https://doi.org/10.48048/tis.2023.5005

A Versatile Molecular Probe of Napthalimide-Derivative for Zn(II) Sensor: A Mini-Review

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Received: 30 June 2022, Revised: 6 August 2022, Accepted: 13 August 2022, Published: 17 March 2023

Abstract

In recent years, many more chemists have been focused on fluorescent probe research, and significant progresses, which has been made in terms of design and use. This review begins with a brief overview of the most prevalent chemosensor design concepts, followed by a discussion of the photophysical characteristics of the 1,8-naphthalimide structure, such as great photostability, high fluorescence quantum yield and ease of modification which has been used in Zn^{2+} cation sensing to date. The contributions of the fluorescent probes built on the 1,8-naphthalimide based platform in the field of chemical sensing, biological sensing, pharmaceutical chemistry, environment and food safety in the last 10 years are then systematically introduced by discussing the probe's fluorescence behavior in the corresponding recognition process. Simultaneously, we intend to build an overall review on fluorescent chemical sensor that will be able to play larger and more interesting role in the future.

Keywords: 1,8-naphthalimide base, Chromo fluorogenic sensor, Zinc(II), Sensing mechanism

Introduction

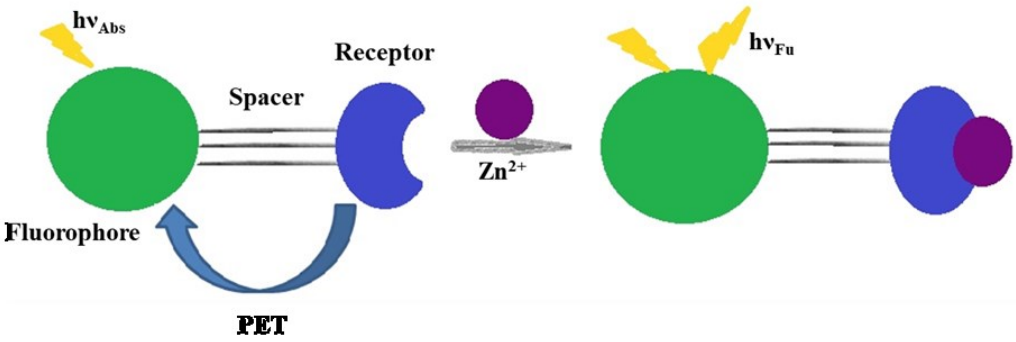
In recent years, low and high molecular weight fluorescent compounds capable of sensing metal cations and protons in the environment have been extensively studied [1-3]. Researcher's advances in modifying the chemical and physical properties of compounds to satisfy specific needs have increased the importance of these new compounds in the development of sensing devices. Fluorescent probes for detecting metal ions have inherent benefits over other detection technologies developed, such as high performance liquid chromatography [4] and capillary electrophoresis [5], due to their high sensitivity, good selectivity, specificity, ease of implementation and quick response time. Fluorescent receptors can be used for *in vitro* tests as well as *in vivo* imaging studies [6]. The potent analytical techniques for detecting metal ions are fluorescent PET (Photo-induced Electron Transfer) sensors [7]. The design of multi-component PET fluorescence sensors is such that when electrons travel between the fluorophore as a signaling unit and the receptor, the fluorescent intensity "switches off" [8-11]. As a result, additional fluorophore spacer-receptor sensors trigger an electron transfer from the electron donating receptor to the fluorophore in the excited state, which can subsequently be influenced by metal cations. The PET interaction is ceased and the system's fluorescence is "switched on" when guests enter the system and are able to bind to the receptor's lone pair electrons. The development of fluorescence sensors for quantifying and investigating the role of Zn^{2+} in various aspects is currently of significant interest. The development of a fluorescent receptor for Zn^{2+} in the presence of a variety of other metal ions, in particular, has gained a lot of attention [12,13].

Zinc plays a vital role in environmental as well as in biological process. It's the second most common transition metal ion in physiology, and it has a variety of roles in both extracellular and intracellular processes [14]. It was an essential part of the human body that was frequently found in dietary supplements. It's an important component of enzymes and proteins. Disorders of zinc homeostasis are thought to have a role in a variety of disorders, including's Alzheimer's disease, cerebral ischemia, infantile diarrhea and epilepsy [15,16]. Zn^{2+} is also said to be a powerful killer of neurons through oxidative stress [17]. A decline in the ability of the pancreas' islet cells to generate and secrete insulin can be caused by a fall in Zn^{2+} concentration [18]. As a result, the development of Zn^{2+} selective fluorescent sensors and practical methods for detecting intracellular Zn^{2+} ions has become a priority in recent years. Taking too much zinc, on the

other hand, might be harmful to human beings. Despite the fact that chelatable Zn^{2+} plays a variety of critical roles in biological systems. It's mechanisms of action are less well understood than those of other cations like Ca^{2+}, Na^{+} and K^{+}. As a result, there is a strong demand for detecting and monitoring the zinc levels in human bodies, biological systems and the environments [19].

For sensing Zn^{2+} in biological environment, several Zn^{2+} selective fluorescent sensor molecules have been created. Only a few ligands have been proven to detect zinc ions in aqueous solution [20]. In most cases, however, organic solvents and surfactants are utilized to solubilize the ligands in aqueous medium, resulting undesired cytotoxicity *in vitro* and *vivo* [21]. Because of its desirable properties, such as excellent photo stability, a significant stokes shift, strong fluorescence and a high quantum yield, 1,8- napthalimide is often utilized as a fluorophore among other fluorophores. As a result it has a wide range of applications in the field of optical storage [22], nucleic acid intercalators [23], polymers [24], DNA photo cleavage [25] and photophysical dyads [26]. Several research groups have produced napthalimide-based fluorescent chemo sensors due to their advantageous properties and numerous applications [27-30]. The binding site at 4 or 4,5-positions of napthalimide are the major components of these chemosensors for the detection of transition metal ions. Furthermore, the majority of them works in an organic or organic/water environment [31-34]. The photoinduced electron transfer that occurs in tailored 1,8-napthalimide complexes and the possible application of these receptors as sensors for cations in the environment received considerable attentions [35-45]. The photoinduced electron transfer (PET) mechanism is used in these chemosensors, which have been successfully used to image intracellular Zn^{2+} [46].

When some photoactive materials contact with light, an electron transfer called photo-induced electron transfer (PET). The "fluorophore-spacer-receptor (ionophore)" configuration is the most common design for a PET-type fluorophore (**Scheme 1**). A non-*p*-electron conjugating spacer group, such as an aryl group with 1 to 4 carbons, is used to covalently bind a fluorescent moiety (fluorophore) to an ion receptor. The ionophore will usually contain a tertiary amine, whose electrons can ligate the cation. The HOMO (highest occupied molecular orbital) of the unbound receptor has a higher energy than the half-filled HOMO of the excited fluorophore in the absence of a bound cation. Because of the energy difference, electrons travel quickly from the receptor to the excited-state fluorophore, and the fluorescence is quenched or "switched off" [47]. When the ionophore is attached to a cation, however, the receptor's electron pair has a lower energy level than the excited fluorophore's HOMO. As a result, the ionophore is energetically stabilized, electron transfer is inhibited, and fluorescence is "turned on". The 1,8-napthalimide based chemosensors have various biomedical applications, environmental application, and biological application like bio imaging in living cell, in mammalian cell, *in vitro* and *vivo* imaging. This work presents a thorough review of numerous 1,8-napthalimide derivatives and their sensing behaviors toward Zn^{2+} against other metal ions.



Scheme 1 Schematically representation of fluorescence chemosensor.

Results and discussion

Zhao *et al.* [48] designed and developed a 1,8-Napthalimide derivative 1 as a selective fluorescence sensor for the detection of Zn^{2+} over other competing metal ions in CH_3CN/HEPES buffer (6:4, v/v) [48] (**Figure 1**). The receptor 1 in acetonitrile displayed the maximum absorption peak at 397 nm. Upon the addition of Zn^{2+} to the receptor 1 in acetonitrile solution resulted a red shift in absorption peak. On the other hand, the receptor 1 showed a very weak fluorescence emission at 518 nm due to the photo induced electron transfer (PET). The addition of Cu^{2+} resulted a red shift in emission peak from 518 to 556 nm with a 13-fold enhancement. The color of the solution changed from light yellow to saffron yellow. The change in

spectra behaviour and color of the receptor signified the formation of complex with a stoichiometry ratio of 1:1. The association constant and the detection limit were calculated and found to be 3.02×10^{3} M^{-1} and 1.03×10^{-6} M, respectively. The receptor was used for fluorescence imaging study in various cell.

Liu *et al.* [49], synthesised a novel naphthalimide fluorescent sensor 2 from 4-amino-1,8-naphthalimide and iminodiacetic acid, which was utilised as a selective fluorescent sensor for the detection of Zn^{2+} in HEPES buffer solution (20 mM, pH = 7.4) (**Figure 1**). The receptor 2 in HEPES buffer solution (20 mM, pH = 7.4) displayed a green colour emission centred at ~550 nm. The addition of Zn^{2+} induced a 50 fold of enhancement in emission peak at 550 nm due to photo-induced electron transfer. It resulted the formation of complex. This complex formation was also confirmed from H^1 NMR spectroscopy as there was a down field shift from 3.909 and 6.361 to 7.001 ppm. The dissociation constant of this complexation was calculated and assessed to be 2.4×10^{-5} M. The receptor was used for bio-imaging study in Hela cells.

Liu *et al.* [50], used iminoacetic acid and iminoethoxyacetic acid as receptors in a novel 4-amino-1,8-naphthalimide-based fluorescence sensor 3 (**Figure 1**). It was applied to detect Zn^{2+} in aqueous solutions and living cells successfully. At 470 nm excitation the receptor 3 in HEPES buffer displayed a weak green colour emission at 550 nm. The addition of Zn^{2+} to the receptor 3 induced a 20-fold increase in the fluorescence emission intensity due to the restriction of photo-induced electron transfer (PET). The detection limit of Zn^{2+} was calculated to be 4.2×10^{-6} mol·L^{-1}. The receptor was used for bio imaging study in various living cell.

Sali *et al.* [51], designed and synthesized a novel blue emitting fluorescent sensor 4 for the selective detection of Zn^{2+}, Ni^{2+}, Ce^{3+}, Cu^{2+}, Co^{2+} and Ag^{+} (**Figure 1**). After the investigation it has been found that the monomeric naphthalimide was used as a sensor for Zn^{2+} cation. The receptor 4 in DMF solution, displayed an absorption maximum at 367 nm and a weak fluorescence peak at 435 nm. In the presence of Zn^{2+} the receptor 4 in DMF displayed an enhancement of emission peak at 435 nm due to the inhibition of photoinduced electron transfer. The presence of monomeric napthalimide unit in the receptor was responsible for the restriction of PET transition. The complex was formed between nitrogen atom of dimethyl amino group and Zn^{2+}.

The bis-1,8-naphthalimide based fluorescent sensor 5 was applied for the selective detection of Zn^{2+} over other metal ions in acetonitrile (**Figure 1**). The sensor 5 in acetonitrile displayed 2 UV-vis absorption bands at 334 and 336 nm near UV-vis region, and displayed dual blue fluorescence at 430 and 439 nm. The addition of Zn^{2+} resulted an enhancement of fluorescence emission peak due to inhibition of photo induced electron transfer (PET). The emission in intensity was due to the coordination of metal cations with the receptor's lone pairs. As a result, the electron transfer was switched off and it induced a fluorescence "switch-on" in the complex.

The 4-amino-1,8-naphthalimide based fluorescent chemosensor 6 was synthesized by Hanaoka *et al.* [53], and was served as a selective sensor of Zn^{2+} in HEPES buffer solution (**Figure 1**). The addition of Zn^{2+} to the receptor 6 in HEPES buffer displayed a blue shift in absorption peak from 437 to 380 nm with 2 clear isosbestic points at 408 and 324 nm. The receptor 6 also exhibited a fluorescence peak at 527 nm due to intra molecular charge transfer (ICT). The addition of Zn^{2+} induced a green fluorescence with 57 nm of blue shift in emission intensity due to the photo-induced electron transfer (PET). This signified the formation of complex between the receptor 6 and Zn^{2+} in a 1:1 stoichiometry ratio. The dissociation constant K_d for Zn^{2+} was estimated to be 1.1 nm. The receptor 6 was applied for fluorescence bio imaging study.

Moniz *et al.* [54], developed a novel fluorescent sensor 7 having 4-amino-1, 8-naphthalimide and 3-hydroxy-4-pyridinone moieties, was applied for the selective detection of Zn^{2+}, Fe^{3+} and Cu^{2+} in DMSO (**Figure 1**) [54]. The receptor 7 in DMSO displayed an absorption band at 450 nm and a strong green fluorescence at 550 nm due to the inter-molecular charge transfer (ICT) transition between the electron donating amine and the electron withdrawing imide. The addition of Zn^{2+} to the receptor 7 in DMSO resulted a quenching in fluorescence with 91 % due to the photo induced electron transfer (PET). The job's plot analysis confirmed 1:2 stoichiometry ratio of 7:Zn^{2+} complex.

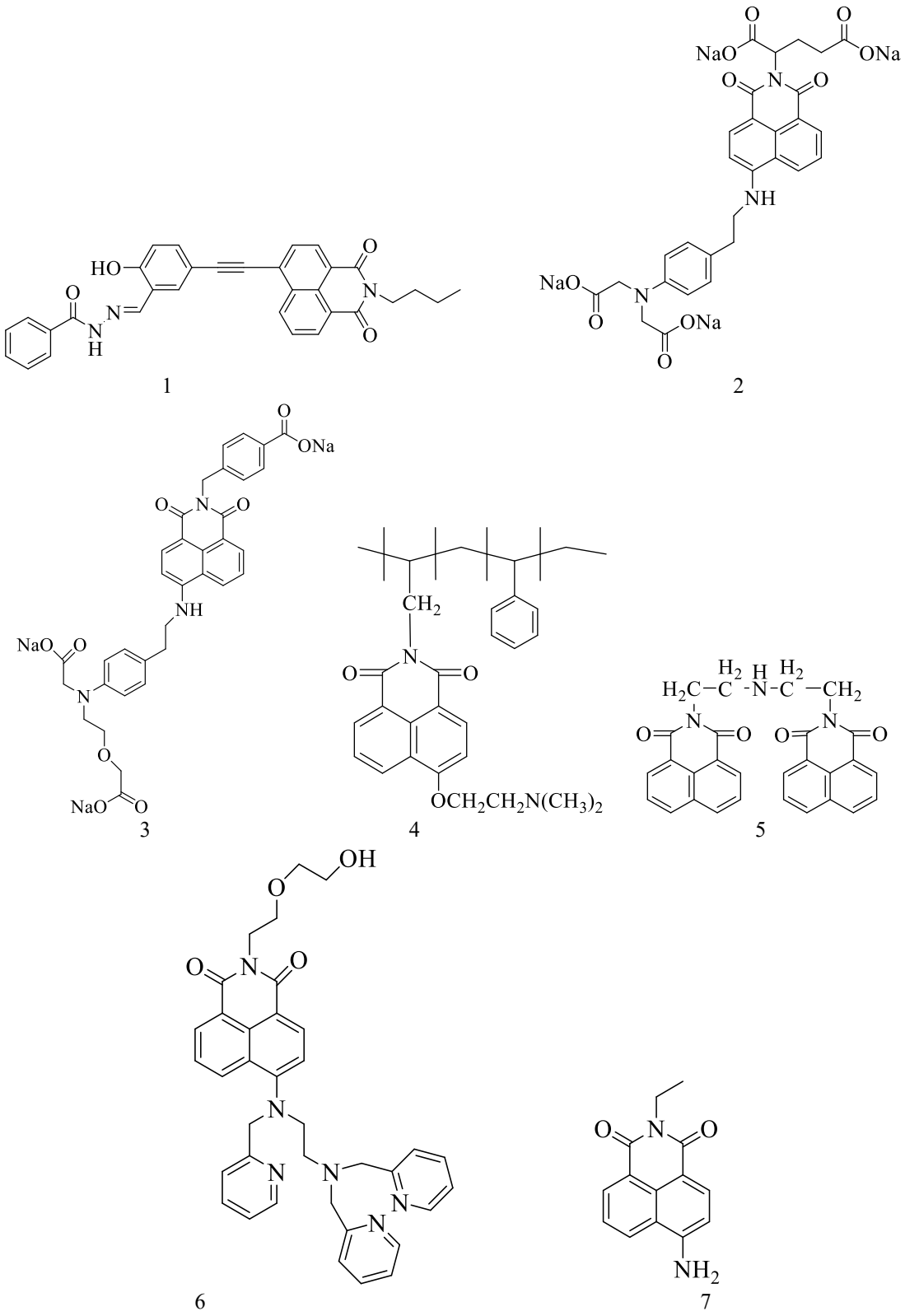


Figure 1 Napthalimide based receptor as zinc ion sensor.

Xu *et al.* [55], designed a new naphthalimide-based fluorescent chemosensor, *N*-butyl-4-[di-(2-picoly)amino]-5-(2-picoly)amino-1,8-naphthalimide 8 for the selective detection of Zn^{2+} in acetonitrile/water (80:20, v/v) (**Figure 2**). The receptor 8 in acetonitrile showed an absorption peak at 451 nm. The addition of Zn^{2+} induced a decrease in absorption band at 451 nm with appearance of 2 new peaks at 309 and 507 nm. The 2 isosbestic points at 382 and 470 nm suggested the formation of 1:1 complex between 8 and Zn^{2+}. On the other hand, the receptor 8 in acetonitrile showed a strong emission peak at 537 nm. In the presence of Zn^{2+}, the fluorescence intensity at 537 nm was quenched and a new peak appeared at 593 nm with a large red shift of 56 nm. The isoemissive point at 630 nm resulted the formation of complex with a binding constant of 6.76×10^5.The addition of Zn^{2+} influenced the protonation process of secondary amine conjugated to 1,8-naphthalimide and it resulted the formation of complex.

The naphthalimide based fluorescent sensor 9 having polyamino carboxylate moiety was applied for the detection of Zn^{2+} in HEPES buffer solution (**Figure 2**) [56]. The receptor 9 in HEPES buffer displayed no fluorescence. The addition of Zn^{2+} to the receptor **9** resulted an enhancement in emission peak at 447 nm due to photo-induced electron transfer (PET). It suggested the formation complex in 1:1 stoichiometry ratio. The dissociation constant (K_d) was calculated to be 9.00×10^{-7} M. This probe was used for fluorescence imaging in various live cell.

Liu *et al.* [57], synthesized a 4-amino-1,8-naphthalimide-based fluorescent sensor 10 for the selective detection of Zn^{2+} in HEPES buffer (**Figure 2**) [57]. The receptor 10 displayed an absorption maximum at 470 nm and a weak green emission peak at 550 nm. Addition of Zn^{2+} to the receptor 10 in HEPES buffer resulted a 5-fold gradual increase in fluorescence intensity at 550 nm due to restriction of photo-induced electron transfer. From fluorescence titration plot the limit of detection was calculated to be 7.72×10^{-7} $mol\cdot L^{-1}$ or 50.5 ppb. In ^1H NMR the down field shift of proton confirmed the formation of 1:1 complex between 10 and Zn^{2+}. The receptor 10 was applied to image Zn^{2+} in living cells.

The naphthalimide based fluorescent sensor 11 was synthesized and applied for the selective detection of Zn^{2+} in HEPES buffer (**Figure 2**) [58]. The receptor 11 in HEPES buffer solution showed a weak fluorescence peak at 394 nm due to the quenching effect through photo induced electron transfer. Upon the addition of Zn^{2+}, the fluorescence peak at 394 nm was continuously increased due to the inhibition of photoinduced electron transfer from nitrogen lone pair electron of Dpa to napthalimide. The fluorescence intensity was increased by 5-fold. It suggested the formation of 1:1 complex between receptor 11 and Zn^{2+} with a binding constant of 1.22×10^6 M^{-1}. This receptor 11 was applied in the fields of polymers, photophysical dyads, optical storage, nucleic acid intercalators and DNA photocleavage.

The 1,8-naphthalimide based receptor 12 was synthesized by Dimov *et al.* [59] for the selective detection of Zn^{2+} in H_2O/DMF (4:1, v/v) (**Figure 2**). The receptor 12 in DMF exhibited an absorption peak centre within the range of 280 to 320 nm due to the intramolecular charge transfer and a weak blue fluorescence emission at 411 nm due to the photo-induced electron transfer transition. Addition of Zn^{2+} resulted a gradual enhancement of emission peak at 411 nm due to the inhibition of PET transition. The jobs plot analysis confirmed the formation of 1:1 complex between 12 and Zn^{2+}. From the fluorescence titration data, the detection limit of sensor 12 was estimated to be 2.5×10^{-7}. The receptor was used as a molecular sensor for Zn^{2+}.

The noble dopamine-naphthalimide-dipicolylamine (DPA) based fluorescent sensor 13 was applied for the selective detection of Zn^{2+} in DMSO/HEPES buffer (50:50, v/v) (**Figure 2**) [60]. The receptor 13 in DMSO displayed a weak fluorescence peak at 527nm upon excitation at 370 nm. Further the addition of Zn^{2+} induced an enhancement of fluorescence peak at 527 nm. This signified the formation of complex in 1:1 ratio with a binding constant value of 1.55×10^{-1} M. The limit of detection (LOD) of the receptor 13 was calculated and finds to be 0.0345 ppb. The receptor 13 was applied for the sensing and removal of Zn^{2+} ions in biological specimens and environmental pollution.

The 4-amino-1,8-naphthalimide-based fluorescence sensor 14, was devised by Liu *et al.* [61], for the detection of Zn^{2+} in HEPES buffer (**Figure 2**). The receptor 14 in HEPES buffer resulted a new fluorescence emission peak at 550 nm due to the photo induced electron transfer. In the presence of Zn^{2+}, the fluorescence emission peak at 550 nm was gradually enhanced by 20-fold due to the restriction of photo induced electron transfer (PET). This receptor was used for the fluorescence imaging study in living cells.

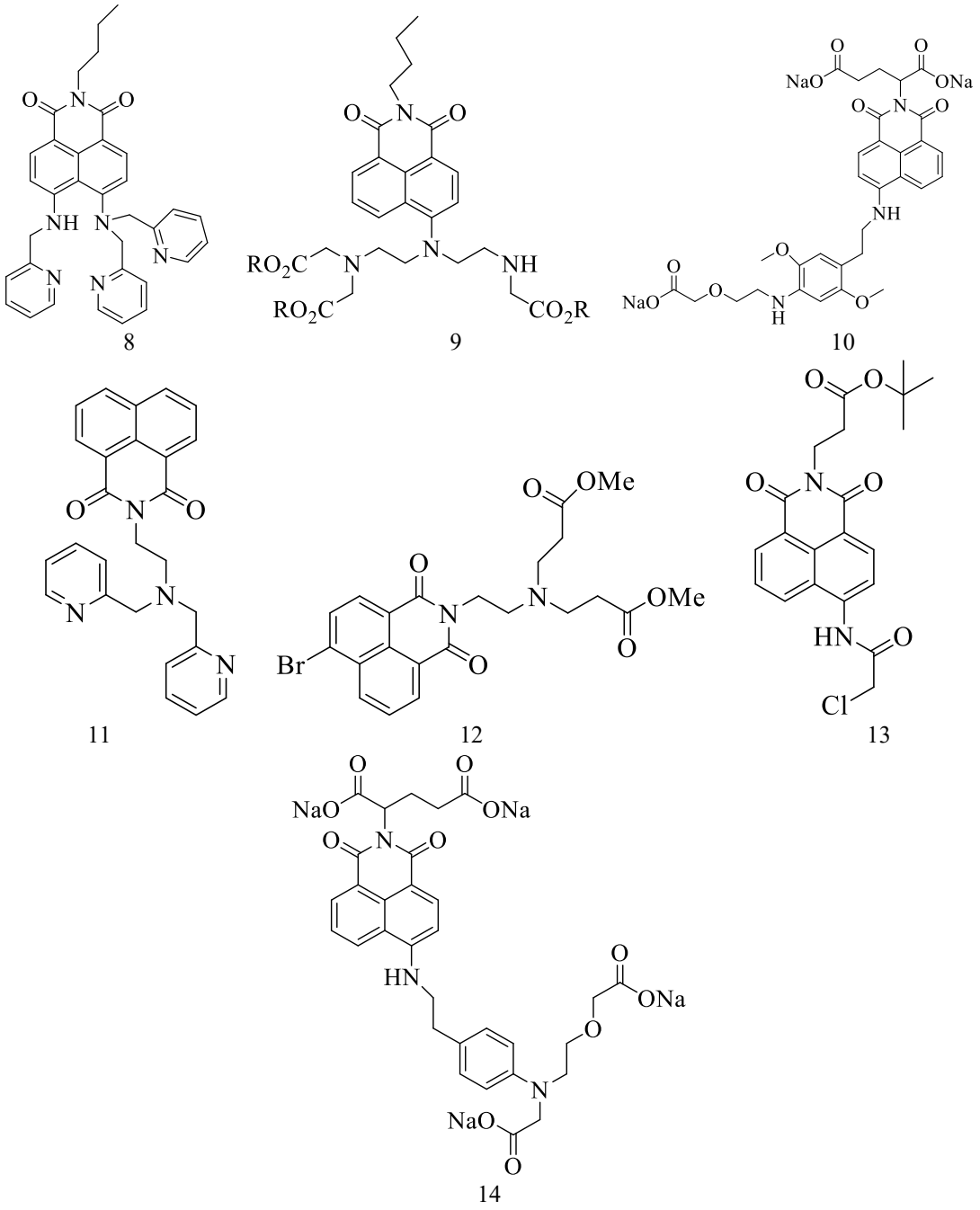


Figure 2 Napthalimide based receptor as zinc ion sensor.

The 1,8-naphthalimide based fluorescent sensor 15 having di-2-picolylamine (DPA) group was devised by Fan *et al.* [62], for the selective detection of Zn^{2+} in tris-HCl buffer (**Figure 3**). The receptor 15 in tris-HCl buffer displayed an absorption maximum at 453 nm. Addition of Zn^{2+} to the receptor 15 resulted a blue shift in absorption band from 453 to 443 nm. On the other hand, the receptor 15 showed an emission maximum at 549 nm due to photo-induced electron transfer. The addition of Zn^{2+} resulted a 5-fold enhancement of emission peak with a slight blue shift from 549 to 539 nm due to the inhibition of PET transition. It signified the formation of 1:1 complex between 15 and Cu^{2+} with a dissociation constant of 0.83 nM.

Xiang *et al.* [63], synthesized a Schiff base fluorescent sensor 16 for the selective recognition of Zn^{2+} in DMSO/H_2O (9:1, v/v) with a detection limit of 39 nM (**Figure 3**). The addition of Zn^{2+} to the receptor 16 in DMSO/H_2O induced an increase in absorption intensity at 400 nm and a concurrent decrease in absorption intensity at 500 nm. The isosbestic points at 450 nm signified the formation of complex in 1:1

ratio. On the other hand, the receptor 16 displayed a weak fluorescence emission peak at 506 nm. In the presence of Zn^{2+}, the emission peak at 506 nm was gradually increased due to the inhibition of photoinduced electron transfer (PET) and excited state intramolecular proton transfer (ESIPT). The fluorescence titration data suggested 1:1 complex formation between 16 and Zn^{2+}. The association constant was calculated to be 1.18×10^5 M^{-1} from the fluorimetric titration. This sensor 16 was used for the detection of Zn^{2+} in water samples as well as test strips.

Bojinov *et al.* [64], designed and synthesized 2 novel, 8-naphthalimide based sensor 17a and 17b, for the selective detection of Zn^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+} and Co^{2+} in H_2O/DMF (4:1, v/v) (**Figure 3**). Sensor 17a and 17b in DMF showed an absorption band centre in the region of 340-342 nm. Both the receptors showed a weak emission peak in the range of 440 - 444 nm. Upon the addition of Zn^{2+}, the fluorescence intensity increased by 3.17 and 10.06 nm for 17a and 17b, respectively due to the restriction of photo-induced electron transfer. It suggested the formation of complex in 1:2 ratio.

Liu *et al.* [65], devised a novel 4-amino-1,8-naphthalimide based fluorescence sensor 18 for the selective recognition of Zn^{2+} in HEPES buffer solution with a detection limit of 1.72×10^{-6} $mol\cdot L^{-1}$ (**Figure 3**). The receptor 18 in HEPES buffer displayed a weak green fluorescence peak at 550 nm due to the photo-induced electron transfer (PET). The addition of Zn^{2+} resulted a 34-fold enhancement in emission peak at 550 nm. The job's plot analysis confirmed the formation of 1:1 complex within 18 and Cu^{2+}. The receptor 18 was successfully applied for fluorescence imaging in living cells.

Parkesh *et al.* [66], synthesized 2 4-amino-1,8-naphthalimide based fluorescent sensors 19a and 19b for the selective detection of Zn^{2+} in HEPES buffer solution (**Figure 3**). The receptor in HEPES buffer displayed an absorption maximum at 450 nm and a weak green fluorescence emission peak at 550 nm. Addition of Zn^{2+} ions to both the receptor 19a and 19b in HEPES buffer, it induced an enhancement of fluorescence peak at 550 nm with a slight redshift from 550 to 554 nm due to the suppression of photo-induced electron transfer transition from receptor to fluorophore. The binding affinity of sensor 19a and 19b with Zn^{2+} was calculated to be 1:1, and the dissociation constant for receptor 19a was calculated to be 4 nM. This receptor was applied in various biological applications.

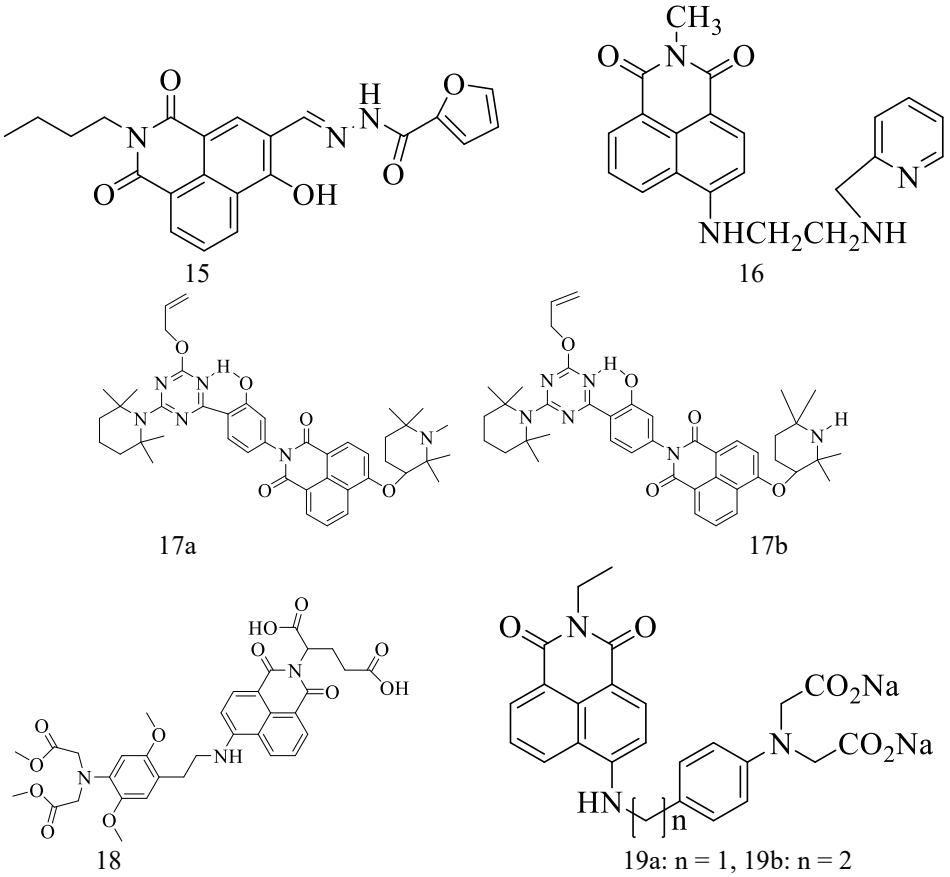


Figure 3 Napthalimide based receptor as zinc ion sensor.

Kumar *et al.* [67], designed and synthesized 1,8-naphthalimide linked quinoline based fluorescence sensor 20 to detect Zn^{2+} ions in H_2O/CH_3CN (2:8, v/v) with a detection limit of 20×10^{-8} mol·L^{-1} (**Figure 4**). The addition of Zn^{2+} to the acetonitrile solution of 20 resulted a red shift in absorption peak from 363 to 375 nm with a clear isosbestic point at 368 nm. On the other hand, the addition of Zn^{2+} induced a redshift in emission peak from 448 to 550 nm with quenching in fluorescence intensity at 448 nm. The quenching in fluorescence was due to the inhibition of photo-induced electron transfer (PET). The change in fluorescence spectral behaviour and the color from blue to orange red suggested the formation of 1:1 complex between the receptor 20 and Zn^{2+}. The 20: Zn^{2+} complex was also applied for the selective detection of pyrophosphate and hydrogen peroxide. This receptor was used to study the fluorescence imaging in various biological samples.

Zhang *et al.* [68], prepared a novel 4-amino-1,8-naphthalimide based fluorescent sensor 21 used to sense Zn^{2+} in HEPES buffer (**Figure 4**). Addition of Zn^{2+} to the receptor 21 resulted a hypsochromic shift from 453 to 442 nm with a clear isosbestic point at 442 nm. Further the addition of Zn^{2+} to the receptor 21 induced a 4 fold enhancement in fluorescence emission at 540 nm due to inter-molecular charge transfer (ICT). This suggested the formation of 1:1 complex between 21 and Zn^{2+} with a dissociation constant of 4 Nm. The detection limit was calculated to be 57 Nm. This receptor was used to study fluorescence bio-imaging in Hela cells, HepG2 cells and Zebra fish.

The novel 1,8-naphthalimide based fluorescence "off-on" sensor 22 was devised by Dimov *et al.* [69], to detect Zn^{2+} inH_2O/DMF (4:1, v/v) (**Figure 4**). The receptor 22 in DMF displayed an absorption band in the region of 280 - 320 nm due to the ICT transition. The receptor 22 also displayed a weak fluorescence peak at 411 nm due to the photo-induced electron transfer (PET). The interaction of Zn^{2+} to the receptor 22 in DMF resulted an enhancement of emission peak at 411 nm due to the restriction of PET transition. The jobs plot analysis confirmed 1:1 complex formation within 22 and Zn^{2+}. From the fluorescence titration plot the limit of detection was assessed to be 2.5×10^{-7} mol·L^{-1}.

The 1,8-naphthalimide based 2 fluorescent sensors 23a and 23b were synthesized by Gravchev *et al.* [70] for the selective detection of various metal cations like Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+}, Fe^{3+} and Ag^{+} (**Figure 4**). Both 23a and 23b in DMF displayed a strong fluorescence peak at 523 nm due to photo-induced electron transfer (PET). Upon addition of Zn^{2+} to both the receptors 23a and 23b in DMF, it displayed a gradual increase in the intensity of emission peak at 523 nm and was blue shifted to lower wavelength region. The intensity of 23a and 23b increased gradually with a quantum yield of 0.216 and 0.184, respectively due to the inhibition of photo-induced electron transfer.

Panchenko *et al.* [71], designed and synthesized a novel fluorescence sensor 24 from 4-methoxy-1,8-naphthalimide derivative and salicylideneamino for the selective recognition of Zn^{2+} in acetonitrile (**Figure 4**). The receptor 24 in acetonitrile showed an absorption spectrum at 363 nm was associated with the intramolecular charge transfer (ICT) transition from the methoxy group at position 4 to the carbonyl groups of the dicarboximide moiety. Upon the addition of Zn^{2+} to the receptor 24 in acetonitrile induced a decrease in absorption peak at 363 nm with slight red shift in absorption band. On the other hand the addition of Zn^{2+} also resulted an enhancement in emission peak at 461 nm due to the inhibition of photoinduced electron transfer (PET). The binding stability of the ligand-metal complex was estimated to be 2:1.

Fan *et al.* [72], synthesized a new fluorescent sensor 25 from 1,8-naphthalimide and di-2-picolylamine for the selective detection of Zn^{2+} (**Figure 4**). Receptor 25 showed a maximum absorption band at 453 nm and a fluorescence emission peak at 549 nm, respectively. The addition of Zn^{2+} to the receptor 25 resulted a 5-fold enhancement in the emission peak at 549 nm with a slight blue shift from 549 to 539 nm. On the other hand the addition of Zn^{2+} to the receptor 25, also induced a blue shift in absorption band from 453 to 443 nm signified the 1:1 complex formation between 27 and Zn^{2+}. The dissociation constant was calculated to be 0.83 nm. This fluorescent probe was used to determine the Zn^{2+} in mammalian cells [70].

The novel 4-amino-1,8-naphthalimide hydrazine based receptor 26 was synthesized to serve as a selective detector of Zn^{2+} in THF (**Figure 4**). The receptor 26 in THF displayed the absorption band at 268 and 429 nm due to inter-molecular charge transfer (ICT). The addition of Zn^{2+} resulted a slight increase in absorption intensity at 268 nm. The receptor 26 displayed a quenched fluorescence peak at 508 nm due to photo-induced electron transfer (PET). After the addition of Zn^{2+} to the receptor 26 displayed an increase in fluorescence intensity at 508 nm due to inhibition of PET transition. The association constant was estimated to be 62.007 M^{-1} and the binding constant was calculated to be 1.13×10^{4} M^{-1}. The 26:Zn^{2+} complex was formed at a 1:2 stoichiometry ratio.

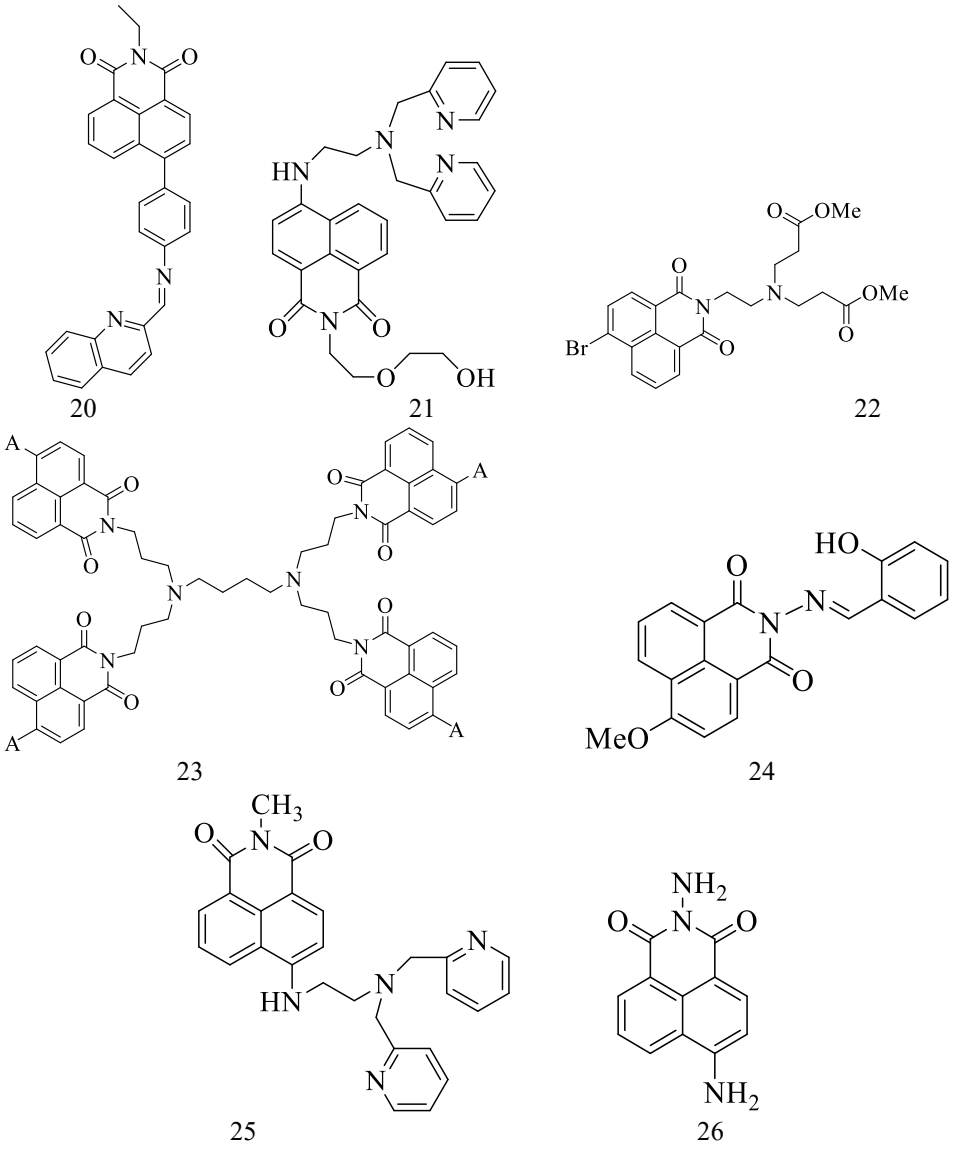


Figure 4 Napthalimide based receptor as zinc ion sensor.

Table 1 Selective parameters of receptors 1 - 26.

Sensors	Solvent	λ_{exc} (nm)	λ_{emi} (nm)	Binding constants (M^{-1})	Detection limit	Application	Ref.
1	Acetonitrile/ HEPES buffer	397	518	3.02×10^{3}	1.03×10^{-6} M	Bioimaging	48
2	HEPES buffer	470	550	2.4×10^{-5}	---	living cell	49
3	HEPES buffer	470	550	---	4.25×10^{-6} M	Biological application	50
4	DMF	367	435	---	---	Environmental application	51
5	Acetonitrile	334,336	430,439	---	---		52
6	HEPES buffer	437	527	---	---	Biological application	53
7	DMSO	450	550	---	---	Biomedical application	54
8	Aqueous acetonitrile solution	451	537	6.76×10^{5}	---	---	55

Sensors	Solvent	λ_{exc} (nm)	λ_{emi} (nm)	Binding constants (M^{-1})	Detection limit	Application	Ref.
9	HEPES buffer	346	447	9.00×10^{-7}	---	Biological application	56
10	HEPES buffer	470	550	---	7.72×10^{-7} M	Biological application	57
11	HEPES buffer	335	394	1.22×10^{6}	---	Application in field of polymers, optical storage, photophysicals dyads, nucleic acid intercalators and DNA photo cleavage	58
12	DMF/ water	280 - 320	411	---	2.5×10^{-7} M	Environmental and biological application	59
13	DMSO	370	527	1.55×10^{5}	0.0345 ppb	Environmental and biological application	60
14	HEPES buffer	470	550	---	---	Biological application	61
15	Tris-HCl buffer	453	549	0.83×10^{9}	---	Application in mammalian cell	62
16	DMSO/H_2O	400,500	506	1.18×10^{5}	39 nM	Biological application	63
17	DMF	340 - 342	440 - 444	---	---		64
18	HEPES buffer	470	550	---	1.72×10^{-6} M	Imaging in living cell	65
19	HEPES buffer	450	550	---	---	Biological application	66
20	Acetonitrile	363,214,239	550	5.19×10^{9}	20×10^{-8} M	Biological application	67
21	HEPES buffer	453	540	0.19×10^{9}	57 nM	*In vitro* and *in vivo* imaging	68
22	DMF	280-320	411	---	2.5×10^{-7} M	---	69
23	DMF		523	---	---	---	70
24	Acetonitrile	363	461				71
25	Tris-HCl buffer	453	549	5.8×10^{9}	---	Application in mammalian cell	72
26	THF	268,429	508	1.13×10^{4}	---	Biological application	73

Conclusions

Fluorescence is well known for its high sensitivity, reproducibility, low detection limits, ease of use, and potential for real-time monitoring due to its fast reaction times. These features made metal ion fluorescence sensing one of the most powerful detection methods ever developed. The importance of 1,8-naphthalimide as Zn^{2+} sensor in fluorescence sensor design has been reported in recent years, and the result of their study have been presented in this review. Depending on the system and experimental parameters, such as the kind of metal salt employed, pH, buffer, solvent utilized and the analytes concentrations, zinc sensors were involved via different binding modes and varied fluorescence response mechanisms. All the specified sensors, however, were turned off, allowing for the selective detection of Zn^{2+} ions in a variety of environmental or biological samples. Because nitrogen is preferable and forms relatively simple geometries with Zn^{2+}, most receptors employ it as a binding site. According to this research, the derivative of 1,8-naphthalimide as receptor still has lot to for improvement, notably in term of quick response and biocompatibility, which are important for biological applications. For a better understanding of the variety of coordination complexes and geometries, more research is recommended. This review may help in the discovery, development and exploration of novel 1,8-naphthalimide derivatives for future chemosensor applications that are much more specific and sensitive to zinc ions. 1,8-naphthalimide derivatives show excellent selectivity and sensitivity to detection of various cations with good anti-interference ability. Due to their great photostability, high quantum yields, prominent visible absorption bands and significant Stokes shifts, 1,8-naphthalimide derivatives are currently frequently utilised as precursors or fluorescent sensors. This method has benefits over other conventional metal ion detection techniques.

Acknowledgements

Dr. Jali acknowledges a fund from UGC-Startup grant (F.30-391/2017(BSR), UGC New-Delhi, India. The authors also thank to Department of Chemistry, VSSUT, Burla, India for providing research facility.

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