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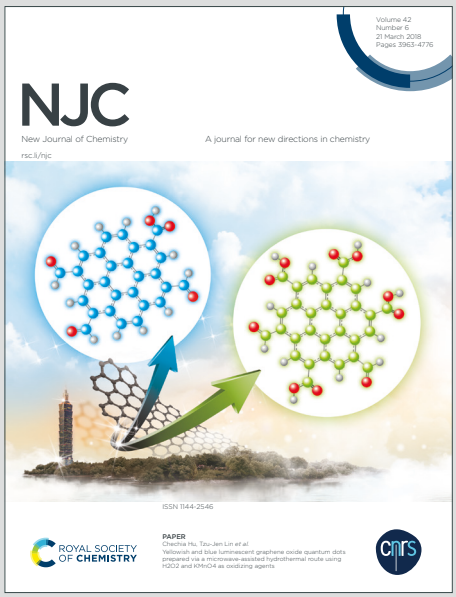

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Zn(II) phthalocyanines Tetra Substituted by Aryl and Alkyl Azides: Design, Synthesis and Optical Detection of H_2S

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Abstract

Novel two Zn(II)-phthalocyanines having: i) aryl azide (**3**) and ii) alkyl azide (**7**) functional groups at the peripheral positions have been designed/synthesized for hydrogen sulfide (H_2S) sensing purposes, and their photocharacteristic properties were investigated in DMSO and THF. In these designs, it is aimed to understand the effect of the groups (aryl or alkyl) bonding azide groups on H_2S sensitivity. The reduction of four azide groups on compound **3** changed the characteristics of zinc phthalocyanine core, and it leaded an appearance of new band with 32 nm bathochromic spectral shift in the absorption band and 88% emission quenching of **3** compared to the original intensity. The detection limits were determined to be 0.14 and 0.68 μM in DMSO and THF, respectively. Besides, compound **7** did not show any response toward H_2S.

Keywords: Zinc (II) phthalocyanine, H_2S probe, Azide group, Fluorescence quenching.

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Introduction

Hydrogen sulfide (H_2S), a gaseous molecule, plays a crucial role in various physiological systems, such as the immune, nervous, cardiovascular and gastrointestinal systems.[1] H_2S is produced endogenously by enzymes such as cystathionine-β-synthase (CBS), cystathionine-γ-lyase (CSE), and 3-mercaptopyruvate sulfur transferase in a controlled fashion. Sulfur-containing amino acids such as cysteine and homocysteine produce H_2S by enzymatic decomposition in several organs such as the heart, brain, kidneys, liver, lungs, and pancreas and vasculature.[2] However, an imbalance of endogenous H_2S production induces several diseases including Alzheimer's disease, Parkinson's disease, and other neurodegenerative diseases.[3] Occasionally, excessive production of H_2S in vital organs invites inception of other diseases like diabetes.[4,5]

Owing to the intricacy of physiological reactivity and rapid catabolism of H_2S in biosystems, it is still important to develop rapid and efficient methods to monitor H_2S. The physiological concentration of H_2S varies from nano-milli-molar levels.[6] H_2S can be detected in a several of ways, such as fluorescence probes and polarographic sensors[7], colorimetric assays, gas chromatography.[8,9] The method based on fluorescence probe is very attractive, for selective analysis of H_2S due to its non-destructive and high sensitivity.[10] Recently, a number of fluorescent probes have been reported for the detection of H_2S but most of these probes suffer from the limitation of poor detection limit, and a relatively long response time. Because the

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catabolism of H_2S is so rapid that the concentration of H_2S in biosystems varies very quickly and largely (10–600 mM), the realtime imaging of H_2S in living cells requires fluorescent probes to respond at a fast rate.[11-13] Fluorescent probe development has emerged as the most common imaging strategy and has relied on three main detection strategies, which include metal precipitation[14], nucleophilic attack[15-17], and reduction of azide[18-27] or nitro groups[28-31] for H_2S detection.

In previous studies, H_2S was detected using fluorescent probes, such as azido-BODIPY reduced into amino-BODIPY by H_2S.[32-34] Another fluorescent probe designed for the detection of both H_2S and NO (two biologically interactive signaling molecules) consisted of a phenylenediamine-modified rhodamine and an azide-linked naphthalimide connected with a rigid piperazine linker that prevented close contact of the two fluorophores and provides promoted efficient Förster resonance energy transfer (FRET) from excited naphthalimide to rhodamine. This fluorescent probe showed different fluorescence signals towards NO and H_2S in living cells and in aqueous media.[35] In another example, the reversible coordination of -SH modulated the fluorescence emission of tetra (N-methylpyridine)porphine zinc complex.[36]

Phthalocyanines (Pcs) are highly stable synthetic macrocyclic compounds with strong absorption bands in the visible region (680-700 nm). Various studies have shown that the photochemical and photophysical properties of Pc can be altered by introducing different substituents at the peripheral position or by changing the central metal.[37] Tetrasubstituted phthalocyanines have the advantage of exhibiting improved solubility[38] and are more easily accessible on a synthetic point of view. The fact that they are usually obtained as a mixture of regioisomers (especially for peripherally substituted derivatives)[38-39] has been demonstrated to have no significant effect on their photoproperties.[38-39]

In the past decade, our laboratory has been interested in the design and characterization of novel types of phthalocyanines with sensing properties.[40-45] Recently, our interest focused on the design of Pc-based H_2S probes, which to the best of our knowledge has not been explored yet. Therefore, two novel Zn(II)-phthalocyanines having aryl azide (**3**) and alkyl azide (**7**) were designed and synthesized for the first time to investigate their sensing abilities towards H_2S by using UV-visible and fluorescence spectroscopy. The results indicated that **3** exhibited huge fluorescence quenching, although compound **7** did not respond toward H_2S.

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Results and discussion

Molecular design

In these designs, it is aimed to understand the effect of the aryl- and alkyl-azide groups on the Pc core on H_2S sensitivity. Recently, fluorescent probes are used for the detection of specific analytes, because of their high specificity, sensitivity, and remarkable temporal resolutions.[46-49]

Up to now, many fluorescent probes have been developed using H_2S's distinctive chemical reactivity to trigger selective nucleophilic additions[50], azido[51-56] and nitro group reduction,[14,57,58] copper sulfide precipitation[14] or thiolysis reactions.[59-61] Due to sensitive non-invasive, non-radioactive, and real-time capacities of fluorescence imaging, these probes provide a useful tool for detecting H_2S.

H_2S probes working by reducing azido groups to amines are existing in the literature.[13,32-34,62] However, to the best of our knowledge, no previous works have described about a phthalocyanine-based H_2S probe. We wished to design H_2S sensing phthalocyanines and evaluate their H_2S sensing ability. Owing to phthalocyanines have intense absorption and fluorescence emission bands in the visible region (600–750 nm) with high quantum yield, phthalocyanine-based probes might be present magnificent sensitivity over the existing ones. Herein, novel Zn(II)-phthalocyanines having aryl (**3**) and alkyl azide (**7**) functional groups at the peripheral position (Fig. 1) were synthesized and their H_2S sensing properties were investigated in two different solvents (DMSO and THF) in detailed by using UV-visible and fluorescence spectroscopy.

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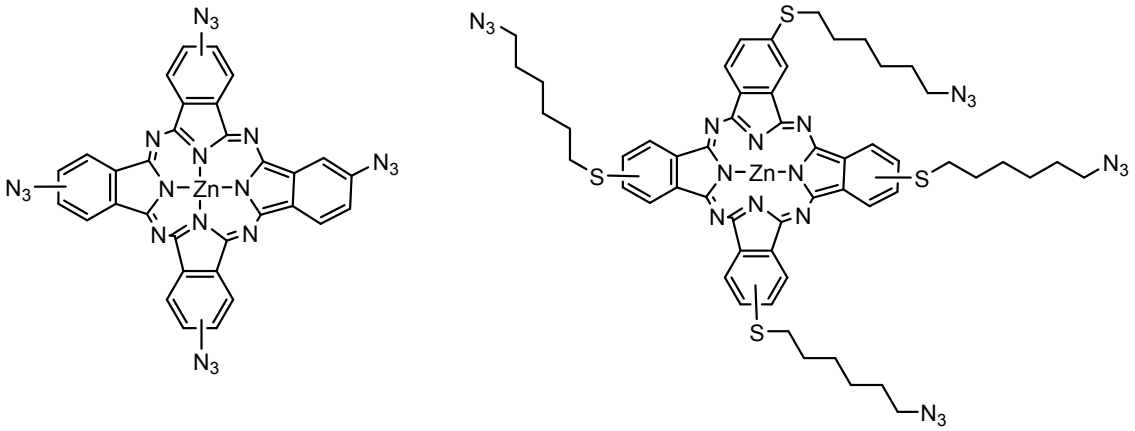

3 **7**

Fig 1. Molecular structures of the molecules **3** and **7** tested for H_2S sensitivity.

3.2. Synthesis

As known the phthalonitrile derivatives are the key intermediates in the synthesis of phthalocyanine derivatives. It is well known that cyclotetramerization of monosubstituted phthalonitriles leads to the formation of four constructional isomers.[38,39] The conclusions of this paper do not depend on having a pure isomer, thus no further purification. Azide-functionalized phthalocyanines can be easily prepared from phthalonitriles already bearing azide functional groups. As shown in Scheme 1 and 2, two new zinc Pc derivatives (**3** and **7**) having four azide functional groups were successfully prepared by cyclotetramerization of related to phthalonitriles (**2** and **6**) to ensure relatively high yields of the required complexes.

Initially, we synthesized phthalonitriles (**2** and **6**) having azide groups. The aryl azide compounds are generally synthesized from aromatic amines through diazotization reaction followed by azidotion procedure.[63-68] Aryl azides are also obtained by coupling reactions of aryl halides, arenediazonium salts[64], aryl boronic acids or esters,[69,70] and aryl metal reagents[71] with azide group sources. Also, the aryl azides has been synthesized in one step from aromatic nitro compounds under mild conditions with good to excellent yields as the starting materials using zinc powder.[72] 4-Azidophthalonitrile has been synthesized starting from 4-aminophthalonitrile using a $NaNO_2/NaN_3$ system in acidic aqueous acetonitrile.[73] In this study, we developed a modified method for the synthesis of aryl azide functionalized phthalonitrile (**2**) from 4-nitro

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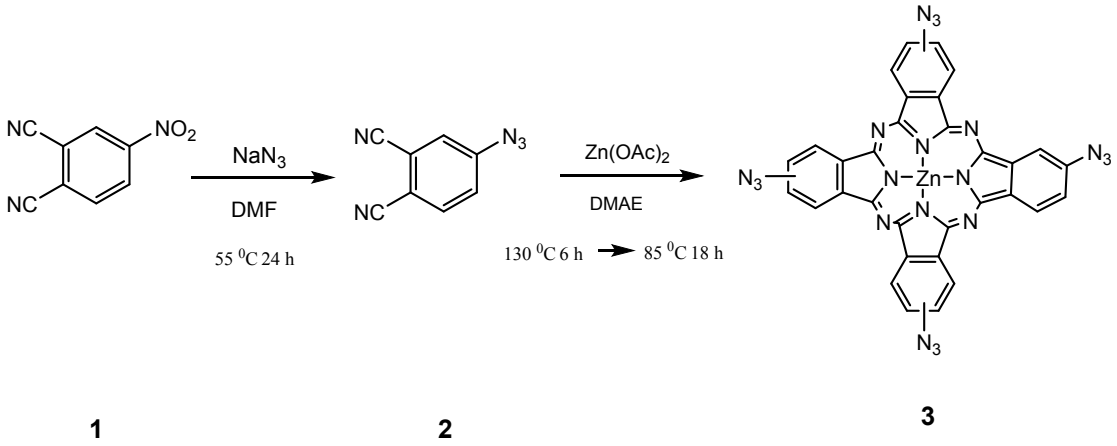
phthalonitrile **1** in one step by nucleophilic substitution by sodium azide, with an overall yield of practically 73%, according to literature.[74]



Scheme 1. Synthesis of tetra 2,9(10),16(17),23(24) azido phthalocyaninato zinc (II) (**3**).

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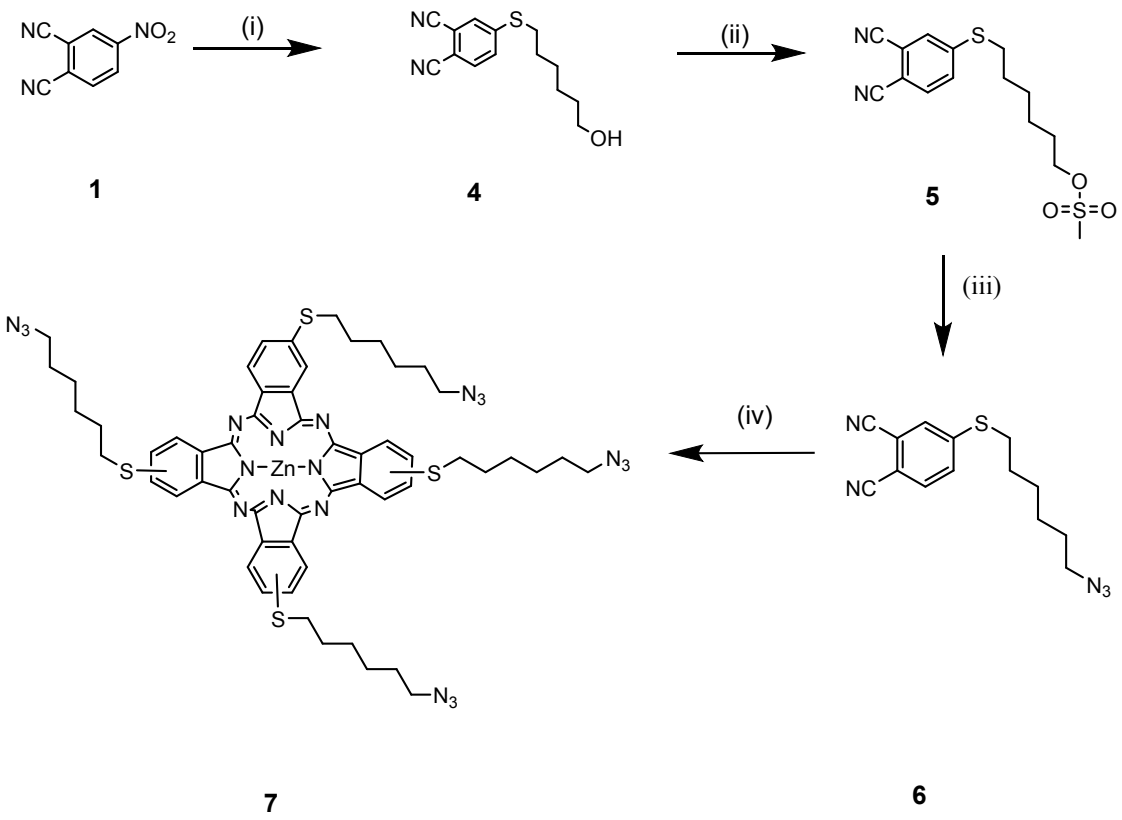

1 4 5 7 6

Scheme 2 Synthesis of ZnPc (**7**). (i) 6-Mercapto-1-hexanol, dry DMF, K_2CO_3. (ii) Methane sulfonyl chloride, DCM, triethylamine. (iii) DMF, NaN_3. (iv) DMAE, $Zn(AcO)_2$.

The other phthalonitrile derivative (**6**) containing alkyl azide groups was prepared from 4- nitro phthalonitrile **1** in three steps: hydroxylation, mesylation followed by nucleophilic substitution by sodium azide, with an overall yield of practically 55 %.

Most of metalated phthalocyanines are prepared in one-step by the cyclotetramerization of phthalonitriles in the presence of an appropriate metal salt. The first envisaged synthetic strategy was therefore the simultaneous preparation of symmetric Pc derivatives **3** and **7** by cyclotetramerization reaction of the phthalonitriles **2** and **6** in the presence of $Zn(OAc)_2$.

Both Pcs (**3** and **7**) exhibited solubility in DMSO and THF, but compound **7** containing alkyl azide groups is soluble in organic solvents of different polarities such as dichloromethane, chloroform, toluene, DMF, and acetonitrile. The new compounds were all characterized by MALDI-MS, NMR, UV-Vis and FT-IR methods, (Figs. S1-S26), the analyses being consistent with the predicted structures. ^{1}H- NMR spectra of **3** in DMSO-d_6 and **7** in $CDCl_3$ (Figs. show

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broad chemical shifts likely due to the self-aggregation at the NMR concentration as well as the presence of positional isomers.[75] As known $CDCl_3$ is non-coordinating solvent. Although DMSO-d_6 is a useful coordinating solvent for NMR spectroscopy, disadvantage to the use of DMSO-d_6 is its high viscosity, which broadens signals. Nevertheless, ^{1}H and ^{13}C NMR spectra of **3** and **7** were obtained clearly satisfying spectra in THF-d_8 which is a coordinating solvent with low viscosity for both Pc derivatives. The undesired aggregations of **3** and **7** in solution were easily prevented by using THF-d_8 in ^{1}H- and ^{13}C-NMR measurements. The integrated intensities of the signals correspond to the number of hydrogens in the pure phthalocyanine derivatives **3** and **7** (Figs S6, and S25). FT-IR spectral analysis results were also consistent with the proposed structures (Figs. S1, S5, S9, S13, S17, S21 and SI†) and confirm their purity.

3.3. Photophysical properties

The zinc phthalocyanines **3** and **7** both showed good photostability and solubility in all the organic solvents such as dimethylformamide (DMF), pyridine, dimetylsulfoxide (DMSO) and tetrahydrofurane (THF). They exhibited intense absorption at ~690 nm in the near-infrared region of the visible spectrum, indicating no solvatochromic effect (Figs. S27 and S28). From their electronic absorption spectra, maximum absorption wavelengths and the extinction coefficients of **3** and **7** can be found. The Lambert-Beer law indicating linear relationship between absorbance and concentration was obeyed for compounds **3** and **7** in the whole concentration measurement range (Figs. S29 and S30). By plotting the Q band absorption intensities versus (*vs*) concentration, log Ɛ values were determined 4.90 and 5.34 for **3** and **7** in DMSO, respectively. It should be noted that Ɛ value of compound **7** was remarkably high, even higher than value of unsubstituted zinc phthalocyanine (**ZnPc**)[76] (See Table 1).

Fluorescence emission spectra were recorded in DMSO and THF. **3** and **7** exhibited fluorescence spectra at 698 and 714 nm. The fluorescence quantum yields were calculated via the fluorescence area integration of compounds **3**, **7** and **ZnPc** *vs* absorbance (Fig. S31), using the fluorescence quantum yield of **ZnPc** in DMSO (Φ_F = 0.18). The fluorescence quantum yields of **3** and **7** were calculated as 0.16 and 0.20, respectively. Compound **7** exhibited higher fluorescence emission compared to **3**, even higher than **ZnPc**.

Optical determination of singlet oxygen was performed by indirect measurement based on the use of DPBF as a chemical quencher. Singlet oxygen quantum yields were calculated using

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ZnPc as a reference (Table 1). Absorption spectra for the determination of singlet oxygen quantum yields of **3**, **7** and **ZnPc** in DMSO were presented in Figs. S32-S34. The Φ_Δ value for **7** was higher than the determined value for **3**, indicating that **7** produces more singlet oxygen. Absorption wavelength maxima (λ_{max}^{Abs}), epsilon (Ɛ) value, fluorescence emission (λ_{max}^{em}) and excitation wavelength maxima (λ_{max}^{ex}), Stoke's shift, fluorescence quantum yield (Φ_F) and singlet oxygen quantum yield (Φ_Δ) and of **3** and **7** in DMSO were presented in Table 1.

Table 1. Photochemical characterization of **3** and **7** in comparison with unsubstituted **ZnPc** in DMSO.

Compounds	λ_{max}^{Abs} (nm)	Log Ɛ	λ_{max}^{em} (nm)	λ_{max}^{ex} (nm)	Stoke's shift	Φ_F	Φ_Δ
3	688	4.90	698	688	10	0.16	0.52
7	693	5.34	714	693	21	0.20	0.57
ZnPc	672	5.14[76]	682	673	9	0.18[77]	0.67[78]

3.4. H_2S sensitivity and effect of used solvents on the sensitivity

Absorption and fluorescence emission-based H_2S sensing response of compounds **3** and **7** were recorded in DMSO and THF to understand the effect of the used solvents on the sensitivity.

3.4.1. H_2S sensing studies of compounds 3 and 7 in DMSO

With the addition of H_2S (25 μM) (Na_2S was used as H_2S source), it was observed ~75% absorption decrease at 688 nm and appearance of new absorption band at 716 nm in DMSO, which corresponds to color change from blueish green to light green (Figure 2-A). An isosbestic point at 705 nm was obtained, indicating the existence of two forms that can be assigned to the azido Pc and reduced amino Pc forms of **3** (Scheme 3). The isosbestic point refers to a specific wavelength at which two chemical species have the same molar absorptivity, and indicates that there is a change from one state to another. Error bar of the absorption signal change of **3** in the concentration range of 0.0-205.0 μM of H_2S was presented in the Fig. 2-B. Data points represent the mean of three independent experiments (n=3). In Fig. 2-B inset shows the calibration graph

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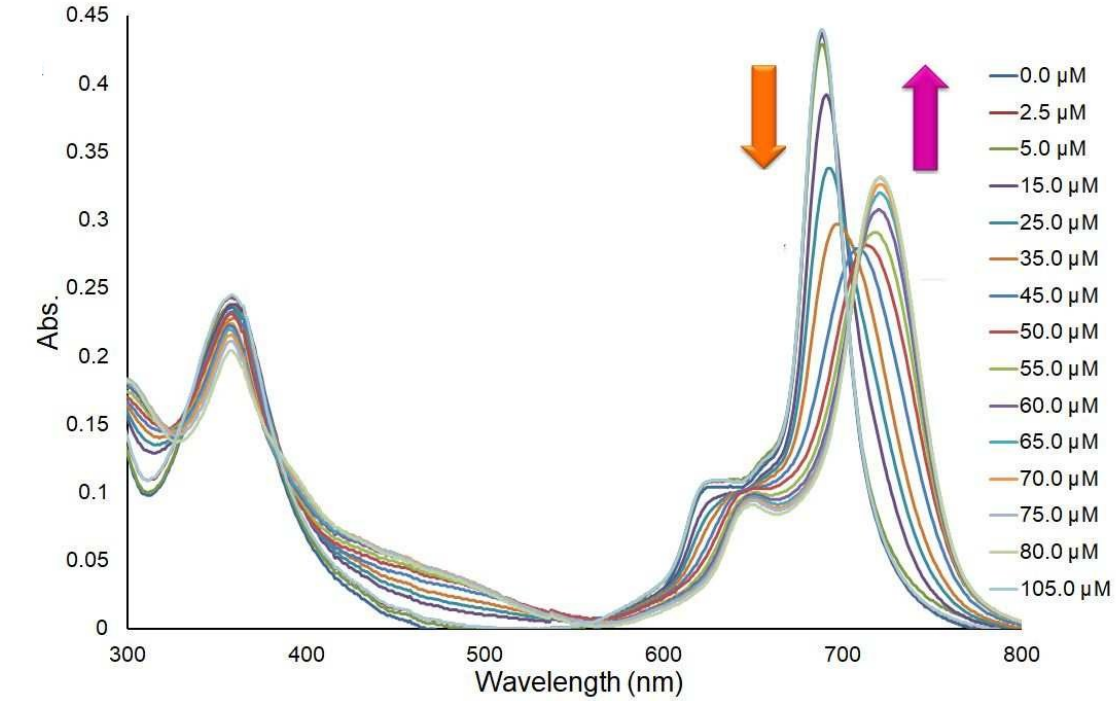
of absorption-based changes of **3** between the linear concentration ranges of 5-55 μM of H_2S. The calibration curves were plotted exploiting the algorithm $[(A_0\text{-}A)/A_0]$ for y-axis where A_0 is the initial absorbance value and A is the absorbance intensity in the different concentrations of the H_2S. Due to the applied algorithm, good straight lines were obtained. In the concentration range of 0.0-55.0 μM quite good linear correlation was obtained with R^2 value of 0.9863 for compound **3** in DMSO (See Table 2).



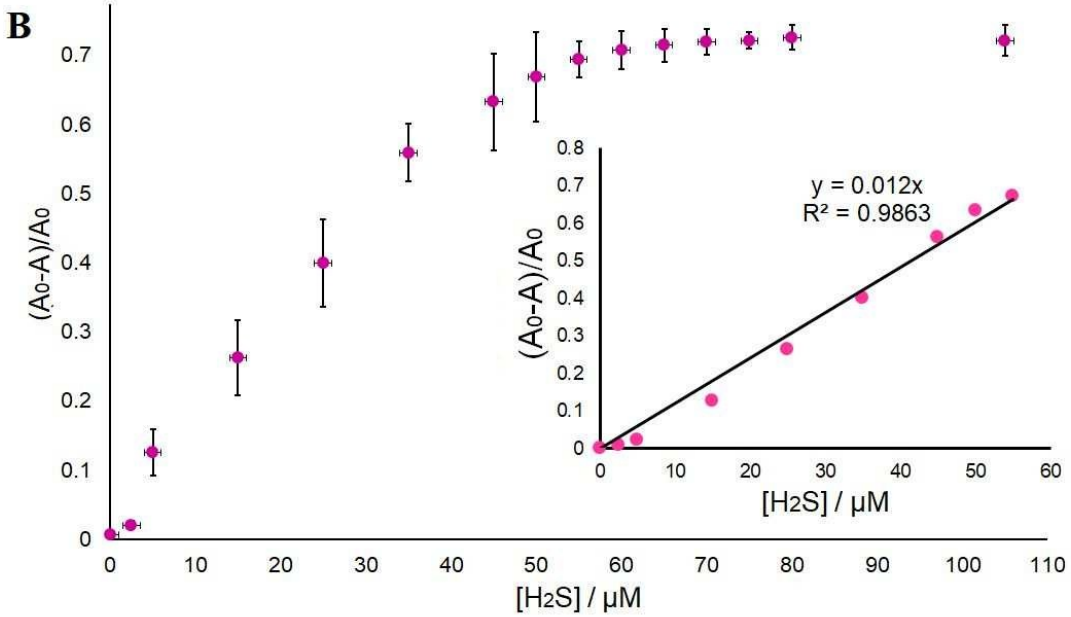


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Fig. 2. (A) Changes in the absorption spectra of compound **3** (5.0×10^{-6} M) in DMSO by the successive of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ DMSO (5:5, pH= 7.0)). (B) Error bar of the ratiometric absorption signal change $(A_0\text{-}A)/A_0$ of **3** vs H_2S for the concentration range of 0.0-105.0 μM. Inset: The calibration plot of **3** in the linear concentration range of 0.0-55.0 μM.

The fluorescence spectra of **3** were monitored upon the addition of increasing amounts of Na_2S. Figure 3A presents the fluorescence intensity-based changes of **3** by the addition of H_2S in DMSO. The fluorescence quenching of **3** depends on the concentration of HS^-. Compound **3** exhibited 88% of emission quenching at 698 nm compared to the original intensity, and saturation was stated after the addition of 13.5 μM H_2S. Compound **3** displays a decreasing fluorescence intensity-based response at 698 nm and the red shifted emission maxima from 698 nm to 748 nm by the addition of H_2S above the concentration of 23.5 μM. In total, 50 nm red shift was observed towards to H_2S. The error bar of the Stern–Volmer plot $(I_0\text{-}I/I_0)$ of **3** for the various concentration range of 0.0-58.5 μM of H_2S (See Fig. 3B). The emission-based linear calibration graph of **3** was presented in the inset of the Fig. 3B. The calibration curve was plotted exploiting the algorithm $[(I_0\text{-}I)/I_0]$ for y-axis where I_0 and I are the fluorescence intensities in the different concentration of the H_2S. In the concentration range of 0.0-28.5 μM, the linear correlation was obtained with R^2 value of 0.9635. Limit of detection (LOD) of **3** in DMSO was found 0.14 μM. With the addition of H_2S (0-160 μM), the absorption and emission spectra of the molecule **7** in DMSO were recorded (See Figs. S35 and S36). Compound **7** did not show any absorption and emission-based responses to H_2S.

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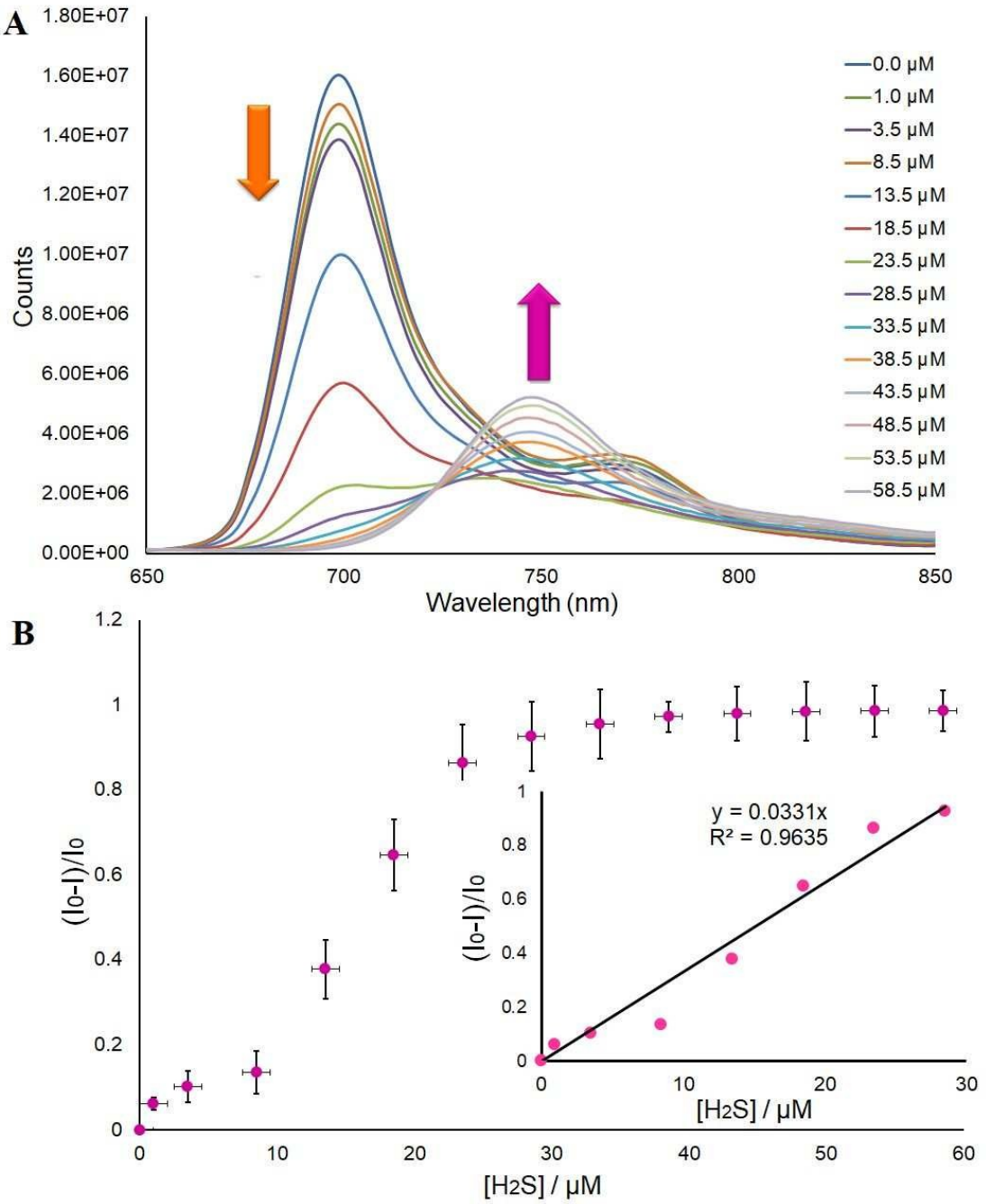

Fig. 3. (A) Changes in the emission spectra of compound **3** (5.0×10^{-6} M) in DMSO by the addition of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ DMSO (5:5, pH= 7.0)). (B) Error bar of the Stern–Volmer plot (I_0-I/I_0) for **3** *vs* H_2S for the concentration range of 0.0-58.5 µM H_2S, Inset: The calibration plot of compound **3** in the between the linear concentration range of 0.0-28.5 µM.

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3.4.2. H_2S sensitivity of compounds 3 and 7 in THF

Fig. 4A shows the absorption based response of compound **3** in THF for the addition of different concentration of H_2S. The sensing molecule exhibited an approximately 76.5% relative signal change in direction of decrease at 681 nm and an increase at 705 nm. As well as new peak formation at 700 nm, the accompanying the obvious color change of the dye from dark green to light is the evidence of the complex formation. The isosbestic point at 698 nm also indicates presence of two species in the medium. The Fig. 4B shows the error bar graphic of the absorption signal change (A_0-A/A_0) in the large concentration range of 0.0-1092.0 μM. In the concentration range of 0.0-242.0 μM of H_2S, **3** exhibited a good linear correlation with R^2 value of 0.9855 in THF (See Fig. 4B inset and Table 2).

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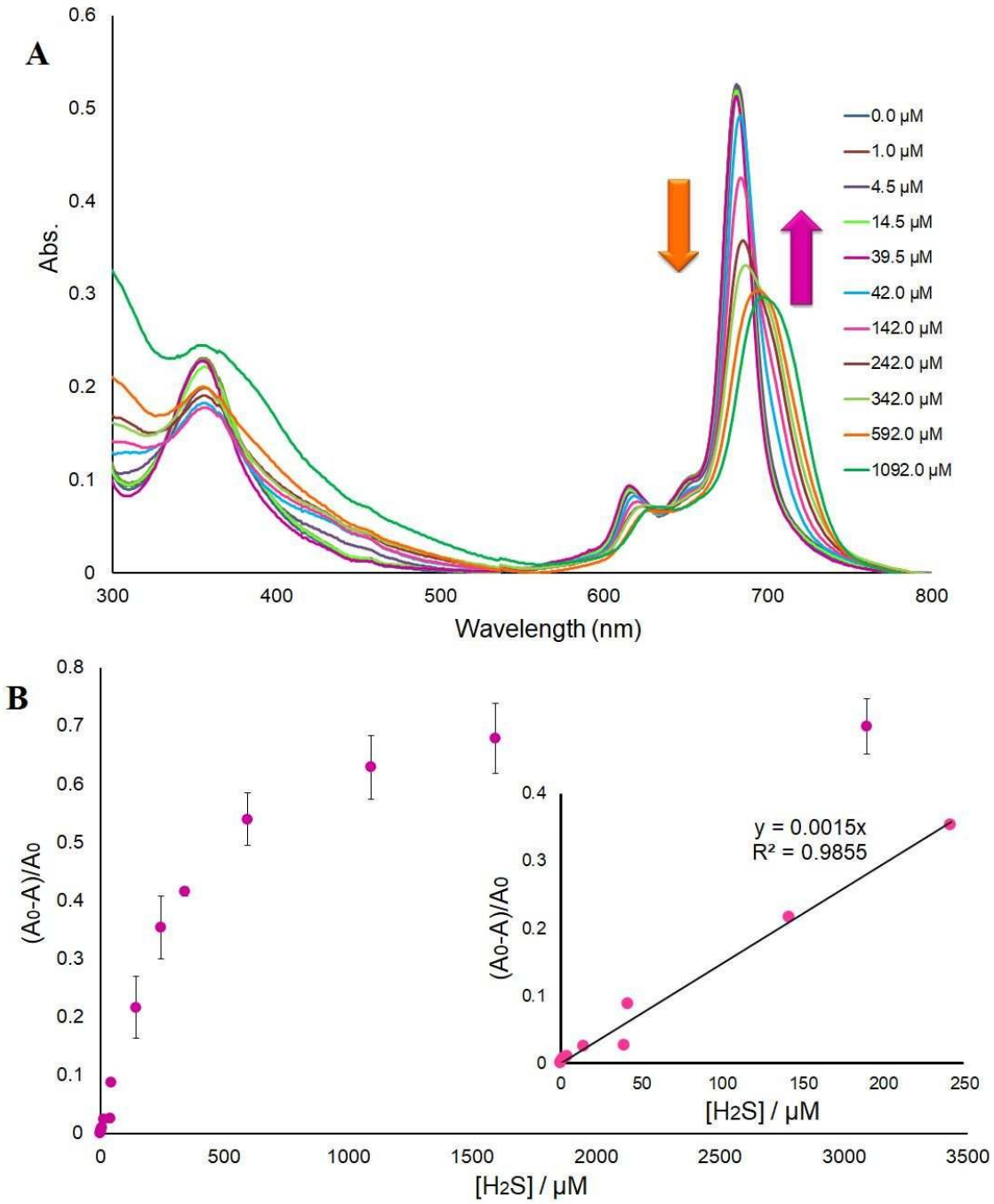

Fig. 4. (A) Changes in the absorption spectra of compound **3** (5.0×10^{-6} M) in THF by the successive of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ THF (5:5, pH= 7.0)). (B) Error bar of the absorption signal change $(A_0\text{-}A)/A_0$ of **3** *vs* H_2S for the concentration range of 0.0-1092.0 μM. Inset: The calibration plot of **3** in the linear concentration range of 0.0-242.0 μM.

As shown in the fluorescence spectra (Fig. 5A), the emission of **3** was quenched upon increasing Na_2S concentrations in 20 μM HEPES/THF solutions ($Na_2S.9H_2O$ in 5:5, v/v, pH= 7.0). By the

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addition of Na_2S, the Q band at 690 nm gradually decreased and new band at 726 nm occurred and increased (saturated when 1592.0 μM Na_2S was added), exhibiting an unclear isosbestic point at 712 nm. In total, 36 nm red shift was obtained towards to H_2S in THF (in DMSO, 50 nm red shift was obtained). A linear working range for H_2S was found between 0.0 and 14.5 μM. The regression results yielded a response with coefficients of regression (R^2) of 0.9322 (See Table 2). The detection limit was determined as 0.68 μM. By the addition of H_2S (0-1000 μM), the absorption and emission spectra of the compound **7** in THF were recorded, and compound **7** did not show any absorption and emission-based responses to H_2S (Fig. S32 and S33).

When compared to solvent effect on H_2S response for both solvents (DMSO and THF), more red shifting, better LOD value, higher relative signal changes in absorption and emission spectra, especially in linear working range were obtained in DMSO.

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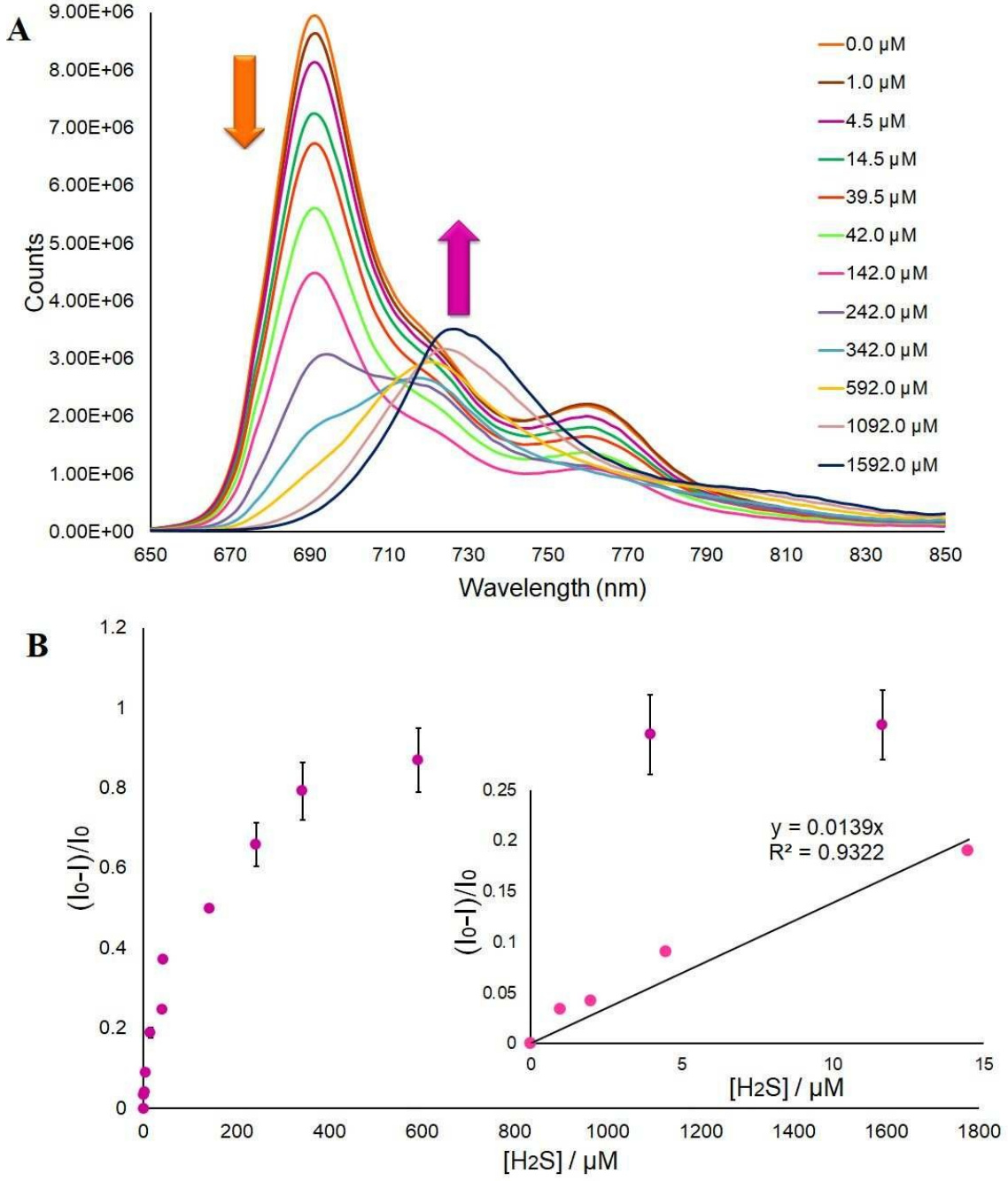

Fig. 5. (A) Changes in the emission spectra of compound **3** (5.0×10^{-6} M) in THF by the addition of hydrogen sulfide ($Na_2S.9H_2O$ in HEPES/ THF (5:5, pH= 7.0)). (B) Error bar of the Stern–Volmer plot $(I_0\text{-}I)/I_0$ for **3** for the concentration range of 0.0-1592.0 µM H_2S. Inset: The calibration plot of **3** in the linear concentration range of 0.0-14.5 µM.

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Table 2. The absorption and the emission-based calibration characteristics, the linear working ranges, the regression equations and the coefficients of regression of phthalocyanine **3** towards to H_2S in THF and DMSO.

Dye	Solvent	Absorbance			Emission		
		Linear Range (μM)	Regression Equation	R^2	Linear Range (μM)	Regression Equation	R^2
3	DMSO	0.0-55.0	y=0.012x	0.9863	0.0-28.5	y=0.0331x	0.9635
3	THF	0.0-42.0	y=0.0015x	0.9855	0.0-14.5	y=0.0139x	0.9322

3.5. Possible Mechanism for H_2S sensing properties

In previous studies, H_2S was determined using fluorescent probes depending on reduction of the azide group to the amine group by H_2S in BODIPY derivative having azide groups at the peripheral phenyl rings[32-34]. Aryl azide group reduced to amine group by H_2S but alkyl azide didn't, probably because of the presence of the aromatic ring. Azide group on the aromatic ring as electron-withdrawing substituents can stabilize the nitrene intermediate and assist the formation of the amino group,[79] whereas nitrene can't be stable in alkyl azide. In addition to that, compound **7** has hetero atom that may impact on reduction of alkyl azide group to amine group.

The reduction of aryl azido Pc **3** by H_2S was presented in Scheme 3. In the presence of an excess of Na_2S, a significant quenching of the fluorescence emission as well as new emission band appearance was observed (see Fig. 3 and Fig. 5) with immediate color change (visible to the naked eye) from blue to green for aryl azido Pc **3**.

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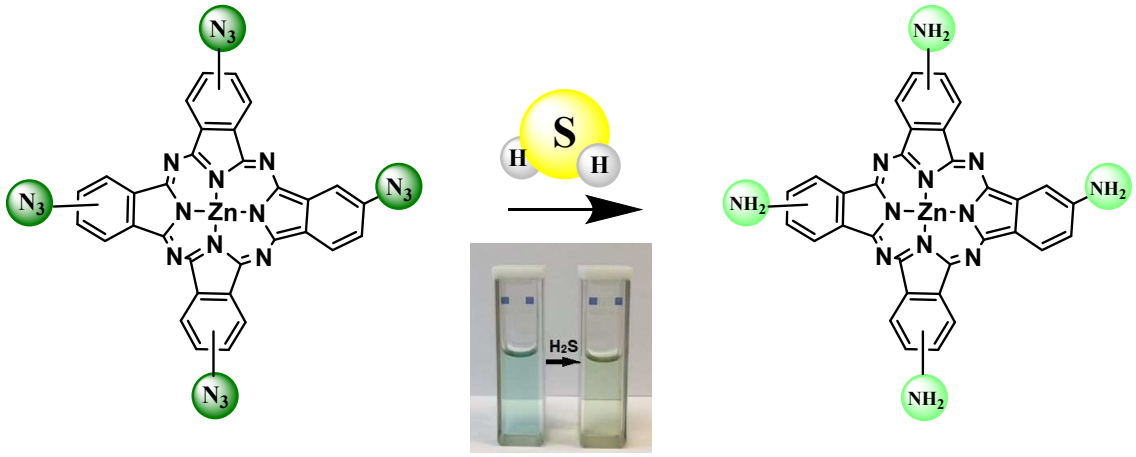

Scheme 3. Proposed sensing mechanism for **3** through the reduction of aryl azido Pc **3** to amino Pc (**Pc-NH$_2$**) by H_2S

The reduction of the azido group to the amine group (possible mechanism presented in the Fig. S37 provides an alternative excited state process (photoinduced electron transfer, PET), which is responsible for quenching of the fluorescence emission. The mass spectral data (Fig. S38) after sulfide treatment of compound **3** supports our structure assignment for the reduction product.

In shed light on the H_2S driven molecular fluorescence turn on-off response, the reduced product, tetra amino phthalocyanine derivative (**Pc-NH$_2$**) (Synthesis in SI) was synthesized and characterized. On the other hand, the treatment of compound **3** with Na_2S afforded the product, which was isolated and characterized by standard FTIR, NMR and mass spectrometry (Figs. S39–S41). FTIR and ^{1}HNMR spectra of compound **3** after treatment with H_2S was compared with the product **Pc-NH$_2$**, and the peaks of NH_2 in **Pc-NH$_2$** were obviously observed, indicating that the product should be reduced compound.

3.6. Selectivity Studies

In order to investigate the selectivity and interference effects on the compound **3**, the influence of some anions were examined in DMSO. Tests were performed for Na_2S, $Na_2S_2O_3$, $C_{10}H_{17}N_3O_6S$, NaN_3, $C_3H_7NO_2S$, KNO_3, Na_2SO_3, Na_2SO_4 and $NaHCO_3$. The fluorescence intensity was dramatically decreased in the presence of H_2S exhibiting a relative signal change ratio of 94.5 %. Relative signal changes of less than 5% were observed to all tested anions except $S_2O_3^{2-}$.Compound **3** exhibited in the direction of decrease almost 18% to $S_2O_3^{2-}$.

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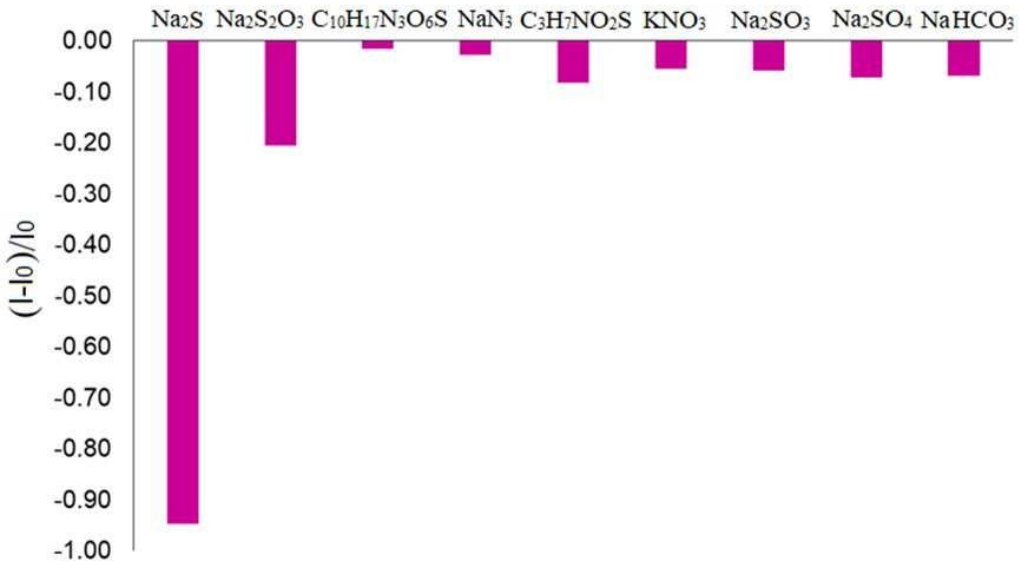

Fig. 6. Selectivity plot showing the changes in fluorescence emission of **3** in DMSO at 700 nm by the addition of various anions like; Na_2S, $Na_2S_2O_3$, $C_{10}H_{17}N_3O_6S$, NaN_3, $C_3H_7NO_2S$, KNO_3, Na_2SO_3, Na_2SO_4 and $NaHCO_3$ alone under identical conditions.

Conclusions

In this study, phthalocyanine-based dual functional fluorescent molecules; novel two Zn(II)-phthalocyanines having aryl azide (**3**) and alkyl azide (**7**) functional groups at the peripheral position were designed and synthesized for detection of H_2S. Their H_2S sensing optical responses were investigated in DMSO and THF. The fluorescence intensity of the molecule **3** was monitored after the addition of increasing amounts of Na_2S to assign whether the amount of fluorescence quenching **3** was dependent on the HS^- concentration.

The Pc molecule **3** bearing aryl azide groups respond to the H_2S through reduction of two azido groups, resulting in 99% quenching of the emission band with highly noticeable red shift in the absorbance and emission spectra. Although molecule **3** exhibited sensitive and ultrafast response to H_2S, **7** did not present any absorption and emission-based change. It is noteworthy that **3** responded more sensitively to H_2S in DMSO (LOD is 0.14 μM) than in THF (LOD is 0.68 μM). The highly selective and sensitive nature of **3** towards H_2S over other tested species demonstrated the potential utility of the molecule.

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Experimental

Materials and instruments

Synthetic procedures were carried out under a dry argon atmosphere. All of the related chemicals were obtained at the highest quality and utilized without further purification. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 A), and TLC on aluminum sheets pre-coated with silica gel 60 F254 (E. Merck). Perkin Elmer Spectrum 100 FT-IR spectrophotometer was used for FT-IR measurements. Normal resolution mass spectra were recorded on a single quadrupole mass spectrometer (Agilent 7800 Quadrupole ICP-MS) with fast LC and high-throughput APCI method. MALDI-TOF MS mass spectrometry was carried out on Bruker microflex. Positive ion and linear mode MALDI-TOF-MS spectrum of phthalocyanine derivatives were obtained in 2,5-dihydroxybenzoic acid (DHB) or dithranol (DIT) MALDI matrix using nitrogen laser accumulating 50 laser shots. Mass spectra of some phthalonitrile derivatives were obtained using Thermo Scientific- TSQ Fortis mass spectrometer by using ESI technique. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker and Varian 500MHz spectrometers using TMS ($\delta = 0$) as an internal reference. The steady-state fluorescence spectra were recorded on an Edinburg spectrofluorometer and the absorption spectra were recorded with a Shimadzu 2001 UV spectrophotometer.

Synthesis

The synthetic pathways for synthesis of **3** and **7** were given in Scheme 1 and Scheme 2.

Synthesis of 4-azido phthalonitrile **(2)**

To 15 ml of dry DMF was added 4- nitro phthalonitrile (1.56 g, 9 mmol) and sodium azide (5.85 g, 90 mmol). The mixture was heated to 55 °C with stirring for 24 hour under an argon atmosphere. After that, the reaction mixture was poured with stirring into 150 ml of ice water. Then the precipitate was filtered and washed water. The obtained product was dissolved in ethanol then, water was added to recrystallize the product. The product was isolated by vacuum filtration and dried to give 1.1g of a white color solid, yield : 72.3%. m.p: 84 °C. Anal. calc. for $C_8H_3N_5$ (169.15): C 56.81; H 1.79; N 41.40; Found: C 56.12; H 1.81; N 41.45. FT-IR [(ATR) υ_{max}/cm^{-1}]: 3103.4 (w) , 3070.8 (w) , 3039.4(w) (Ar C–H), 2230.3 (m)(-CN), 2124.4(s)(-N_3), 1594.8(s) , 1560.3(m), 1486.6(s), 1410.3 (m) , 1310.0(s), 842.9(s). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.37 (d, 1H, ArH), 7.42 (s, 1H, ArH), 7.81 (d, 1H, ArH). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 145.94, 135.05, 123.83, 123.29, 117.75, 115.02, 114.53, 111.34. APCI-MS *m/z*: 141.03 $[M - 2N]^+$.

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Synthesis of tetra 2,9(10),16(17),23(24) azido phthalocyaninato zinc (II) **(3)**

To 1 ml of dried DMAE was added 4- azido phthalonitrile (0.254 g, 1.5 mmol) under argon atmosphere and stirred for 20 min at room temperature. Then $Zn(OAc)_2$ (92 mg ,0.5 mmol) was added and the mixture was heated to 130 ^oC with stirring for 6 hour, then stirred overnight at 85 ^oC. After this time, the reaction mixture was stirred into 50 ml of hot ethanol and the resulting precipitate was collected by centrifugation. The product was washed firstly with water then hot ethanol, ethyl acetate, DCM, and diethyl ether then dried in *vacuo* over P_2O_5 to give 95 mg of compound **3**, yield: 34%. Anal. calc. for $C_{32}H_{12}N_{20}Zn$ (741.97) C 51.80; H 1.63; N 37.76 %; Found: C 51.52; H 1.81; N 37.45 %. FT-IR [(ATR) υ_{max}/cm^{-1}]: 3231.8 (w), 2103.4 (s) (-N_3), 1713.7 (w), 1649,1(m), 1608.8 (s), 1472.6 (m), 1292.8 (s), 742.1 (s) cm^{-1}. ^1H NMR (500 MHz, THF-d_8, ppm): δ 7.55-7.99 (m, 4H, ArH), 8.32-8.58 (m, 4H, ArH), 8.78-9.05 (m, 4H, ArH). ^{13}C NMR (126 MHz, THF-d_8, ppm): δ 150.97, 146.32, 135.57, 129.39, 124.32, 123.85, 113.23. APCI-MS *m/z*: 141.03 $[M - 2N]^+$.APCI-MS *m/z*: 741.54 $[M]^+$.

Synthesis of 4 -(6-hydroxyhexylsulfanyl)-1,2-dicyanobenzene **(4)**

4- Nitrophthalonitrile (3.00 g, 17 mmol) and 6-mercapto-1-hexanol (2.39 g, 17 mmol) were dissolved in dry DMF at 40°C under an argon atmosphere and finely grounded potassium carbonate (4 g, 0.029 mol) was added in portions to the mixture. The reaction mixture was stirred under argon at 40°C for 2 days. After that the reaction mixture was cooled to room temperature then poured into 500 mL ice-water. The creamy precipitate formed was filtered and washed with water. The obtained product was dissolved in small amount of ethanol, then, diehtylether was added to the solution to recrystallize the product. The product was isolated by vacuum filtration to give 2.11g (46 %). Anal. calc. for $C_{14}H_{16}N_2OS$ (260.63) : C 64.59; H 6.19; N 10.76, Found: C 64.52; H 6.09; N 10.45 % FT-IR [(ATR) υ_{max}/cm^{-1}]: 3332.9 (w) (CH_2OH), 3139.4(w) (Ar C–H), 2930.7, 2890.3, 2860.6 (m) (Aliph-CH_2), 2232.8 (m) (-CN), 1580.2 (s), 1473.3 (s), 1398.5 (m), 1192.5 (m), 1073.3 (s) , 831.6 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$, ppm): δ 7.65 (d, 1H, ArH), 7.56 (bs, 1H, ArH), 7.50 (m, 1H, ArH), 3.67 (t, 2H, OCH_2), 3.03 (t, 2H, SCH_2), 1.76 (m, 2H, CH_2), 1.61 (m, 3H, CH_2, OH), 1.53 (m, 2H, CH_2), 1.45 (m, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 147.3, 133.1, 129.9, 129.8, 116.2, 115.5, 115.1, 62.6, 32.4, 31.7, 28.5, 28.1, 25.2. ESI-MS *m/z*: 278.20 $[M+H_2O]^+$.

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Synthesis of 4 -(6- methanesulfonatehexylsulfanyl)-1,2-dicyanobenzene **(5)**

Compound **4** (0.9 g, 3.4 mmol) was dissolved in a mixture of dichloromethane (80 mL) and triethylamine (5 mL) and cooled down to ~0 °C in an ice bath. Then, methane sulfonyl chloride (6 ml, 77.5 mmol) was added drop-wise to this mixture. The reaction mixture was stirred over night at room temperature. The solvents were evaporated under reduced pressure. The product was purified over a silica gel column using dichloromethane as an eluent to give 830 mg of dry product, yield: 71 %. Anal. calc. for $C_{15}H_{18}N_2O_3S_2$ (338.44): C 53.23; H 5.36; N 8.28; Found: C 53.35; H 5.51; N 8.45 %. FT-IR [(ATR) υ_{max}/cm^{-1}]: 3108.2, 3024.5 (w) (Ar C–H), 2965.9, 2937.7, 2856.9 (m) (-CH_2), 2229.6 (m) (-CN), 1583.1 (s), 1461.6(m), 1344.2(s) (S=O), 1165.3(s) (S=O), 915.4 (s), 837.7 (s). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.67 (d, 1H, ArH), 7.58 (d, 1H, ArH), 7.51 (m, 1H, ArH), 4.26 (t, 2H, O-CH_2), 3.05 (t, 2H, SCH_2), 3.03 (s, 3H, CH_3), 1.79 (m, 4H, CH_2), 1.52 (m, 4H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 147.12, 133.22, 130.2, 129.94, 116.33, 115.51, 115.16, 110.86, 69.66, 37.44, 31.69, 28.97, 28.13, 27.98, 25.00. ESI-MS *m/z*: 356.10 $[M+H_2O]^+$

Synthesis of 4 -(6-azidohexylsulfanyl)-1,2-dicyanobenzene **(6)**

Compound **5** (0.390 g, 1.15 mmol) was dissolved in dry DMF (5 mL). Then sodium azide (0.75 g, 11.5 mmol) was added to the mixture. The mixture was heated to 55 °C with stirring under argon for 24 hour. After this time, the reaction mixture was poured with stirring into 150 ml of ice water. The white product was isolated by vacuum filtration. The obtained product was dissolved in DCM, then dried with Na_2SO_4 and filtered off, then it was purified over a silica gel column using dichloromethane/ hexane (10:1) as eluent to give 181 mg of dry product, yield: 55 %. Anal. calc. for $C_{14}H_{15}N_5S$ (285.37): C 58.93; H 5.30; N 24.54, Found: C 58.52; H 5.61; N 24.45 %. FT-IR [(ATR) υmax/cm^{-1}]: 3108.2,(w) (Ar C–H),2925.3, 2855.5,(m) (Aliph-CH_2) , 2229.6 (m)(-CN), 2091.0 (s)(-N_3), 1581.8 (s), 1462.7(m) , 1256.7(m), 1068.9 (s), 872.1 (m) , 830.3 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.66 (d, 1H, ArH), 7.57 (bs, 1H, ArH), 7.51 (d, 1H, ArH), 3.30 (t, 2H, N_3-CH_2), 3.04 (t, 2H, S-CH_2), 1.76 (m, 2H, CH_2), 1.63 (m, 3H, CH_2), 1.51 (m, 2H, CH_2), 1.45 (t, 2H, CH_2). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 147.29, 133.20, 130.02, 129.91, 116.21, 115.57, 115.19, 110.71, 51.27, 31.73, 28.66, 28.29, 28.02, 26.22 ESI-MS *m/z*: 303.20 $[M+H_2O]^+$

Synthesis of tetra 2,9(10),16(17),23(24) (6-azidohexylsulfanyl) phthalocyaninato zinc (II) **(7)**

To 1 ml of dried DMAE was added compound **6** (0.170 g, 0.6 mmol) of and stirred for 20 min at room temperature under argon atmosphere. Then $Zn(OAc)_2$ (60 mg ,0.33 mmol) was added

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and the mixture was heated to 130 ˚C with stirring for 24 hour. After that, the solvent was evaporated under reduced pressure. The main product was purified by preparative thin layer chromatography on silica gel using CH_2Cl_2 / n-hexane (5:3) as eluent to give 65 mg (36 %) of dry product. Anal. calc. for $C_{56}H_{60}N_{20}S_4Zn$ (1206.9): C 55.73; H 5.01; N 23.21, found: C 55.52; H 4.98; N 23.45 %. FT-IR [(ATR) υ_{max}/cm^{-1}]: 3108.2,(w) (Ar C–H),2929.1, 2855.8,(m) (Aliph-CH_2) , 2086.6 (s)(-N_3), 1598.4 (s), 1484.2 (m) , 1382.2 (m), 1301.3 (m), 1253.7 (m), 1069.3 (s), 1033.5 (s), 909.5 (s) , 741.7 (s) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.58 (m, 4H, ArH), 6.94 (m, 4H, ArH), 6.57 (m, 4H, ArH), 3.29-3.21 (m, 8H, N_3-CH_2 and SCH_2), 2.75-2.30 (m, 8H), 1.68 (t, 32H). ^{1}H NMR (500 MHz, THF-d_8, ppm): δ 9.05-8.82 (m, 8H, ArH), 8.07-7.97 (m, 4H, ArH), 3.56 (t, 8H, N_3-CH_2), 3.43 (m, 8H, SCH_2), 2.49 (m. 8H) 2.13 (m, 8H), 1.85 (m, 8H), 1.68 (t, 8H). ^{13}C NMR (126 MHz, $CDCl_3$, ppm): δ 150.20, 138.06, 136.65, 133.21, 126.24, 121.30, 119.28, 51.33, 32.80, 28.74, 28.51, 26.42, 26.22. ^{13}C NMR (126 MHz, THF-d_8, ppm): δ 151.78, 139.46, 138.69, 135.18, 128.19, 122.34, 121.30, 120.83, 28, 51.22, 33.33, 29.19, 28.88, 28.66, 26.43. MALDI-TOF-MS *m/z*: 1203.2 $[M-3H]^+$.

Spectral measurements

The spectral measurements for H_2S sensing were carried out using $Na_2S.9H_2O$ in HEPES/ DMSO (5: 5, v/v) or HEPES/THF (5: 5, v/v). The emission spectra were observed with an excitation wavelength of 360 nm. The slit widths were set up as 5.0 nm for both excitation and emission. In error bar graphics, data points represent the average of three independent tests.

Fluorescence and Singlet Oxygen Quantum Yield Determinations

Quantum yield values of compounds **3** and **7** (Φ_F) were determined by the comparative with William's method[80] using reference molecule ZnPc (Φ_F = 0.18 in DMSO[77] (See SI for further information). Singlet oxygen quantum yield (Φ_Δ) measurements were carried out a 1 mL part of the solutions including the quencher irradiated in the Q band area with the photo-irradiation set-up described in the literature.[81] DPBF was utilized as the quencher for singlet oxygen measurements (Φ_Δ = 0.67 in DMSO[78]) (See SI for further information).

The limit of detection

The limit of detection (LOD) was calculated with respect to Eq. 1, where k is the slope between the intensity and S^{2-} concentration and s is the standard deviation of the blank.

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$$LOD = 3s/k \qquad \text{(Eq. 1)}$$

Conflicts of interest

There are no conflicts to declare.

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Zn(II) phthalocyanines Tetra Substituted by Aryl and Alkyl Azides: Design, Synthesis and Optical Detection of H_2S

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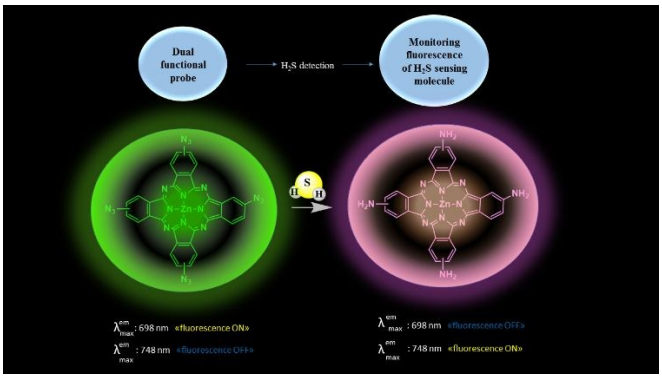

Experimental examination of novel two Zn(II)-phthalocyanines having aryl and alkyl azide functional groups at the peripheral positions have been designed/synthesized for hydrogen sulfide (H_2S) sensing purposes.