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Fluorescence Dyes for Determination of Cyanide

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Abstract

Cyanides being highly poisonous to living beings and pollutants to our environment are among the most important anions studied over the years. As cyanide usage continues to sky-rocket, it is extremely important and high time that chemists devised methods for their detection to ensure harmless usage and safer working conditions for people coming into contact with cyanide and its compounds, day in day out. In this book, an attempt has been made to provide an in-depth commentary of literature for the synthesis of fluorescent dyes and mechanisms for the molecular recognition and detection of cyanide ions. It also covers some current entropy on colorimetric and fluorescent organic chemical probes for the detection and quantification of cyanide anions via fluorogenic and chromogenic procedures.

Keywords: fluorescent dyes, molecular recognition, fluorogenic, chromogenic procedures, cyanide detection, sensing mechanisms

1. Introduction

The design of protocol for selective optical signaling probes for anions has received much attention over the years as a result of the significant roles they play in biological and environmental procedures [1]. The recognition of cyanide has become an area of increasing significance in supramolecular chemistry as a result of the vital role it plays in environmental, clinical, chemical, and biological applications, and the fact that much attention has been given to the preparation of artificial probes that have the capability of uniquely recognizing and sensing anion species [2, 3]. Cyanide is famous for being one of the most toxic materials and is very dangerous to the environment and human health [4]. As a result of the extreme toxicity of cyanide ions in physiological [4–6] and environmental [7] systems, many investigators have designed optical probes [8, 9] for the sensitive and bias detection of cyanide. Till date,

many strategies have been designed and developed for the detection of cyanide, including the formation of cyanide complexes with transition metal ions [10–14], boron derivatives [15, 16], CdSe quantum dots [17, 18], the displacement approach [19], hydrogen-bond interactions [20–22], deprotonation [23], and luminescence lifetime measurement [24]. For the interferences of competing anions to be curtailed in the sensing of cyanide, the nucleophilicity of the cyanide ion has been utilized, which includes its nucleophilic reactions with oxazine [25–27], pyrylium [28], squaraine [29], acyltriazene [19], acridinium [30], salicylaldehyde [31–33], trifluoroacetophenone [34–38], trifluoroacetamide derivatives [39–43], and other highly electrophilic carbonyl groups or imine [22, 44–48].

A lot of chemosensors for cyanide ion have been developed [49], chromogenic and fluorogenic probes for the detection of cyanide by the naked eye have attracted much interest as a result of the facile, fast usage, and their high sensitivity. As it is well-known, the probes are normally designed by the combination of a luminophore and an anion binding unit. Mostly, the anion binder is basically composed of H-bonding donors [50]. Herein, concise literature reports have been made on some strategies employed in the sensing of cyanide ions, dating from 2008 to 2017.

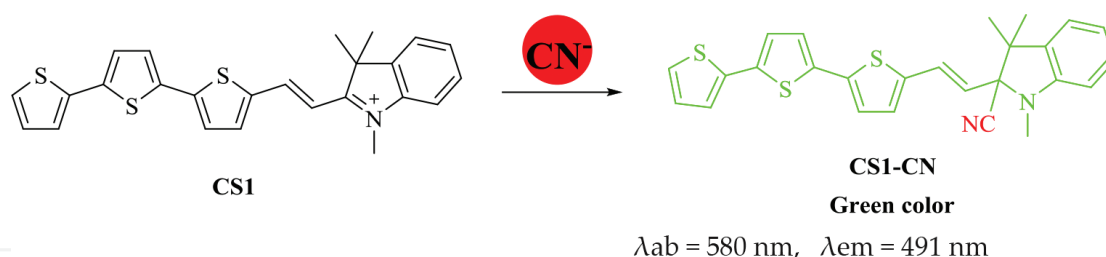
2. Sensing mechanisms and synthesis of cyanide sensors (CS)

The official methods of determining cyanides include titration [51, 52], spectrophotometry [65, 66], potentiometry with cyanide-selective electrodes [51, 53], flow injection (FI)-amperometry [54]. Analysis of cyanide in various matrices including water, soil, air, exhaled breath, food, and biological fluids (blood, urine, saliva, etc.), have been reviewed in official documents [55, 56], books [57] and journal articles [58, 59–61]. Quiet recently, Xu et al. [62] and Zelder and Mannel-Croise [63] have respectively written reviews on optical sensors and colorimetric measurement of cyanide. Herein, different sensing strategies have been discussed.

2.1. Cyanide sensing via aggregation induced emission (AIE)

This uncommon fluorescence phenomenon was perceived by Luo et al. [64] in 2001 via a solution of 1-methyl 1,2,3,4,5-pentaphenylsilole, and the term aggregation-induced emission was given to it. Tang et al. gave an explanation on the AIE phenomenon through a series of experimental analyses. They realized that the main cause of the AIE phenomenon was due to restriction of intramolecular rotation in the aggregates.

Sun et al. [65] have prepared a turn-on fluorescent probe **CS1** based on terthienyl for the detection of cyanide through the aggregation-induced emission (AIE) behavior of terthienyl units in aqueous solutions (**Scheme 1**). They confirmed the AIE behavior of **CS1** using the dynamic light scattering (DLS) measurements and the scanning electron microscopy (SEM) studies. The UV-vis titration of the free **CS1** showed absorption at 530 nm with a distinct color. Upon adding CN^- , the absorption was quenched and eventually disappeared when the concentration of CN^- reached 40 μM . In the fluorescence studies of the solution of the probe, it showed non-emissiveness in the absence of CN^- . Upon addition of cyanide to the solution



Scheme 1. Sensing mechanism of cyanide employing CS1.

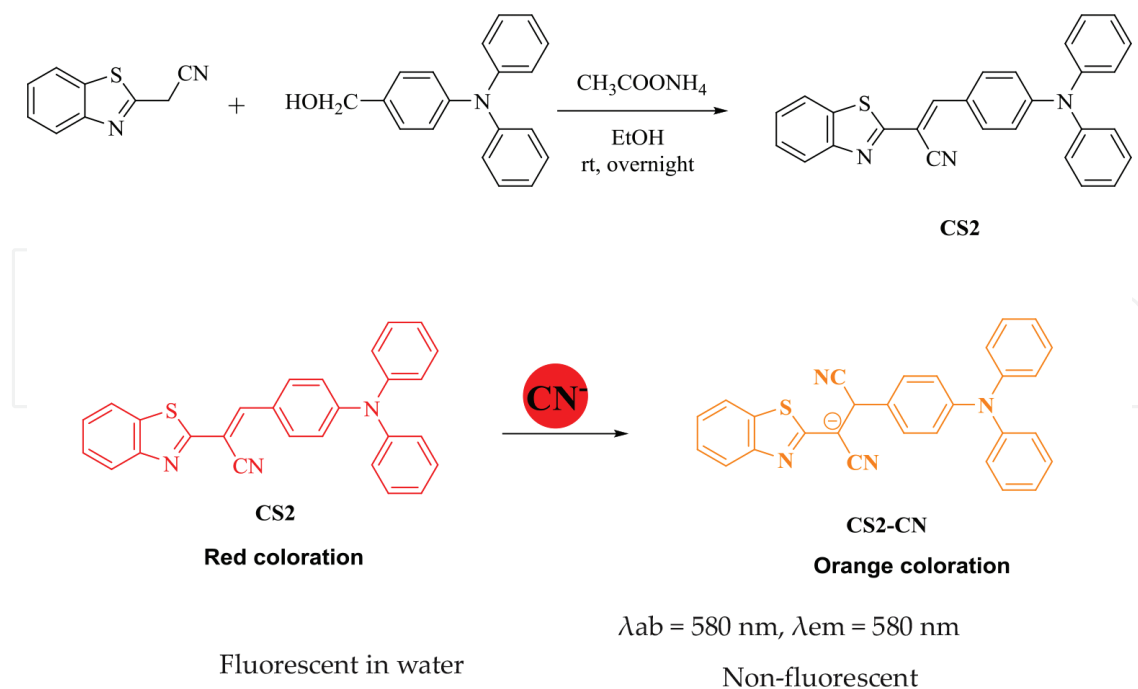
of **CS1**, an increase in its intensity at 491 nm was observed, and the fluorescence intensity further increased by the addition of more than 170 times. As the concentration of CN^- reached 40 μM , a bright green fluorescent emission was observed which can easily be noticed by the naked eyes.

Another AIE probe **CS2** has been prepared by Chen et al. [66]. The sensor was synthesized using 2-benzothiazoleacetonitrile and 4-(diphenylamino)-benzaldehyde in 73% yield. The investigators synthesized the probe by placing equimolar (10 mmol) of 2-Benzothiazoleacetonitrile, ammonium acetate, and 4-(diphenylamino)benzaldehyde in ethanol (30 mL). The reaction was stirred at room temperature overnight. Then obtained product was filtered and recrystallized from dichloromethane (5 mL) and ethanol (50 mL) to afford the product. The absorption and fluorescence titrations of the probe (5 μM) were used to ascertain its AIE properties in acetonitrile/water (1: 99, v/v) solvent mixture at room temperature. The researchers employed different anions including CN^- , HSO_4^- , SO_4^{2-} , HSO_3^- , CH_3COO^- , Cl^- , Br^- , I^- , F^- , NO_3^- and H_2PO_4^- in the analysis. All the anions, with the exception of cyanide, exhibited almost no changes in the fluorescence intensity. However, the addition of cyanide led to 99% decrease in the fluorescence intensity of **CS2**, which confirmed that **CS2** could significantly sense cyanide. When **CS2** was dissolved in acetonitrile, a weakly fluorescent was seen. The authors found **CS2** to be non-emissive in acetonitrile. However, upon addition of large amounts of water (fw > 80 vol%) to acetonitrile, an orange fluorescence ($\lambda_{em} = 580 \text{ nm}$) was observed under identical measurement conditions (**Scheme 2**). However, the group found the absorbance of the solution to be weak as the fraction of water was below 80%. Additionally, the fluorescence intensity with 90% water content was a bit intense than that with 99% which may be attributed to a more perfect aggregation state. Nonetheless, the characterizations were carried out in CH_3CN /water (1:99, v/v) (almost 100% aqueous solution) in consideration of practical use and environment protection. They therefore proposed cyanide sensing mechanism using probe **CS2** as illustrated in **Scheme 2**.

2.2. Cyanide sensing via the chemodosimeter approach

The special nucleophilic character of cyanide has been utilized for the preparation of different chemodosimetric sensors for cyanide, mostly in aqueous solutions.

In 2009, Kim and Kim [67] prepared, through the condensation reaction of nitromethane and a coumarinyl aldehyde, a new fluorescent chemodosimeter **CS3**, and investigated it for the detection of cyanide ions. The sensor has a coumarin moiety as the fluorescent signaling unit



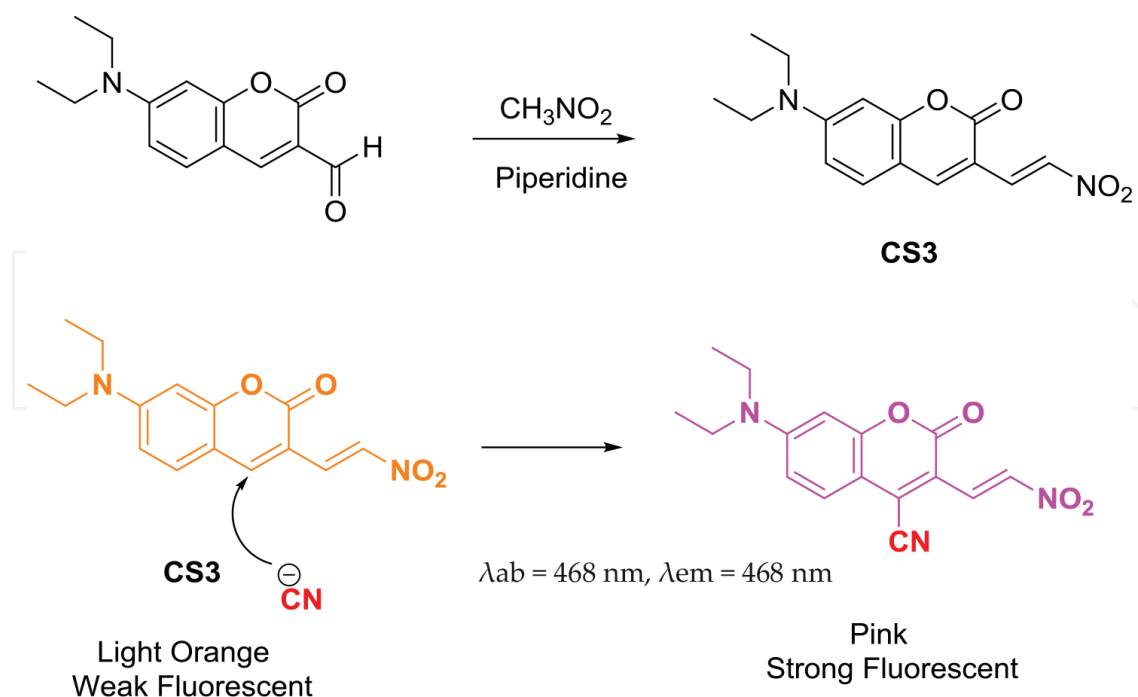
Scheme 2. Synthesis and sensing mechanism of probe CS2.

and a Michael acceptor unit being an unsaturated nitro group toward the cyanide. The authors proposed, using spectroscopic and chromatographic evidence, a plausible mechanism for the Michael acceptor type chemodosimeter **CS3**. Because the unsaturated nitro group of **CS3** is one of the good Michael acceptors, cyanide can be added to the β - or δ -position of the unsaturated nitro group, where the δ -position is doubly activated. The chemical reaction of **CS3** with a cyanide nucleophile was reported to be capable of causing a change in the electronic structure of the sensor thereby inducing a color change from light orange to pink at 468 nm (**Scheme 3**).

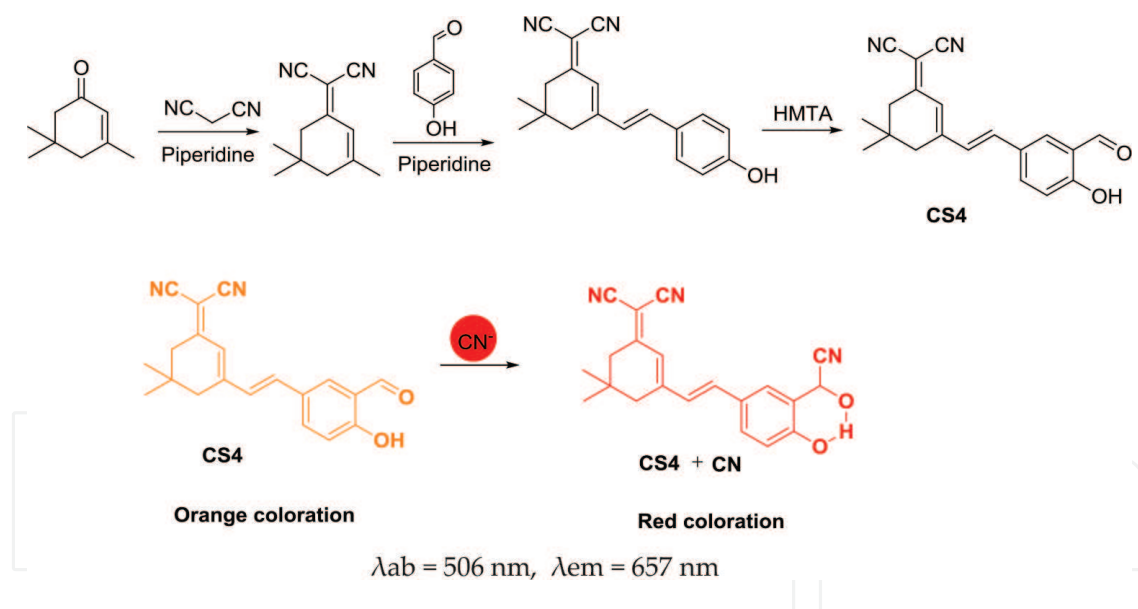
Hu et al. [68] have successfully synthesized and reported a 1,3-indanedione-based chemodosimeter that could be employed in sensing cyanide ions via both aggregation-induced emission enhancement (AIEE) and intramolecular charge transfer (ICT) in 90% aqueous medium. They prepared a solution of the chemodosimeter (1.0×10^{-5} M) in aqueous solution (THF:H₂O = 1:9 [v/v], containing 10×10^{-3} M HEPES, pH = 7.3). In the aqueous medium, the chemodosimeter showed a strong ICT absorption band at 425 nm, and upon adding CN[−], the ICT band was said to have disappeared and the color of the solution changed from yellow to colorless.

2.3. Cyanide sensing via the excited state intra- and inter-molecular proton transfer (ESIPT)

In 2017, Huo and co-workers [69] reported the synthesis of a novel isophorone-based red-emitting fluorescent probe **CS4** that can be used in signaling cyanide ion through hampering of its ESIPT (**Scheme 4**). With the addition of cyanide ions, as reported by the investigators, the absorption spectrum of **CS4** (5 mM) exhibited an obvious peak at 419 nm. Upon further



Scheme 3. Synthesis and plausible mechanism for cyanide using CS3.



Scheme 4. Sensing mechanism for cyanide using CS4.

addition of CN^- , the absorption band gradually weakened followed by a rapid step-up in the peak at 506 nm, intimating that CS4 has involved in a nucleophilic reaction with the CN^- , which led to a distinct color change from orange to red. The authors observed the fluorescence spectra of CS4 (5 mM) without CN^- to have shown an emission at 616 nm with orange color under a handheld UV lamp. After adding CN^- , the emission at 616 nm was said to have attenuated sharply and then followed by a peak increased at 657 nm, which induced a fluorescence chromogenic change from orange to red (**Scheme 4**).

Shymaprosad Goswami and co-researchers [70] have reported an ESIPT exhibiting benzothiazole receptor possessing two aldehyde groups; one ortho and the other para to an OH group. The ortho aldehyde group being very reactive, was reported to have undergone a nucleophilic reaction with CN^- selectively, thereby hampering an ESIPT. The investigators confirmed the process via DFT and TD-DFT computations. The affinity of the benzothiazole receptor toward different competing ions was investigated using UV-vis absorption and emission spectrometry in aqueous acetonitrile solution. The probe showed a green emission at 521 nm, a peculiar benzothiazolyl phenol ring emission. Upon adding CN^- , the emission was reported to have drastically decreased, followed by an increase at 436 nm. This suggested that, as thought by the authors, a chemical reaction between the cyanide and the aldehyde group has interrupted the conjugation and thereby hampering the ESIPT process leading to a color change from green to blue. In the UV-vis absorption study, they found that, only CN^- had induced the perturbation of the electronic behavior of benzothiazole receptor.

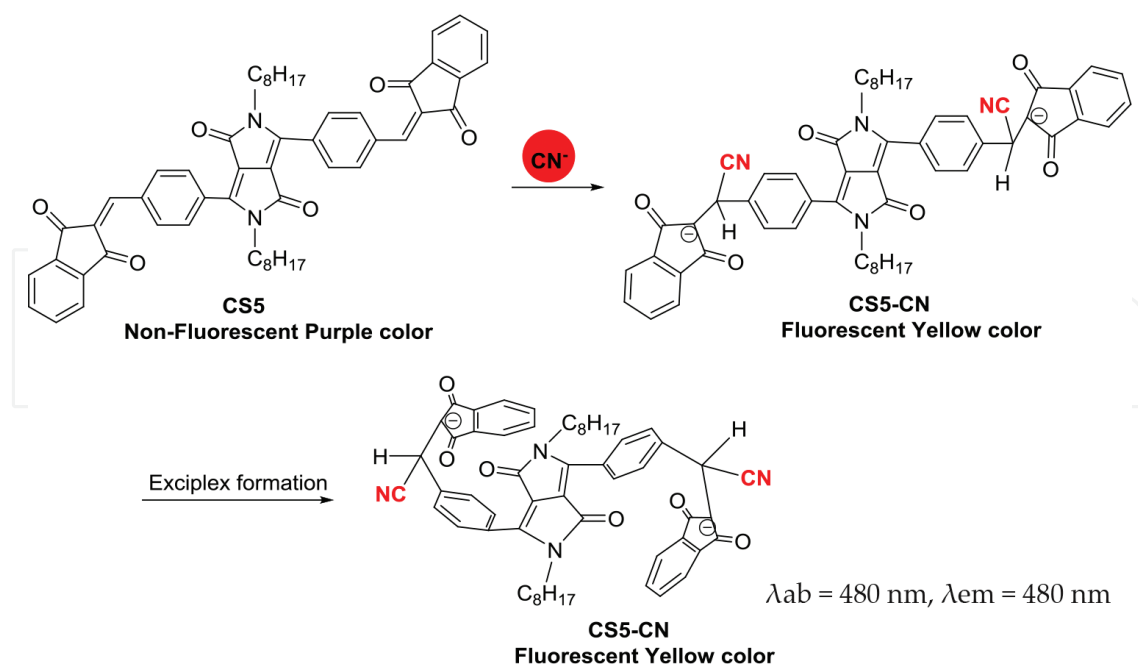
2.4. Cyanide sensing via the excimer/exciplex form

Wang et al. [71] have successfully designed and reported the synthesis of a novel probe **CS5** comprising diketopyrrolopyrrole and indanedione-based Michael receptor. The sensor could be employed in the recognition of cyanide anion. The researchers realized that, as an aqueous solution of cyanide was added to **CS5** in THF, it induced a sudden color change from purple to yellow, as well as a large blue shift from 553 to 480 nm, without any interference from the other interfering ions (F^- , Cl^- , Br^- , I^- , H_2PO_4^- , SO_4^{2-} , CO_3^{2-} , PO_4^{3-} , and OAc^-). They also studied the binding of CN^- with **CS5**. Therein, they found out that, the absorption spectra of **CS5** in THF changed upon addition of an aqueous solution of cyanide. This led to absorption peaks of **CS5** at 359 and 553 nm, which gradually attenuated following the formation of two new bands centered at 314 and 480 nm with color change from purple to yellow (**Scheme 5**).

Shahid et al. [72] have prepared and described a new simple organic scaffold based on acenaphthene. The fluorogenic and chromogenic properties of the probe were investigated for signaling metal cations and anions in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (8:2, v/v) solvent mixture. The authors employed a metal chelate based sensing strategy of copper complexes for fluorescent sensing of cyanide.

2.5. Cyanide sensing via the Förster/fluorescence resonance energy transfer (FRET)

Goswami et al. [73] investigated a chemosensor **CS6** having a naphthalene and fluorescein chromophores acting as an energy donor and an acceptor, respectively. The authors reported that, the emission of the naphthalene chromophore and the absorption of the ring-opened fluorescein dye indicated that, there was an overlap between these two spectra, implying that the FRET from the naphthalene chromophore to the fluorescein moiety had occurred. Additionally, they found out that, the probe **CS6**- Zn^{2+} complex for signaling cyanide was generated *in situ* by adding 1 equiv of ZnCl_2 to $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (3:7, v/v) solution of probe **CS6**. They conducted the UV-vis and fluorescence studies at pH 7.1, and realized that there was the disappearance of yellow color of the **CS6**- Zn^{2+} with increased concentration of CN^- . The researchers suggested that, the observed decrease of yellow coloration of the solution



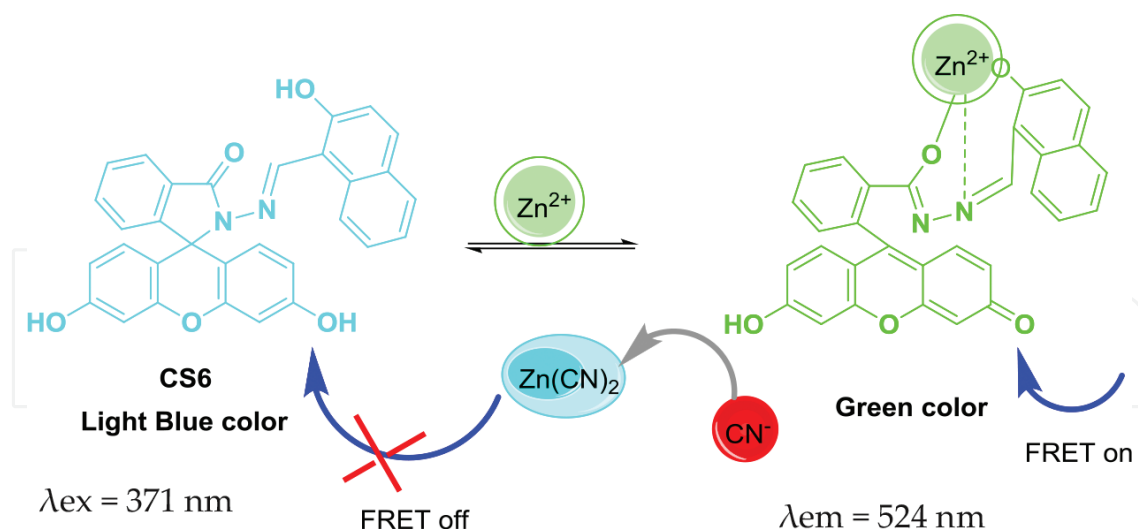
Scheme 5. Structure of CS5 and its cyanide sensing.

containing the **CS6-Zn²⁺** complex was a result of the ring opened amide form of **CS6-Zn²⁺** has been converted to the spirolactam form of **CS6** in the presence of CN⁻. Again, the authors investigated the selectivity of cyanide through the UV response of **CS6-Zn²⁺** in the presence of competing anions such as Br⁻, Cl⁻, I⁻, F⁻, ADP, ATP, PPI, OAc⁻, Pi, SH⁻, SCN⁻, and N₃⁻. As cyanide solution was added to the solution of the **CS6-Zn²⁺** complex, there was a reverse change in the fluorescence spectra due to the occurrence of a reverse FRET phenomenon (**Scheme 6**).

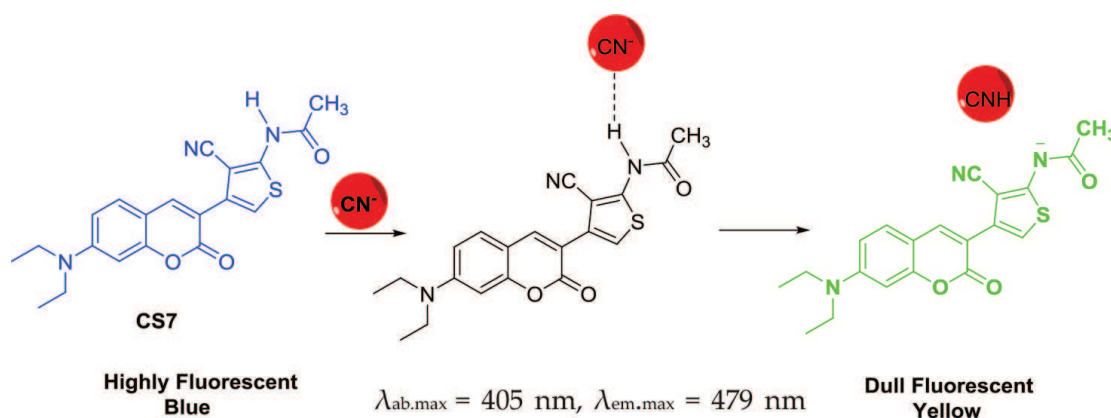
In 2009, Chung and co-workers [74] successfully developed a cyanide sensor for fluorescence study. In the fluorescence study, different anions, such as CN⁻, SCN⁻, AcO⁻, F⁻, Cl⁻, Br⁻, I⁻, H₂PO₄⁻, HSO₄⁻, NO₃⁻, and ClO₄⁻ were evaluated at pH 7.4 (0.02 M pH 7.4 HEPES). Using 100 equiv. of each of these anions, and 6 mM of the probe in the presence of Cu²⁺ (1 equiv.), only CN⁻ was observed to have shown a large fluorescence enhancement.

2.6. Cyanide sensing via H-bonding

In 2015, our group [75] designed and reported the synthesis and application of chemosensor **CS7** as cyanide sensor. The signaling performance of **CS7** was investigated using UV-vis absorption and fluorescence spectroscopy in DMSO against F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, CN⁻, HSO₄⁻ and ClO₄⁻ anions with tetrabutylammonium (TBA) as the counter cation. The absorption maximum of **CS7** was observed at 405 nm in DMSO. This absorption band shifted hypsochromically upon addition of one equiv of CN⁻ to the solution of the probe, and a new band at 392 nm was observed. Apparently, the electrostatic interaction between probe **CS7** and CN⁻ deprotonated the amide -NH function and negative charge accumulated around the amide function giving rise to the observed hypsochromic shift. To gain, an insight into the binding of **CS7** with anions and fluorescence titrations were performed



Scheme 6. Structure of CS6 and cyanide sensing on the via a Zn-complex.



Scheme 7. Binding mode of CS7 for cyanide sensing.

in DMSO with excitation wavelength of 405 nm. Free sensor, **CS7** displayed an emission maximum at 479 nm in DMSO with a high intensity. Upon addition of CN^- (>1 equiv) to the solution of **CS7**, the fluorescence intensity gradually decreased and emission color changed. Addition of 20 equiv of CN^- almost wiped out the fluorescence of **CS7**. Similar results were observed for the competing anions (**Scheme 7**).

A group of researchers [76] reported the synthesis of two receptors of specific signaling of cyanide ions in sodium cyanide solution. The authors associated the visual detection of CN^- via color changes, with the formation of hydrogen bonded adducts. They found the probes to have limited solubility in water, and therefore employed mixed solvent, such as CH_3CN /HEPES buffer (1:1, v/v), for the sensing studies. The fluorogenic and visually detectable chromogenic changes of the receptors were verified using aqueous solutions of the sodium salt of all the employed common anionic analytes such as F^- , Cl^- , Br^- , I^- , CN^- , SCN^- , CH_3COO^- , H_2PO_4^- , $\text{P}_2\text{O}_7^{3-}$, HSO_4^- , NO_3^- , and NO_2^- present in excess (0.1 mM). For the contending anions, no spectral changes in their spectral patterns was observed by the investigators. However, the researchers observed changes in spectral pattern, naked-eye color, and fluorescence, only in

the presence of added CN^- . Interference studies conducted by them revealed that, the spectral response for CN^- remained unaffected in the presence of 10 equiv of all interfering anions.

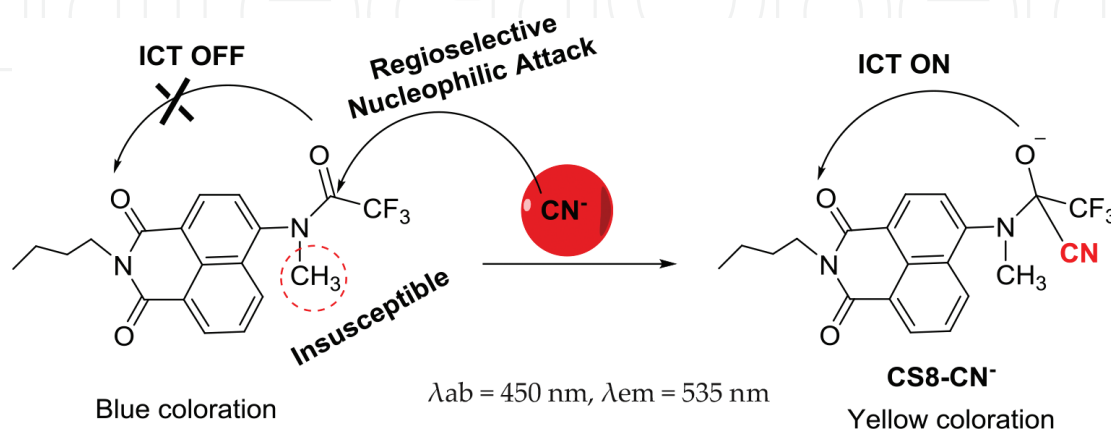
2.7. Cyanide sensing via the inter- or intra- molecular charge transfer (ICT)

In 2017, Hao et al. [77] designed and synthesized a probe **CS8** having a naphthalimide unit as the fluorophore and a methylated trifluoroacetamide moiety as the acceptor part, which can be employed for selective and ratiometric signaling of cyanide. The group also employed the probe to study the sensing recognition of cyanide using HPLC, UV-vis, and emission spectroscopic analyses. The regioselective nucleophilic attack of cyanide ion to the methylated trifluoroacetamide unit in the sensor was reported to induce an enhanced ICT process, and therefore causing a sudden red shift in both absorption and emission spectra of the sensor at 450 nm and 535 nm, respectively (**Scheme 8**).

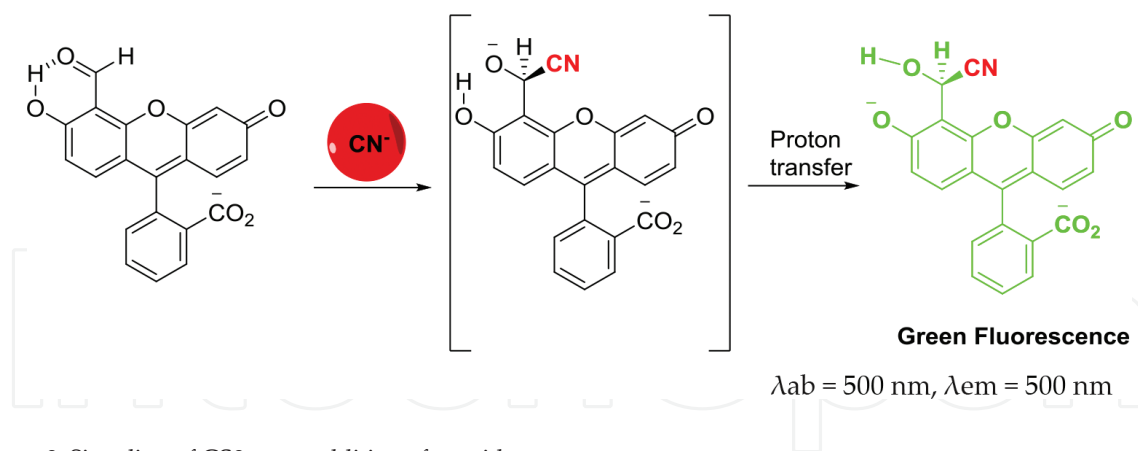
Mashraqui and co-workers [78] have developed a novel chemodosimeter that has the structural capabilities to convert the CN^- -binding event into an enhanced ICT process, inducing absorbance red shifts and a high fluorescence turn-on response. The use of the probe toward sensing different anions was investigated by the group via optical spectral analysis. The group realized that, the absorption spectra of the chemosensor (28 μM) in DMSO- H_2O (7:3, v/v) in tris-HCl buffer pH 7.0, was insensitive to each of the competing anions (F^- , AcO^- , SCN^- , HSO_4^- , NO_3^- , Br^- , Cl^- , I^- , and H_2PO_4^-) up to 75 mM. On the contrary, the concentration of cyanide (7.6 mM) which was at a 10-fold lower than that of the interfering anions, was noticed to have elicited a monumental interaction, which was followed by an instant color change from colorless to deep yellow, an event that allowed selective visual detection of cyanide by the naked eye.

2.8. Cyanide sensing via the nucleophilic approach

Kwon et al. [79] successfully introduced a fluorescent chemodosimeter **CS9** which exhibited a green fluorescence coloration upon adding cyanide ions. The investigators analyzed the probe in aqueous solution and noticed that the probe showed an 'OFF-ON' type of emission change which could be utilized as a monitoring device for cyanide over 500 nm (**Scheme 9**).



Scheme 8. Mechanism for the signaling of **CS8** with cyanide.



Scheme 9. Signaling of CS9 upon addition of cyanide.

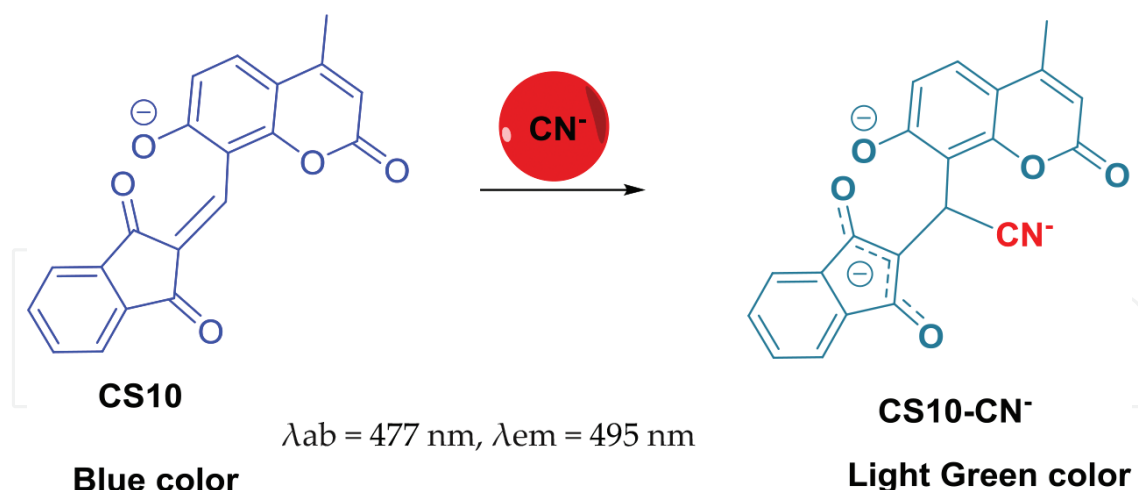
For the fluorescent analysis, 100 equiv of different anions (CN^- , AcO^- , F^- , Cl^- , Br^- , I^- , H_2PO_4^- , HSO_4^- , NO_3^- , and ClO_4^-) were investigated in acetonitrile–HEPES (9:1, v/v, 0.01 M pH 7.4 HEPES), containing probe **CS9** (3 μM). The authors attributed the selective recognition of cyanide as a result of the high nucleophilic nature of CN^- in aqueous solution. Finally, they further studied the practical application of the sensor by applying it for the selective detection of cyanide in the living cells.

Li et al. [80] reported the development of selective and sensitive red-emitting fluorogenic and colorimetric dual-channel sensor for detection of cyanide. The group realized that, adding cyanide ion to the probe led to the display of huge blue-shift in both fluorescence (130 nm) and absorption (100 nm) spectra. The authors found that, the probe could be capable of selective signaling of cyanide by the naked-eye. They therefore concluded that, the mechanism for the detection of cyanide was due to the nucleophilic attack of cyanide toward the benzothiazole group of probe, which could block conjugation between benzothiazole unit and the naphthopyran moiety, resulting in both color and spectral changes.

$\lambda_{ab} = 500 \text{ nm}, \lambda_{em} = 500 \text{ nm}$.

2.9. Cyanide sensing via the photoinduced electron transfer (PET)

Qu et al. [81] described the synthesis of a fluorescent and colorimetric chemosensor **CS10** derived from a naphtho[2,1-*b*]furan-2-carbohydrazide and 2-hydroxy-1-naphthaldehyde, through a straightforward reaction, from inexpensive reagents, for a swift signaling, superior selectivity, and superb sensitivity toward cyanide ions. The researchers observed that, the mechanism for the recognition of cyanide ions was as a result of the photo-induced electron transfer (PET) (**Scheme 10**). The investigators found the probe **CS10** to possess a strong anti-interference toward other common anions (F^- , AcO^- , H_2PO_4^- , and SCN^-). The authors applied the sensor for detection of CN^- in food samples, which they found to be an easier and selective platform for on-site monitoring of CN^- in agriculture samples. The investigators carried out both UV-vis and the fluorescence spectroscopy experiments in EtOH/ H_2O (7:3, v/v) HEPES solution of sensor **CS10**. A significant color change from colorless to yellow, which was visible to the naked eyes, and it was accompanied by a strong and broad absorption red shift from 373 nm to 477 nm in the UV-visible spectrum of solution of the sensor in EtOH/ H_2O (7:3, v/v) HEPES solution. When



Scheme 10. Mechanism for the recognition of cyanide using sensor **CS10**.

50 equivalents of CN^- was added to the solution of the probe, the fluorescence intensity of the sensor **CS10** increased rapidly and the observed change in coloration from dim blue to blue-green was said to be distinguishable by the naked eye under the UV-lamp.

A group of researchers [82] successfully prepared a Co(II)-salen based fluorescent sensor that is applicable for selective recognition of cyanide anions in 1:2 binding stoichiometry. The scientists related the fluorescence enhancement of the solution of the probe, upon the addition of cyanide, to an interruption of photoinduced electron transfer from the coumarin fluorophore of the sensor to the cobalt(II) ion. In order to address the origin of the fluorescence enhancement of the sensor by the coordination of cyanide anions, the authors measured the HOMO and LUMO energy levels of the cobalt-salen complex of the chemosensor in the absence and the presence of cyanide anions via cyclic voltammetric and UV-vis spectroscopic measurements.

3. Conclusion

In summary, this chapter is limited to literature reports that have been published from 2008 to 2017. Some papers that have been published pre-2008 may have been used to illustrate important points. Some of the schemes for the synthetic pathways of the reported literature have not been illustrated in this chapter due to the limited space available to the authors. There are also a few papers that have been published within the period captured herein but could not be included. The omission of such literature does not in any way connote that such papers are of lesser importance.

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Conflict of interest

There is no conflict of interest, whatsoever, in publishing this piece.

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References

- [1] (a) Lee C-H, Miyaji H, Yoon D-W, Sessler JL. Strapped and other topographically non-planar calixpyrrole analogues. Improved anion receptors. *Chemical Communications*. 2008;(1):24-34 (b) Yoon J, Kim SK, Singh NJ, Kim KS. Imidazolium receptors for the recognition of anions. *Chemical Society Reviews*. 2006;**35**(4):355-360 (c) Gunnlaugsson T, Glynn M, Tocci GM, Kruger PE, Pfeffer FM. Anion recognition and sensing in organic and aqueous media using luminescent and colorimetric sensors. *Coordination Chemistry Reviews*. 2006;**250**(23-24):3094-3117 (d) Gale PA. From anion receptors to transporters. *Accounts of Chemical Research*. 2011;**44**(3):216-226 (e) Koskela SJM, Fyles TM, James TD. A ditopic fluorescent sensor for potassium fluoride. *Chemical Communications*. 2005;(7):945-947 (f) Kim SK, Kim HN, Xiaoru Z, Lee HN, Lee HN, Soh JH, Swamy KMK, Yoon J. Recent development of anion selective fluorescent chemosensors. *Supramolecular Chemistry*. 2007;**19**(4-5):221-227 (g) Martínez-Máñez R, Sancañón F. Fluorogenic and chromogenic chemosensors and reagents for anions. *Chemical Reviews*. 2003;**103**(11):4419-4476 (h) Czarnik AW. Chemical communication in water using fluorescent chemosensors. *Accounts of Chemical Research*. 1994;**27**(10):302-308 (i) Lee HN, Xu Z, Kim SK, Swamy KMK, Kim Y, Kim S-J, Yoon J. Pyrophosphate-selective fluorescent chemosensor at physiological pH: formation of a unique excimer upon addition of pyrophosphate. *Journal of the American Chemical Society*. 2007;**129**(13):3828-3829
- [2] Beer PD, Gale PA. Anion recognition and sensing: The state of the art and future perspectives. *Angewandte Chemie, International Edition*. 2001;**40**(3):486-516
- [3] Amendola V, Esteban-Gómez D, Fabbrizzi L, Licchelli M. What Anions do to N-H-containing receptors. *Accounts of Chemical Research*. 2006;**39**(5):343-353
- [4] Bianchi A, Bowman-James K, Garcia-Espana E. *Supramolecular Chemistry of Anions*. New York, NY, USA: Wiley-VCH; 1997
- [5] Timofeyenko YG, Rosentreter JJ, Mayo S. Piezoelectric quartz crystal microbalance sensor for trace aqueous cyanide ion determination. *Analytical Chemistry*. 2007;**79**(1):251-255

- [6] Vennesland B, Comm EE, Knownles CJ, Westly J, Wissing F. Cyanide in biology. London: Academic; 1981
- [7] Young C, Tidwell L, Anderson C. Cyanide: Social, Industrial, and Economic Aspects, Minerals, Metals, and Materials Society. Warrendale; 2001
- [8] Xu Z, Chen X, Kim HN, Yoon J. Sensors for the optical detection of cyanide ion. Chemical Society Reviews. 2010;**39**(1):127-137
- [9] Cho DG, Sessler JL. Modern reaction-based indicator systems. Chemical Society Reviews. 2009;**38**(6):1647-1662
- [10] Kim YH, Hong JI. Ion pair recognition by Zn-porphyrin/crown ether conjugates: Visible sensing of sodium cyanide. Chemical Communications. 2002;**5**:512-513
- [11] Liu H, Shao XB, Jia MX, Jiang XK, Li ZT, Chen GJ. Selective recognition of sodium cyanide and potassium cyanide by diaza-crown ether-capped Zn-porphyrin receptors in polar solvents. Tetrahedron. 2005;**61**(34):8095-8100
- [12] Chow CF, Lam MH, Wong WY. A heterobimetallic ruthenium (ii)-copper (ii) donor-acceptor complex as a chemodosimetric ensemble for selective cyanide detection. Inorganic Chemistry. 2004;**43**(26):8387-8393
- [13] Zelder FH. Specific colorimetric detection of cyanide triggered by a conformational switch in vitamin B12. Inorganic Chemistry. 2008;**47**(4):1264-1266
- [14] Zeng Q, Cai P, Li Z, Qin J, Tang BZ. An imidazole-functionalized polyacetylene: Convenient synthesis and selective chemosensor for metal ions and cyanide. Chemical Communications. 2008;**9**:1094-1096
- [15] Badugu R, Lakowicz JR, Geddes CD. Enhanced fluorescence cyanide detection at physiologically lethal levels: Reduced ICT-based signal transduction. Journal of the American Chemical Society. 2005;**127**(10):3635-3641. DOI: 10.1021/ja044421i
- [16] Ros-Lis JV, Martínez-Máñez R, Sato J. A selective chromogenic reagent for cyanide determination. Chemical Communications. 2002;**19**:2248-2249
- [17] Jin WJ, Fernández-Argüelles MT, Costa-Fernández JM, Pereiro R, Sanz-Medel A. Photoactivated luminescent CdSe quantum dots as sensitive cyanide probes in aqueous solutions. Chemical Communications. 2005;**7**:883-885
- [18] Touceda-Varela A, Stevenson EI, Galve-Gasíon JA, Dryden DT, Mareque-Rivas JC. Selective turn-on fluorescence detection of cyanide in water using hydrophobic CdSe quantum dots. Chemical Communications. 2008;**17**:1998-2000
- [19] Chung Y, Ahn KH. N-acyl triazines as tunable and selective chemodosimeters toward cyanide ion. The Journal of Organic Chemistry. 2006;**71**(25):9470-9474
- [20] Sun SS, Lees AJ. Anion recognition through hydrogen bonding: a simple, yet highly sensitive, luminescent metal-complex receptor. Chemical Communications. 2000;**17**:1687-1688

- [21] Miyaji H, Sessler JL. Off-the-shelf colorimetric anion sensors. *Angewandte Chemie, International Edition*. 2001;**113**(1):158-161
- [22] Saha S, Ghosh A, Mahato P, Mishra S, Mishra SK, Suresh E, Das S, Das A. Specific recognition and sensing of CN⁻ in sodium cyanide solution. *Organic Letters*. 2010;**12**(15):3406-3409
- [23] Gimeno N, Li X, Durrant JR, Vilar R. Cyanide sensing with organic dyes: Studies in solution and on nanostructured Al₂O₃ surfaces. *Chemistry - A European Journal*. 2008;**14**(10):3006-3012
- [24] Anzenbacher P, Tyson DS, Jursíková K, Castellano FN. Luminescence lifetime-based sensor for cyanide and related anions. *Journal of the American Chemical Society*. 2002;**124**(22):6232-6233
- [25] Tomasulo M, Sortino S, White AJ, Raymo FM. Chromogenic oxazines for cyanide detection. *The Journal of Organic Chemistry*. 2006;**71**(2):744-753. DOI: 10.1021/jo052096r
- [26] Ren J, Zhu W, Tian H. A highly sensitive and selective chemosensor for cyanide. *Talanta*. 2008;**75**(3):760-764
- [27] Tomasulo M, Raymo FM. Colorimetric detection of cyanide with a chromogenic oxazine. *Organic Letters*. 2005;**7**(21):4633-4636. DOI: 10.1021/ol051750m
- [28] Garcia F, Garcia JM, Garcia-Acosta B, Martínez-Máñez R, Sancenón F, Soto J. Pyrylium-containing polymers as sensory materials for the colorimetric sensing of cyanide in water. *Chemical Communications*. 2005;(22):2790-2792
- [29] Ros-Lis JV, Martínez-Máñez R, Sato J. A selective chromogenic reagent for cyanide determination. *Chemical Communications*. 2002;(19):2248-2249
- [30] Yang Y, Tae J. Acridinium salt based fluorescent and colorimetric chemosensor for the detection of cyanide in water. *Organic Letters*. 2006;**8**(25):5721-5723. DOI: 10.1021/ol062323r
- [31] Lee KS, Kim HJ, Kim GH, Shin I, Hong JI. Fluorescent chemodosimeter for selective detection of cyanide in water. *Organic letters*. 2008;**10**(1):49-51
- [32] Kwon SK, Kou S, Kim HN, Chen X, Hwang H, Nam SW, Yoon J. Sensing cyanide ion via fluorescent change and its application to the microfluidic system. *Tetrahedron Letters*. 2008;**49**(26):4102-4105
- [33] Lee KS, Lee JT, Hong JI, Kim HJ. Visual detection of cyanide through intramolecular hydrogen bond. *Chemistry Letters*. 2007;**36**(6):816-817
- [34] Kim YK, Lee YH, Lee HY, Kim MK, Cha GS, Ahn KH. Molecular recognition of anions through hydrogen bonding stabilization of anion-ionophore adducts: A novel trifluoroacetophenone-based binding motif. *Organic Letters*. 2003;**5**(21):4003-4006
- [35] Chung YM, Raman B, Kim DS, Ahn KH. Fluorescence modulation in anion sensing by introducing intramolecular H-bonding interactions in host-guest adducts. *Chemical Communications*. 2006;(2):186-188

- [36] Ryu D, Park E, Kim DS, Yan S, Lee JY, Chang BY, Ahn KH. A rational approach to fluorescence “turn-on” sensing of α -amino-carboxylates. *Journal of the American Chemical Society*. 2008;**130**(8):2394-2395
- [37] Kim DS, Chung YM, Jun M, Ahn KH. Selective colorimetric sensing of anions in aqueous media through reversible covalent bonding. *The Journal of Organic Chemistry*. 2009;**74**(13):4849-4854
- [38] Kim DS, Ahn KH. Fluorescence “turn-on” sensing of carboxylate anions with oligothiophene-based o-(carboxamido) trifluoroacetophenones. *The Journal of Organic Chemistry*. 2008;**73**(17):6831-6834
- [39] Niu HT, Jiang X, He J, Cheng JP. A highly selective and synthetically facile aqueous-phase cyanide probe. *Tetrahedron Letters*. 2008;**49**(46):6521-6524
- [40] Niu HT, Su D, Jiang X, Yang W, Yin Z, He J, Cheng JP. A simple yet highly selective colorimetric sensor for cyanide anion in an aqueous environment. *Organic & Biomolecular Chemistry*. 2008;**6**(17):3038-3040
- [41] Ekmekci Z, Yilmaz MD, Akkaya EU. A monostyryl-boradiazaindacene (BODIPY) derivative as colorimetric and fluorescent probe for cyanide ions. *Organic Letters*. 2008;**10**(3):461-464
- [42] Yu H, Zhao Q, Jiang Z, Qin J, Li Z. A ratiometric fluorescent probe for cyanide: convenient synthesis and the proposed mechanism. *Sensors and Actuators B: Chemical*. 2010;**148**(1):110-116
- [43] Peng L, Wang M, Zhang G, Zhang D, Zhu D. A fluorescence turn-on detection of cyanide in aqueous solution based on the aggregation-induced emission. *Organic Letters*. 2009;**11**(9):1943-1946
- [44] Sessler JL, Cho D. The benzil rearrangement reaction: Trapping of a hitherto minor product and its application to the development of a selective cyanide anion indicator. *Organic Letters*. 2008;**10**(1):73-75. DOI: 10.1021/ol7027306
- [45] Miyaji H, Kim DS, Chang BY, Park E, Park SM, Ahn KH. Highly cooperative ion-pair recognition of potassium cyanide using a heteroditopic ferrocene-based crown ether-trifluoroacetylcarboxanilide receptor. *Chemical Communications*. 2008;(6):753-755
- [46] Sun Y, Liu Y, Chen M, Guo W. A novel fluorescent and chromogenic probe for cyanide detection in water based on the nucleophilic addition of cyanide to imine group. *Talanta*. 2009;**80**(2):996-1000
- [47] Sun Y, Liu Y, Guo W. Fluorescent and chromogenic probes bearing salicylaldehyde hydrazone functionality for cyanide detection in aqueous solution. *Sensors and Actuators, B: Chemical*. 2009;**143**(1):171-176
- [48] Cho D, Kim JH, Sessler JL. The benzil-cyanide reaction and its application to the development of a selective cyanide anion indicator. *American Chemical Society*. 2008;**130**(36):12163-12167. DOI: 10.1021/ja8039025

- [49] Kim HJ, Ko KC, Lee JH, Lee JY, Kim JS. KCN sensor: Unique chromogenic and 'turn-on' fluorescent chemodosimeter: Rapid response and high selectivity. *Chemical Communications*. 2011;**47**(10):2886-2888 (b) Lee JH, Jeong AR, Shin S, Kim HJ, Hong JI. Fluorescence turn-on sensor for cyanide based on a cobalt (II)- coumarinylsalen complex. *Organic Letters*. 2010;**12**(4):764-767 (c) Saha S, Ghosh A, Mahato P, Mishra S, Mishra SK, Suresh E, Das S, Das A. Specific recognition and sensing of CN⁻ in sodium cyanide solution. *Organic Letters*. 2010;**12**(15):3406-3409 (d) Chen X, Zhou Y, Peng X, Yoon J. Fluorescent and colorimetric probes for detection of thiols. *Chemical Society Reviews*. 2010;**39**(6):2120-2135
- [50] (a) Lee KS, Kim HJ, Kim GH, Shin I, Hong JI. Fluorescent chemodosimeter for selective detection of cyanide in water. *Organic Letters*. 2008;**10**(1):49-51 (b) Kumara V, Kaushika MP, Srivastava AK, Pratapa A, Thiruvengatamb V, Rowb TG. Thiourea based novel chromogenic sensor for selective detection of fluoride and cyanide anions in organic and aqueous media. *Analytica Chimica Acta*. 2010;**663**(1):77-84 (c) Li H, Li B, Jin LY, Kan Y, Yin B. A rapid responsive and highly selective probe for cyanide in the aqueous environment. *Tetrahedron*. 2011;**67**(38):7348-7353 (d) Martínez-Máñez R, Sancenón F. Chemodosimeters and 3D inorganic functionalised hosts for the fluoro-chromogenic sensing of anions. *Coordination Chemistry Reviews*. 2006;**250**(23-24):3081-3093. DOI: 10.1016/j.ccr.2006.04.016 (e) Chung SY, Nam SW, Lim J, Park S, Yoon J. A highly selective cyanide sensing in water via fluorescence change and its application to in vivo imaging. *Chemical Communications*. 2009;(20):2866-2868 (f) Shang L, Jin L, Dong S. Sensitive turn-on fluorescent detection of cyanide based on the dissolution of fluorophore functionalized gold nanoparticles. *Chemical Communications*. 2009;(21):3077-3079 (g) Zeng Q, Cai P, Li Z, Qin J, Tang BZ. An imidazole-functionalized polyacetylene: Convenient synthesis and selective chemosensor for metal ions and cyanide. *Chemical communications*. 2008;(9):1094-1096 (h) Zhang P, Shi BB, Wei TB, Zhang YM, Lin Q, Yao H, You XM. A naphtholic Schiff base for highly selective sensing of cyanide via different channels in aqueous solution. *Dyes and Pigments*. 2013;**99**(3):857-862
- [51] Federation WE. American Public Health Association. Standard methods for the examination of water and wastewater. Washington, DC, USA: American Public Health Association (APHA); 2005
- [52] United States Environmental Protection Agency (EPA), Titrimetric and manual spectrophotometric determinative methods for cyanide, Method 9014, 1996, <http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/9014.pdf> [Accessed January 9, 2010]
- [53] United States Environmental Protection Agency (EPA), Potentiometric determination of cyanide in aqueous samples and distillates with ion-selective electrode, Method 9213. 1996. www.epa.gov/waste/hazard/testmethods/sw846/pdfs/9213.pdf [Accessed January 9, 2010]
- [54] United States Environmental Protection Agency (EPA), Available cyanide by flow injection, ligand exchange and amperometry, Method OIA-1677. 2004. <http://www.epa.gov/waterscience/methods/method/cyanide/1677final.pdf> [Accessed January 9, 2010]
- [55] World Health Organization. Concise international chemical assessment document 61, Hydrogen cyanide and cyanides: Human health aspects, Geneva. 2004. pp. 4-5. <http://www.who.int/ipcs/publications/cicad/en/cicad61.pdf> [accessed January 09, 2009]

- [56] The Agency for Toxic Substances and Disease Registry, Toxicological profile for cyanide, Atlanta, GA, US Department of Health and Human Services. Analytical Methods for Determining Cyanide in Biological Samples. pp. 201-219. <http://www.atsdr.cdc.gov/toxprofiles/tp8-c7.pdf> [Accessed January 9, 2010]
- [57] Mudder TI, Botz M, Smith A. Chemistry and treatment of cyanidation wastes. London, UK: Mining Journal Books. pp. 21-46
- [58] Mak KK, Yanase H, Renneberg R. Cyanide fishing and cyanide detection in coral reef fish using chemical tests and biosensors. *Biosensors and Bioelectronics*. 2005;**20**(12):2581-2593. DOI: 10.1016/j.bios.2004.09.015
- [59] Singh HB, Wasi N, Mehra MC. Detection and Determination of Cyanide—A Review. *International Journal of Environmental Analytical Chemistry*. 1986;**26**(2):115-136
- [60] Out EO, Byerley JJ, Robinson CW. Ion chromatography of cyanide and metal cyanide complexes: A review. *International Journal of Environmental Analytical Chemistry*. 1996;**63**(1):81-90. DOI: 10.1080/03067319608039812
- [61] Lindsay AE, Greenbaum AR, O'Hare D. Analytical techniques for cyanide in blood and published blood cyanide concentrations from healthy subjects and fire victims. *Analytica Chimica Acta*. 2004;**511**(2):185-195. DOI: 10.1016/j.aca.2004.02.006
- [62] Xu Z, Chen X, Kim HN, Yoon J. Sensors for the optical detection of cyanide ion. *Chemical Society Reviews*. 2010;**39**(1):127-137
- [63] Zelder FH, Männel-Croisé C. Recent Advances in the colorimetric detection of cyanide. *CHIMIA International Journal for Chemistry*. 2009;**63**(1):58-62. DOI: 10.2533/chimia.2009.58
- [64] Luo J, Xie Z, Lam JW, Cheng L, Chen H, Qiu C, Kwok HS, Zhan XW, Liu YQ, Zhu DB, Tang BZ. Aggregation-induced emission of 1-methyl-1, 2, 3, 4, 5-pentaphenylsilole. *Chemical Communications*. 2001;(18):1740-1741
- [65] Sun Y, Li Y, Ma X, Duan L. A turn-on fluorescent probe for cyanide based on aggregation of terthienyl and its application for bioimaging. *Sensors and Actuators B: Chemical*. 2016;**224**:648-653. DOI: 10.1016/j.snb.2015.10.057
- [66] Chen X, Wang L, Yang X, Tang L, Zhou Y, Liu R, Qu J. A new aggregation-induced emission active fluorescent probe for sensitive detection of cyanide. *Sensors and Actuators B*. 2017;**241**:1043-1049
- [67] Kim G, Kim H. Doubly activated coumarin as a colorimetric and fluorescent chemodosimeter for cyanide. *Tetrahedron Letters*. 2010;**51**(1):185-187. DOI: 10.1016/j.tetlet.2009.10.113
- [68] Hu J-W, Lin W-C, Hsiao S-Y, Wu Y-H, Chen H-W, Chen K-Y. An indanedione-based chemodosimeter for selective naked-eye and fluorogenic detection of cyanide. *Sensors and Actuators B*. 2016;**233**:510-519
- [69] Huo F, Zhang Y, Yue Y, Chao J, Zhang Y, Yin C. Isophorone-based aldehyde for "ratio-metric" detection of cyanide by hampering ESIPT. *Dyes and Pigments*. 2017;**143**:270-275

- [70] Goswami S, Manna A, Paul S, Das AK, Aich K, Nandi PK. Resonance-assisted hydrogen bonding induced nucleophilic addition to hamper ESIPT: Ratiometric detection of cyanide in aqueous media. *Chemical Communications*. 2013;**49**:2912
- [71] Wang L, Jiqing D, Cao D. A colorimetric and fluorescent probe containing diketopyrrolopyrrole and 1,3-indanedione for cyanide detection based on exciplex signaling mechanism. *Sensors and Actuators B*. 2014;**198**:455-461
- [72] Shahid M, Razi SS, Srivastava P, Ali R, Maiti B, Misra A. A useful scaffold based on ace-naphthene exhibiting Cu^{2+} induced excimer fluorescence and sensing cyanide via Cu^{2+} displacement approach. *Tetrahedron*. 2012;**68**:9076-9084
- [73] Goswami S, Paul S, Manna A. FRET based selective and ratiometric 'naked-eye' detection of CN^- in aqueous solution on fluorescein-Zn-naphthalene ensemble platform. *Tetrahedron Letters*. 2014;**55**:3946-3949
- [74] Chung S-Y, Nam S-W, Lim J, Park S, Yoon J. A highly selective cyanide sensing in water via fluorescence change and its application to in vivo imaging. *Chemical Communications*. 2009:2866-2868
- [75] Yanar U, Babür B, Pekyılmaz D, Yahaya I, Aydıner B, Dede Y, Seferoğlu Z. A fluorescent coumarin-thiophene hybrid as a ratiometric chemosensor for anions: Synthesis, photophysics, anion sensing and orbital interactions. *Journal of Molecular Structure*. 2016;**1108**:269-277
- [76] Saha S, Ghosh A, Mahato P, Mishra S, Mishra SK, Suresh E, Das S, Das A. Specific recognition and sensing of CN^- in sodium cyanide solution. *Organic Letters*. 2010;**12**(15)
- [77] Hao Y, Nguyen KH, Zhang Y, Zhang G, Fan S, Li F, Guo C, Yuanyuan L, Song X, Peng Q, Liu Y-N, Maotian X. A highly selective and ratiometric fluorescent probe for cyanide byrationally altering the susceptible H-atom. *Talanta*. 2018;**176**:234-241
- [78] Mashraqui SH, Betkar R, Chandiramani M, Estarellas C, Frontera A. Design of a dual sensing highly selective cyanide chemodosimeter based on pyridinium ring chemistry. *New Journal of Chemistry*. 2011;**35**:57-60
- [79] Kwona SK, Kou S, Ha NK, Chen X, Hwang H, Nama S-W, So HK, Swamy KMK, Park S, Yoon J. Sensing cyanide ion via fluorescent change and its application to the microfluidic system. *Tetrahedron Letters*. 2008;**49**:4102-4105
- [80] Li J, Qi X, Wei W, Zuo G, Dong W. A red-emitting fluorescent and colorimetric dual channel sensor for cyanide based on a hybrid naphthopyran-benzothiazol in aqueous solution. *Sensors and Actuators B*. 2016;**232**:666-672
- [81] Qu W-J, Li W-T, Zhang H-L, Wei T-B, Lin Q, Yao H, Zhang Y-M. A rational designed fluorescent and colorimetric dual-channel sensor for cyanide anion based on the PET effect in aqueous medium. *Sensors and Actuators B*. 2017;**241**:430-437
- [82] Lee JH, Reum Jeong A, Shin I-S, Kim H-J, Hong J-I. Fluorescence turn-on sensor for cyanide based on a cobalt(II)-coumarinylsalen complex. *Organic Letters*. 2010;**12**(4)