions that have a comparable hydration energy (ΔGh = −365, −340, −315, and −300 kJ/mol for OAc^-, Cl^-, Br^-, and NO_3^-, respectively) to cyanide anion. Here comes a question: Why does **1** only respond to CN^- in water? The much stronger basicity of CN^- in water may be the main reason. The pK_a value of HCN in water (9.30) is much higher than that of other acid (pK_a = 4.75, 3.17 for HOAc and HF in water, respectively). When the strong basic CN^- anion gets close to the acidic N-H fragment of **1**, hydrogen bonding interaction occurs, leading to a partial proton transfer from **1** to CN^-, an increase of electron density on DPP center, and red-shifts of the absorption and decrease of emission intensity. The excellent selectivity of **1** toward CN^- can be attributed to the

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DOI: 10.1039/C6RA21669B

fitness in the activity of its NH groups in **1**, which is tuned to be able to distinguish the subtle difference in the affinity of CN^- to proton in water.

To test whether **1** can detect CN^- selectively even in the presence of other anions, competitive anion titrations were carried out. **1** was treated with 6 equiv of CN^- in the presence of 6 equiv of all other anions. The results indicated miscellaneous competitive anion did not lead to any significant spectral change and CN^- ions still resulted in the similar fluorescence quenching in the presence of competitive anions, as shown in Fig. S5. Thus, the selectivity of **1** toward CN^- was not affected by the presence of other anions. All the above results clearly indicated that **1** could be used as a new chemosensor for CN^- by the colorimetric and fluorescence dual mode.

For determination of stoichiometry between **1** and CN^-, Job's plot analyses were used. The method is that keeping total concentration of **1** and CN^- at 10.0 μM, and changing the molar ratio of CN^- (X_M; $X_M = [CN^-]/\{[\mathbf{1}] + [CN^-]\}$) from 0.1 to 0.9. From Fig. S6, when molar fraction of CN^- was 0.3, the I_0-I value got to maximum, indicating that forming a 1:2 complex between **1** and CN^-.

Moreover, the binding stoichiometry and the binding constant to CN^- were determined by Benesi-Hildebrand double reciprocal method following Eq. (1). Here I_0 and I_{min} are the fluorescence intensities at zero and the maximum concentrations of CN^-, $[CN^-]$ is the total CN^- concentration, K_b is the binding constants for 1:2 binding mode. For receptor **1**, a good linear fit could be obtained by Eq. (1), indicative of the binding stoichiometry of 1:2, which conformed to the presence of two N-H groups in receptor **1** (Fig. S7). The binding constant was found to be 2.02×10^{10} M^{-2}. In addition,

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limits of detection (LOD) were determined from the equation LOD = $K\times Sb_1/S$, where K=3, Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve (Fig. S8). The obtained result was 0.23 μM for CN^- with **1** using emission measurements.

$$\frac{1}{I_0 - I} = \frac{1}{K(I_0 - I_{\min})[CN^-]^2} + \frac{1}{I_0 - I_{\min}} \quad (1)$$

Active materials-based test strips represent a group of convenient probing substrate for practical utilization. **1**-based test strip was thus fabricated by immersing filter paper into the THF solution of **1** (1.0×10^{-3} M) and drying in air, which was energy- and cost-effective. The corresponding probing experiments were carried out subsequently. The results indicated that this protocol really took effect. The obvious color change from pink to indigo was observed by immersing this test strips in solution of CN^-, exhibiting colorimetric changes differentiable to naked eyes (Fig. S9).

3.3 ^{1}H NMR studies

The cyanide ion binding to receptor **1** was also monitored by ^{1}H NMR titration studies in $CDCl_3$. The changes in ^{1}H NMR signals of **1** upon addition of increasing amounts of cyanide ion were shown in Fig. 5. The signal of proton on the hydrazone N-H at 11.4 ppm disappeared entirely upon addition of 2 equiv of cyanide owing to the hydrogen bonding between this proton and cyanide. The deprotonation of the hydrazone N-H group was supported by the fact that aromatic protons showed distinct upfield shifts when 2 equiv of cyanide was introduced compared with the free

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receptor arising from an overall change of the electron distribution in the chromophore when the hydrazone N-H group was deprotonated.

3.4 DFT calculations

To gain insights into spectroscopic responses of **1** cyanide anions, receptor **1** and the corresponding deprotonated species were also examined by DFT calculations at the B3LYP/6-31 G(d) level of the Gaussian 03 program. The optimized structures of receptor **1** and deprotonated species were shown in Fig. 6. For receptor **1**, the phenyl ring was tilted by about 74.3° toward the DPP core and the twisted angle between hydrazone (-CH=N-NH) and phenyl spacer was 41.3°. For deprotonated species, the phenyl ring was tilted by about 82.8° toward the DPP core, and the hydrazone moiety was almost coplanar with the phenyl spacer moiety with twisted angle 3.4°. The bathochromic shift of maximum absorption of receptor **1** when binding with cyanide could further be understood in terms of decrease in the potential energy of its HOMO and LUMO. The HOMO and LUMO orbitals of receptor **1** and deprotonated species were shown in Fig. 7. For receptor **1**, the HOMO was distributed on the DPP core, hydrazone moiety and 2,4-dinitrophenyl moiety, while the LUMO was more distributed on the 2,4-dinitrophenyl and hydrazone moiety. For the deprotonated species, the HOMO was mostly located on both the hydrazone moiety and 2,4-dinitrophenyl moiety, while the LUMO was more distributed on both the DPP core, 2,4-dinitrophenyl and the hydrazone moiety. As described above that the LUMO was the electron-deficient, and cyanide would prefer it more rather than the HOMO.

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Hence, on binding with cyanide, the potential energy of the LUMO was raised to comparatively lesser extent than that of the HOMO, which was less preferred by cyanide. This led to narrowing of the energy gap between HOMO and LUMO (3.37 eV and 2.76 eV for **1** and its deprotonated species, respectively), which was ultimately responsible for the bathochromic shift of maximum absorption of receptor **1** on binding with cyanide. This indicated that the binding of cyanide with receptor **1** made a polar due to the homogenization of electron density through extended π-conjugation. In other words, the binding of cyanide introduced a high extent of planarity into the receptor **1**, which led to the homogeneous distribution of electron density throughout. This phenomenon had been well documented in the literature as planar intramolecular charge transfer. The ^{1}H NMR studies also indicated similar type of electron density changes crossing the receptor **1** in form of upfield shifting of the signals and merging of a few of them.

*3.5 Reversibility and Reusability of the receptor **1***

Most of the CN^{-} ion sensors available in the literature are irreversible and can be used only one time. It is very beneficial if a probe can be reversible in nature and be reusable for sensing selective anion. To test the reversibility and reusability of **1**, we carried out systematic titration studies of **1**-CN^{-} complex upon addition of increasing amounts of trifluoroacetic acid (TFA) by absorption and fluorescence techniques. The absorption spectral titration of **1**-CN^{-} complex with increasing addition of TFA (0-2 equiv) in aqueous solution is shown in Fig. 8. Addition of increasing equivalents of

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TFA to a solution of **1**-CN^- complex resulted in the significant increase in the absorption bands at 396 and 516 nm, whereas two absorbance peaks at 462 and 646 nm were greatly decreased. It was clearly shown that only addition of 2 equiv of TFA to **1**-CN^- complex was needed to go back to the initial spectrum of original **1**. These findings supported protonation of the N-H negative ion. Similarly, we also monitored the systematic titration studies of **1**-CN^- complex upon addition of increasing equivalents of TFA by fluorescence studies. Upon addition of increasing amounts of TFA to **1**-CN^- complex, the fluorescence emission gradually increased, and emission peak underwent a minor red shift from 593 nm to 601 nm. Finally, 34-fold enhancement was observed on addition of 2 equiv of TFA (Fig. 9). Thus, upon CN^- ion addition, the N-H moiety was electron-rich via deprotonation and engaged in photoinduced electron transfer quenching of the DPP excited state. But, upon titration with TFA, the photoinduced electron transfer quenching was prevented because of protonation of N-H negative ion. So, the absorption and fluorescence properties were reverted (Scheme 2). The reversible and reusable response of **1** was demonstrated by carrying out four alternate cycles of titration of **1** with CN^- ion followed by addition of TFA by absorption measurement (Fig. 10). The repeated demonstration of visual color changes from pink to indigo and then back to pink was shown in Fig. 11, demonstrating the reversibility and reusability of probe **1**. Herein, in the presence of 2 equiv TFA, the color change from indigo to pink and fluorescence recovery occurred very rapidly (within 10 seconds), indicating high efficiency was the unique feature of **1**.

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DOI: 10.1039/C6RA21669B

3.6 The reversible colorimetric switch with complementary"IMP/INH" logic functions

As discussed above, concomitant with a color change from pink to indigo, a drastic red-shift of 130 nm was observed in the UV-vis spectra of receptor **1** upon cyanide binding. More interestingly, we found that the cyanide-induced chromogenic process is totally reversed with TFA (see Figs. 8 and 9). The eye-detected change was clearly reflected in the UV-vis spectra, in which the addition of 2 equiv of TFA results in vanishing of the band at 646 nm and reappearance of the absorption at 516 nm (Fig. 4). The reversible pink-indigo-pink cycle could be repeated for several times by alternating addition of 6 equiv of cyanide and 2 equiv of TFA. However, this reversible chromogenic switching process did not occur when TFA, instead of cyanide, is previously added to the solution. A set of comparison experiments demonstrated that the successive addition of 2 equiv of TFA and 6 equiv of cyanide does not produce **1** any change in both its color and absorption spectrum. The results indicate that the presence of TFA would inhibit the interaction of cyanide with the sensor **1**, since TFA is a more acidic species compared to **1**. As elucidated in Scheme 2, the interaction of TFA with the complex **1**-2CN^- reproduces the receptor **1**; meanwhile the released cyanide ions could be converted into other species. This also explains why the colorimetric switch can work in a reproducible manner, despite the fact that the added cyanide and TFA are not of equal molar amount in one single cycle. The reversible and reproducible colorimetric switching process may be represented by a

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molecular "INHIBIT" logic gate, employing CN^- (InC) and TFA (InF) as the inputs and the absorbance at 646 nm as the output. When using the absorbance at 516 nm as another output, an "IMPLICATION" logic gate is fabricated. In this way, a complementary IMP/INH logic function can be realized based on the receptor **1**, as shown in Fig. 12. Thus, the color changes of **1** in THF (optical output) are controlled by the input of two anions: CN^- "switches" ON the optical output, while TFA "switches" OFF the optical output. By alternately adding CN^- (6 equiv) and TFA (2 equiv.) into the receptor solution, a reversible colorimetric switch could be created in a reproducible manner (Fig. 12). To the best of our knowledge, this kind of reversible and reproducible switch is of great interest for molecular-level information processing. In the field of information technology, the switching process must be based on a reversible chemical process to perform any useful calculation.[31] Therefore, the present logic device has a great advantage over early reported relative systems at least in terms of the reversible and reproducible characteristics.

4. Conclusions

In summary, a new colorimetric and on-off fluorescence receptor **1** based diketopyrrolopyrrole (DPP)-hydrazone conjugate for cyanide anion detection in aqueous media was designed and synthesized. Receptor **1** displayed a rapid response, high selectivity and sensitivity toward cyanide over other anions, with a significant 130 nm bathochromic shift of the absorption maximum. Meanwhile, it could be easily observed that the receptor **1** for cyanide ion changed from pink to indigo by the naked

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eye, and from fluorescence red to non-fluorescence dark under UV lamp immediately after the cyanide ion was added. The experimental results revealed that the formation of anionic species from deprotonation of the hydrazone moiety by cyanide ion was responsible for the spectral changes. Density function theory calculations were conducted to rationalize the optical response of the receptor **1**. In addition, receptor **1** has been used to construct the molecular-level complementary "IMPLICATION/INHIBIT" logic gate employing CN^- and TFA as the inputs. The present work provides deep insights for the future design of anions sensors as multifunctional logic devices.

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View Article Online
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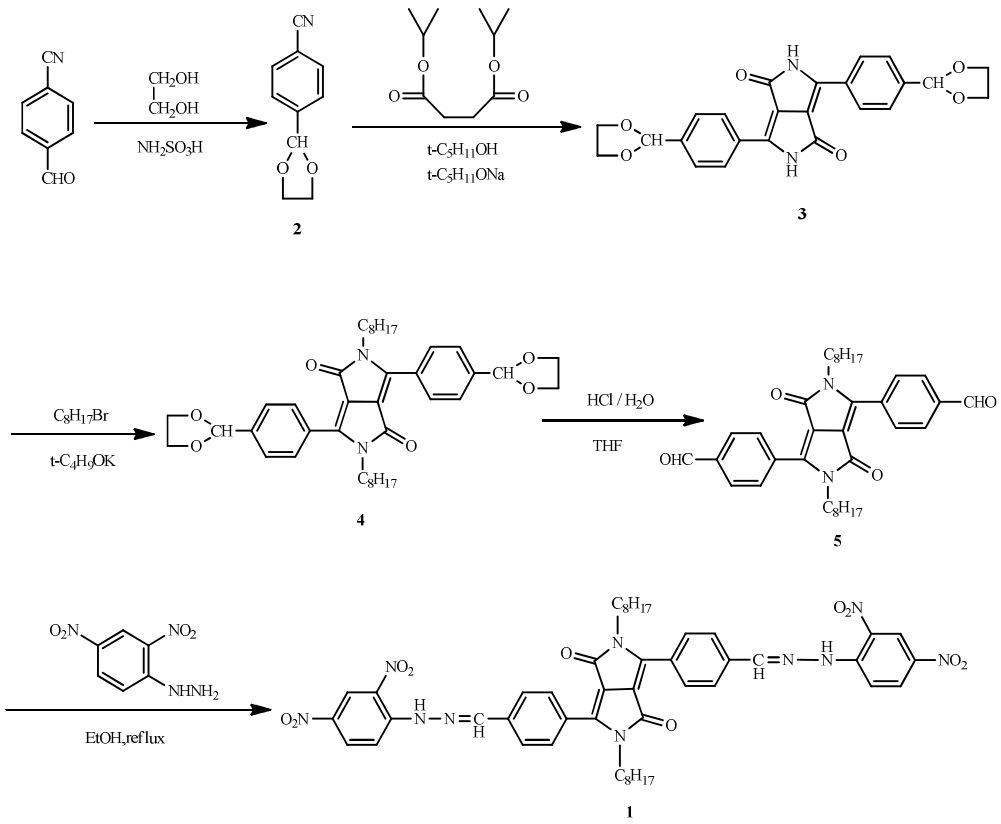

Scheme 1. Synthesis of receptor **1**.

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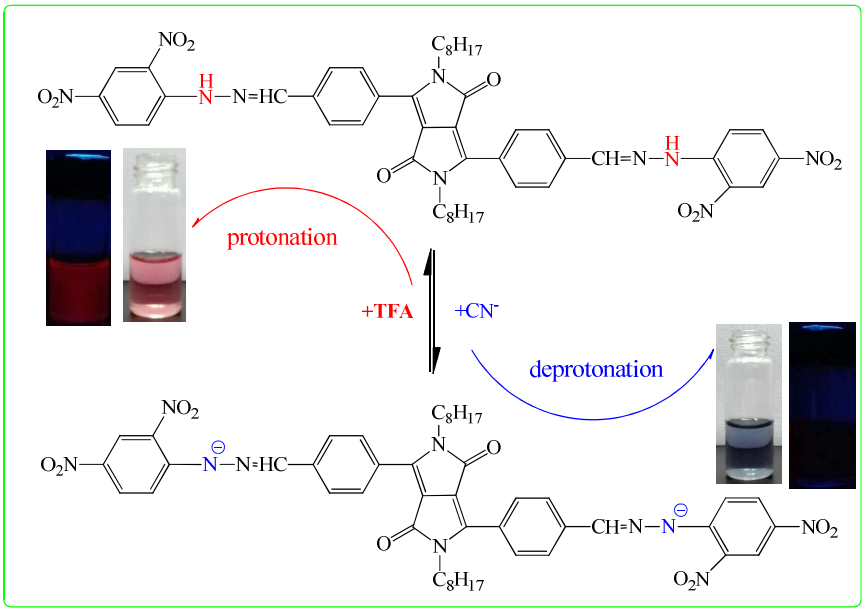

Scheme 2. Proposed interaction mode of receptor **1** with CN^- and TFA.

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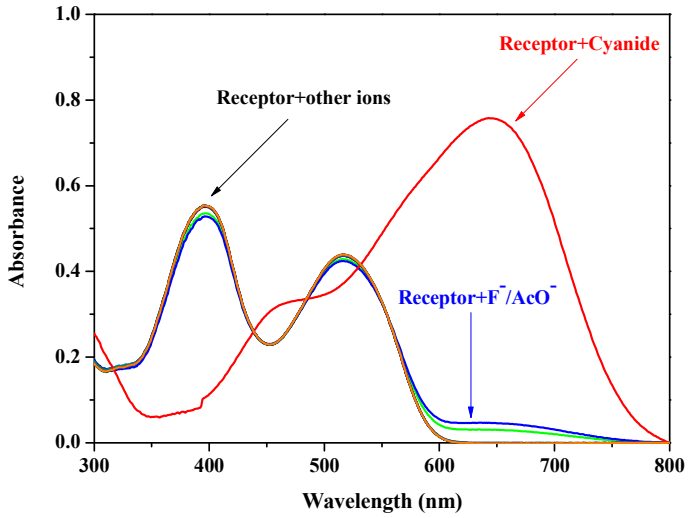

(b)

Figure 1. (a) The absorption spectra and (b) color changes of receptor **1** (10 μM) in THF/H_2O (93/7, v/v) upon addition of 6 equiv of various ions.

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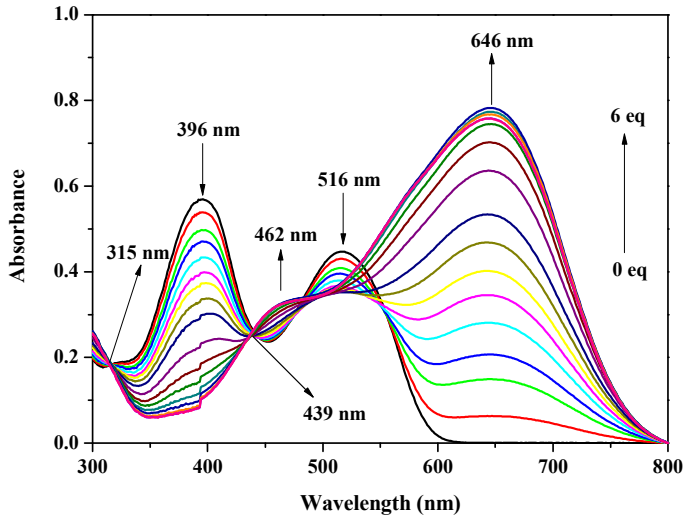

Figure 2. The absorption spectra of receptor **1** (10 μM) in THF/H_2O (93/7, v/v) with the addition of different equivalents of cyanide ions.

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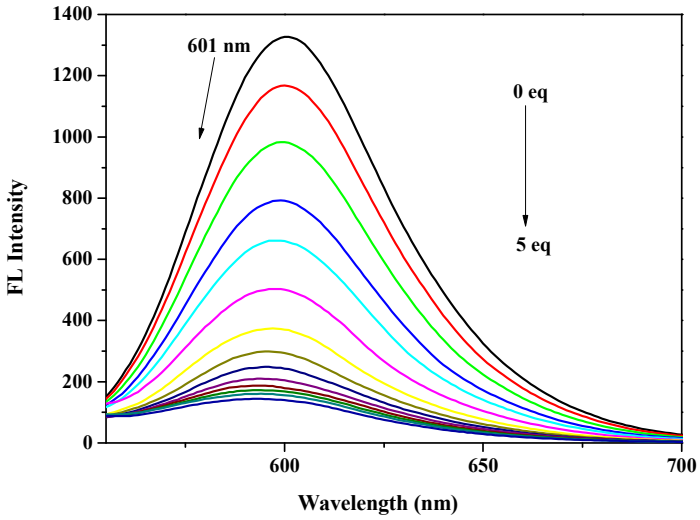

Figure 3. The emission spectra of receptor **1** (10 μM) in THF/H_2O (93/7, v/v) with the addition of different equivalents of cyanide ions (λ_{ex}=516 nm).

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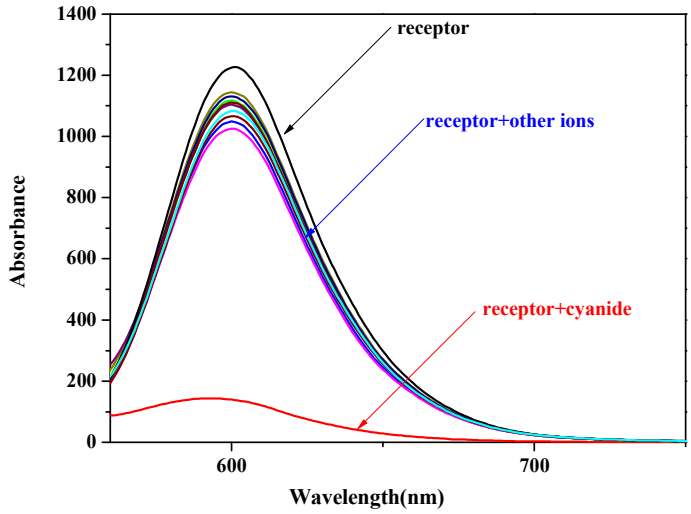

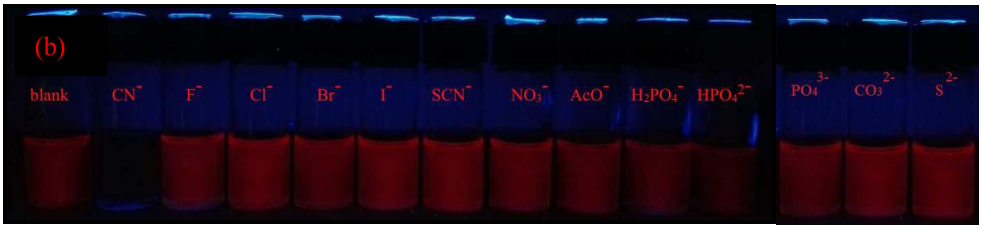

Figure 4. The fluorescence spectra of receptor **1** (10 μM) in THF/H_2O (93/7, v/v) solution upon addition of 5 equiv of various ions (λ_{ex}= 516 nm).

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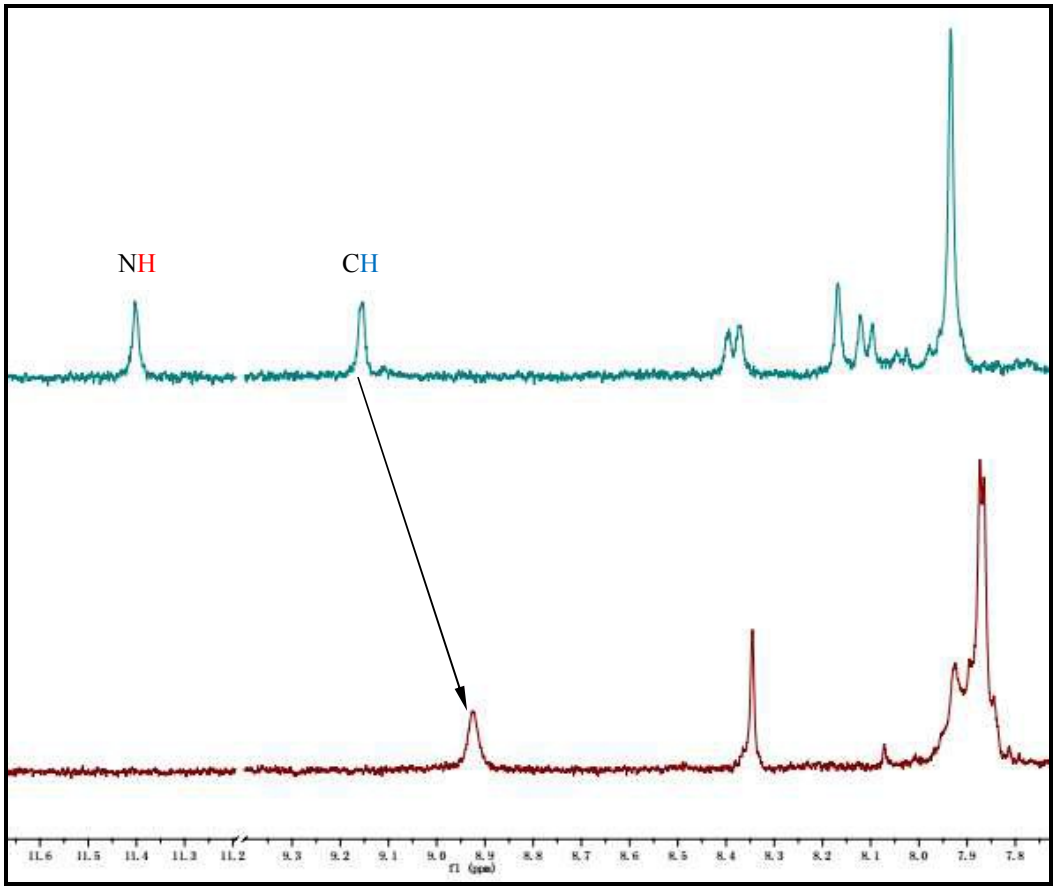

Figure 5. Partial ^{1}H NMR spectra of receptor in $CDCl_3$ in the absence and presence 2.0 equiv of cyanide ions.

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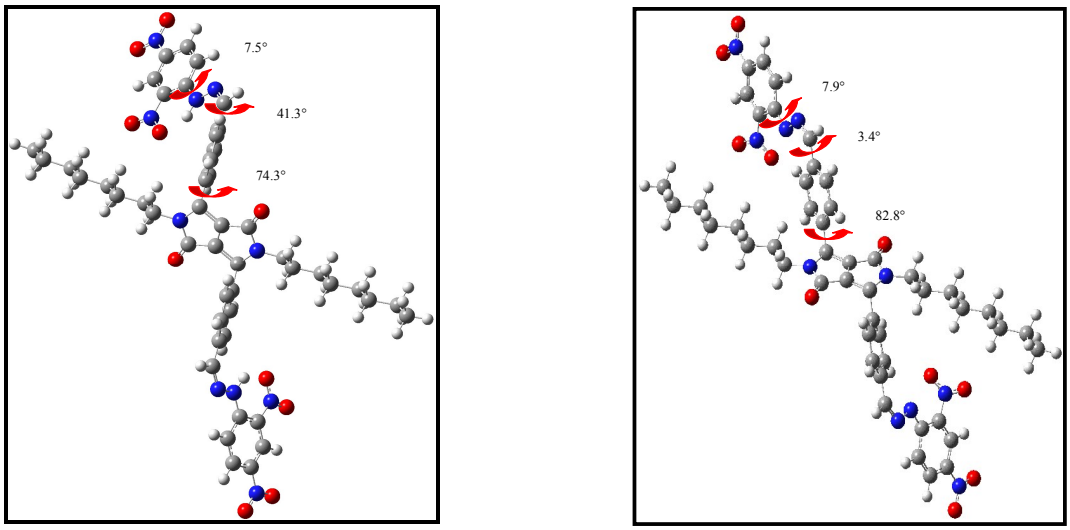

receptor **1** receptor **1**-cyanide

Figure 6. Optimized geometry of the receptor **1** (left) and the deprotonated species (right) at the B3LYP/6-31G* level of theory.

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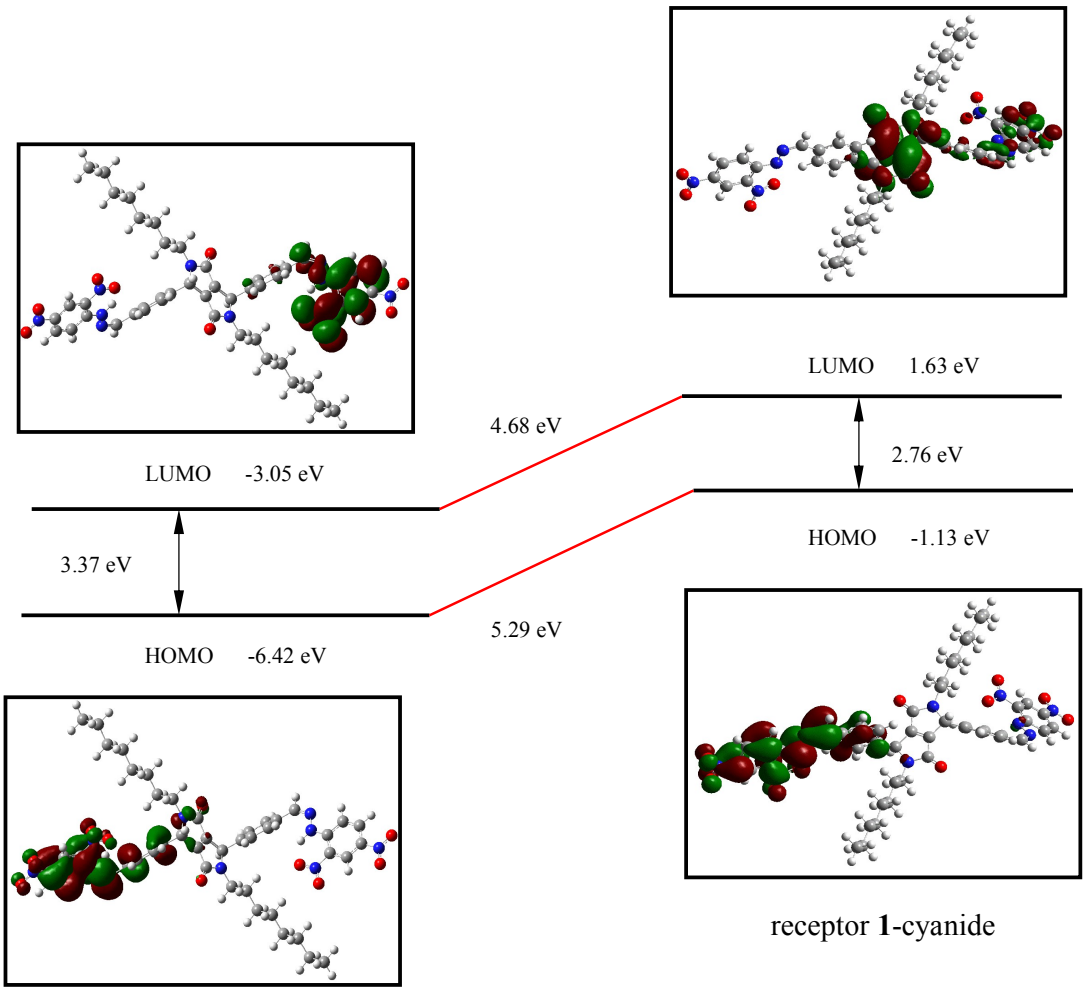

Figure 7. HOMO-LUMO orbitals and energy level diagrams of receptor **1** and its deprotonated species calculated on the DFT level using a B3LYP/6-31G* level of theory.

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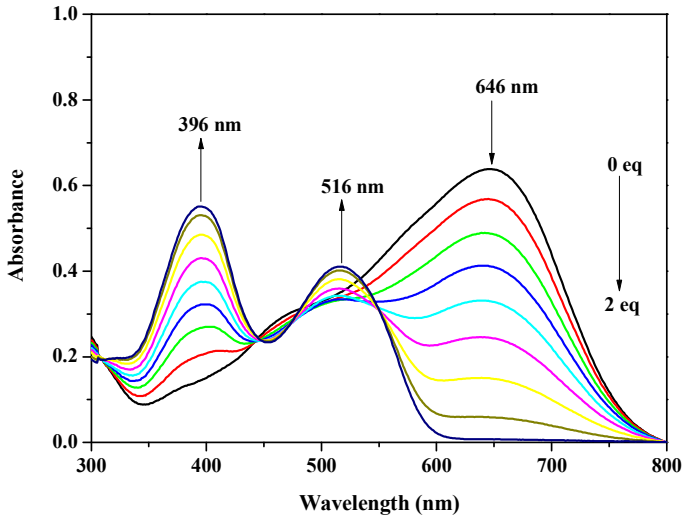

Figure 8. Absorption spectral changes of receptor **1**-cyanide solution (10 μM) in THF/H_2O (93/7, v/v) upon addition of increasing equivalents of TFA (10 mM) aqueous solution.

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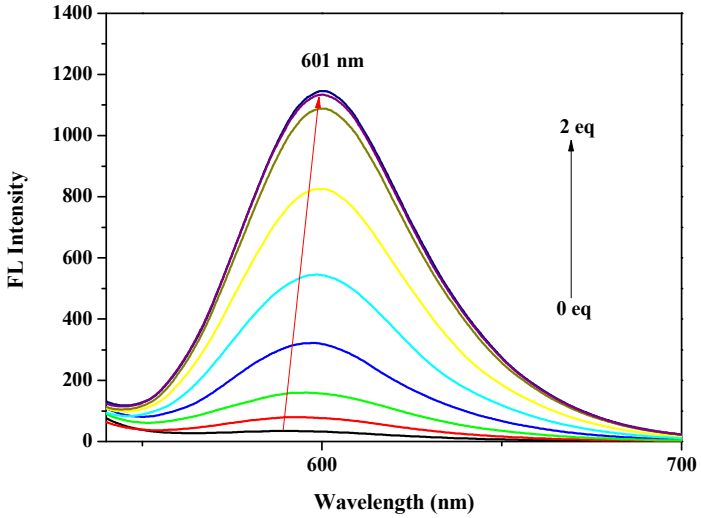

Figure 9. Emission spectral changes of receptor **1**-cyanide (10 μM) in THF/H_2O (93/7, v/v) upon addition of increasing equivalents of TFA aqeous solution.

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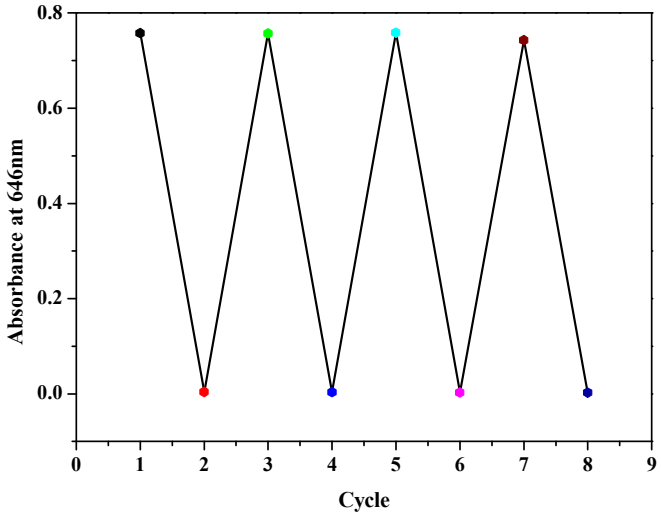

Figure 10. Relative absorbance intensity at 646 nm obtained during the titration of receptor **1**-cyanide and TFA.

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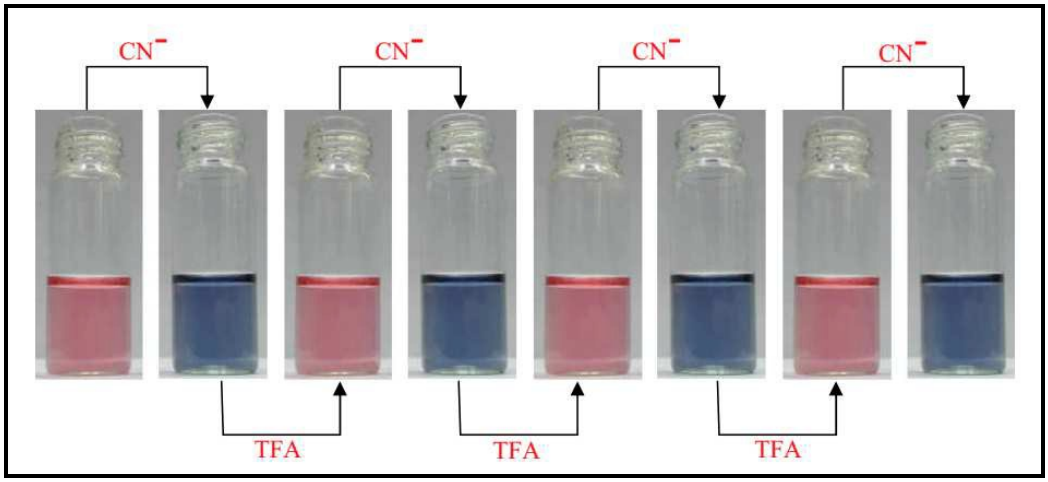

Figure 11. Visual color changes of receptor **1** after each sequential addition of cyanide ions and TFA aqueous solution.

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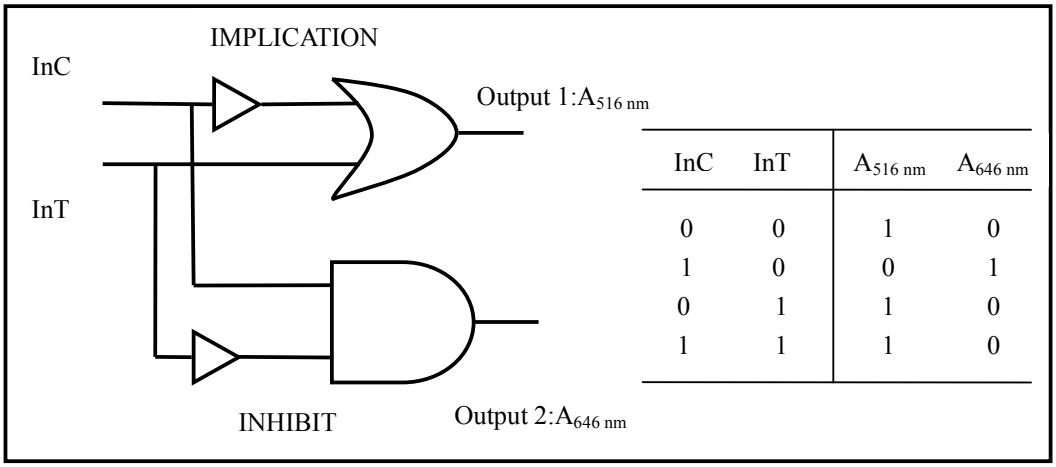

InC	InT	$A_{516\ nm}$	$A_{646\ nm}$
0	0	1	0
1	0	0	1
0	1	1	0
1	1	1	0

Figure 12. The complementary IMP/INH logic gate and its truth table. InC and InT represent Input CN^- and Input TFA, respectively.

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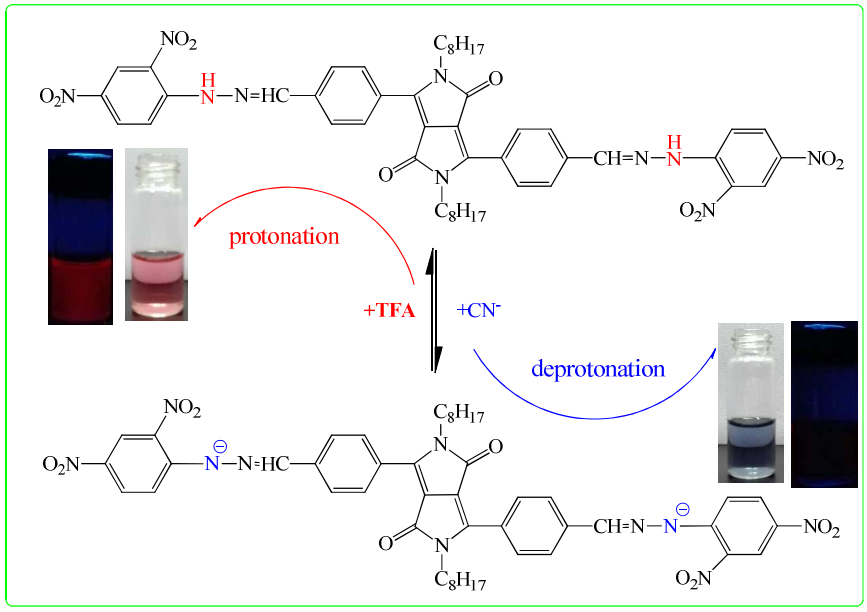
Graphic Abstract



A novel diketopyrrolopyrrole (DPP)-hydrazone based receptor **1** was designed and synthesized as a selective fluorescent and colorimetric chemosensor for cyanide in aqueous media *via* deprotonating between the hydrazide moiety of probe and cyanide. Notably, this probe serves as a recyclable component in sensing materials by adding of trifluoroacetic acid (TFA).