REVIEW

D-π-A based Diaminomalenonitrile Imine Compounds as Sensors: From Ion Recognition to Logic Arithmetic Applications

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In this review article, exciting highlights on highly π-conjugated (π-D-A) 2,3-diaminomaleonitrile (DAMN) based imines or Schiff base chemosensors have been reviewed and discussed. Owing to the typical free -NH$_2$ anion recognition site and 1,2-ethylenediamine based chelating structure, both anion and cation sensing has been achieved with such designed molecules. It has been found that ion interactions strongly alter the electronic push-pull and hence intramolecular charge transfer (ICT) properties across the molecular system. So far such molecular recognition strategy has successfully detected ions like F$^-$, CN$^-$ and Cu^{+2} in aqueous as well as non-aqueous media. Importantly, recognition is usually reversible and changes are clearly perceived through naked eyes. In this work, various sensing aspects like mechanism of interaction, type of recognition, sensitivity, reversibility, binding constants and spectral changes (absorption and emission) have been thoroughly discussed. Herein, the designed and fabricated sensor reports have been arranged in systematic order since 2010 so that the reader gets complete and trending picture of how the developments have taken place in the area of this research. In last, essential shortcomings and future challenges existing with the current approaches have also been highlighted.

Keywords: DAMN, Chemosensor, Recognition, Schiff base, Mechanism, ICT.

INTRODUCTION

Molecular recognition chemistry has achieved tremendous impetus during last few decades attributed to the diverse applications of new and explored molecules in food analysis, environmental analysis, cell/organelle imaging, material sciences, *etc.* [1,2]. Such molecular receptors or sensors with the help of supramolecular analytical chemistry provide an alternate tool to the analytical and environmental chemists, as it is advantageous and attractive in the sense that it is user-friendly, cost-effective, portable and reusable [3,4].

The exploration, design, fabrication and development of such chemical sensors for detection and quantification of target analytes in certain media remain to be the fundamental challenge [5,6]. In this direction many novel molecular fragments and design motifs have been explored. On the other hand, with the help of advances and developments in the synthetic organic chemistry, synthesis of numerous challenging molecular structures has been produced in limelight of the field. In this context, one of the molecular designs which caught attention of researchers in the recent past is the highly conjugated donor-pi-acceptor (D-π-A) diaminomaleonitrile (DAMN in Fig. 1) [7,8].

Researchers have utilized an easy to achieve synthetic procedure by one-side Schiff-base condensation reaction of DAMN with any aromatic aldehydes to form thermally stable mono-imine compounds and explored diverse applications [9-16]. Besides, the synthesized molecules are usually coloured because of extensive π-conjugation. The single side condensation products are easy to achieve rather than two-side condensation. This can be understood by the fact that upon imine condensation
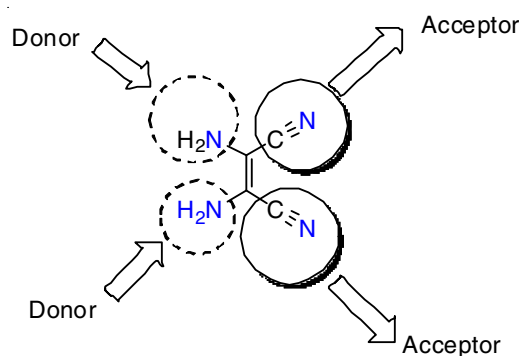
Fig. 1. Structure of diaminomaleonitrile (DMAN) with D-π-A sites assigned

on one side of DAMN, lone pair of electrons on the free amine (–NH$_2$) nitrogen atom strongly exists in conjugation with the nitrile (–CN) acceptor. This dramatically reduces the nucleophilicity of this free –NH$_2$ group and thus avoids the Schiff base formation on the other side of DAMN backbone. However, under harsh conditions, two side condensation is plausible on DAMN. Interestingly as such an asymmetric DAMN Schiff base molecular structure bears free -NH$_2$ anion recognition site which possess highly polarized N-H bonds. Such polarized N-H motifs have been the basic target of various researchers across the community of interest. Similarly, existence of 1,2-ethylenediamine based chelating site in the molecules sensed the researchers to explore the cation binding and hence sensing aspects in different matrices [17]. In addition to the field of anion recognition research, innovative work has given rise to a fascinating new area of material science called molecular logic mathematics and information processing [18,19]. Such an unconventional molecular basis of digital processing has emerged as area of considerable interest over the last few decades. Even though it is debatable as far as practical utility is concerned, but then it represents a real bottom-line approach for quick and complex information processing [20]. In brief, herein we have put our all efforts for compiling crucial aspects put forward by various scientists for exploring cation and anion recognition performances of D-π-A based diaminomaleonitrile imine compounds and further exploring their logic arithmetic application will be discussed here.

Ion recognition studies: Amid exploration of ion sensing characteristics of asymmetric DAMN based imines with D-π-A charge transfer (CT) channels, Wu *et al.* [21] in 2010 synthesized pyrene fluorophore tethered chemosensor (R$_1$). The UV-visible spectroscopy analysis in CH$_3$CN/H$_2$O (v/v 1:1, 10 mM HEPES, pH = 7.0) showed that after gradual addition of Cu^{2+} to R$_1$, characteristic absorbance peak of R$_1$ at 420 nm got reduced with emergence of new peak at 355 nm. This was further visually observed by missing of yellow colour of sensor solution. Moreover, R$_1$ exhibited very weak fluorescence (quantum yield, Φ = 0.0045) as a result of photoinduced electron transfer (PET) from two -CN groups to pyrene moiety. In presence of Cu^{2+} PET process got inhibited in R$_1$ and hence fluorescence "turn on" response was observed and a sharp emission peak was observed at 417 nm (Φ = 0.59). The 1:1 stoichiometric ratio of R$_1$ and Cu^{2+} complex was shown by Job plot and binding constant (K$_a$) was calculated to be 5.55×10^3 M^{-1}.

The coumarin fluorophore was also condensed with DAMN to produce the molecular sensor R$_2$ [22]. The sensor is capable of hypochlorite anion (OCl$^-$) detection in living cells *via* de-diaminomaleonitrile reaction. Molecule R$_2$ in phosphate buffer and N,N-dimethylformamide solvent (PBS/DMF, pH = 7.4, v/v 8:2) displays emission peak at 585 nm. Upon addition of NaOCl, emission peak decreases gradually with appearance of new blue shifted emission peak around 505 nm. The emission changes were seen with colour changes from orange to green. The spectral shift is attributed to the strong intramolecular charge transfer (ICT), which was further confirmed by solvent effect. The results were further validated by DFT calculations, wherein it was confirmed that donor unit bears a partial positive charge and the acceptor unit bears partial negative charge. Regarding quantative aspects, linear calibration curve of R$_2$ for OCl$^-$ was obtained at µM concentrations; hence R$_2$ can be quantitatively used to detect OCl$^-$ at micro molar level. The receptor is highly selective to OCl$^-$ with a detection limit of 0.2 µM. The proposed molecular sensor is permeable to cell membrane and hence a prospective for ratiometric imaging of OCl$^-$ in living cells.

Lan *et al.* [23] reported the another type of molecular receptor R$_3$ by condensing naphthalimide moiety with DAMN, where R$_3$ interacted with Cu^{2+} showed fluorescence "turn on" response. This was ascribed to the prevention of PET from indole moiety to the DAMN. In presence of Cu^{2+} at very low concentrations, the absorbance peaks of molecule at 325 nm and 405 nm got decreased. But in presence of greater than 1.0 equiv. of Cu^{2+} absorption peak got increased at 325 nm with a monotonic decrease of peak at 405 nm. The lowest detection limit of R$_3$ was found to be 6.18×10^{-8} mol L^{-1}.

One of the interesting reports to explore anion recognition performance of DAMN Schiff base compounds was put forward by Sankar & Kaloo in 2013 [24]. They came out with an interesting case of exclusive fluoride ion sensing with the help of simplest Schiff base produced by condensation reaction of DAMN and *p*-nitro benzaldehyde, 2-amino-((*E*)-(4-cyanobenzalidine)-amino), R$_4$. In this, -NH$_2$ group acted as donor (D) and -CN group acted as acceptor (A). As a result of such a strong π-D-A channels strong ICT was proposed. Anion recognition was explored in polar aprotic solvents like dimethysulphoxide (DMSO) and tetrahydrofuran (THF). Fluoride anion (F$^-$) used as tetrabutylammonium (TBA) salts strongly modulated the absorption and emission properties of the molecule. Free R$_4$ displays a strong CT absorption band at 376 nm and upon interaction with F$^-$ ion, strong red shift (89 nm) was observed in its absorption band towards 465 nm was observed. An intermolecular proton transfer (IPT) from the amine group of R$_4$ to the fluoride ion was proposed to be the vent responsible for it. The resulting negatively charged anion of R$_4$ shows a strong push pull effect, which is visible to naked eye along with colour changes from yellow to red. The binding constant (K$_a$) of R$_4$ with F$^-$ ion was estimated 5.36×10^4 M^{-1}. The R$_4$ shows high selectivity for F$^-$ ion in the range of 0-10 µM concentration. The anion sensing of F$^-$ further resulted in fluorescence "turn on" response.

In another study, Zhou *et al.* in 2013 [25] made use of foundational supramolecular chemistry based approach and

introduced azacrown ether and tethered them over DAMN. A typical condensation reaction was carried out between DAMN and 4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzaldehyde (R_5) or 4-(1,4,7,10,13-pentaoxa-16-azocyclooctadecyl)benzaldehyde (R_6) in benzene solvent. Molecule R_5 possess small cavity, this upon interaction with Hg^{2+} turned pale yellow where as with Cu^{2+} it turned colourless under the pH range of 5.5-10.5. The UV-vis spectrum of R_5 showed that addition of Cu^{2+} resulted in the decrease of its characteristic absorption peak 420 nm and appearance of new peak at 336 nm with isosbestic point at 336 nm. In Jobs plot, 1:1 binding stoichiometry was observed between Cu^{2+} and receptor R_5. The stability constant was found to be $1.04 \times 10^4 M^{-1}$. Other molecular sensor, R_6 with large cavity (compared to R_5) in absorption spectroscopy showed characteristic absorption maximum at 420 nm, which decreases upon continuous addition of Cu^{2+} to 300 nm with a clear isosbestic point at 316 nm. The basic mechanism as anticipated was proposed to be the coordination of Cu^{2+} with the nitrogen and oxygen atoms of the crown compounds. Interestingly, once the ion coordination behaviour was studied under emission spectroscopy, "turn on" was observed.

Similarly, Zhang *et al.* in 2013 [26] designed a novel molecular receptor R_7. In presence of NaOCl, the optical spectrum of R_7 in phosphate buffer:EtOH = 7: 3 (v/v, 20 mM, pH = 7.4) showed that the fluorescent intensity increases rapidly in 30 s and then leveled off. Upon addition of ClO^-, the emission peak decreases gradually and a new emission peak emerged at 542 nm. This further accompanied with colour changes from purple to pink. A linear calibration curve was obtained for OCl^- from 0 to 20 μM. The receptor is highly selective to OCl^- with a detection limit of 2.88×10^{-8} M. The mechanism of anion interaction was proposed to be the breakdown of -C=N bond of the imine receptor.

Kaloo & Sankar in 2014 [27] came up with another imine Schiff base, R_8 (2-amino-3-((*E*)-(napthalen-1-ylmethylene)-amino)maleonitrile) by condensing naphthalene aldehyde with DAMN. R_8 displayed a unique CT absorption band at 385 nm in dry THF. The TBA salt of F^- induced a red shift of 75 nm along with a remarkable colour change of R_8 from yellow to red. The stoichiometry of 1:1 was obtained between sensor and anion by job's studies. The spectral changes were attributed to the deprotonation to the hydrogen-bond donor interaction of $-NH_2$ group of R_8 with F^- followed by deprotonation at high anion concentrations. In fluorescence, R_8 displayed fluorescence 'turn on' response at 430 nm upon excitation of molecule at 385 nm. The changes were attributed to the modulation of CT characteristics of receptor in presence of anion. In addition to this the R_8 in THF, showed selective detection of Cu^{2+}, which was visualized by colour changes from yellow to blue. The absorption maxima was shifted from 385 nm to 303 nm and proposed that the election withdrawing effect of $-CN$ group is blocked in the unsaturated-five membered ring complex resulting in CT inhibition across the system. Even at 10-20 μM concentration instant response of Cu^{2+} with R_8 occurs. The molecule was suitable to shown ionic recognition at micro molar level. For the first time, such D-π-A based asymmetric DAMN Schiff bases were also explored for Boolean logic applications.

In this direction, the chemical inputs (anions and cations, *etc.*) were utilized as logic inputs, while as absorption signal and emission signals were proposed to be logic outputs. Presence of inputs or outputs is represented by "1" while as absence corresponds to "0". Authors perceive the phenomena from the viewpoint of R_8 in the form of logical operations such as OR and NOR gates. Besides, a complex logic circuit was also constructed (Fig. 2).
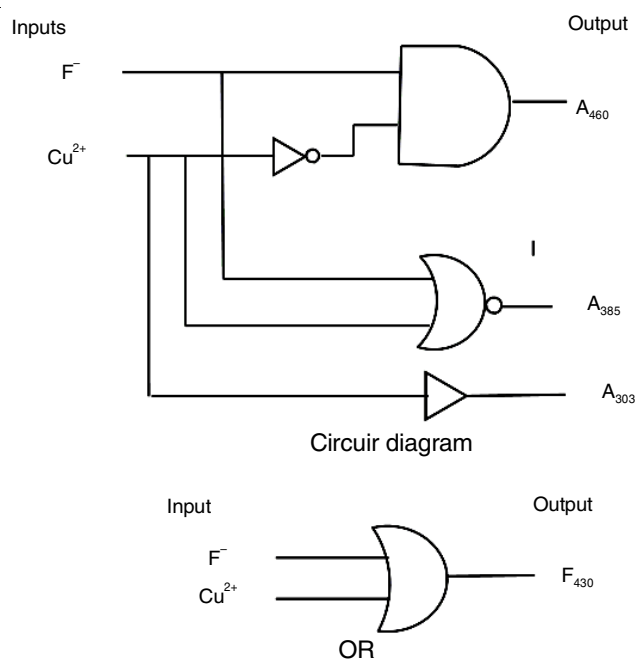

Fig. 2. Logic array gate for DAMN-based molecular sensor R_8

In same year, 2014 two new molecular sensors (R_9 and R_{10}) were reported by Xi *et al.* [28]. The molecules were based on triphenylethene, 9-phenylcarbazole and DAMN blocks. Both these compounds exhibited similar structures and UV-visible spectra with characteristic absorption maxima around 420 and 382 nm for R_9 and R_{10}, respectively. The molecules also displayed solvatochromic behaviour upon screening them from non-polar to polar solvents. The free receptor R_{10} displays absorbance at 420 nm; however upon titration with Cu^{2+}, 420 nm based peak diminished with appearance of new absorption signal at 350 nm. Naked eye colour changes from pale yellow to colourless were seen and ascribed to the metal-ligand (ML) charge transfer. Upon examination in fluorescence spectroscopy, the presence of Cu^{2+} resulted in the off and on type of fluorescent signaling. This increase of fluorescence intensity was attributed to the formation of the coordination complex that actually leads to the chelation-enhanced effect (CEE). In addition to Cu^{2+}, 0-2.0 equiv. of Hg^{2+} absorption peak at 382 nm got red shifted to 420 nm, proposed due to the metal-ligand (ML) transition.

In 2014, Sankar *et al.* [29] came up with ferrocene-DMN Schiff base molecule R_{11} as a selective F^- sensing and Cu^{2+}. The proposed sensor recognizes F^- with the help of polarized $-NH_2$ recognition site and Cu^{+2} through chelating 1,2-diamine. Interestingly, the research proposed exciting logic arithmetic behaviour from such ionic interaction with molecules and

resulting the optical outputs. Several simple and complex logic functions like YES, NOT, NOR, INH, IMP and complementary (INH/IMP) sequential circuits were obtained (Fig. 3). Most importantly, reversible switching behaviour of F^- interaction by influx of H^+ was presented with "Writing-Reading-Erasing-Reading-Memory" function deciphering multi-write ability.
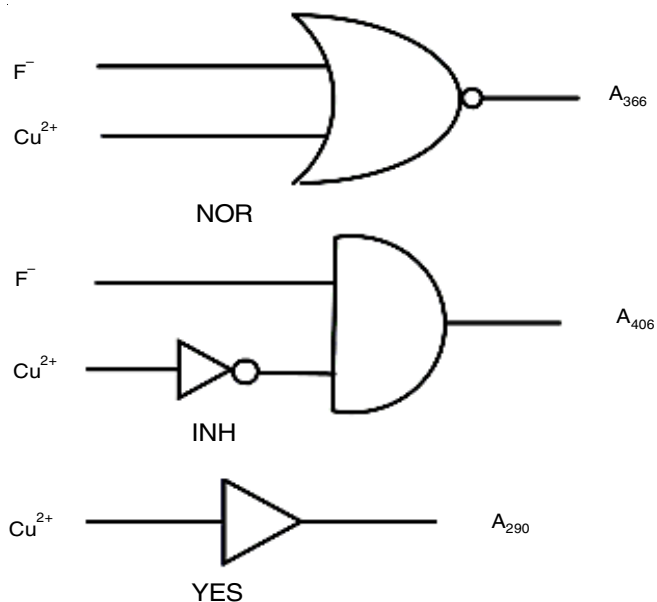

Fig. 3. Logic array gate for DAMN-based molecular sensor R_{11}

Ma *et al.* in 2014 [30] proposed and designed highly photostable fluorescent Coumarin derivative (R_{12}). Owing to 7-diethylamino group as electron donor, while as DAMN fragment as strong electron acceptor, strong ICT process exists in the molecular system and R_{12} exhibited weak fluorescence which was proposed due to the quenching effect of -CN group as well as due to its flexible structure. The addition of Zn^{2+} resulted in the enhancement of emission response at 620 nm up to 35-folds. This was further accompanied with blue shift of 50 nm. The fluorescence enhancement as a result of reduced ICT process was proposed and the inhibition of conformational change upon complexation with Zn^{2+}. Most importantly, R_{12} was utilized for Zn^{2+} ion imaging in HepG2 cells.

Khanmohammadi *et al.* in 2014 [31] reported a new molecular sensor (R_{13}), which is an N-monosubstituted DAMN-based azo-azomethine dye and selectively recognizes F^- as TBA salt in mixed (9:1, v/v: DMSO-H_2O) solvent system. Herein the presence of F^- in the receptor solution resulted in the red shift of characteristic absorption maxima by 94 nm. This is further accompanied by the prompt colour change of receptor solution from light green to greenish blue. This visual colorimetric signalling could be ascribed to the deprotonation of free -NH_2 group of R_{13}. The incident of proton transfer signalling (PTS) resulted in the enhancement of negative charge on the nitrogen atom, which leads to the enrichment of push–pull effect of the ICT transitions in the molecule. Hence, the absorption maxima of molecule got red shifted in presence of highly electronegative or basic F^-. Further by introducing strong electron-withdrawing group like -NO_2 increases the acidity of H atoms on the amine

N. This in turn facilitates the deprotonation. The detection limit of F^- ion was found 1.50×10^{-6} M and the binding constant (K_a) towards F^- was found to be 1.59×10^5 M^{-1}. Moreover, the proposed molecular sensor was successfully used for qualitative and quantitative estimation of inorganic fluoride in toothpaste and mouthwash samples.

In a similar manner, Park *et al.* [32] developed a dual colorimetric sensor 2-(3-nitro-2-oxo-2*H*-chromen-4-ylamino)-3-aminomaleonitrile (R_{14}) for the sensing of Al^{3+} and F^-. In UV-Vis spectroscopy, absorption peaks displayed by molecule at 250, 334 and 432 nm continuously decreased with simultaneous emergence of new peak at 302 nm upon continuous addition of Al^{3+} in presence of other competing ions in the medium. The occurrence of colour transformations could be attributed to the binding of Al^{3+} ion with NH and NH_2 groups of R_{14}. The binding of this cation weakened the ICT transition in the sensor molecule. More importantly, R_{14} sensor performance can be recycled and reused upon handling with ethylenediaminetetraacetic acid (EDTA). Contrary to cations, molecule R_{14} showed selective colorimetric sensing of F^- also. Here F^- ion induced the deprotonation of amine moiety which led to decrease in the ICT. The detection limit of sensor for Al^{3+} was found to be 38.2 mM.

An interesting example of exploration and development of already existing pyrene-DAMN Schiff base (R_{15}) (2-amino-((*E*)-(pyren-1-ylmethylene)amino)maleonitrile) for solid phase and solution based NaCN sensing was reported by Sankar & Kaloo in 2015 [33]. Prompt, selective and reusable recognition of water soluble CN^- was achieved through colorimetric and fluorescent means. Under DMSO/HEPES (8:2, v/v) solvent conditions free R_{15} posses a strong absorption peak at 430 nm along with another weak signal at 345 nm. Presence of CN^- triggered a red shift of 430 nm peak. A new band was observed at 505 nm with concomitant decrease of 430 nm absorption. These spectral changes were associated with two isosbestic points at 468 nm and 367 nm. The observations in UV-Vis spectrum envisage two different chemical species in equilibrium. Such occurrence is ascribed to the strong ICT transitions from -NH_2 to -CN. The K_a value was calculated to be $1.35 \ 10^4$ M^{-1} and the high value of hydration energy (-295 KJ mol^{-1}) in contrary to other competing anions along with strong basicity was proposed to be an important reason for selective sensing of CN^- by molecule R_{15}.

Jo *et al.* in 2015 [34] achieved selective detection of Cu^{2+} and F^- of new DAMN based symmetric Schiff base (R_{16}). The selective sensing of R_{16} for Cu^{2+} was monitored by UV-Vis absorption spectroscopy under mixed solvent system, CH_3CN/tris buffer (6:4, v/v). Among a range of competing metal ions, only Cu^{2+} induced a distinctive spectral change along with visual naked-eye detection from yellow to colourless. In presence of Cu^{2+}, R_{16} showed gradual decrease of its absorption maxima at 450 nm with concomitant appearance of a new band at 375 nm. The significant blue shift in the spectral behaviour indicated weakness in the push-pull electronic effect. The same was ascribed to the binding of Cu^{2+} to the -OH and -NH_2 groups on molecule R_{16}. A clear isosbestic point was achieved at 396 nm indicating existing of some equilibrium in the solution

between receptor and its cation bound form. The binding constant (K_a) of R_{16} for Cu^{2+} ion was obtained to be 2.3×10^4 M^{-1} with the help of Benesi-Hildebrand equation. Detection limit of molecule R_{16} in drinking water was low in comparison to the WHO recommendation. The sensing behaviour of R_{16} with TBA salts or sodium salts of various anions was further tested in mixed solvent system, DMSO/*bis*-tris buffer (97:3, v/v). Interestingly, addition of F^- was selectively seen to come up with colour change from yellow to orange within few second. Under the UV-Vis spectroscopic analysis, R_{16} showed a strong absorption band around 300 nm and 460 nm. Presence of F^- decreased such bands along with gradual emergence of 520 nm. It was proposed that F^- deprotonotes the phenol and leads to enhancement of ICT across the molecule.

Interestingly, Sankar *et al.* in 2016 [35] designed and synthesized environmental challenging matrices for sensing the water soluble bicarbonates using conjugated molecule (R_{17}) (2-amino-3-((*E*)-(-((*E*)-3-(4)-nitrophenyl)allyidene)amino)-maleonitrile). The sensor molecule was achieved by condensation between DAMN and *p*-nitro cinamaldehyde. The screening of ion sensing characteristics of R_{17} was carried out in which DMSO/H_2O:8/2 (v/v) solvent and the anions were directly added in the form of sodium or potassium salts. Among the various anions existing in environmental waters, only bicarbonate (HCO_3^-) ion produced instantaneous and prompt colour changes. At very lower addition of HCO_3^- yellowish sensor solution turned brown, while as at higher concentrations violet colour was observed from sensor solution under study. Once such changes opted for further examination under UV-Vis spectroscopy, slowly diminished the intensity signal at 415 nm with a consequent increase in absorption at 555 nm was observed. The high value of bathochromic shift in absorption spectra was attributed to the increase of negative charge density –NH_2. The synthesized and developed sensor was utilized for qualitative and quantities estimation of water soluble carbonates in the range of water samples collected from various environments of the region. Based upon the 1:1 stoichiometry by Job's method, the binding constant (K_a) was found to be 3.552×10^3 M^{-1}.

Vengaian *et al.* in 2016 [36] synthesized and developed another molecular sensor (R_{18}) (2-((10-hexyl-10*H*-phenothiazin-7-yl)methyleneamino)-3-aminomaleonitrile based on phenothiazine-DAMN combination. The sensor molecule selectively detected Hg^{2+} ions in ethanol-water (6/4: v/v). In the UV-Vis spectra, molecule R_{18} showed an absorption peak at 425 nm where red shifted towards 448 nm in presence of Hg^{2+}. Once examined under emission spectroscopy, R_{18} upon excitation at 425 nm and in presence of Hg^{2+} intense emission band at 550 nm got quenched. The same solution upon addition of 1 equiv. of Na_2S quenched the fluorescent behaviour at 550 nm. The high concentration of sulphide ion increased fluorescence intensity due to the formation of an ensemble which is concentration dependent. The high sensitivity to S^{2-} leads to the formation of the stable chemical species.

Sarveswari *et al.* in 2017 [37] reported two new molecules wherein fluorine fragment was tethered with DAMN and molecules were named as (2-((*E*)-(9*H*-fluoren-2-yl)methylene)-amino)-3-aminomaleonitrile and (*E*)-2-(amino(((9-ethyl-9*H*-

carbazol-2-yl)methylene)amino)methylene)maleonitrile) (R_{19} and R_{20}). According to them, R_{19} possess an extensive conjugation due to the strong electronic communication between electron donor (-NH_2) and electron acceptor (-CN] groups. Such type of D-π-A electronic properties dedicates strong ICT in the molecule. Anions like CN^- and F^- selectively bought in fast colorimetric changes in the receptor in DMF solvent. Once the molecule was examined under emission spectroscopy, the characteristic emission peak at 460 nm got red shifted by 20 nm with the emergence of new emission peak to 480 nm. Later was attributed to strong ICT from deprotonated amine site (–NH^-) to –CN acceptor moiety and displays the characteristic absorption signal at 400 nm in the presence of F^-, which exhibited a red shift with the emergence of new absorption peak at 450 nm along with colour changes from light yellow to deep yellow. However, in emission spectroscopy upon excitation of molecule at 380 nm, the emission band got shifted to 480 nm. Thus, a fluorescence 'turn on'' response was reported and the molecule could detect CN^- at nano molar level.

Keshav *et al.* [38] prepared a new DAMN derived molecule sensor containing hydroxyl benozothiazole moiety (R_{21}). This molecular sensor is also based on the electronic push-pull effect between –NH_2 donor and –CN acceptor. The CN^- was selectively detected in the mixed-aqueous/DMF (50%) solution. In this sensor, the CN^- binds reversibly with the R_{21} and showed cell visibility in live fibroblast L929 cells at 0.16 μM level. In absorption spectra, in the presence of CN^-, R_{21} shows disappearance of peak at 370 nm with the emergence of new peak 445 nm. The colorimetric changes were observed from yellow to red. In the UV-Visible spectra, the isosbestic point at 390 nm indicated the existence of equilibrium in the solution. The receptor R_{21} also showed an emission band at 517 nm and this peak got strongly intensified in presence of CN^- owing to the enhanced ICT. The strong fluorescence enhancement was proposed to the fact that ICT prevented PET process in the molecule. The K_a was calculated to be 1.96×10^4 M^{-1} and the limit of detection of 1.0 μM was shown for CN^-.

A significant breakthrough in the field of sensor design was achieved by Chang *et al.* in 2017 [39]. He utilized hydroxyl substituted naphthalimide moiety for design and synthesis of DAMN Schiff base sensor (R_{22}). The anion recognition study was conducted in DMSO solvent and observed that R_{22} selectively detects Cu^{2+}. The detection could be seen with the help of naked-eyes as colour changes occur from yellow to pink. Once the Cu^{2+} sensing was examined in UV-Vis spectroscopy, the band at 457 nm got decreased with the emergence of signal at 565 nm was noted. One of the novel applications of this sensor molecule is that it could extract Cu^{2+} from semiconductor wastewaters also. The lower limit of detection for Cu^{2+} was found to be 0.48 μM.

One of the different sensing molecular receptor which incorporated rhodamine fragment (R_{23}) namely (2-amino-3-(((1*E*,2*E*)-2-((33,63-*bis*(diethylamino)-3-oxospiro-[isoindoline-1,93-xanthen]-2-yl)imine) was synthesized and developed by Sakthivel *et al.* in 2017 [40]. The sensing behaviour was investigated in CH_3CN/H_2O (v/v = 7:3) and the molecule displayed the selectivity towards Cd^{2+} ions. In UV-Vis spectroscopy, an absorption

peak at 530 nm appeared from the solution of R₂₃ only in presence of Cd²⁺. Magenta or pink colour appeared in presence of Cd²⁺ in the sensor solution, which is due to the metal-induced delactonization of rhodamine fragment in the sensor. The complexation of Cd²⁺ with R₂₃ converts colourless spirolactam structure into ring opened amide form. Most importantly, the proposed chemical sensor was able to detect Cd²⁺ in HeLa living cells also.

Zhao *et al.* [41] also synthesized a new molecular sensor (R₂₄) by single step condensation of indoline type molecule with DAMN [41]. The probe could selectively sense Cu²⁺ in DMSO/H₂O (9:1; v/v) solvent system through fluorescence 'turn on'. A large stokes shift of 146 nm was achieved in presence of Cu²⁺. In presence of analyte and exciting sensor at 364 nm, the emission peak at 510 nm got enhanced in the intensity. The enhancement of fluorescent intensity was ascribed to the prevention of PET process from donor indole moiety to the acceptor DAMN. Molecule R₂₄ showed very low detection limit with around calculated to be 6.18×10^{-8} M⁻¹.

For selective and sensitive sensing of CN⁻, Son *et al.* [42] used dioctyl fuorene-dibenzenealdehyde for the condensation with DAMN to produce a highly π-conjugated molecular sensor (R₂₅). Here at both the ends of dioctyl fuorene-dibenzene, two molecule of DAMN got condensed [42]. The sensor R₂₅ successfully detected CN⁻ in aqueous medium at nanomolar level. The detection limit reported was much lower than the concentration level recommended by WHO guidelines. The sensor R₂₅ demonstrated intense colour change from yellow to red. Importantly, fluorescence 'turn on' response was recorded in presence of CN⁻. In UV-Vis examination, it was observed that CN⁻ induced the shift of characteristic absorption peak at 406 to 478 nm with a clear isosbestic point at 446 nm. The red-shift was explained through PTS of -NH₂ of DAMN coupled with ICT. The concentration of charge density at nitrogen atom led to enhancement of donor-to acceptor ICT transitions and hence red shift. Job's plot showed that the sensing is basically of 1: 2 between sensor and ion. More importantly the chemical sensor was able to detect CN⁻ in tap water and drinking water samples.

Wang *et al.* [43] prepared novel coumarin-based compound (R₂₆) with thiosemicarbazone as sensing unit. The sensor could detect F⁻ by both colorimetric and fluorometric means in THF solvent. A clear naked-eye colour change from green yellow to organe red was observed from molecular solution in presence of F⁻. The characteristic absorption of R₂₆ in THF was observed to be around 445 nm which upon gradual addition of F⁻ got gradually decreased with concomitant appearance at 510 nm with clear isosbestic point obtained at 480 nm. In emission spectroscopy, quenching of fluorescence at 499 nm was seen in presence of F⁻. The mechanism of anion recognition was proposed to be hydrogen bonding at low concentrations and deprotonation at high concentrations.

Another report of asymmetric DAMN Schiff base (R₂₇) was reported by Das *et al.* in 2018 [44]. The free chemosensor R₂₇ showed two absorption peaks at 263 nm and 378 nm in mixed aqueous media (10 μM, H₂O/MeOH, 1/1, v/v, 1 Mm PBS, pH = 7.1). In presence of ClO⁻ receptor solution changes from yellow to colourless. In presence of analyte, two absorption bands of R₂₇ at 282 nm and 330 nm disappear with appearance of new peaks at 282 nm and 330 nm. Two clear isosbestic points were observed at 272 nm and 300 nm. The changes are due to the oxidation of –C=N bond, followed by hydrolysis to form the aldehyde derivative. In fluorescence, molecule R₂₇ shows an intense peak 572 nm. The presence of ClO⁻ resulted in the decrease of this emission along with appearance of new blue-shifted emission peak around 468 nm. The emission changes were visually by receptor solution changes from orange to cyan. The lowest detection limit was calculated to be 7.87×10^{-7} M. The important aspect of this molecule was that it could be used for live cell imaging by using human white blood cells (monocytes).

Jiang *et al.* [45] reported one of the simple D-π-A DAMN based sensors (R₂₈), which was synthesized by the condensation reaction between 4-(dimethylamino)benzaldehyde and DAMN. The chemosensor displayed ratiometric detection of ClO⁻ and displayed a prompt colorimetric change from the canary yellow to red in DMSO/H₂O (1/1, v/v, pH = 7.4) medium. The fuorometric analysis of the R₂₈ showed that the emission peak at 521 nm was decreases along with appearance of another new peak at 635 nm. The intensity ratio of these two peaks was used as a means for the ratiometric detection of ClO⁻. The mass spectrometric and ¹H NMR of sensor in presence and absence of ClO⁻ revealed the oxidation of amino group of DAMN and hence formation of nitro compound. The LOD of R₂₈ for ClO⁻ was calculated to be 0.5 nM. Importantly, the negligible cell toxicity was observed and hence molecule was suitable for imaging intracellular ClO⁻ in the living cells.

Two highly selective asymmetric DAMN based imine Schiff base molecular sensors (R₂₉ & R₃₀) were developed by Shu *et al.* [46] in 2019. Both these sensors offered colorimetric and fluorescent 'turn on' detection of Cu²⁺ in acetonitrile. Owing the excellent photophysical properties like high molar extinction coefficient and high fluorescent quantum yield, signaling units like BODIPY and pyrene were introduced with the DAMN moiety. Both R₂₉ and R₃₀ were non-fluorescent in free molecular state but selectively in presence of Cu²⁺ dramatic fluorescence enhancement was observed. The mechanism was proposed to be through a Cu²⁺ enhanced hydrolysis reaction of –C=N. Sensing agent R₂₉ showed four absorption bands at 340 nm, 374 nm, 421 nm and 530 nm in the presence of Cu²⁺, which showed a progressive decrease in the intensity. Besides a new band appeared at 508 nm and shifted to 498 nm, two clear isosbestic points were also observed at 551 and 435nm, which indicate the complex formation with Cu²⁺. In fluorescence spectroscopy, addition of Cu²⁺ showed a significant fluorescence enhancement in molecule at 365 nm, which was further observed with bright green fluorescence from the solution. In case of R₃₀, no fluorescence was observed, however Cu²⁺ addition resulted in pyrene emission at 417 nm. The Job's study revealed 1:2 stoichiometry and this sensor molecules could detect the Cu²⁺ in tap water, lake water and drinking water samples.

For selective sensing of reactive oxygen species (ROS), Leng *et al.* [47] in 2022 came up with highly interesting molecular synthetic design wherein highly fluorescent BODIPY-was condensed with DAMN (R₃₁). This BODIPY-DAMN sensor
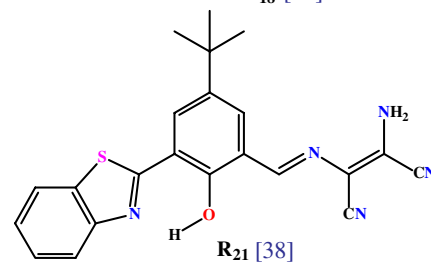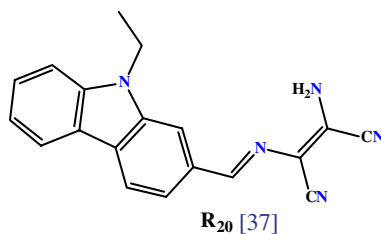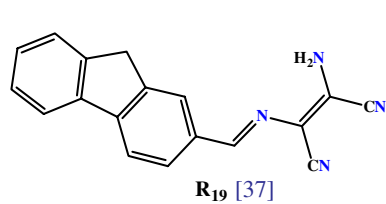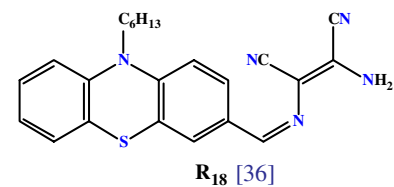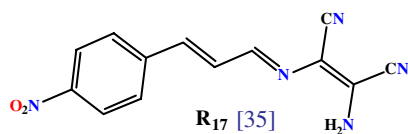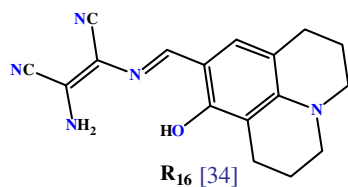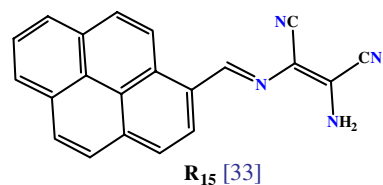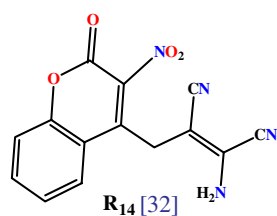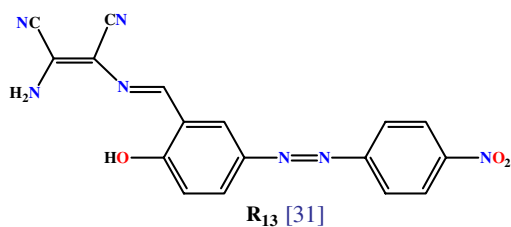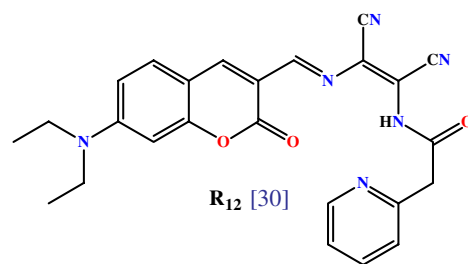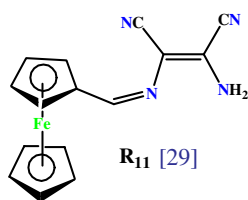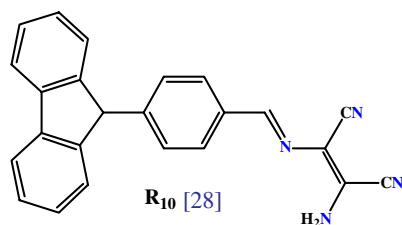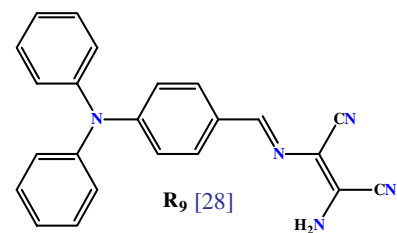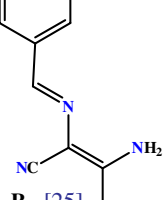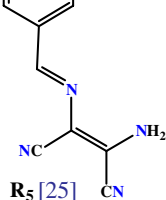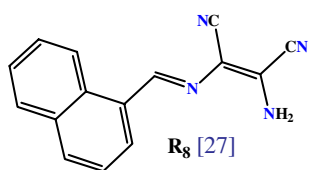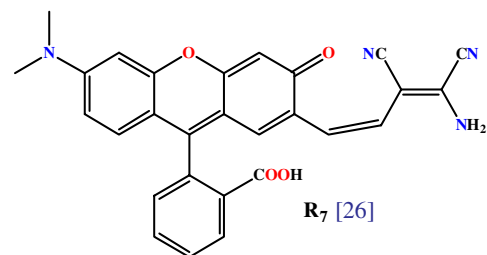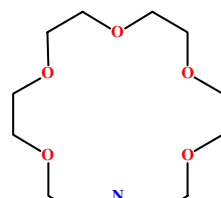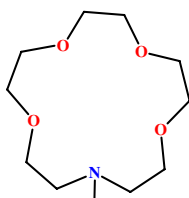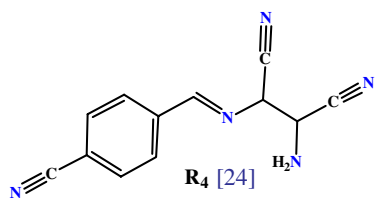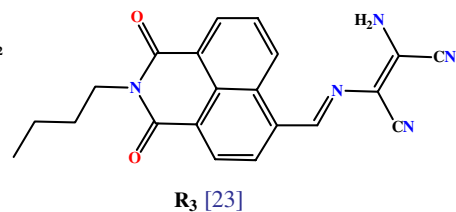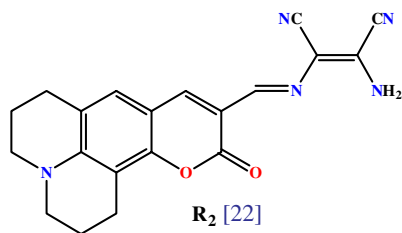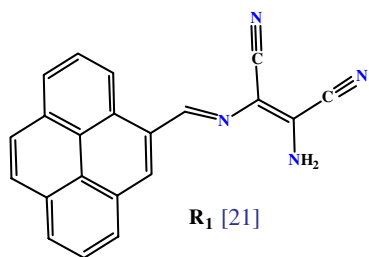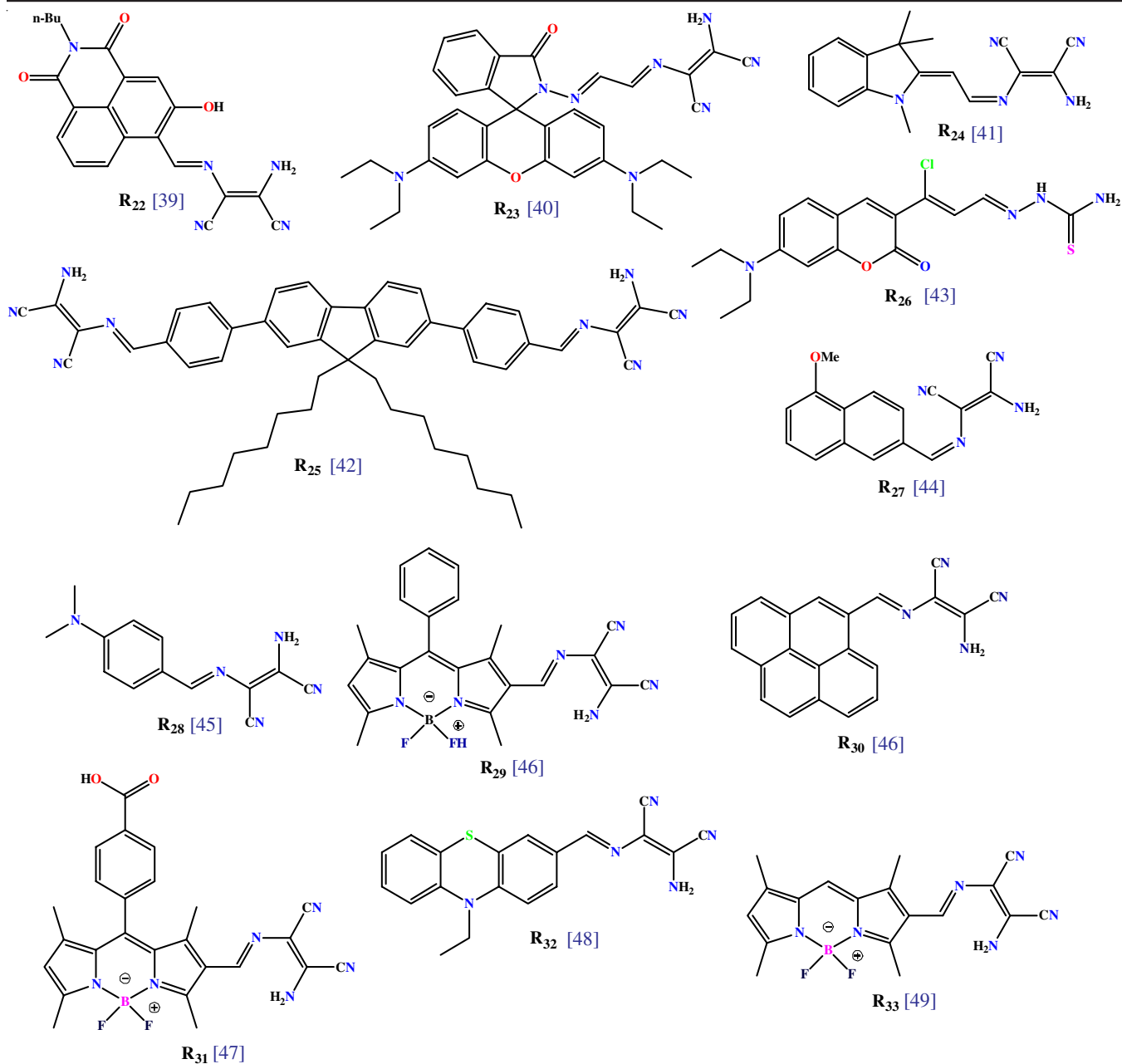
Structures of the diaminomalenonitrile (DMAN) imine compounds as sensors

was water soluble and could offer selective detection of endogenous ClO⁻ in the living organisms through an "off-on" fluorescence signaling response. As far as mechanism of recognition is concerned ClO⁻ encounters with R_{31} and oxidized it back to the aldehyde. The UV-Vis absorption spectrum showed appearance of maximum at 540 nm and in the presence of ClO⁻ under aqueous environment (PBS, pH = 7.4), the absorption peak was shifted to 490 nm. Once examined under fluorescence spectroscopy, R_{31} upon excitation at 480 nm, weak fluorescence signal was achieved. Presence of anion triggered fluorescence 'turn on' response. Most exciting aspect of this report is that the designed sensor could not only detect ClO⁻ in tap water, but was non-toxic to the living cells. For the same reason, authors could successfully, detect the concentration of ClO⁻ in endogenous mouse melanoma cells and human neuroblastoma cells.

Recently Dua *et al.* [48] designed and synthesized a novel DAMN-based molecular sensor *viz.* [(2-amino-3-(((E)-(10-ethyl-10*H*-phenothiazin-3-yl)methylene)amino)maleonitrile] (R_{32}) for Cu^{2+} sensing. The interaction of R_{32} with various ions was investigated in $CH_3CN:H_2O$ (8:2, v/v) solvent. Among various metal ions screened with the receptor, only Cu^{2+} resulted in the pale yellow colour and further under normal light it turned colourless. Once the solution was examined under UV light, R_{32} was non-fluorescent and in presence of Cu^{2+} blue fluorescence was observed. The UV-visible titration of R_{32} with Cu^{2+} in $CH_3CN:H_2O$ (8:2, v/v) shows a gradual decrease of intense absorbance peak at 425 nm, along with emergence of a new band at 282 nm. A clear isosbestic point was observed at 301 nm. The ion recognition behaviour for R_{32} was further utilized and successfully constructed a complex logic circuit by various

permutations of chemical inputs and optical outputs under the given solvent conditions. The circuit was proposed with the help of molecular logic gates like NOT, OR and AND gate (Fig. 4).
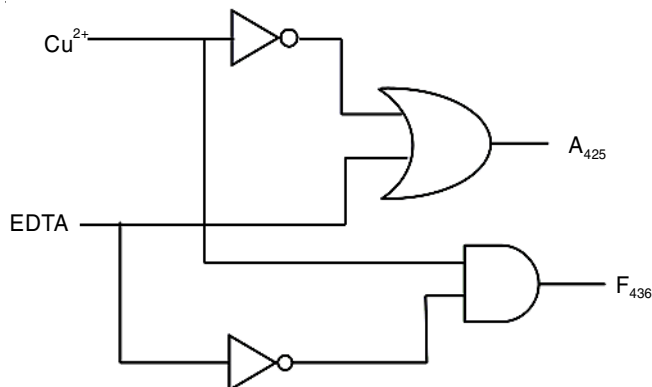

Fig. 4. Logic array gate for DAMN-based molecular sensor R_{32}

Similarly, Li *et al*. [49] reported a new molecular receptor 2-amino-3-(BODIPY methyleneamino)maleonitrile (R_{33}) for Cu^{2+} detection intracellularly in the DrG cell line and zebra fish. Molecule R_{33} in CH_3CN solvent was pink in colour and displayed quenching of fluorescence in the free state. No observable fluorescence change occurred in presence of lot of metal ions except in Cu^{2+}. As molecule R_{33} possess DAMN attached to the BODIPY scaffold *via* C=N. In presence of photon of light, the isomerization of -C=N releases the energy of excited dye through non-radiated thermal vibrations, which leads to the intramolecular cyclization and converts -C=N into a five membered imidazole ring, which is non-emissive in CH_3CN. With the synthesized sensor molecule, high contrast images of Cu^{2+} detection was validated in Hela cells, which demonstrates potential application of molecule R_{33} for bioimaging applications. Most importantly the sensor could penetrate the blood brain barrier of the zebra-fish; hence the neuron cells in the brain could be stained.

Conclusions and future perspectives

In conclusion, all reports on the ion recognition chemistry of imine Schiff bases based on unsymmetrical DAMN have been compiled to the best of our knowledge. Based on the literature survey, it appears that the altering of charge transfer characteristics of molecules has been the primary mechanism of sensing out in the D-π-A accepter based structure. Prompt signaling response has been reported with such molecular structural motifs. In addition to qualitative uses, quantitative uses in highly challenging aqueous environments have also been documented. The sensing of ions like F^-, CN^- and Cu^{2+} has specifically been achieved. Further, the test strips have also been developed for fast and real time applications. Researchers have further moved a step ahead and utilized the concept of tethering of fluorescent moieties with DAMN and imaging of biosystems. Owing to the development of molecular electronics and miniaturization for technology, researchers have focused of such ion sensing platforms to achieve complex logic arithmetic applications and complex information processing at molecular level. But still such applications have been very rarely

documented and achieved with DAMN Schiff bases. At some point, it is believed that there are still numerous areas that demand the close attention like minimization of the complexity of synthetic design, water solubility of receptor, imaging of other cellular organelles and target the range of sensors for detection of other crucial ions which can affects the human life. We also believe that future is bright for scientists and researchers in material chemistry and allied areas to put sincere efforts and utilize potential and futuristic applications of such highly robust D-π-A based charge transfer imine compounds.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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