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Fluorescence Dyes for Determination of Cyanide

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<http://dx.doi.org/10.5772/intechopen.75090>

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.

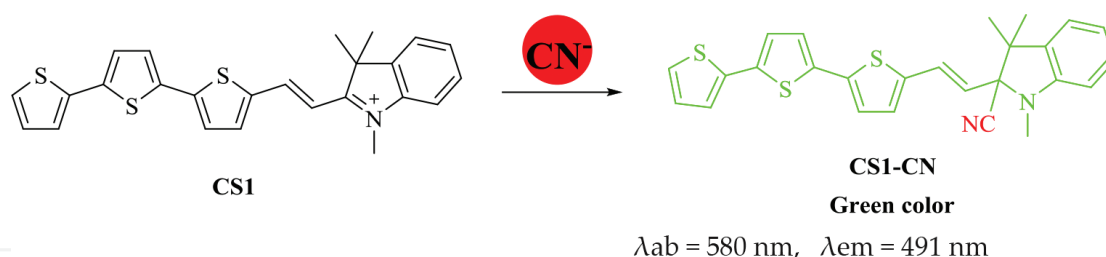
2. Sensing mechanisms and synthesis of cyanide sensors (CS)

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**.

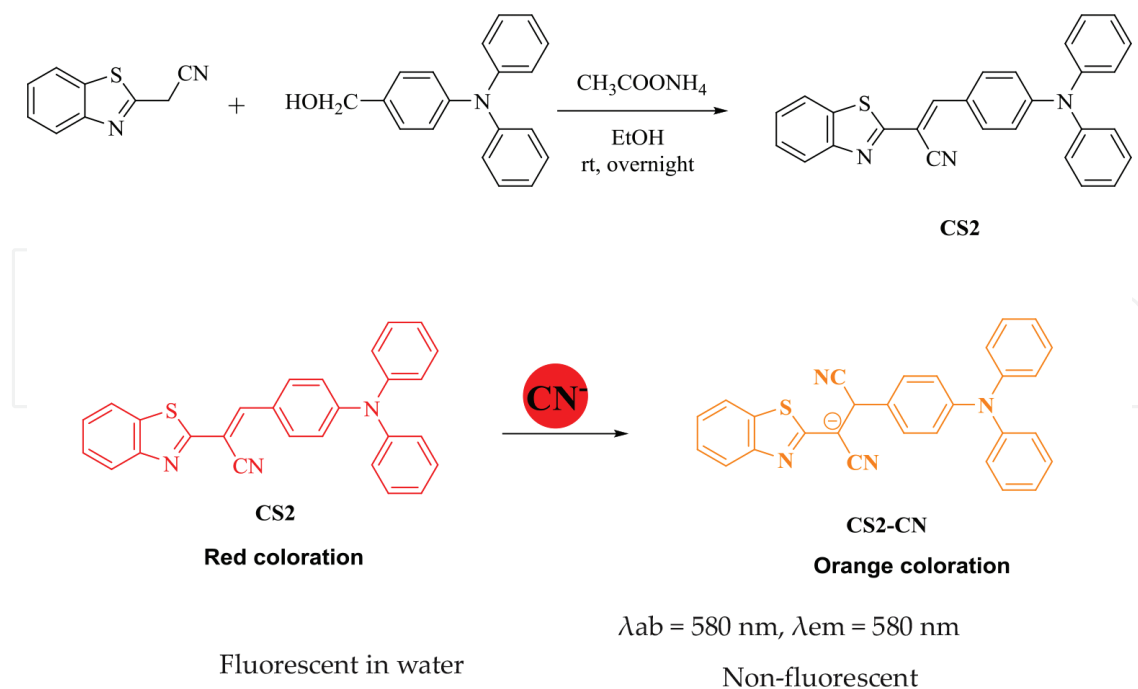
of **CS1**, an increase in its intensity at 491 nm was observed, and the fluorescence intensity further increased by the addition of more than 170 times. As the concentration of CN^- reached 40 μM , a bright green fluorescent emission was observed which can easily be noticed by the naked eyes.

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



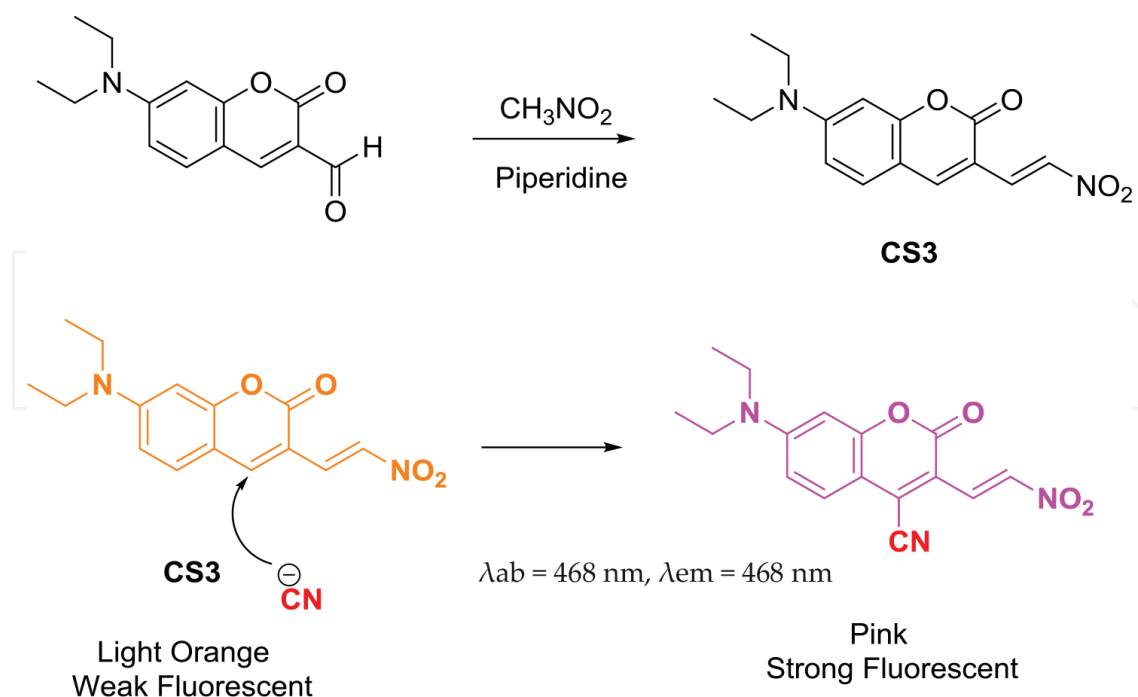
Scheme 2. Synthesis and sensing mechanism of probe CS2.

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**).

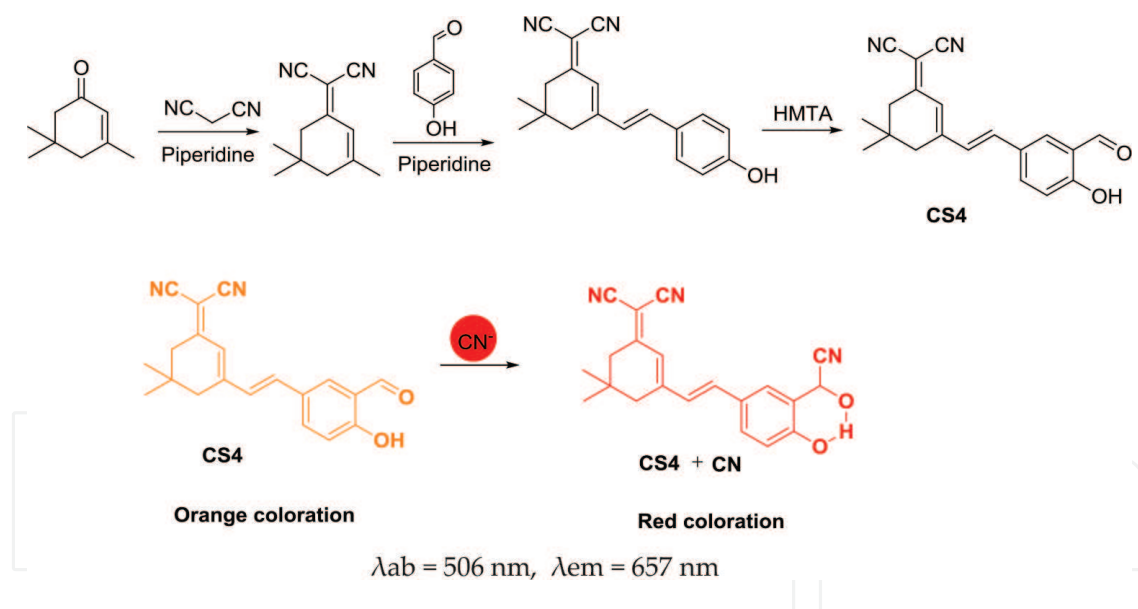
Hu et al. [68] have successfully synthesized and reported a 1,3-indanedione-based chemodosimeter that could be employed in sensing cyanide ions via both aggregation-induced emission enhancement (AIEE) and intramolecular charge transfer (ICT) in 90% aqueous medium. They prepared a solution of the chemodosimeter (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.

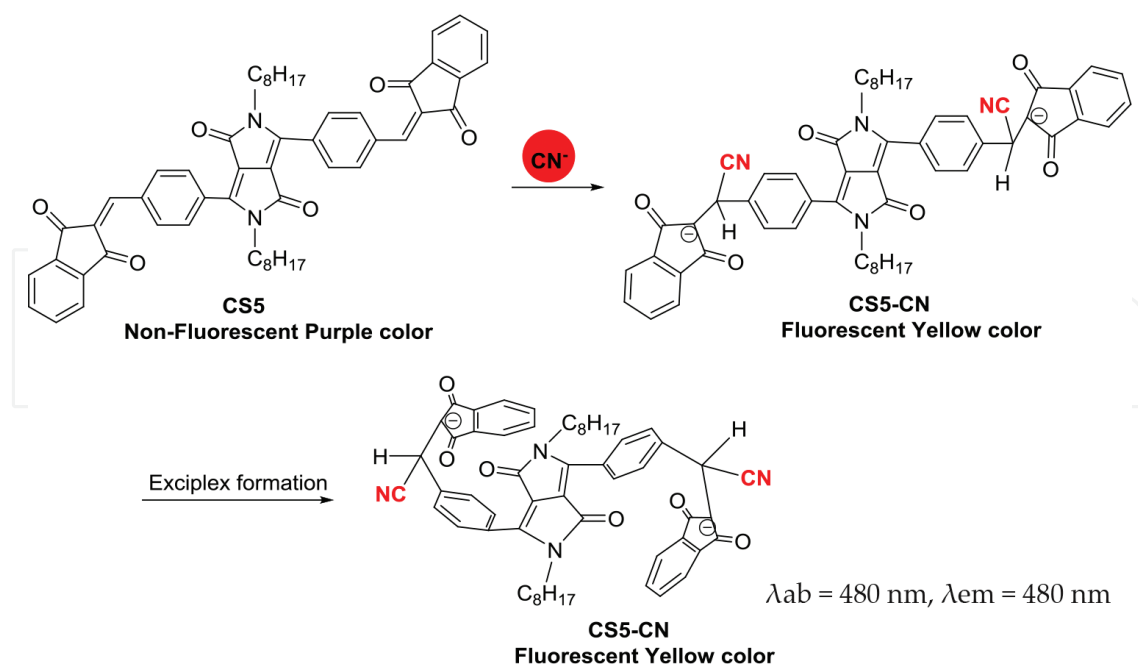
2.4. Cyanide sensing via the excimer/excplex form

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-Zn²⁺** 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-Zn²⁺** with increased concentration of CN^- . The researchers suggested that, the observed decrease of yellow coloration of the solution



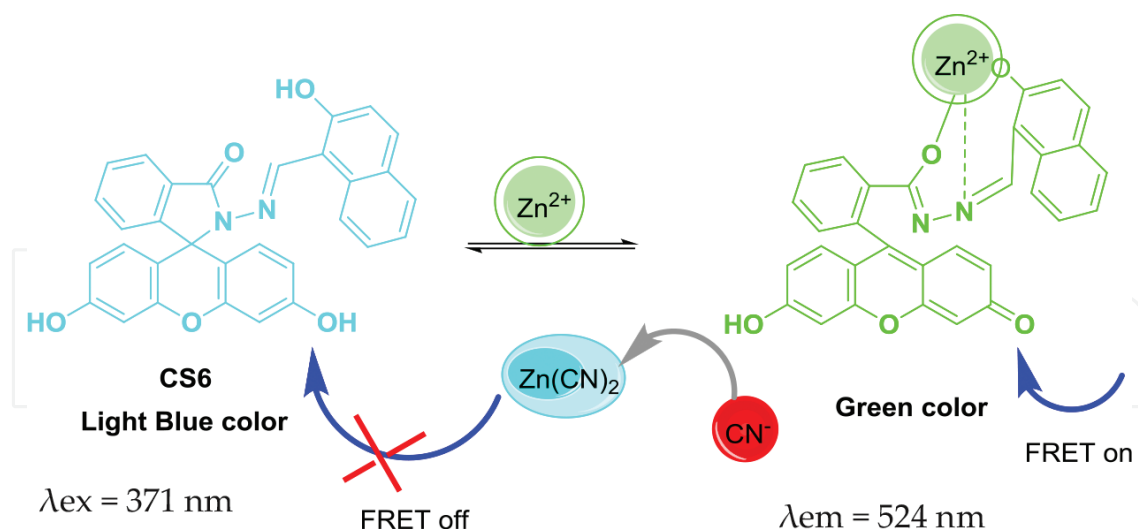
Scheme 5. Structure of CS5 and its cyanide sensing.

containing the CS6-Zn^{2+} complex was a result of the ring opened amide form of CS6-Zn^{2+} 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-Zn^{2+} in the presence of competing anions such as Br^- , Cl^- , I^- , F^- , ADP, ATP, PPI, OAc^- , Pi , SH^- , SCN^- , and N_3^- . As cyanide solution was added to the solution of the CS6-Zn^{2+} complex, there was a reverse change in the fluorescence spectra due to the occurrence of a reverse FRET phenomenon (**Scheme 6**).

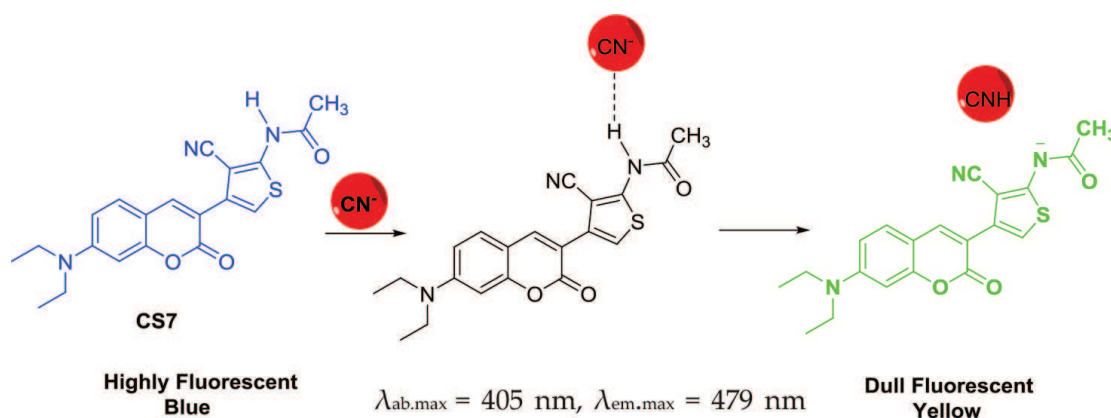
In 2009, Chung and co-workers [74] successfully developed a cyanide sensor for fluorescence study. In the fluorescence study, different anions, such as CN^- , SCN^- , AcO^- , F^- , Cl^- , Br^- , I^- , H_2PO_4^- , HSO_4^- , NO_3^- , and ClO_4^- were evaluated at pH 7.4 (0.02 M pH 7.4 HEPES). Using 100 equiv. of each of these anions, and 6 mM of the probe in the presence of Cu^{2+} (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^- , HSO_4^- and ClO_4^- 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.

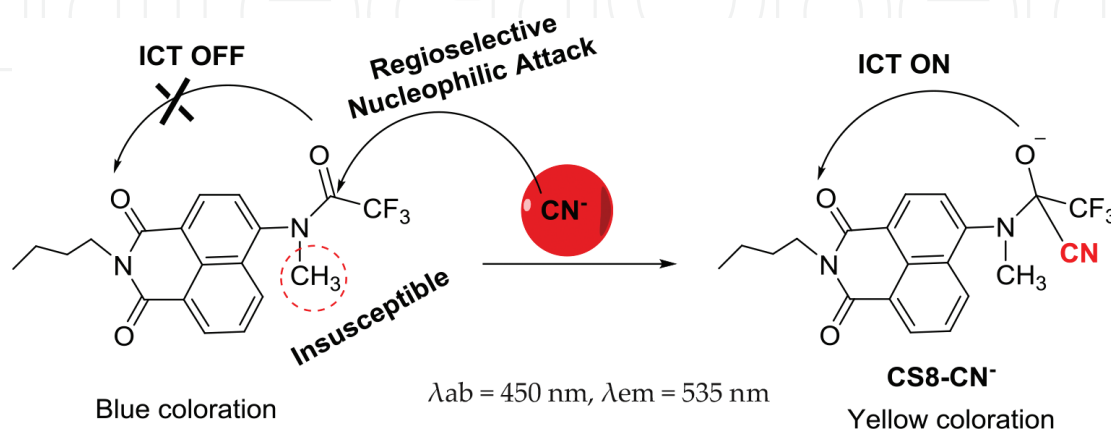
2.7. Cyanide sensing via the inter- or intra- molecular charge transfer (ICT)

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**).

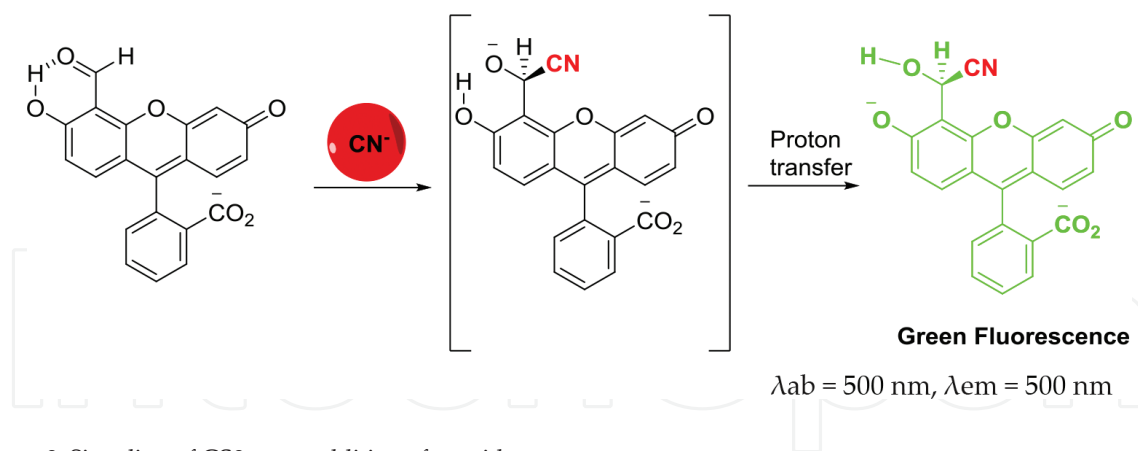
Mashraqui and co-workers [78] have developed a novel chemodosimeter that has the structural capabilities to convert the CN^- -binding event into an enhanced ICT process, inducing absorbance red shifts and a high fluorescence turn-on response. The use of the probe toward sensing different anions was investigated 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.

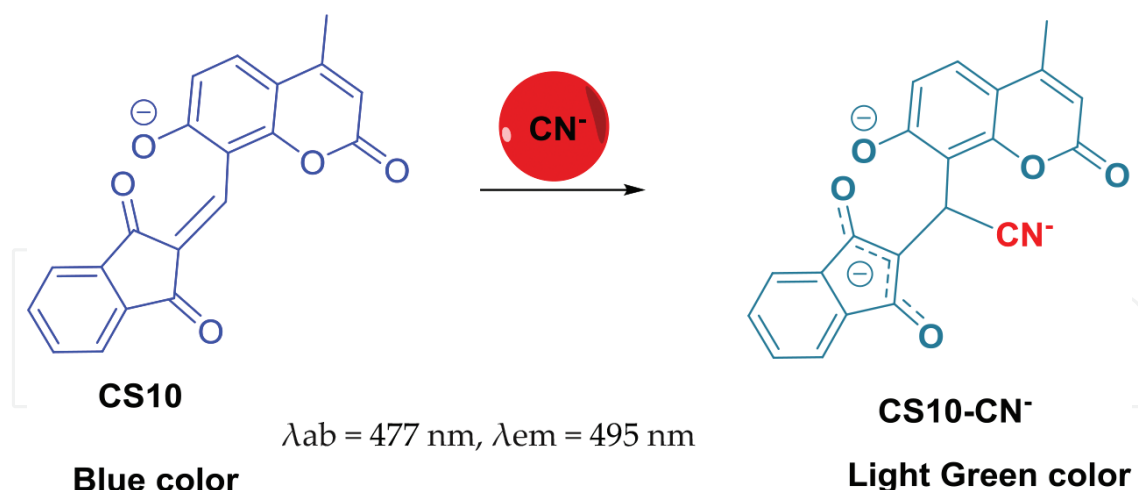
For the fluorescent analysis, 100 equiv of different anions (CN^- , AcO^- , F^- , Cl^- , Br^- , I^- , H_2PO_4^- , HSO_4^- , NO_3^- , and ClO_4^-) were investigated in acetonitrile–HEPES (9:1, v/v, 0.01 M pH 7.4 HEPES), containing probe **CS9** (3 μM). The authors attributed the selective recognition 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.

Acknowledgements

We appreciate, with kind regards, the support and sponsorship of this endeavor by Gazi University and TUBITAK for the grant (Grant numbers; 111 T106, 113Z704, 114Z980, and 215Z567).

Conflict of interest

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

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