


SYNTHESIS OF CYCLEN BODIPY DYAD AND ITS METAL COMPLEXES: EVALUATION OF ANION RECOGNITION FEATURES

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Abstract

In this study, a new compound, viz. 4,4-Difluoro-8-(1,4,7,10-tetraazacyclododecane)methyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (1), and its metal complexes (1-Zn, 1-Cu, and 1-Ni) are synthesized and spectroscopically characterized (UV-Vis, luminescence-fluorescence, NMR, FTIR, and MS). Anion sensing properties of compound 1 and its metal complexes (1-Zn, 1-Ni and 1-Cu) are tested in the presence of various anionic species in acetonitrile media. Fluorescence measurements indicated that, 1-Ni and 1-Cu do not have any selectivity towards various anions except weak interactions. On the other hand 1-Zn shows good response and selectivity toward acetate ion based on fluorescence enhancement. In addition, JOB studies demonstrate that the interaction between 1-Zn and acetate ion were with a ratio of 1:2 and limit of detection (LOD) of 1-Zn was calculated as 4.76×10^{-6} M for acetate ion detection. Moreover, 1-Zn provides a certain change in color in the presence of acetate. The results demonstrate that 1-Zn can be utilized for fluorogenic and naked eye detection of acetate anion.

Keywords: BODIPY, Cyclen, Acetate Ion, Zinc(II), Fluorescence

CYCLEN BODIPY ÇİFTİNİN VE BUNLARIN METAL KOMPLEKSLERİNİN SENTEZİ: ANYON TANIMA ÖZELLİKLERİNİN DEĞERLENDİRİLMESİ

Özet

Bu çalışmada, yeni bir bileşik, 4,4-Difloro-8-(1,4,7,10-tetraazasiklododekan)metil-1,3,5,7-tetrametil-2,6-dietyl-4-bora-3a,4a-diaza-s-indasen (1) ve bu bileşiğin metal kompleksleri (1-Zn, 1-Ni ve 1-Cu) tasarlanmış, sentezlenmiş ve spektroskopik (UV-Vis, luminesans-floresans, FTIR, NMR ve Kütle Spektroskopisi) olarak karakterize edilmiştir. Bileşik 1'in ve metal komplekslerinin (1-Zn, 1-Ni ve 1-Cu) anyon algılama özellikleri, asetonitril ortamında çeşitli anyonik türlerin varlığında test edilmiştir. Floresans ölçümleri, 1-Ni ve 1-Cu'nun bu anyonik türlere karşı zayıf etkileşimlerinin haricinde bir seçiciliğe sahip olmadığını göstermiştir. Diğer taraftan 1-Zn, floresans artışına bağlı olarak asetat anyonuna karşı iyi bir yanıt ve seçicilik göstermektedir. Buna ek olarak, JOB verileri, 1-Zn ile asetat iyonu arasındaki etkileşimin 1:2 oranında olduğunu göstermekte olup asetat iyonunun algılanması için tayin sınırı (LOD) 4.76×10^{-6} M olarak hesaplanmıştır. Ayrıca 1-Zn, asetat varlığında kesin bir renk değişimine olanak sağlamaktadır. Sonuçlar, 1-Zn'nin, asetat anyonunun florojenik ve çıplak gözle algılanması için kullanılabileceğini göstermektedir.

Anahtar Kelimeler: BODIPY, Cyclen, Asetat İyonu, Çinko(II), Floresans

Cite

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1. Introduction

Selective anion sensing is an important topic in supramolecular chemistry due to the critical roles of anions in various biological and environmental processes [1-3]. Among anionic species, acetate anion (AcO⁻) plays significant roles in enzyme activity,

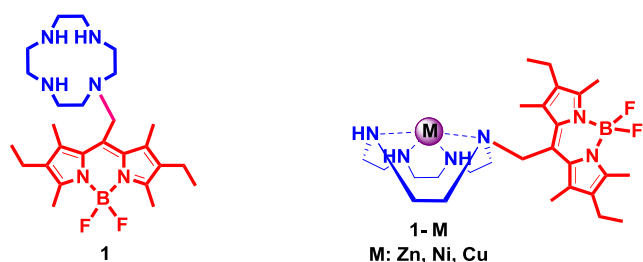
hormones transporting, synthesis of proteins and regulation of DNA expression [4]. Also, AcO⁻ is a remarkable one because of its function in blood washing and blood vessel softening [5]. However, high concentrations of AcO⁻ in human body can interact with Ca²⁺ cation to form calcium acetate which can cause urinary calculi disease [5]. Furthermore, quantity of

AcO⁻ in marine sediments gives information about sedimentation rate in organic decomposition [1]. Therefore, the detection of AcO⁻ is highly important. Fluorescent probes offer one of the best methods for the detection of AcO⁻ ion. Thus, many studies have been performed for synthesis and designing of fluorescent AcO⁻ probes in recent years [1, 4-17].

In anion recognition chemistry, noncovalent interactions between a receptor and an anion can occur by three ways: i) hydrogen bonding, ii) electrostatic interaction or iii) coordination with metal cations [1]. Coordination between metal cations and anions is an efficient way in anion sensing. In addition, other parameters like molecule rigidity, the distance and connection of a binding site between anion and metal ion center are important factors to increase the analyte binding response of a luminescent probe [18]. On the other hand, azole species based on macrocyclic ligand have been generally used for their effect on numerous biological activities such as anticancer, antiviral, antitubercular etc [19]. Among those macrocyclic species, 1, 4, 7, 10-tetraazacyclododecane (cyclen) and its species are defined as good chelators, which can coordinate strongly to various cations. Zn(II) complexes of cyclen derivatives have been used for luminescent sensing of biologically important anions such as phosphate species [18, 20-24], thymine/thymidine nucleotides [25-29] and be used as hydrolytic DNA cleavage promoter [30].

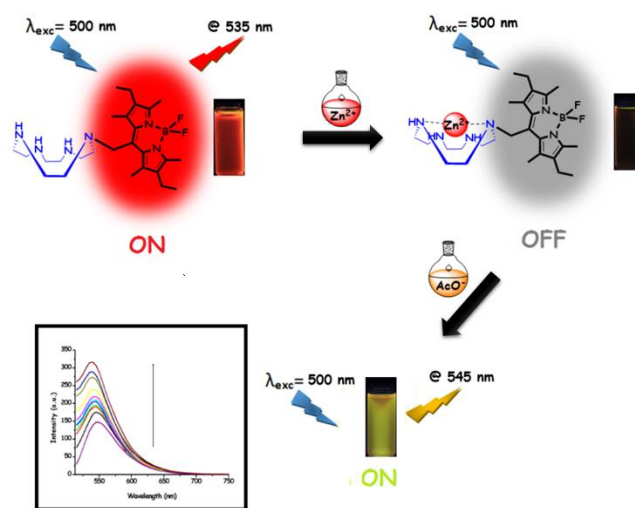
One of the most popular fluorophore family is 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) derivatives [31-41]. BODIPYs are versatile fluorescent dyes and widely used in designing donor-acceptor systems, artificial light harvesters, fluorescent sensors, laser dyes and light emitting devices because of their excellent properties: sharp emission bands and high absorption capacities in the visible region, efficient light-harvesting capability, high fluorescence quantum yields, facility of modification at all positions of the main structure, long excited state lifetimes and remarkable photo-stability and good solubility in organic solvents [42].

In this paper, the design and synthesis of a novel cyclen BODIPY dyad **1** and its metal complexes (**1-M**: **1-Zn**, **1-Cu** and **1-Ni**) (Chart 1) have been reported.



Furthermore, evaluation of anion recognition features of cyclen BODIPY dyads were also described. It was found that **1-Zn** can be used as a dual channel acetate probe,

which enables fluorogenic and naked-eye detection of this anion (Scheme 1). It should be noted that there has been a limited number of reports concerning the design and synthesis of cyclen BODIPY dyads, which can be used as fluorescent probes [43-46]. As far as we know these compounds represent one of the rare examples of cyclen BODIPY dyads.



Scheme 1. Complexation of **1** with Zn(II) ion and *off-on* process.

2. Experimental Section

All chemicals were supplied from Merck or Sigma Aldrich company. FTIR spectrums were recorded using a Perkin Elmer Spectrum 100 model FTIR with an ATR (attenuated total reflectance). ¹H and ¹³C NMR spectrums were recorded on a Bruker DPX-400 or Ultrashield 300 NMR Spectrometers. Mass measurements were recorded using a Bruker microflex LT MALDI TOF MS and Bruker microflex TOF-ESI/MS. UV-vis and fluorescence spectrums were recorded using a Varian Cary 50 and a Varian Cary Eclipse spectrophotometers, respectively. Melting points were measured with a Schorpp MPM-H2 model device. Column chromatography was realized using silica gel (60-200 mesh) from Merck Company. TLC was performed on analytical aluminum plates (Merck 0.2 mm silica gel 60 F254). Compounds **2** and **3** were synthesized by previously published works [47, 48]. The tert-butyl ammonium salts were used to prepare the anion solutions.

2.1. Synthesis of 4,4-Difluoro-8-(1,4,7,10-tetraazacyclo-dodecane) methyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-s-indacene (**1**)

Compound **3** (93.6 mg, 0.211 mmol) in dry CH₂Cl₂ (10 mL) was added dropwise to a solution of compound **2** (145.2 mg, 0.843 mmol) and dry triethylamine (36 μL, 0.253 mmol) in dry CH₂Cl₂ (15 mL) under nitrogen. The reaction mixture was heated under reflux until TLC analysis indicated that all the starting material had been

consumed. The mixture was filtered, then solvent was removed under reduced pressure. The residue was subjected to silica gel column chromatography by eluting with CH₂Cl₂ → Toluene: Hexane 3:1 → Et₂O: MeOH 1:1 to give **1** as red solid: 70 mg, 68%; mp 145-148 °C. ¹H NMR (400 MHz, CDCl₃): δ/ppm 4.13 (s, 2H), 2.98 (m, 8H), 2.76 (m, 8H), 2.52 (s, 6H), 2.42 (m, 10H), 1.06 (t, J = 7.54 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ/ppm 154.29, 136.72, 135.96, 133.72, 132.47, 73.38, 51.30, 49.01, 47.95, 45.78, 17.20, 14.79, 13.87, 12.65; FTIR (cm⁻¹): 3278, 2694, 2930, 2870, 1666, 1602, 1544, 1475, 1404, 1373, 1358, 1264, 1229, 1190, 1405, 976, 750, 723; MALDI-TOF-MS (Matrix: 2,5-Dihydroxybenzoic acid) *m/z* calcd for C₂₆H₄₃BF₂N₆, 488.36 g/mol, found [M]⁺: 489.01 g/mol; Anal Calcd for C₂₆H₄₃BF₂N₆: C, 63.93; H, 8.87; N, 17.20; Found: C, 63.75; H, 8.57; N, 17.50.

2.2. The Synthesis Procedure of Metal Complexes (1-Zn, 1-Ni and 1-Cu)

M(ClO₄)₂·6H₂O (0.2346 mmol) solution of in 10 mL absolute methanol was slowly added to a magnetically stirred solution of compound **1** (114.6 mg, 0.2346 mmol) in 20 mL absolute methanol. The mixture was heated under reflux until TLC analysis confirmed that the starting material was consumed. Solvent was evaporated and a black solid was obtained. It was dissolved in a minimum amount of THF and precipitated out by diethylether or petroleum ether.

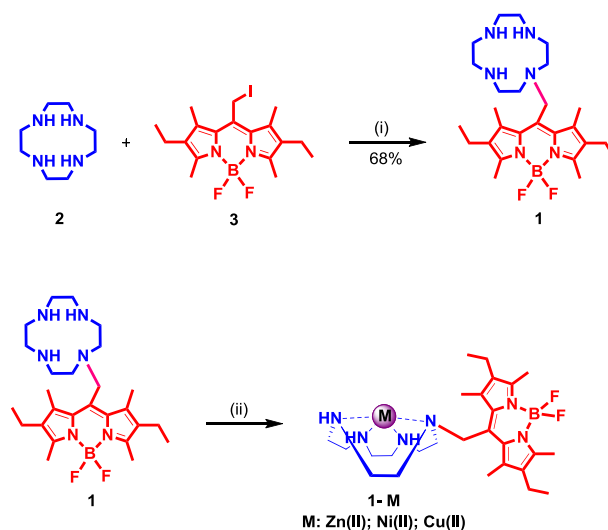
1-Zn: 120 mg, 93% yield; mp 135-137 °C. ¹H NMR (400 MHz, CD₃CN and CDCl₃): δ/ppm 3.84 (s, 2H), 2.99 (m, 8H), 2.78 (m, 8H), 2.39 (m, 16H), 1.08 (t, J = 7.45 Hz, 6H); FTIR (cm⁻¹): 3504, 3457, 2969, 2933, 2875, 1630, 1568, 1444, 1323, 1282, 1056, 957, 713; LC-MS *m/z* calcd for C₂₆H₄₃BF₂N₆Zn: 552.29 g/mol, found [M+CH₃OH]⁺: 583.10 g/mol; MALDI-TOF-MS (no matrix was used) *m/z* calcd for C₂₆H₄₃BF₂N₆Zn: 552.29 g/mol, found [M+H+Na]⁺: 576.77 g/mol; Anal Calcd for C₂₆H₄₃BF₂N₆Zn: C, 56.38; H, 7.83; N, 15.17; Found: C, 56.20; H, 7.70; N, 15.30.

1-Ni: 65 mg, 41% yield; mp 126-128 °C; FTIR (cm⁻¹): 3424, 3331, 3280, 2967, 2933, 2876, 1641, 1538, 1474, 1444, 1191, 1059, 972, 677; MALDI-TOF-MS (Matrix: 1,8,9-Anthracenetriol (Dithranol)) *m/z* calcd for C₂₆H₄₃BF₂N₆Ni: 546.30 g/mol, found [M+H]⁺: 547.05 g/mol; Anal Calcd for C₂₆H₄₃BF₂N₆Ni: C, 57.07; H, 7.92; N, 15.36; Found: C, 57.17; H, 7.70; N, 15.45.

1-Cu: 105 mg, 66% yield; mp 130-133 °C; FTIR (cm⁻¹): 3499, 3280, 2969, 2934, 2876, 1595, 1544, 1442, 1376, 1328, 1266, 1190, 1056, 969, 929, 683; MALDI-TOF-MS (Matrix: 2,5-Dihydroxybenzoic acid) *m/z* calcd for C₂₆H₄₃BF₂N₆Cu: 551.29 g/mol, found [M+H]⁺: 552.16 g/mol; Anal Calcd for C₂₆H₄₃BF₂N₆Cu: C, 56.57; H, 7.85; N, 15.22; Found: C, 56.40; H, 7.70; N, 15.45.

3. Results and Discussions

Synthetic route for some potential luminescent anion probes (**1-Zn**, **1-Ni** and **1-Cu**) based on compound **1** was shown in Scheme 2.



Scheme 2. Reaction conditions: (i) NEt₃, dry CH₂Cl₂, 40 °C, (ii) M(ClO₄)₂·6H₂O, CH₃OH, 65 °C.

First of all, the compounds **2** and **3** were synthesized according to well-established procedures [47, 48]. Then, cyclen (**2**) and iodomethyl BODIPY (**3**) were reacted in presence of NEt₃ in dry CH₂Cl₂ at 40 °C to obtain compound **1** in 68% yield as red solid. Finally, cyclen-BODIPY metal complexes (**1-Zn**, **1-Cu** and **1-Ni**) were acquired by the treatment of **1** with perchlorate salts of Zn (II), Ni (II) and Cu (II) in refluxing methanol. The compounds were characterized by traditional spectroscopic methods (see Supporting Information for details).

Absorption spectra of target compounds **1**, **1-Zn**, **1-Ni** and **1-Cu** were recorded in acetonitrile solution at different concentrations (see Fig. 1a and Fig. S15). The maxima of absorption (λ_{Abs}) and extinction coefficients (ϵ) of **1**, **1-Zn**, **1-Ni** and **1-Cu** (9 μ M) were tabulated in Table 1. Fluorescence properties of the compounds were also examined. Fluorescence spectrum of compound **1** (0.04 μ M) exhibited a broad emission band (λ_{FL}) between 500 nm and 600 nm with a maximum at 545 nm (λ_{exc} = 500 nm) (Fig. 1b).

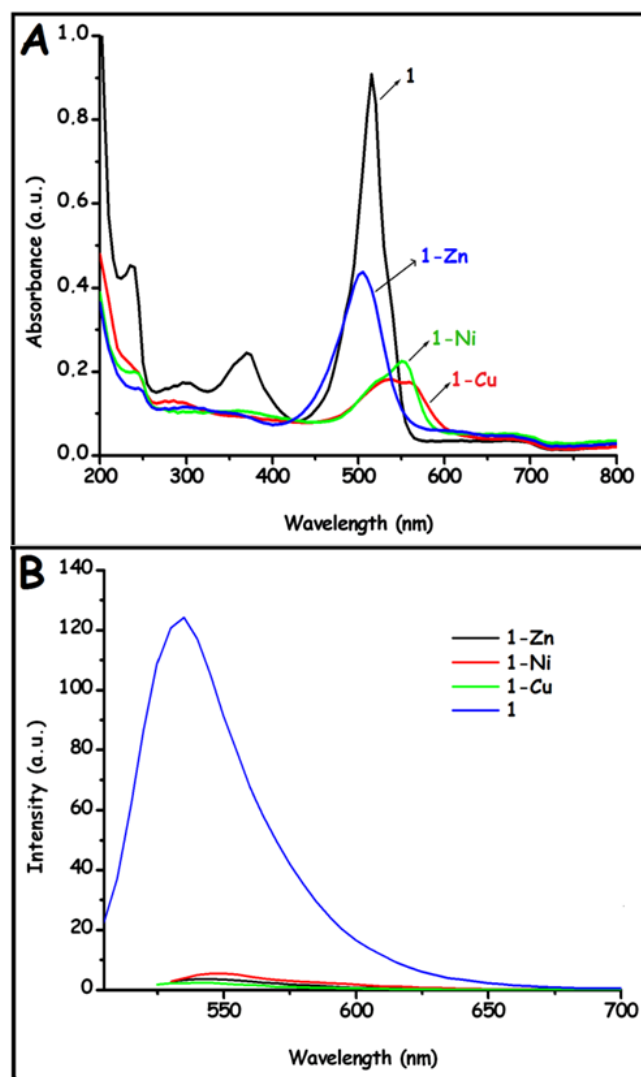


Figure 1. (a) Absorption (9 μM), (b) Emission spectra (0.04 μM) of **1**, **1-Zn**, **1-Ni** and **1-Cu** in CH_3CN ($\lambda_{\text{exc}}=500$ nm).

Table 1. Selected spectroscopic data for **1**, **1-Zn**, **1-Ni**, and **1-Cu**.

Compound	UV-Vis		Fluorescence
	λ_{Abs} [nm]	ϵ [$\text{M}^{-1} \text{cm}^{-1}$]	λ_{FL} [nm]
1	515	114150	545
1-Zn	505	66630	-
1-Ni	550	41140	-
1-Cu	540, 560	30830, 30370	-

On the other hand, it was noted that complexation of compound **1** with metal cations resulted in a complete disappearance of the emission band. The complexation with metal ions might activate the photoinduced electron transfer (PeT) process between BODIPY unit and metal binding site. The activation of PeT process would lead to quenching of the fluorescence, thus a decreased emission is observed. Furthermore, the

HOMO and LUMO energy levels of metallic species of the compound **1** activates PET when compared with the metal-free state and the paramagnetic nature of the transition elements, such as Ni(II) and Cu(II), would play critical role by providing pathways for nonradiative decay of the excited state.

Anion sensing features of compound **1** and metal complexes (**1-Zn**, **1-Ni** and **1-Cu**) were investigated by spectrophotometric titrations. UV-vis and fluorimetric titrations of compounds **1**, **1-Zn**, **1-Ni** and **1-Cu** were carried out with various anions such as AcO^- , F^- , H_2PO_4^- , BF_4^- , ClO_4^- , PF_6^- , I^- , OH^- , Br^- and Cl^- in acetonitrile in order to see the effects of these anions on UV-vis and fluorescence spectra of the metal complexes. It was found that there has been no significant change in the absorption or emission profiles of **1**, **1-Ni** and **1-Cu** during the spectrophotometric titrations. It can be interpreted that **1-Ni** and **1-Cu** show no sensitivity towards any of these anions. By contrast, UV-Vis spectrophotometric titration experiments indicated that there are dramatic changes in the absorption spectra of **1-Zn** upon addition of AcO^- , OH^- and F^- anions whereas the other anions (H_2PO_4^- , BF_4^- , ClO_4^- , PF_6^- , I^- , Br^- and Cl^-) did not cause any significant change (Fig. 2). It was noted that the absorption intensity was decreased upon addition of these anions. The spectral and relative absorption intensity changes were given in Fig. 2. The most significant change was observed for AcO^- . In addition to that, the absorption band of **1-Zn** centered at 505 nm was slightly shifted upon addition of F^- and/or OH^- anions (ca. 5 nm and 10 nm, respectively). It means that F^- and OH^- induced a blue shift in the absorption maxima along with a concomitant decrease in the absorption band of **1-Zn**. However, there was no change at the position of the absorption band (505 nm) in the case of AcO^- when compared with OH^- or F^- anions (Fig. 2a).

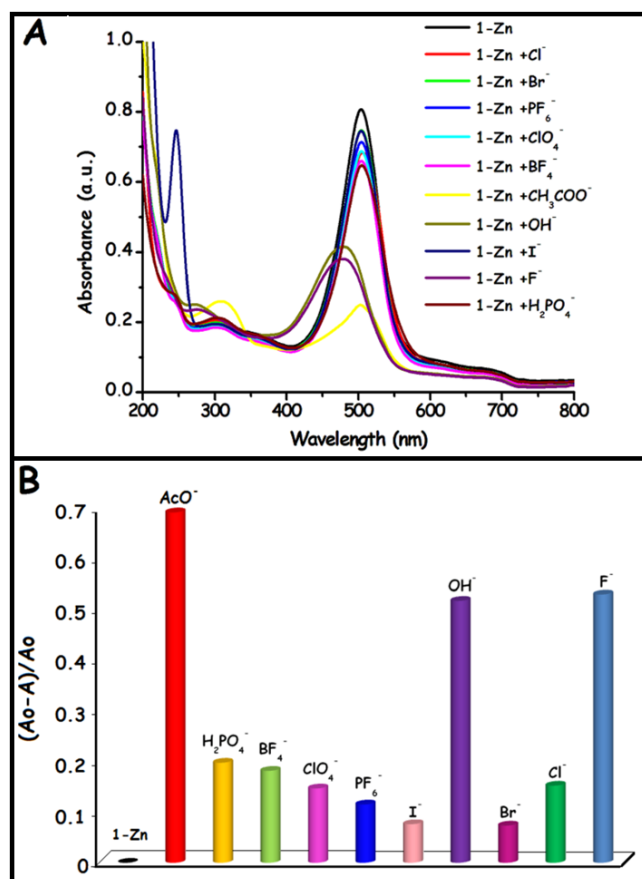


Figure 2. (a) Absorption spectrum and (b) changes in relative absorption intensity of **1-Zn** (33 μM) towards various anions (1.0 equiv.): Cl⁻, Br⁻, PF₆⁻, ClO₄⁻, BF₄⁻, I⁻, H₂PO₄⁻, OH⁻, F⁻ and AcO⁻ in CH₃CN.

Further investigations were focused on the concentration-dependency of these changes. Fig. 3 shows the recorded UV-vis spectrum of **1-Zn** (36 μM) as a function of AcO⁻ concentration. It is noteworthy that there is a progressive decrease in absorbance at 505 nm with a concomitant increase at 310 nm.

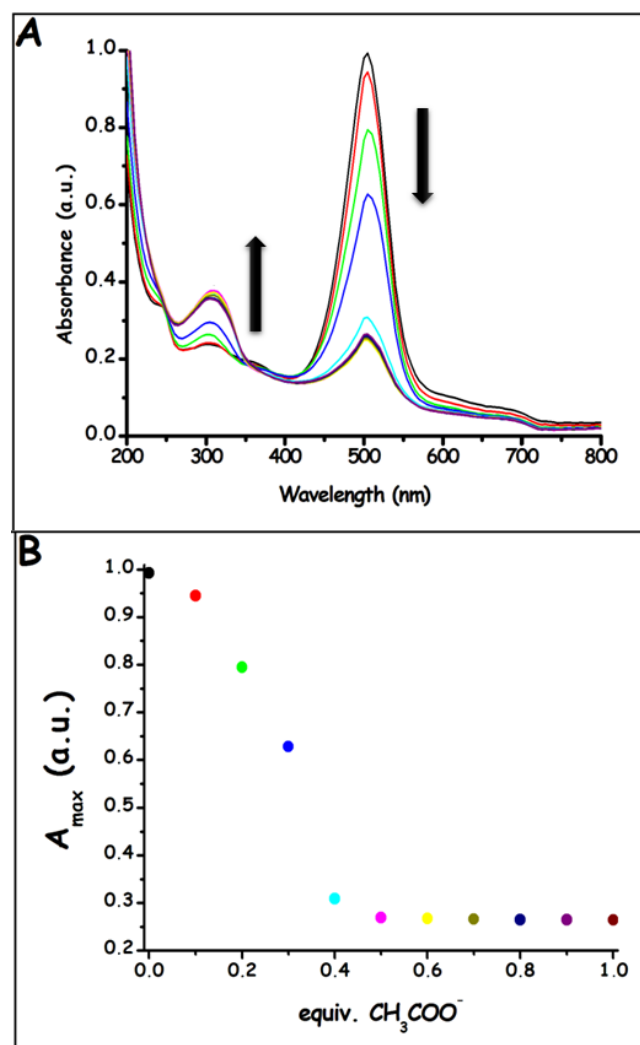


Figure 3. (a) Absorption spectrum of **1-Zn** (36 μM) toward various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.) of AcO⁻ in acetonitrile; (b) Absorption changes of **1-Zn** with respect to the amount of AcO⁻ (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.).

It indicated that **1-Zn** interacts appreciably with AcO⁻. The effect was maximum in the presence of 0.5 equiv of AcO⁻ and no further change was seen by addition of higher amounts. Similar results were also obtained for OH⁻ and F⁻ anions (Fig. S16 and S17). As the amount of the anion increases, the absorption band centered at 505 nm decreases with concomitant increase at the absorption band at 300 nm. When all the changes in the absorption spectra of **1-Zn** with AcO⁻, OH⁻ and F⁻ anions were compared, it was observed that absorbance diminishes explicitly in the cases of AcO⁻ and F⁻ whereas OH⁻ causes a relatively weak for 0.5 equiv of the anion. In all cases, however, titration curves reach a plateau for 0.5 equiv of the anions. To our delight, the changes in the UV-vis absorption spectra of **1-Zn** were quite enough to induce color changes which were easily detectable by the naked-eye in the daylight. Fig. 4 shows the accompanied colors changes of compounds **1**, **1-Zn**, **1-Zn-AcO**, **1-Zn-OH** and **1-Zn-F** in acetonitrile solution. As it can be seen clearly, the intensity of colors

allows the discrimination of these anions from one another to an extent. Note that the color change is a straightforward, cheap and convenient way of visual analysis.



Figure 4. Compounds **1** (33 μM), **1-Zn** (33 μM), **1-Zn-AcO⁻** (36 μM), **1-Zn-OH⁻** (33 μM) and **1-Zn-F⁻** (33 μM) in acetonitrile solution under ambient light (1.0 equiv. of anions).

After the elucidation of UV-vis absorption features of **1-Zn**, fluorescence spectral properties were evaluated. It was found that Cl^- , Br^- , PF_6^- , ClO_4^- , BF_4^- , I^- and H_2PO_4^- anions did not influence the emission spectrum of **1-Zn** significantly (Fig. 5a). Fortunately, the intensity in emission was increased with a concomitant blue shift (ca 5 nm) when AcO^- was added to solution. Surprisingly, however, the intensity of **1-Zn** was decreased in the presence of OH^- and F^- anions. These anions also lead similar blue shift in the emission maxima as in the case of AcO^- . Fig. 5b shows the relative emission intensity changes of **1-Zn** in the presence of all of these anions. It was apparent that AcO^- induced the most significant change when compared to others.

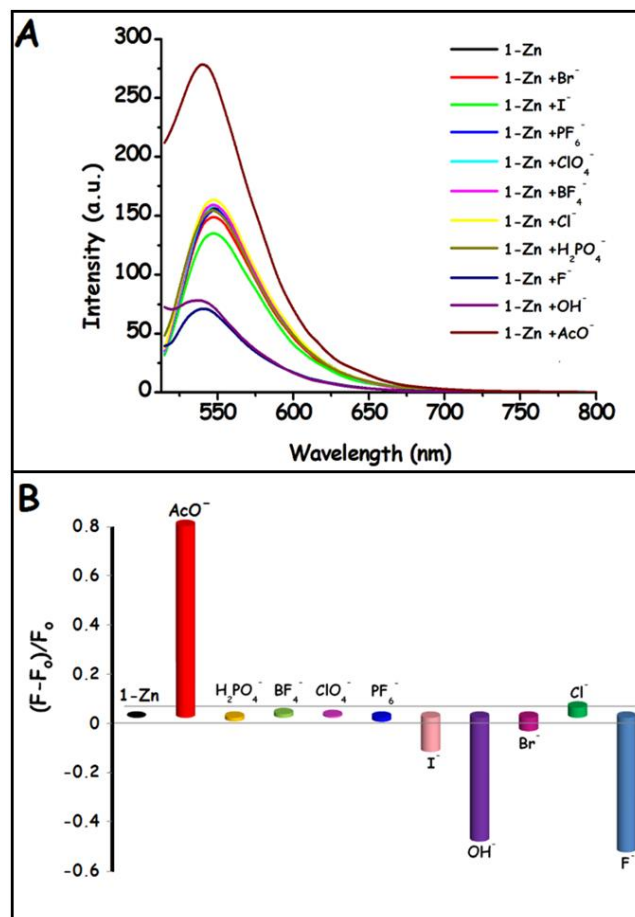


Figure 5. (a) Fluorescence spectra and (b) changes in relative emission intensity of **1-Zn** (24 μM) for various anions (1.0 equiv.): Cl^- , Br^- , PF_6^- , ClO_4^- , BF_4^- , I^- , H_2PO_4^- , OH^- , F^- and AcO^- in CH_3CN ($\lambda_{\text{exc}}=500\text{ nm}$).

Similarly, concentration dependency of the fluorescence spectral changes was also monitored. To this purpose, fluorescence spectra of **1-Zn** were recorded as a function of AcO^- concentration (Fig 6). It was seen that there was a progressive enhancement in the emission intensity as the amount of the anion was increased. A concomitant blue shift was also observed, which pointed out that **1-Zn** interacts appreciably with AcO^- . There was a one-fold increase in the emission intensity for 1.0 equiv of AcO^- .

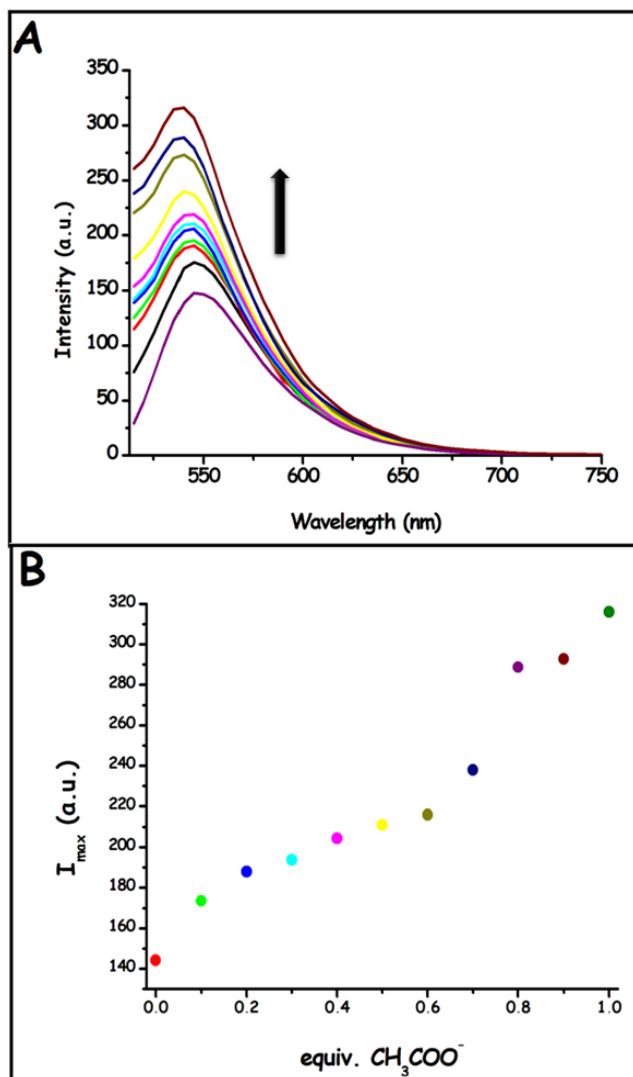


Figure 6. (a) Fluorescence spectra and (b) the emission intensity changes for **1-Zn** (27 μM) upon addition various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 equiv.) of AcO^- in CH_3CN .

In sharp contrast, the addition of OH^- and F^- anions resulted in quenching of the emission (Fig. S18 and S19). As the amount of the anions increase, the emission band centered at 545 nm decreases with a concomitant blue shift around 5 nm. Considering all these changes in the emission spectra of **1-Zn** with OH^- and F^- anions, it was clear that titration curves reach a plateau for 0.5 equiv. of the anions. Gratifyingly, however, the changes in fluorescence spectrum of **1-Zn** were quite enough to induce visual changes which were easily detectable by the naked-eye. Fig. 7 shows the accompanied visual changes for compounds **1**, **1-Zn**, **1-Zn-AcO⁻**, **1-Zn-OH⁻** and **1-Zn-F⁻** in acetonitrile solution. It is noteworthy that **1-Zn** allows the fluorescence detection of AcO^- anion among the others. Importantly, none of the other compounds (**1**, **1-Ni** or **1-Cu**) were promising for fluorogenic recognition of any of these anions, which makes **1-Zn** viable for the detection of AcO^- .

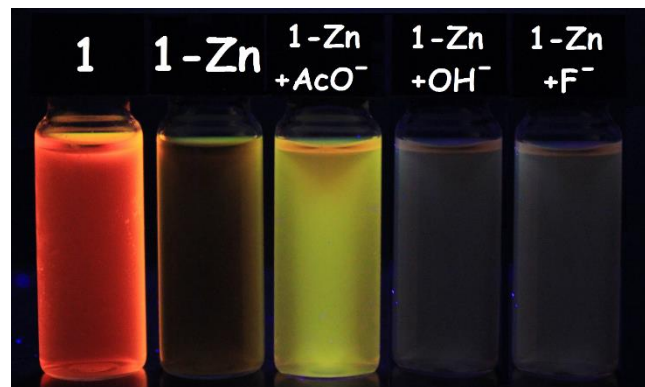


Figure 7. Compounds **1**, **1-Zn**, **1-Zn-AcO⁻**, **1-Zn-OH⁻** and **1-Zn-F⁻** in acetonitrile solution under UV illumination (365 nm).

The fluorescence emission enhancement might be correlated with strong interaction between acetate and metal center of **1-Zn** (Fig. 5b). Moreover, the metal center offers a binding site for AcO^- via electrostatic interaction, which may result in high selectivity of **1-Zn** to AcO^- anion in acetonitrile media [1]. In addition, the shape and/or size of host and guest are important factors for selective recognition. AcO^- has a triangular structure (states O-C-O about 120°) which can provide more stable form and strong complexation between **1-Zn** and AcO^- when compared to F^- and OH^- [1, 4, 7]. On the other hand, it should also be considered that F^- and OH^- can form hydrogen bonding with N-H functional group of cyclen ring. The selectivity for OH^- and F^- can be related to basicity of anions, and also the interactions between the host and the anionic guests. Furthermore, literature search showed that the basicity and binding affinities of these anions can change with the polarity of solvent or solvent mixtures like ACN, DMSO, DMSO/ H_2O and the host [49-51]. For example, an association constant for AcO^- was found to be $5.11 \times 10^5 \text{ M}^{-1}$ in ACN: H_2O /95:5 (8.32×10^6 in this work) medium by Goswami and Chakrabarty using fluorimetric method [1]. Because of their basicity, AcO^- , F^- and OH^- can bound more strongly than other anions. In particular, the triangular structure of AcO^- may well match with **1-Zn** in terms of shape and could form stronger ionic interactions. Consequently, AcO^- can be selectively differentiated from other anions based on dissociation constant [17]. The binding constants of **1-Zn** with OH^- , F^- and AcO^- were calculated from UV-vis and fluorescence titration measurements to reveal the binding properties and selectivity (Table 2). It was found that anion sensing capabilities were found as $\text{AcO}^- > \text{F}^- > \text{OH}^-$ in acetonitrile media, respectively.

Table 2. The association constants of **1-Zn** with OH⁻, F⁻ and AcO⁻.

Compound	UV-Vis	Fluorescence
	Method	Method
OH⁻	1.21 x 10 ⁶	2.77 x 10 ⁶
F⁻	2.45 x 10 ⁶	2.80 x 10 ⁶
AcO⁻	5.68 x 10 ⁶	8.32 x 10 ⁶

^aTetrabutylammonium salts of anions were used.

Evidently, these changes in the emission profile of **1-Zn** in the presence of AcO⁻ demonstrated that a well-defined complex between **1-Zn** and AcO⁻ was formed. When the JOB study was evaluated to find out the interaction between **1-Zn** and acetate, the stoichiometry was found to be 1:2 (Fig. S20). To our knowledge, electrostatic interactions between Zn(II) center and AcO⁻ anion restricts the free rotation to an extent, thus, providing rigidity to the whole molecule. Furthermore, it is possible to assume that this interaction might affect the energy levels of the frontal orbitals of HOMO and/or LUMO. As a result, PeT process between BODIPY unit and metal binding site might be blocked. The deactivation of PeT process would provide a pathway for radiative decay of the excited state, thus, the fluorescence would be turned on. Moreover, JOB studies were performed for OH⁻ and F⁻ (Fig. S21-S22). The results showed that, both of these anions made similar effects to the fluorescence intensity (decrease). The interaction ratio between **1-Zn** and these anions were also found as 1:2 ratio. Finally, LOD of **1-Zn** was calculated as 4.76x10⁻⁶ M for AcO⁻ (Fig. S24).

4. Conclusion

In conclusion, the design and synthesis of a novel cyclen BODIPY dyad and its metal complexes were reported. Furthermore, evaluations of anion recognition features of cyclen BODIPY dyads were described. As far as we know, these compounds represent one of the rare examples of cyclen BODIPY dyads. It was found that **1-Zn** enables fluorogenic and naked-eye detection of acetate anion. It is considered that the multitude of choices in metal selection will allow extending the applications of this class of compounds. Further studies are ongoing in our laboratory to obtain similar complexes, which can be used in sensing and imaging applications.

5. Acknowledgement

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study was produced from master (postgraduate) thesis of S.K.

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Supporting Information

SYNTHESIS OF CYCLEN BODIPY DYAD AND ITS METAL COMPLEXES: EVALUATION OF ANION RECOGNITION FEATURES

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Table of Contents	Page
1. NMR and Mass Spectra for compounds	80-91
2. Additional Graphs and Data	92-99

1. NMR, ESI-MS and MALDI TOF MS Spectra for compounds

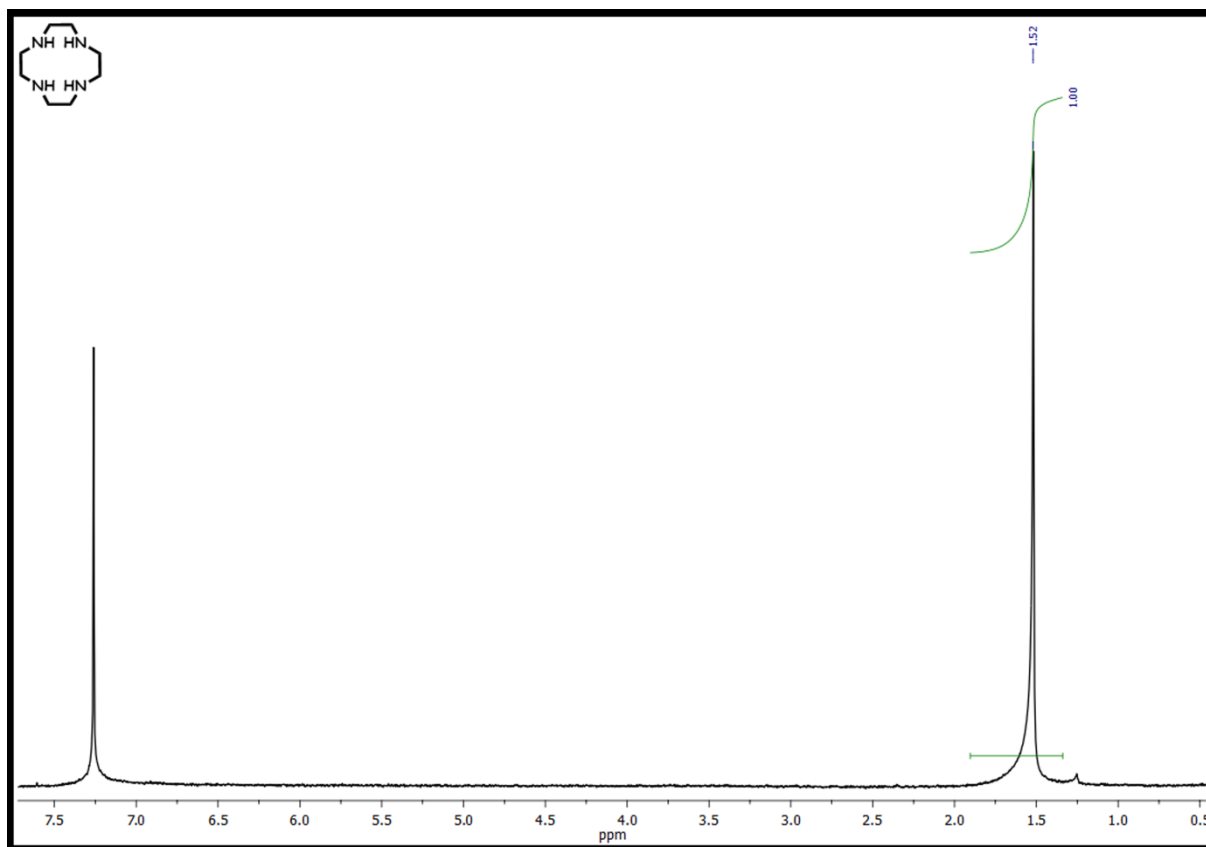


Figure S1. ¹H NMR spectrum of 2 in CDCl₃.

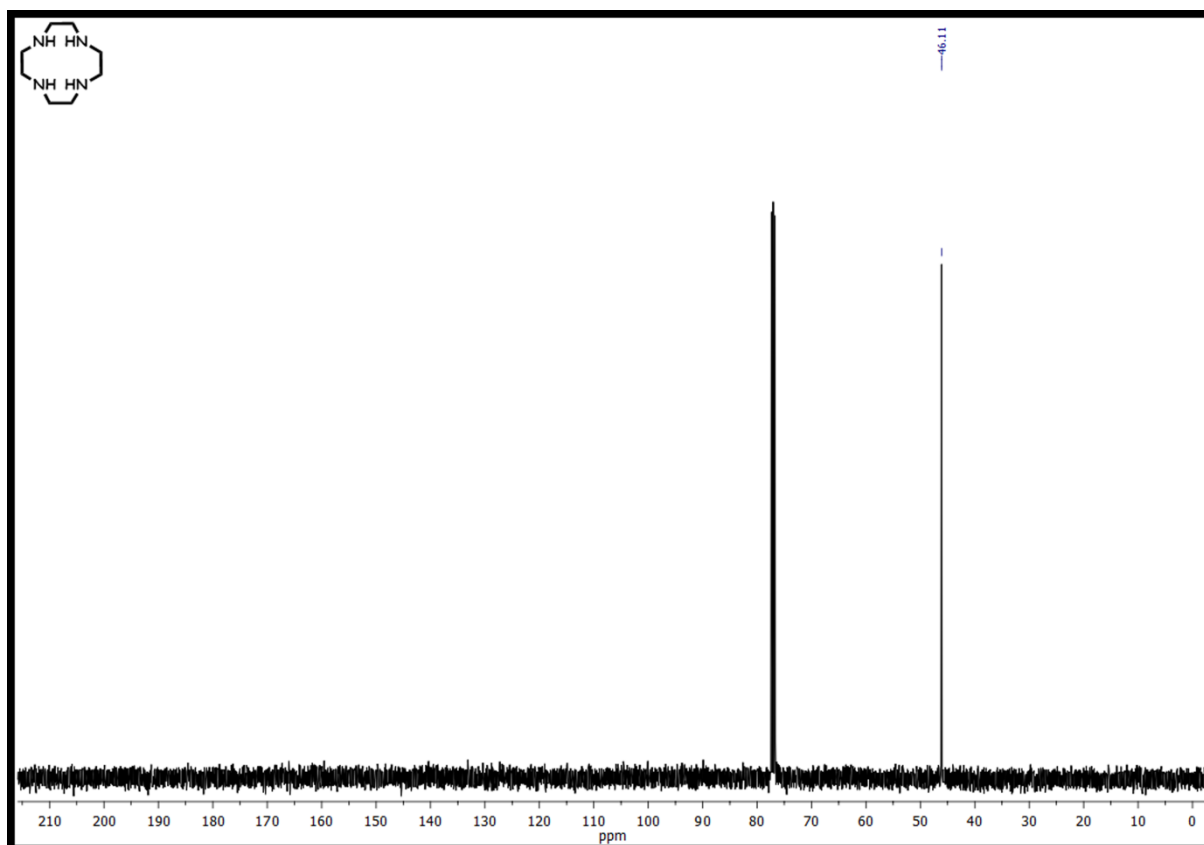


Figure S2. ^{13}C NMR spectrum of **2** in CDCl_3 .

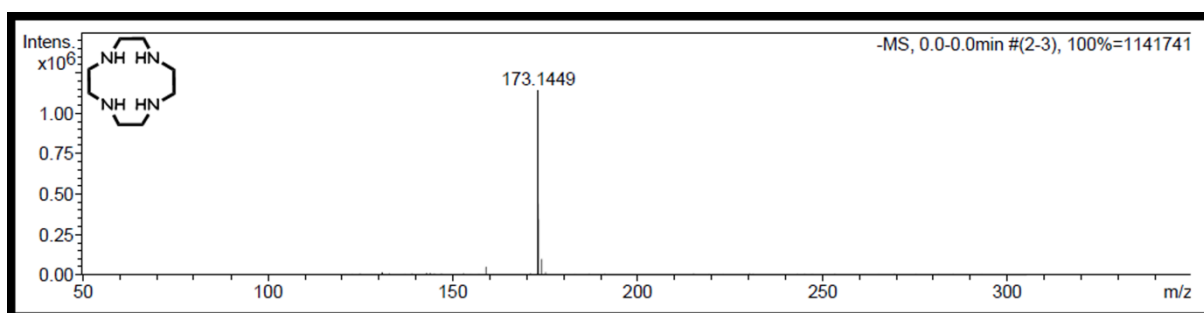


Figure S3. ESI-MASS spectrum of **2**.

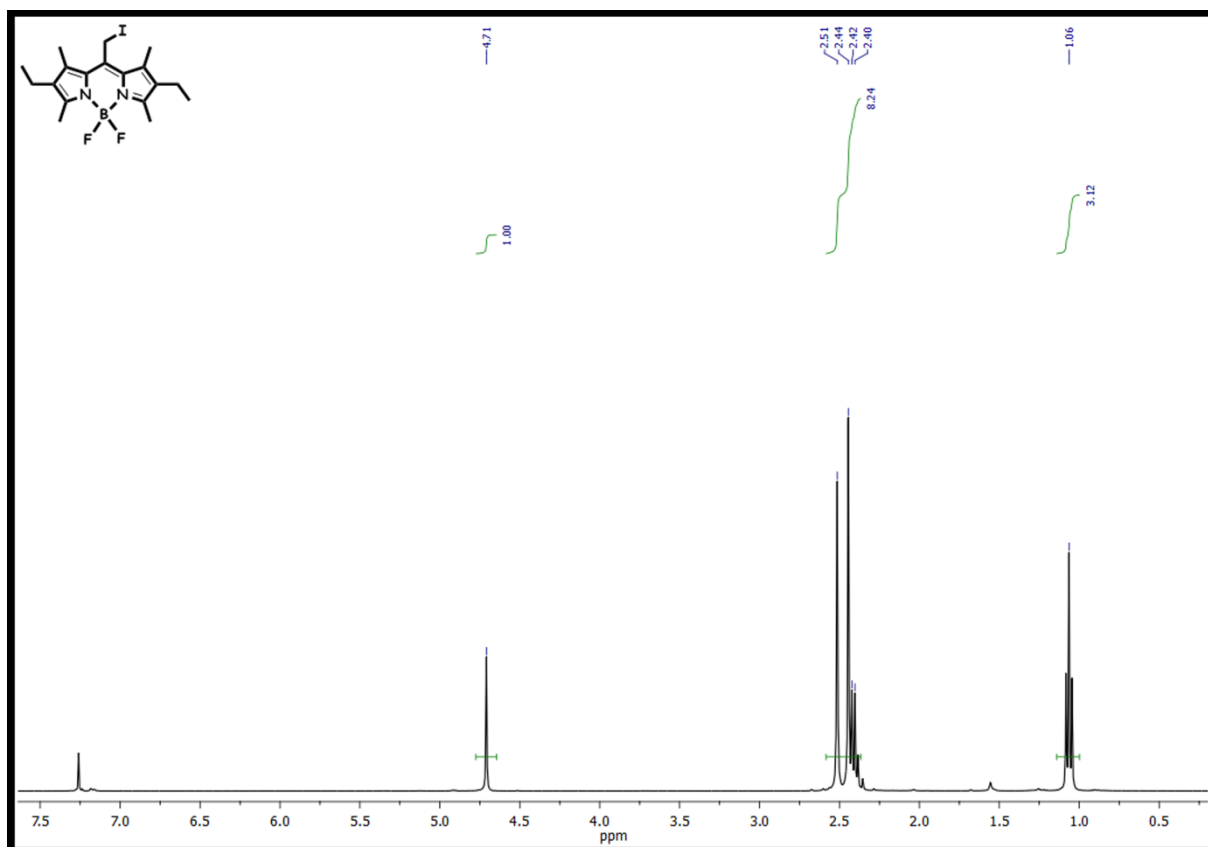


Figure S4. ¹H NMR spectrum of 3 in CDCl₃.

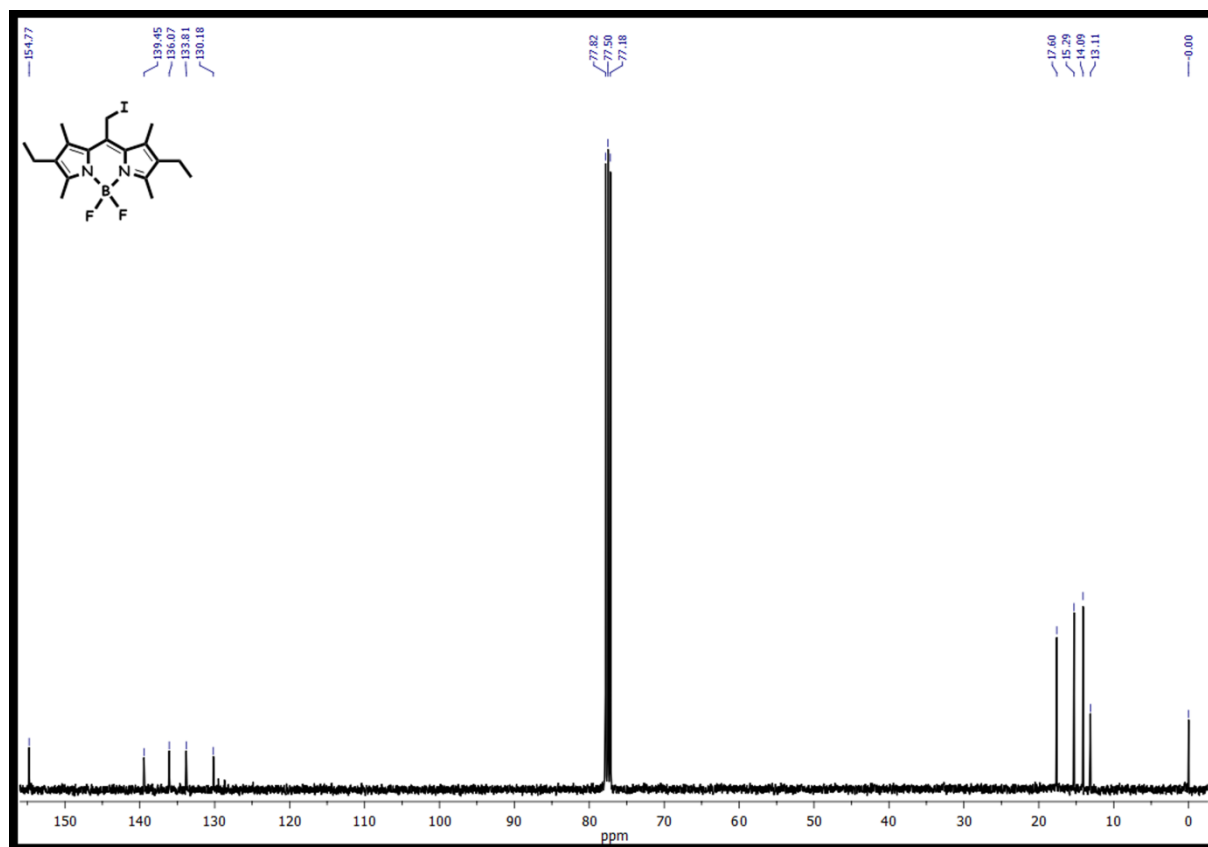


Figure S5. ¹³C NMR spectrum of 3 in CDCl₃.

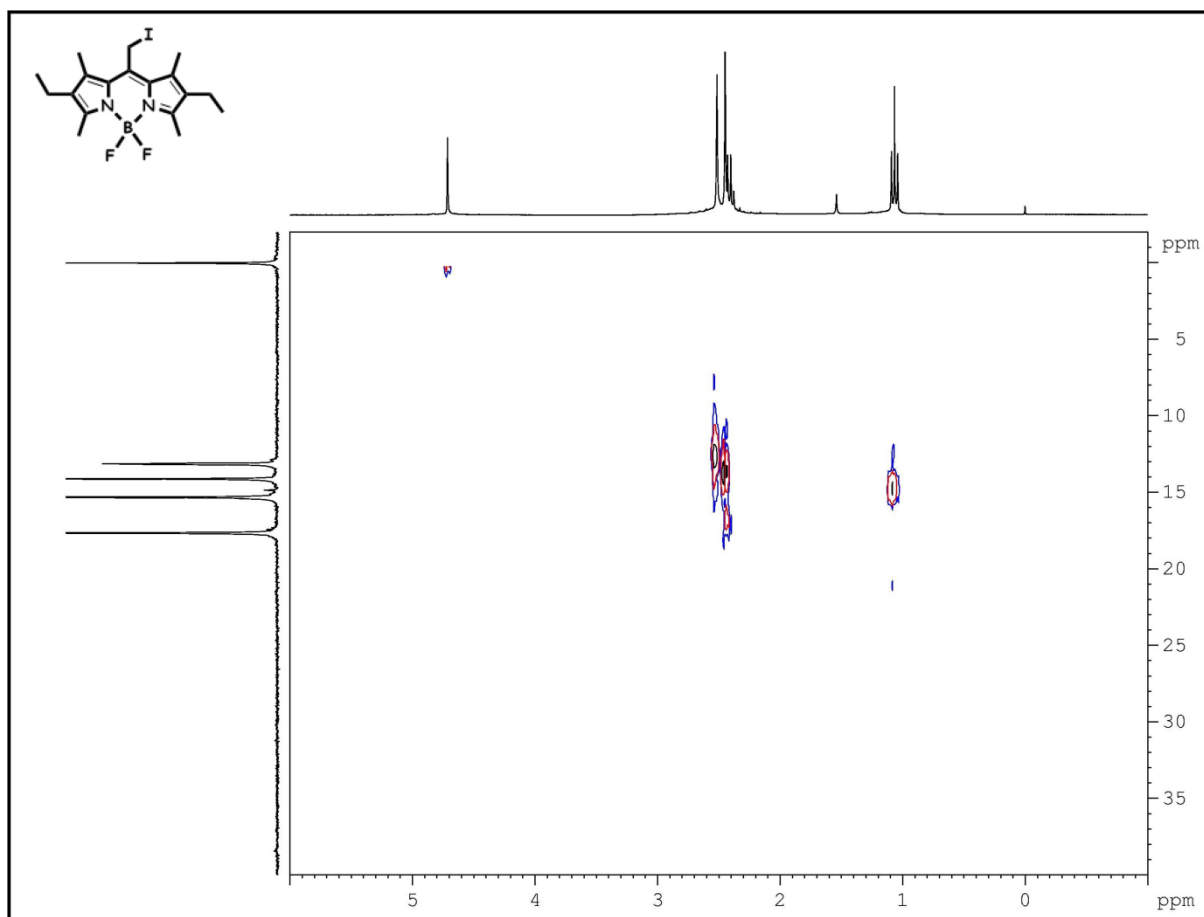


Figure S6. HMQC spectrum of **3** in CDCl₃.

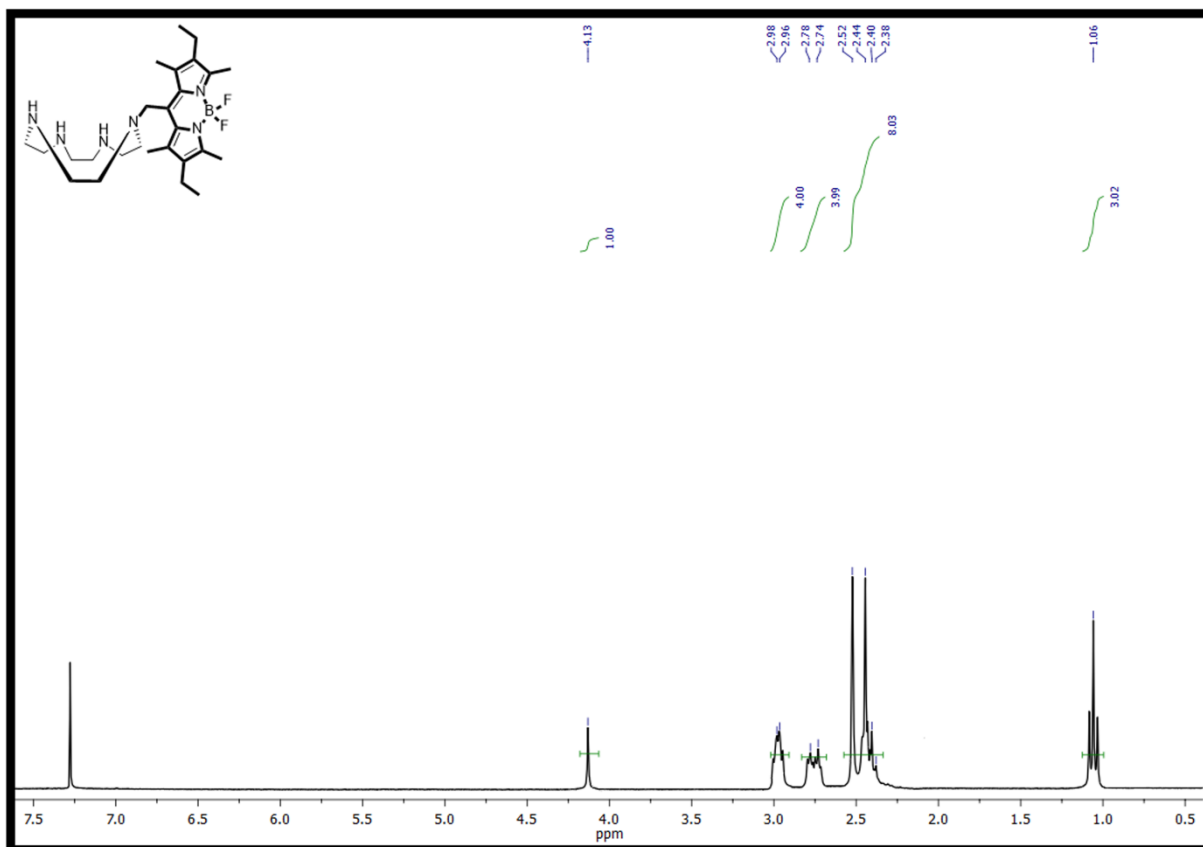


Figure S7. ¹H NMR spectrum of **1** in CDCl₃.

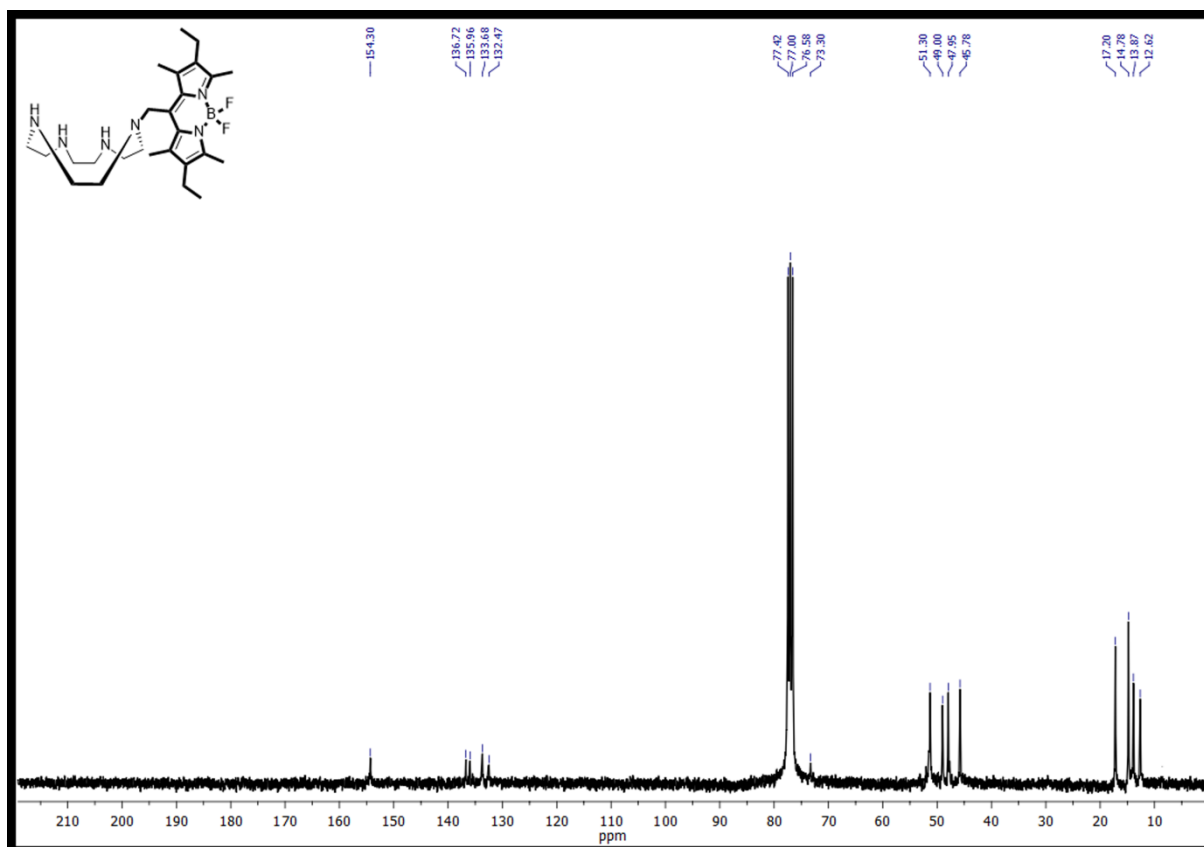


Figure S8. ¹³C NMR spectrum of 1 in CDCl₃.

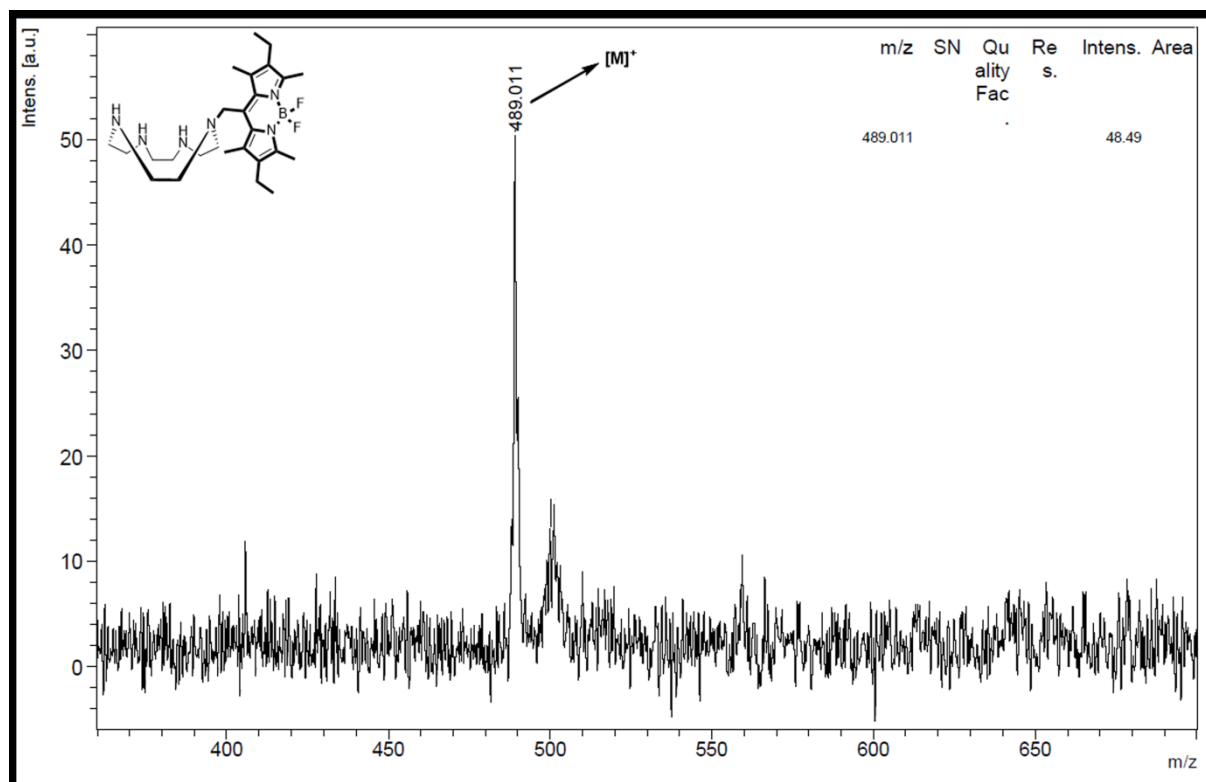


Figure S9. MALDI TOF MS spectrum of **1**.

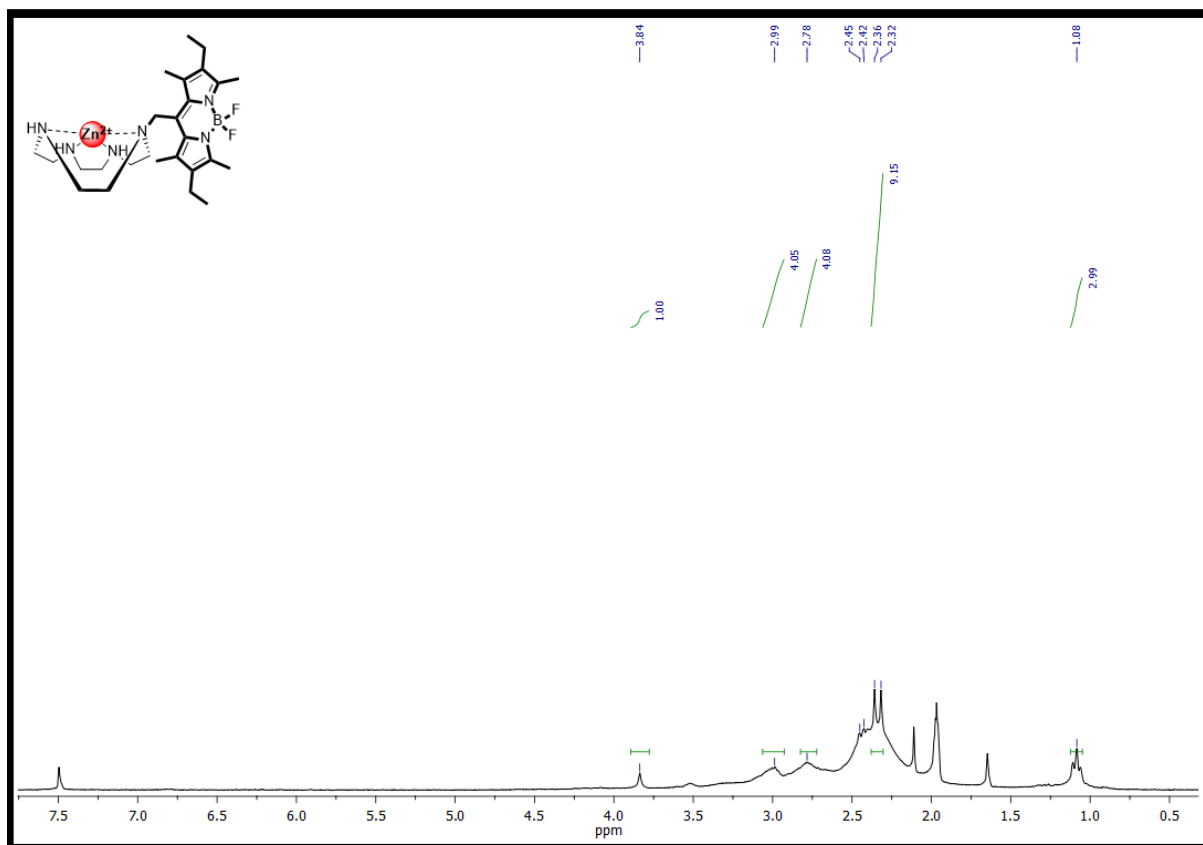


Figure S10. ¹H NMR spectrum of **1-Zn** in mixture of CD₃CN and CDCl₃.

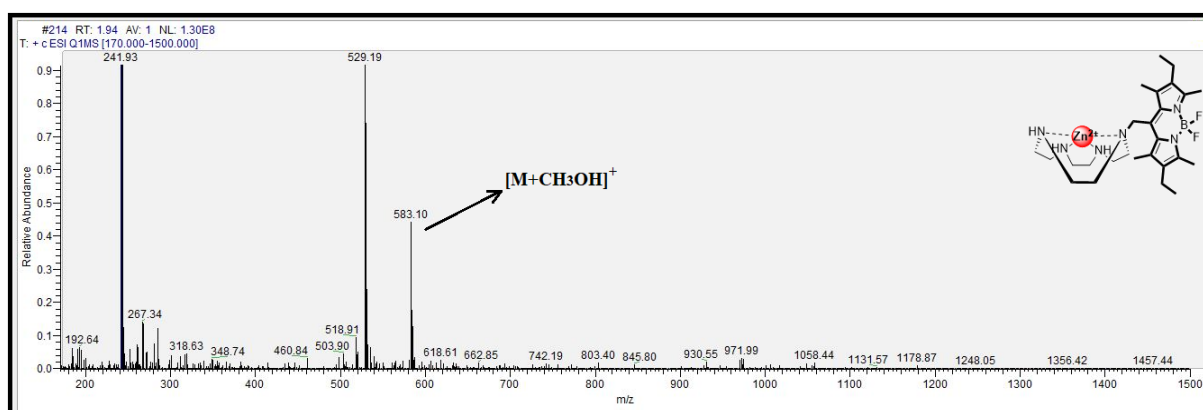


Figure S11. LC-MS spectrum of **1-Zn**.

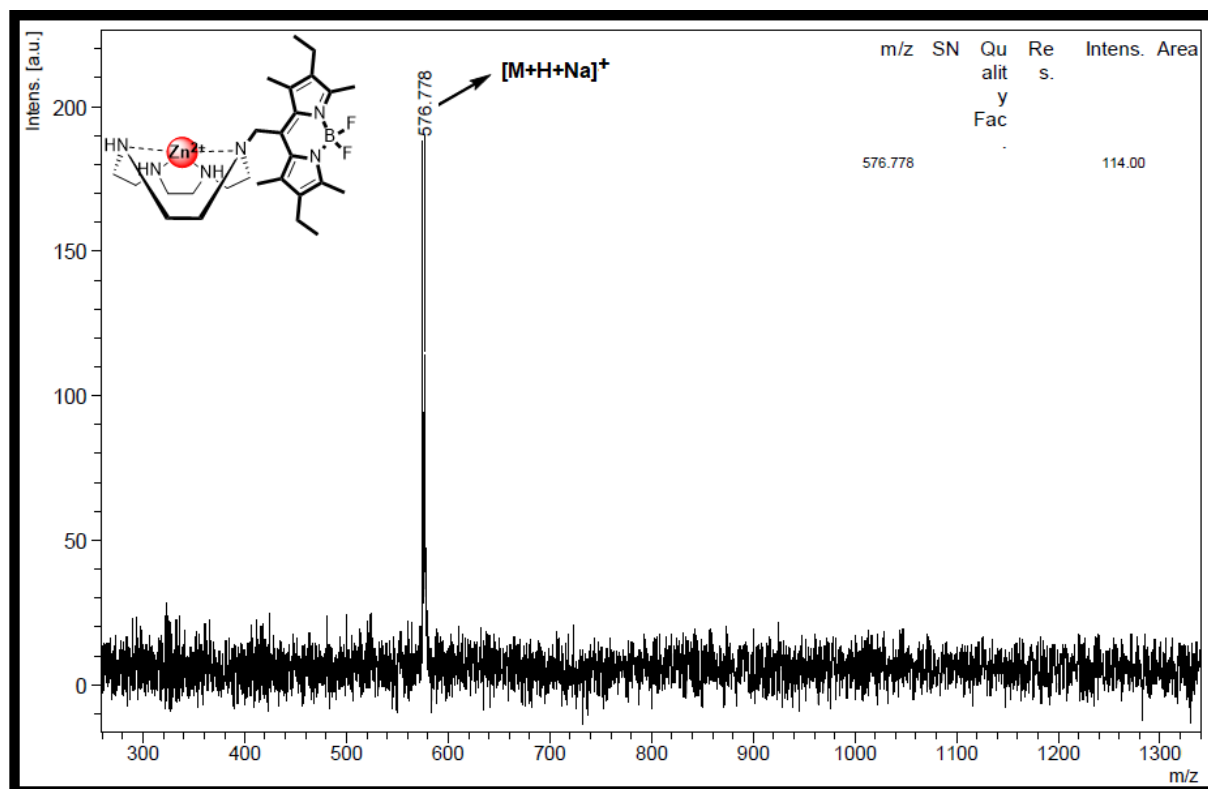


Figure S12. MALDI TOF MS spectrum of 1-Zn.

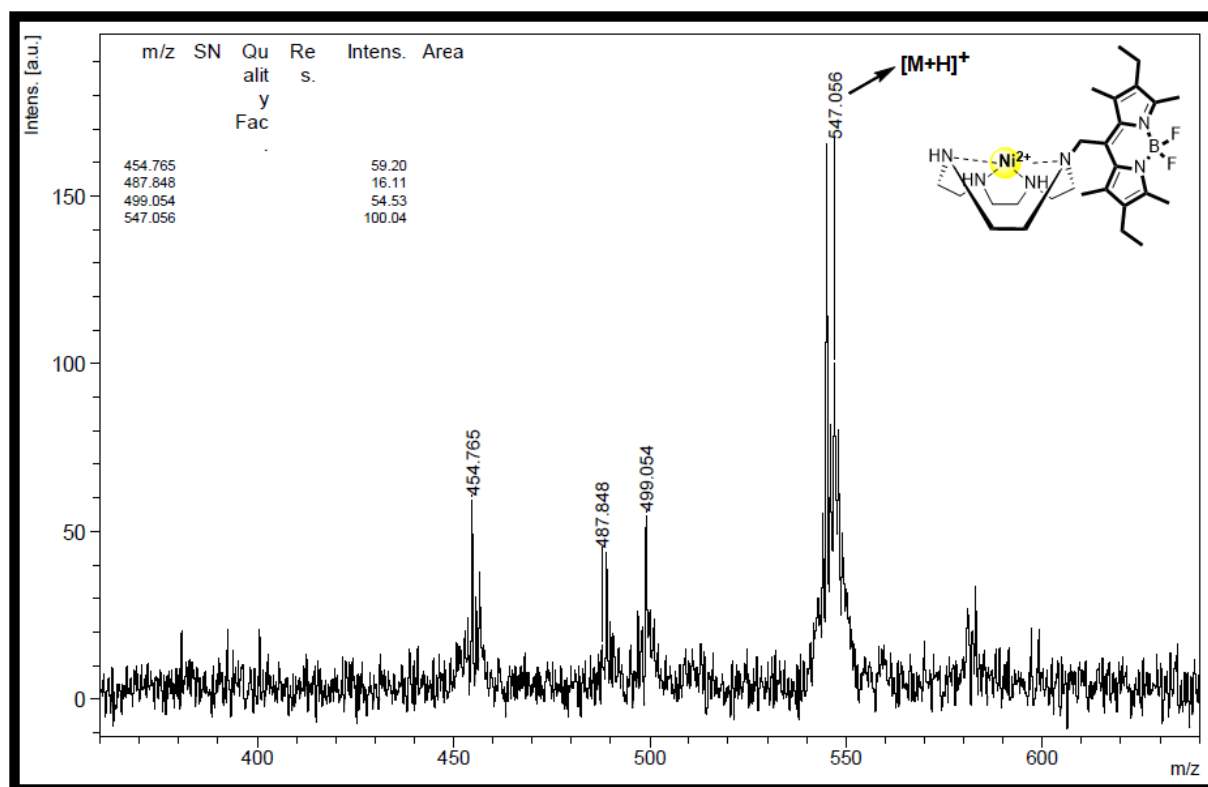


Figure S13. MALDI TOF MS spectrum of 1-Ni.

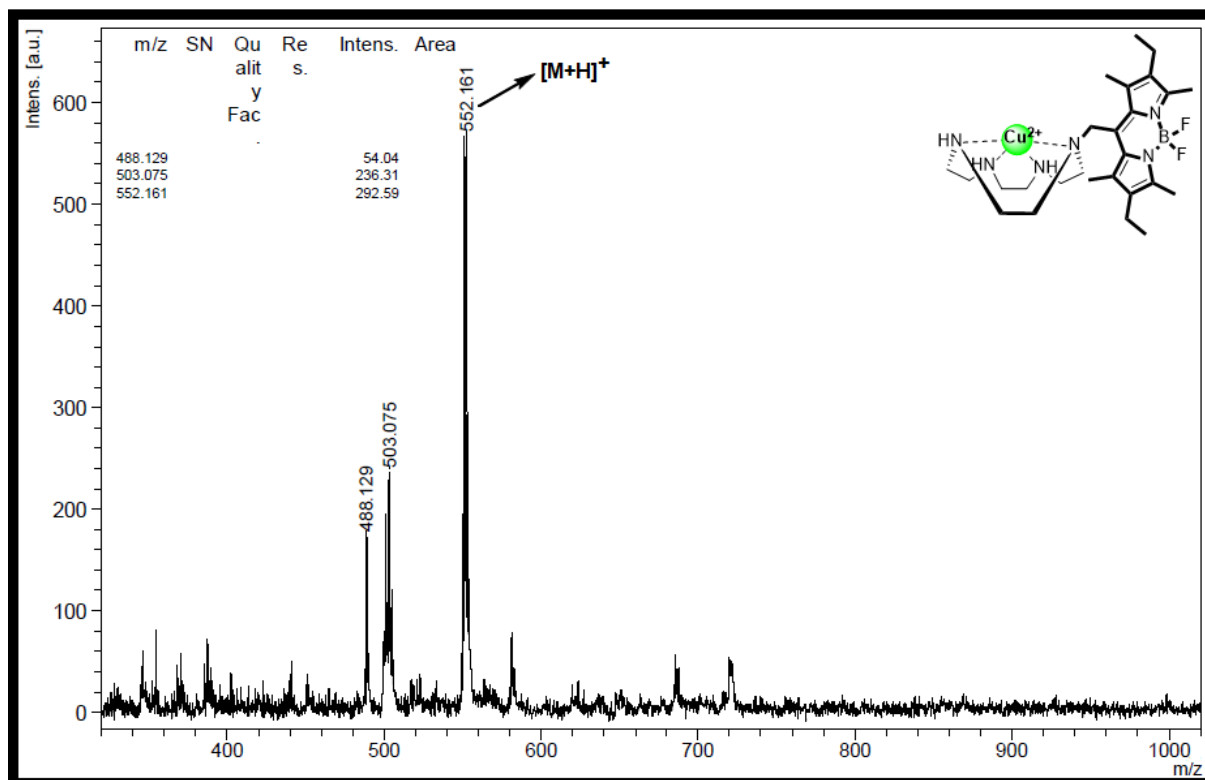


Figure S14. MALDI TOF MS spectrum of **1-Cu**.

2. Additional Graphs and Data

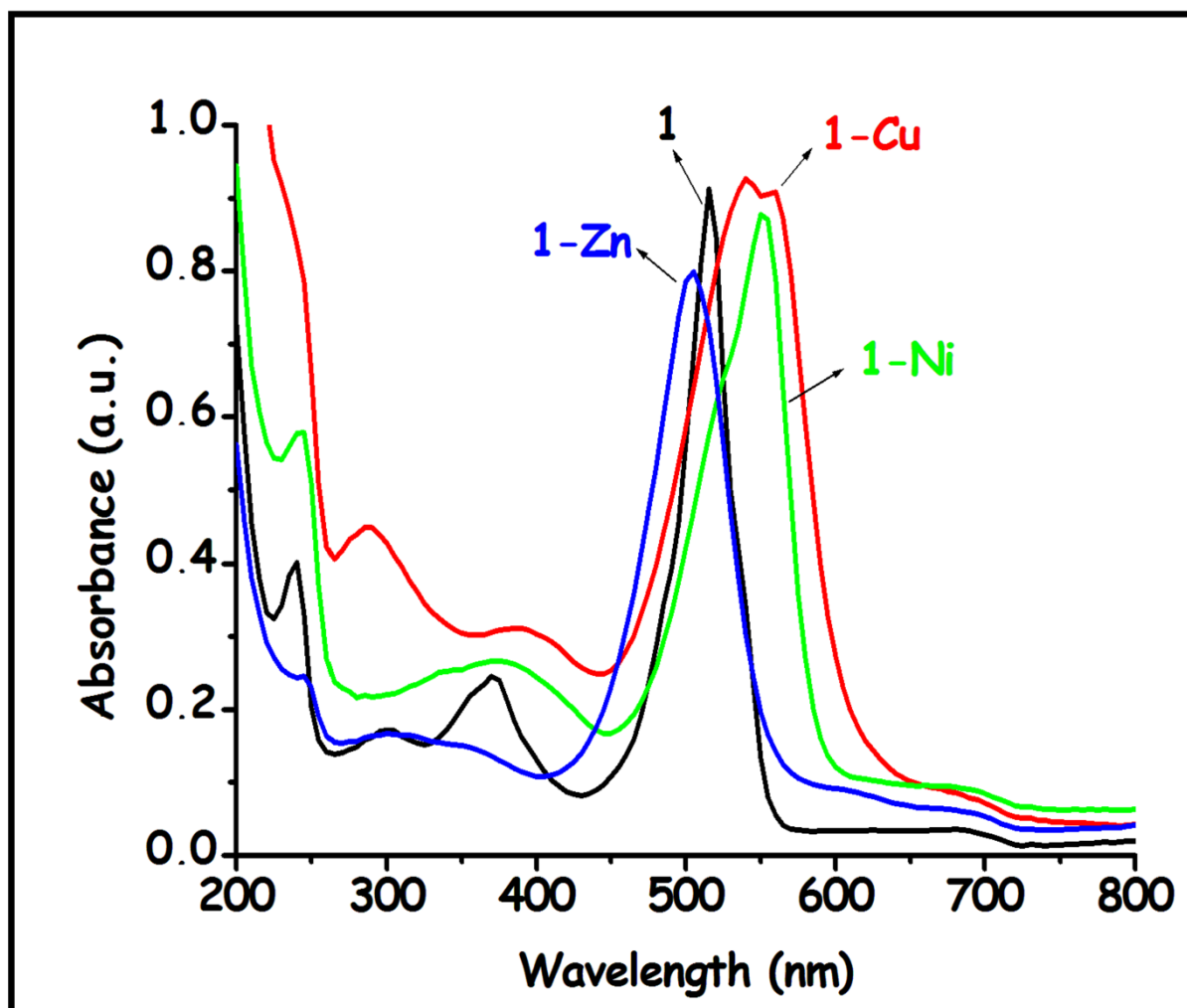


Figure S15. Absorption spectra of compounds 1 (8 μM), 1-Zn (12 μM), 1-Ni (24 μM) and 1-Cu (30 μM) in CH_3CN .

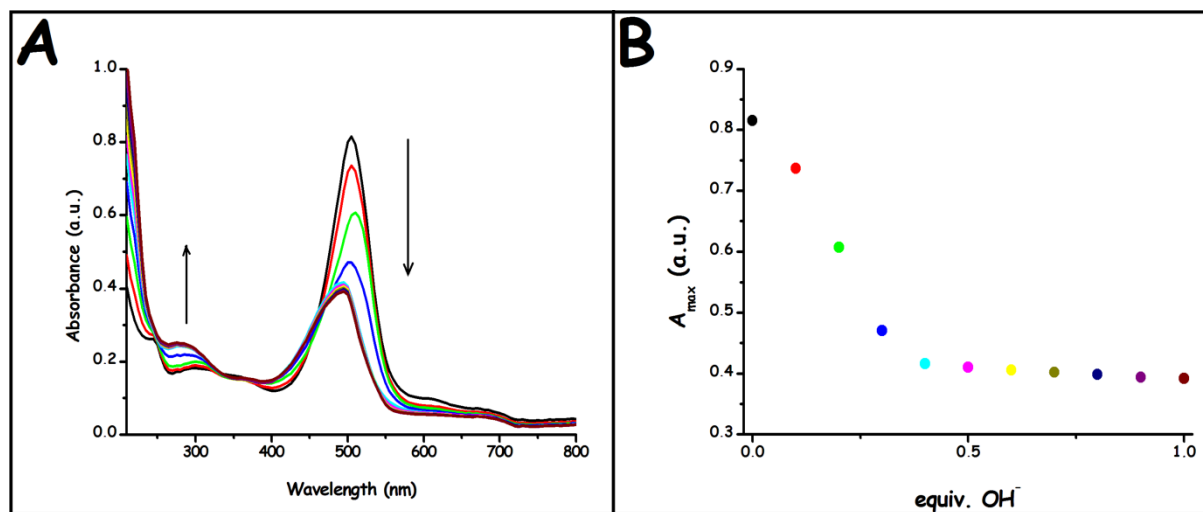


Figure S16. (a) Absorption spectra, (b) the curve of the absorption intensity changes of **1-Zn**(33 μM) upon addition of various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.) of OH^- .

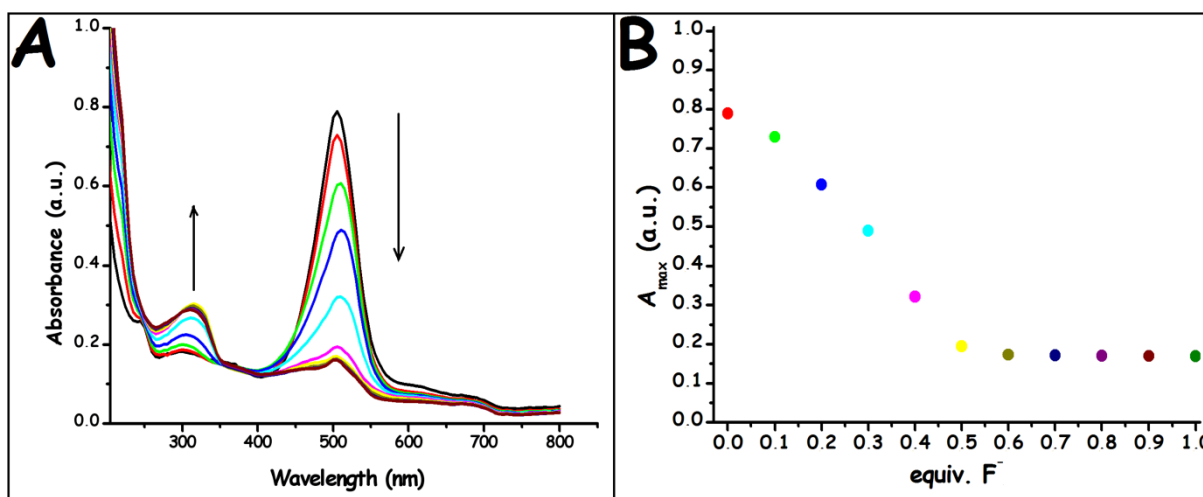


Figure S17. (a) Absorption spectra, (b) the curve of the absorption intensity changes of **1-Zn**(33 μM) upon addition of various concentrations (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.) of F^- .

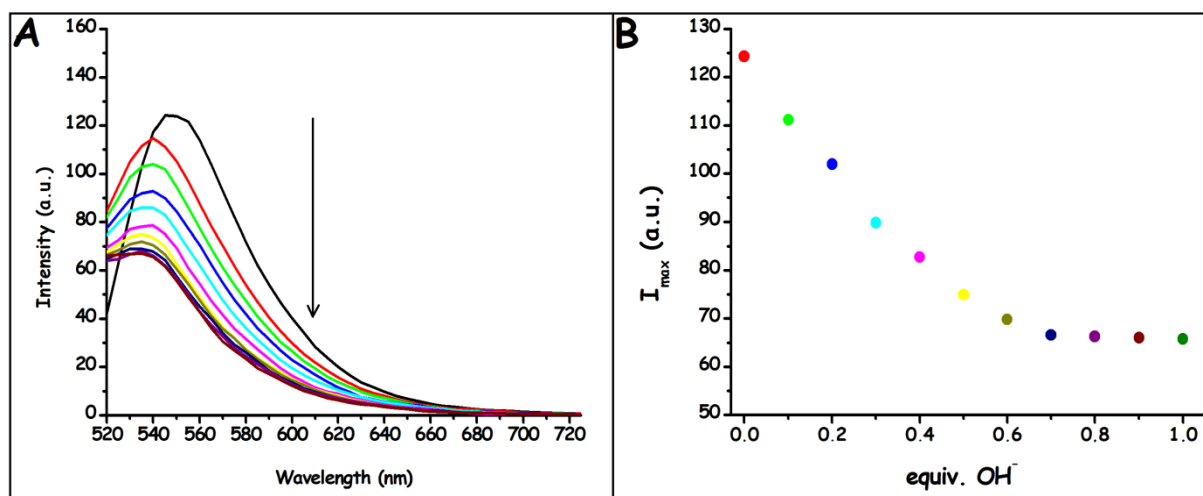


Figure S18.(a) Fluorescence spectra and, (b) the emission intensity changes for **1-Zn** (30 μ M) upon addition of various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.) of OH⁻ in CH₃CN (λ_{exc} =500 nm).

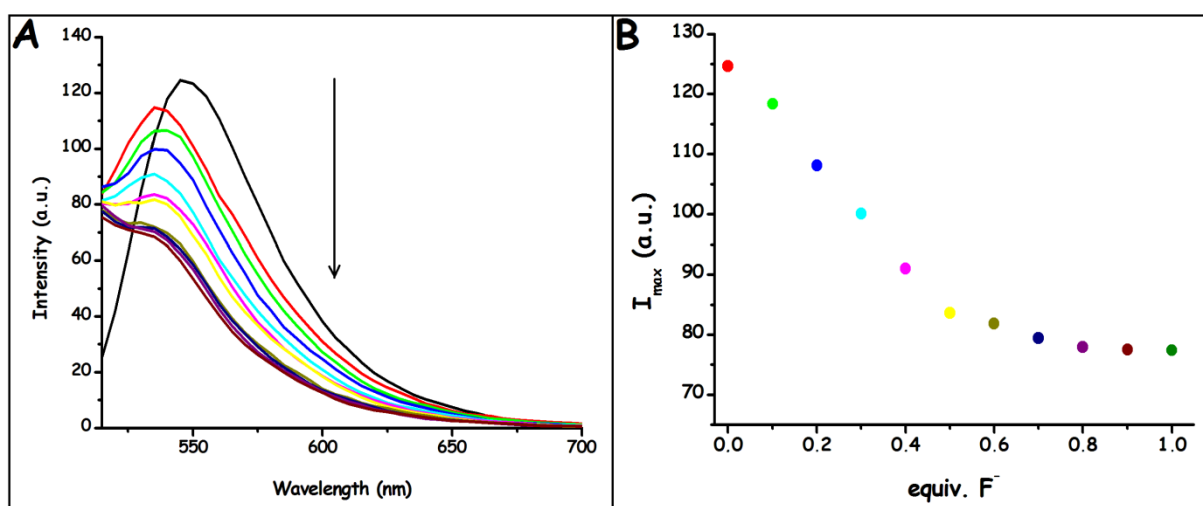


Figure S19.(a) Fluorescence spectra and, (b) the emission intensity changes for **1-Zn** (30 μ M) upon addition of various amounts (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 equiv.) of F⁻ in CH₃CN (λ_{exc} =500 nm).

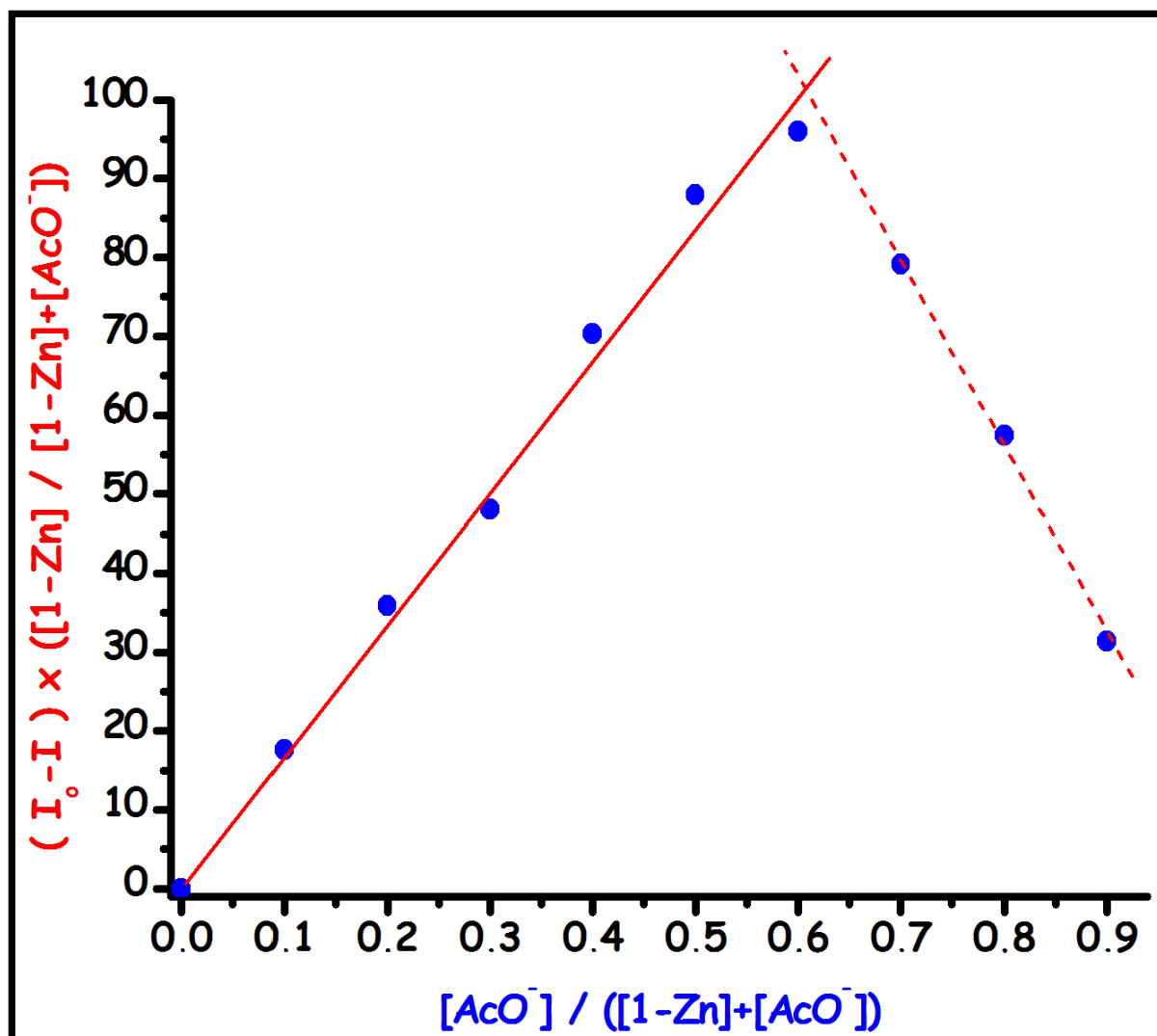


Figure S20. JOB plot diagram of 1-Zn for AcO⁻ at a constant total concentration of 30 μM of 1-Zn in CH₃CN at 545 nm.

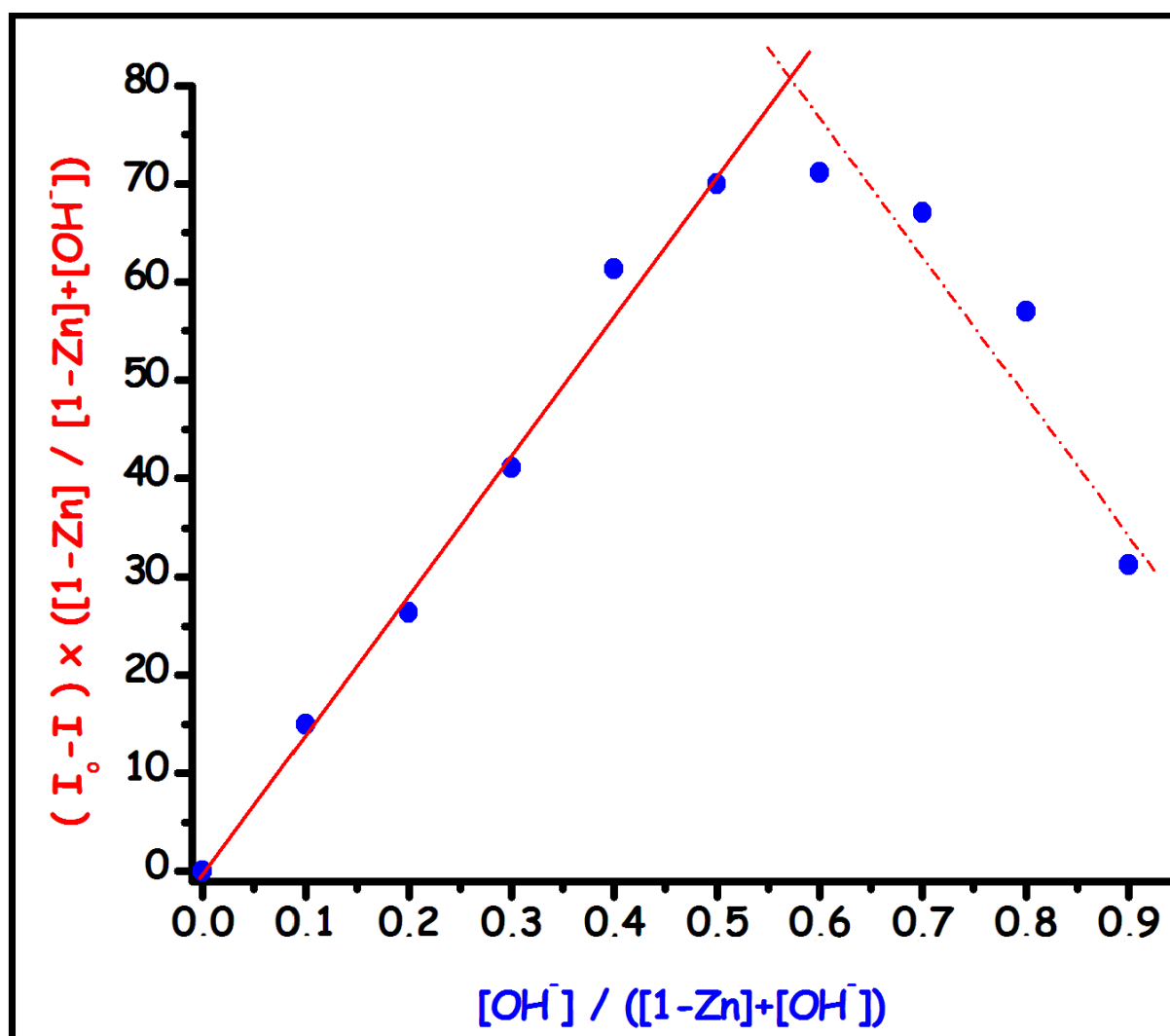


Figure S21. JOB plot diagram of 1-Zn for OH⁻ at a constant total concentration of 30 μM of 1-Zn in CH₃CN at 540 nm.

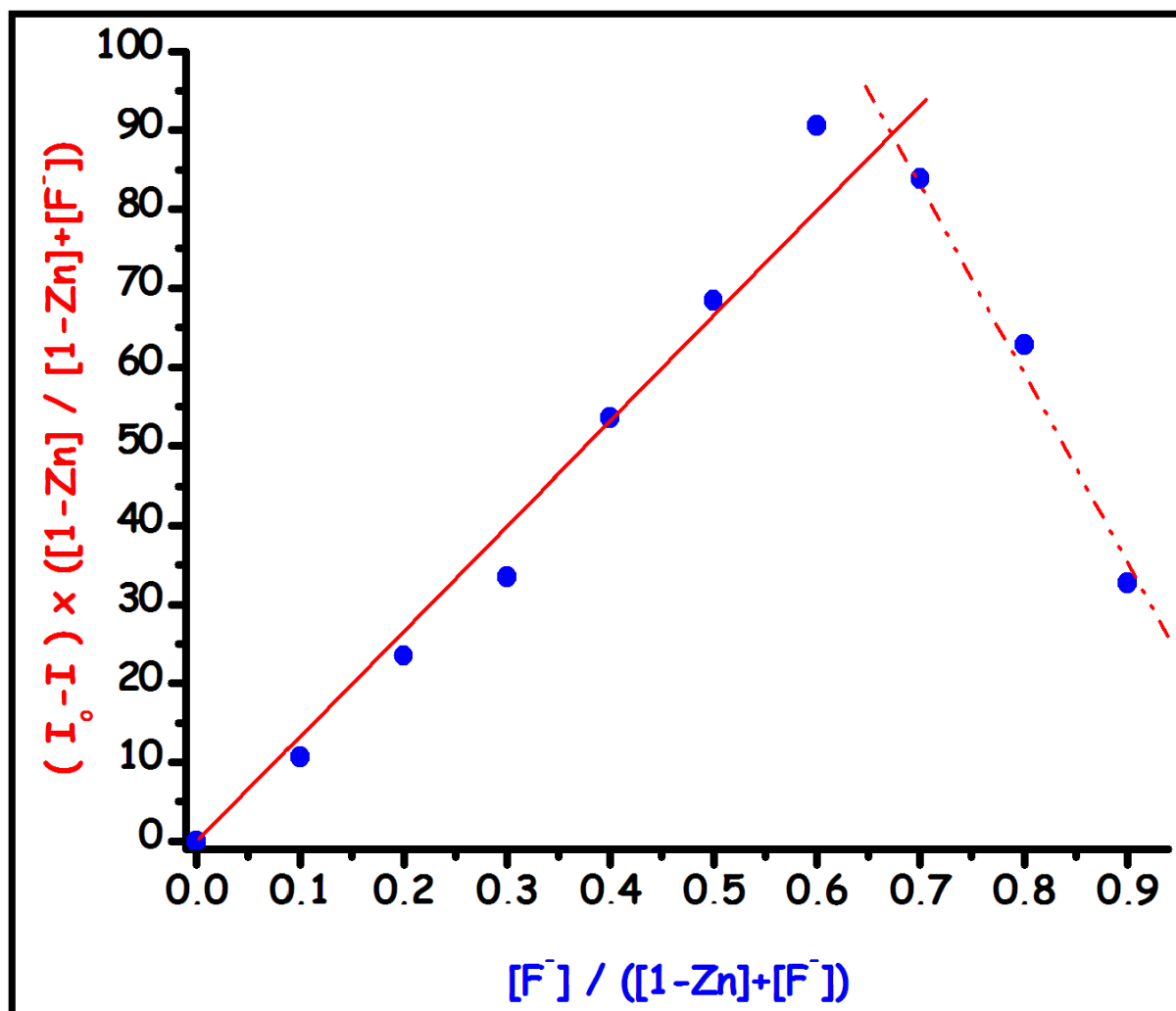


Figure S22. JOB plot diagram of **1-Zn** for F^- at a constant total concentration of $30 \mu M$ of **1-Zn** in CH_3CN at 540 nm .

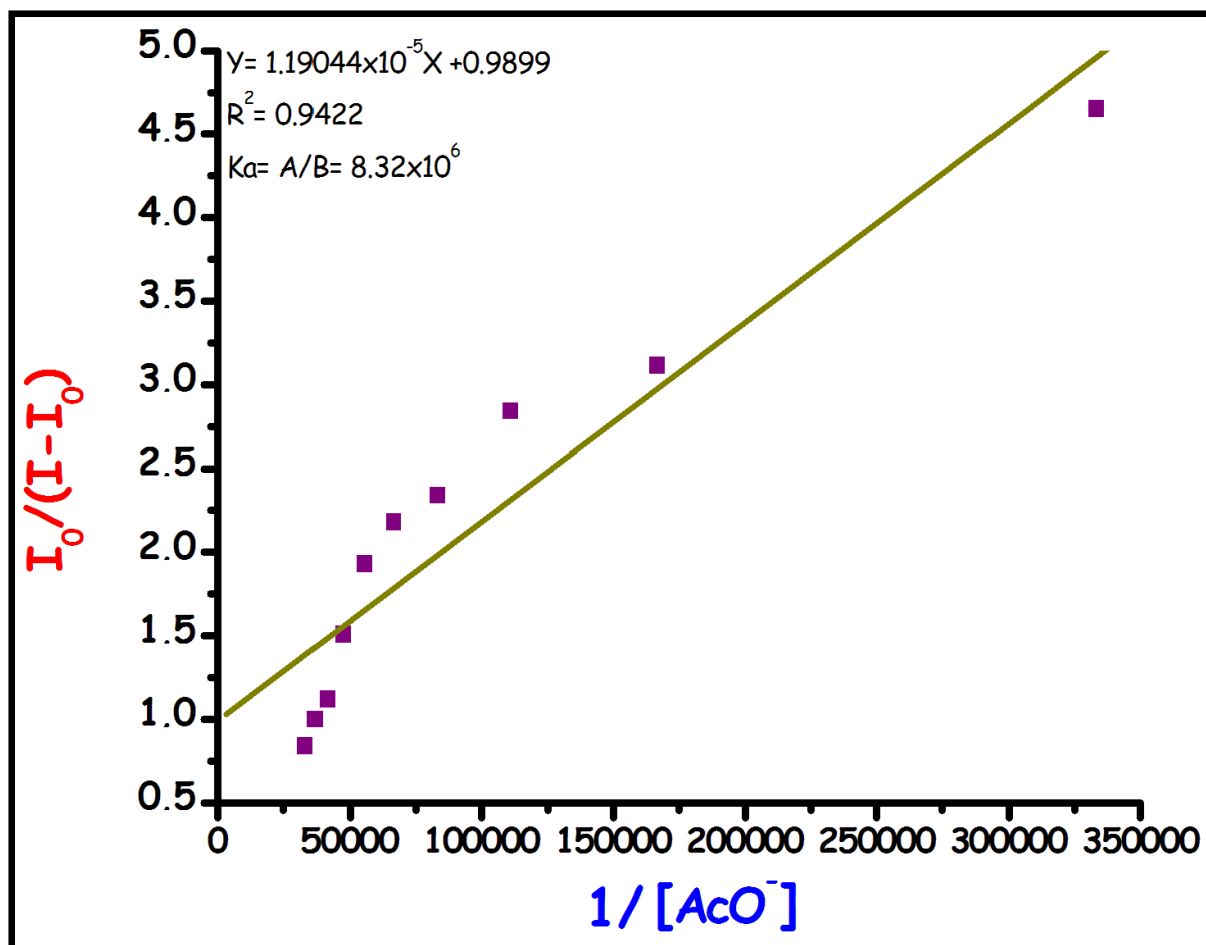


Figure S23. Linear regression curve 1-Zn for AcO⁻.

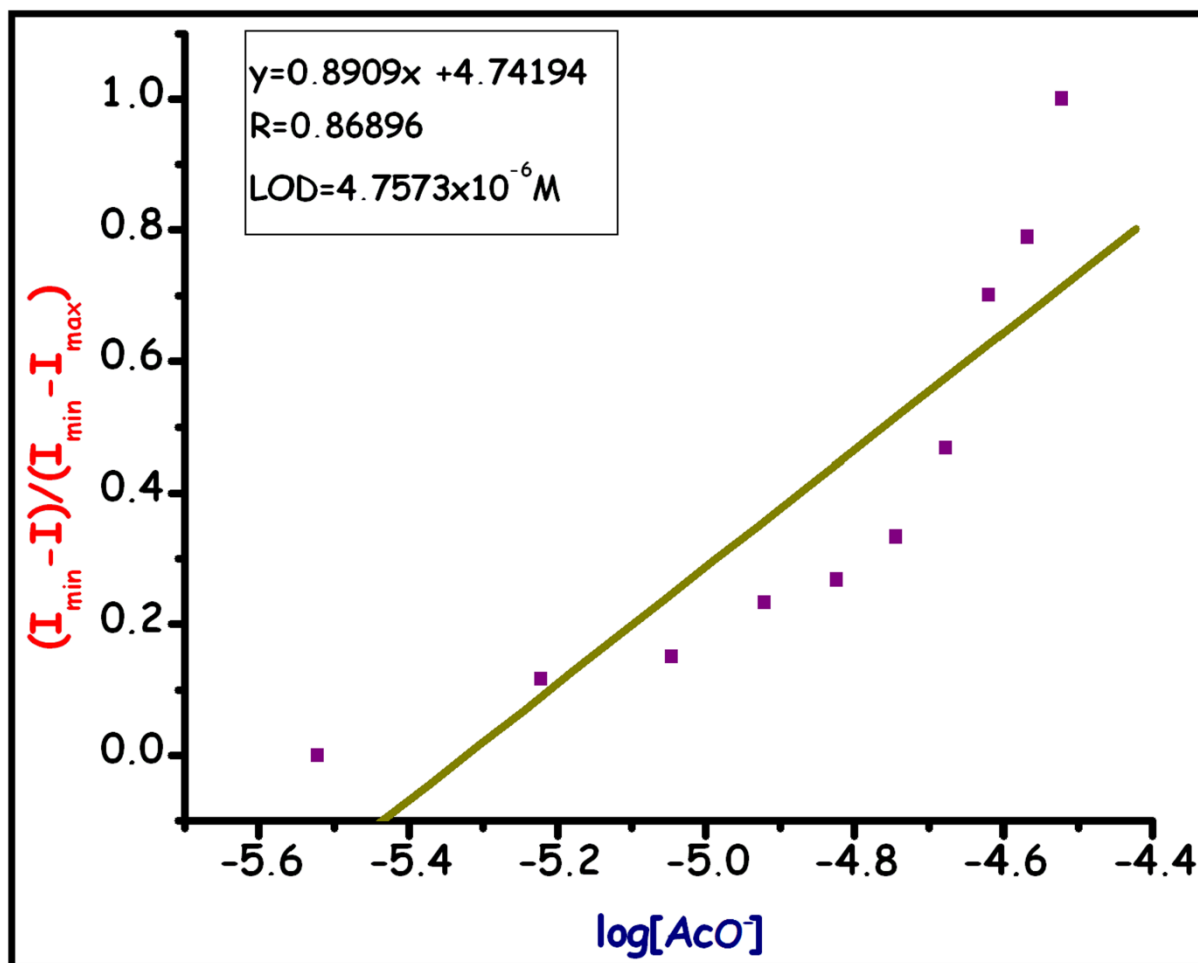


Figure S24. Plot of normalized fluorescence intensity of 1-Zn as a function of $\log[\text{AcO}^-]$ in CH_3CN ($\lambda_{\text{exc}} = 500 \text{ nm}$ and $\log[\text{AcO}^-] = -5.323$).