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A pyrenesulfonyl-imidazolium derivative as selective cyanide ion sensor in aqueous media

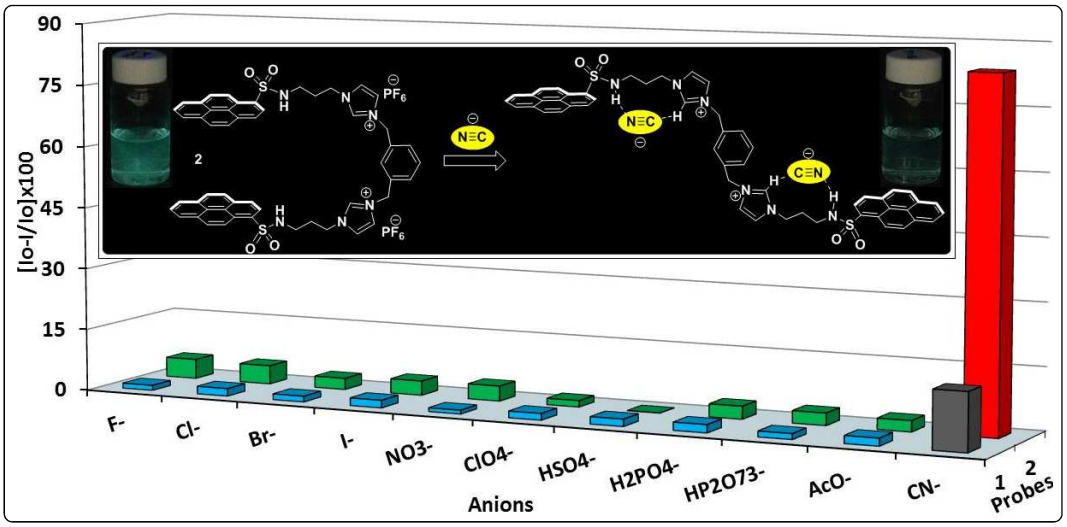
Ashwani Kumar, and Hong-Seok Kim*

Department of Applied Chemistry, Kyungpook National University, Daegu 702-701,

Republic of Korea

Corresponding author: Tel.:+82 53 9505588; fax: +82 53 9506594.

E-mail address: kimhs@knu.ac.kr



A pyrenesulfonyl-imidazolium derivative as selective cyanide ion sensor in aqueous media

Ashwani Kumar, and Hong-Seok Kim*

Department of Applied Chemistry, School of Applied Chemical Engineering,

Kyungpook National University, Daegu 702-701, Republic of Korea

Corresponding author: Tel.:+82 53 9505588; fax: +82 53 9506594.

E-mail address: kimhs@knu.ac.kr

Abstract

In this work, *N*-imidazolylpropyl pyrenesulfonamide **1** and its diimidazolium salt **2** were synthesized to be tested as cyanide (CN^-) sensors. The probes were found to be selective and sensitive toward CN^- in a PBS-EtOH solution. The sensing ability of the probes was examined by UV-Vis, fluorescence, and NMR spectroscopy. CN^- sensing was characterized by the quenching of both the monomer and excimer emissions of probe **2**, owing to unlocking of the π–π interaction; in the case of probe **1**, a small degree of quenching of the monomer emission intensity was observed. The selective sensing of CN^- was associated with a color change and complete quenching of green fluorescence emission under 365 nm illumination. The degree of quenching of the emission intensity was driven by the presence of a positive charge, number of positive charges (which lead to ionic interactions with anions), and hydrogen bonding. Probe **2** exhibited a large association constant with CN^- (K_a = 2.32 x 10^5 M^{-1}), with a 1:2 stoichiometry in

a PBS-EtOH solution. The lowest detection limit for the estimation of CN^- was determined to be 0.5 μM (13 ppb), which is lower than the permissible limit for drinking water established by the WHO.

Keywords: Fluorogenic probe, Pyrenesulfonyl imidazolium, Pyrenesulfonamide, CN^- sensor, Excimer emission.

Introduction

Cyanide salts are widely employed in a range of applications, for example, the synthesis of large tonnage organic chemicals, gold extraction, electroplating, etc.[1] However, this is associated with a serious danger of environmental leaching. CN^- is extremely toxic to mammals as it adversely affects the respiratory system by binding with heme units and causes damage to several metabolic functions. The lethal concentration of CN^- in the blood of fire victims has been suggested to be between 23 and 26 μM.[2] The CN^- limit in drinking water is lower than 2 μM (42 ppb), as established by the World Health Organization (WHO).[3] Therefore, the development of effective and selective CN^- probes is necessary.

Supramolecular chemistry-based molecular probes have received much attention for the selective detection of metal ions, anions, and biologically relevant neutral molecules.[4] Most of the reported CN^- chemosensors are electron-deficient organic molecules; in this case, nucleophilic addition of CN^- to carbon-carbon double bonds,[5] carbon-heteroatom double bonds (i.e., carbonyl of aldehydes, ketones, or amides)[6] and heterocyclium derivatives[7] results in a change in the electron density of the corresponding chromophore/fluorophore. To date, only a

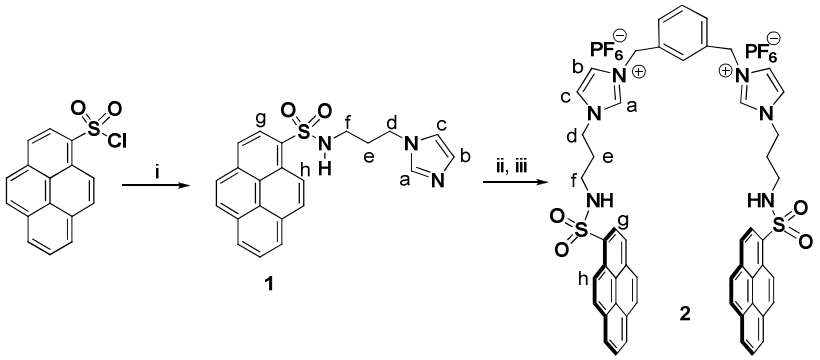
few probes can detect the concentration of CN^- below permissible limits, especially under aqueous conditions. Further, the application of probes for the estimation of CN^- concentration in live cells using confocal imaging has shown poor results.[8]

Only a few studies have clearly described the poor selectivity in CN^- recognition via hydrogen bonding.[9] The CN^- ion is characterized by a small size in aqueous systems because of its lower hydration energy (ΔH_{hyd} = -67 kJ/mol) as compared to that of other anions such as F^- (ΔH_{hyd} = -505 kJ/mol), AcO^- (ΔH_{hyd} = -375 kJ/mol), and $H_2PO_4^-$ (ΔH_{hyd} = -260 kJ/mol),[10] this property has been exploited for selective CN^- sensing via hydrogen bonding with the imidazole N-H group of imidazole anthraquinone systems and ruthenium bipyridine imidazole complexes.[11] In most of the supramolecular probes, the pyrene unit and imidazolium salts are used as fluorophore and anion sensors, respectively.[12] Considering the significant role played by the ionic interactions of the imidazolium salt and the properties of the amidic N-H group, which provides a hydrogen bonding site, and following our previous studies on optical/voltammetric molecular probes,[13] we herein report a preorganized pyrenesulfonamide imidazolium-based probe for the selective determination of CN^- in a PBS-EtOH solution; this was carried out by "switch-off" green fluorescence-emission intensity centered at 495 nm. To the best of our knowledge, this is the first study on the use of hybrid pyrenesulfonamide and imidazolium salts with green emission as selective CN^- sensors in aqueous systems.

Results and Discussion

Pyrene-1-(3-imidazol-1-yl-propyl)sulfonamide (probe **1**) was easily synthesized in good yield by the reaction of pyrenesulfonyl chloride [14] with 1(3-aminopropyl)imidazole in

dichloromethane. The ^{1}H NMR spectrum of probe **1** in DMSO-d_6 showed three CH_2 groups of the propyl chain (two as triplets, one at δ 3.84 for SO_2NHCH_2, the other at δ 2.74 for CH_2Imidazole; and one as a multiplet at δ 1.68–1.72 for middle CH_2 of the propyl chain and three imidazole protons (as singlet, at δ 6.72, 6.88, and 7.36 for the H-b, -c, and -a protons, respectively). The ^{13}C NMR spectrum of probe **1** showed the imidazole C-2 at δ 137.4. In addition, the mass spectrum of probe **1** had a clear molecular ion peak at m/z = 390.1273 $(M + H)^+$. Pyrenesulfonyl imidazolium (probe **2**) was simply synthesized by heating probe **1** with 1,3-bis(bromomethyl)benzene in acetonitrile at 90 °C; a counter-ion exchange with PF_6 (using KPF_6) was then performed to obtain the corresponding solid compound as a PF_6 salt in good yield (Scheme 1). Because of the positive charge, the imidazolium C2-H of probe **2** was strongly deshielded, i.e., the H-a proton appeared at δ 9.16, and the H-b and H-c protons of the imidazolium rings merged together to appear as a singlet at δ 7.68; the CH_2 group of 1,3-bis(methyl)benzene was detected at δ 5.36, in addition to other protons. The mass spectrum of probe **2** clearly showed a molecular ion peak at $(M + PF_6)^+$, m/z = 1027.2667 (see ESI for further details).



Scheme 1: (i) 1(3-aminopropyl)-imidazole, DCM, 0 °C, 3h, rt, 2h; (ii) 1,3-bis(bromomethyl) benzene; 90 °C, CH_3CN; (iii) KPF_6, rt, 3 h.

The UV-Vis absorption spectrum of probe **1** (10 μM, PBS-EtOH (5:95), pH = 7.4) exhibited typical pyrene absorption maxima (λ_{max}) at 322, 336, and 350 nm. The UV-Vis spectrum of probe **2** (10 μM, PBS-EtOH (5:95), pH = 7.4) showed that the absorbance at λ_{max} was twice as that of probe **1**. This finding clearly suggested the presence of two pyrene rings in probe **2** (Fig. 1). Upon the addition of different anions (such as, F^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$, $HP_2O_7^{3-}$, AcO^-, and CN^-) to the solution of probes **1** and **2** (10 μM, PBS -EtOH (5:95), pH = 7.4), no significant changes were observed, with the exception of the CN^- ion, which induced a slight change in the absorbance (Figs. SI 1 - 2).

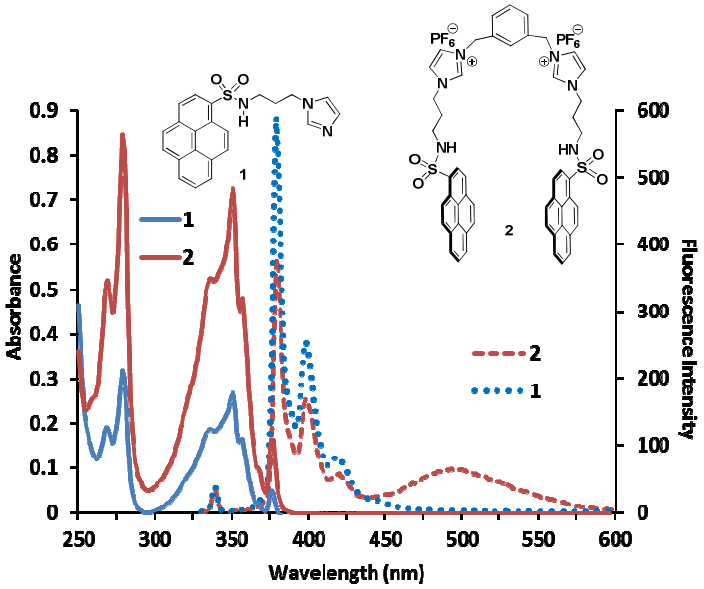


Fig. 1: UV-Vis and fluorescence spectra of solutions of probes **1** and **2** (PBS-EtOH (5:95), pH = 7.4). Solid lines indicate the UV-Vis spectra at 10 μM; dotted lines indicate the fluorescence spectra at 1 μM, λ_{ex} = 336 nm, slit width 3, 3.

Upon excitation at 336 nm, probe **1** exhibited fluorescence emission maxima at 379, 398, and 420 nm with a high quantum yield (Φ = 0.232), while probe **2** exhibited green fluorescence emission with maxima at 379 nm and 495 nm (Fig. 1). In case of probe **2**, the emission maxima at 379 nm is due to the monomer emission of pyrene while the emission maxima at 495 nm responsible for the green emission is due to excimer emission of π-π interaction between the pyrene rings of the same molecule. These interactions were confirmed by the UV-Vis data for probe **2**, which indicated that the absorbance of probe **2** was twice that of probe **1**.

From among the various anions (such as, F^-, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-, $H_2PO_4^-$, $HP_2O_7^{3-}$, AcO^-, and CN^-) added to the solution of probes **1** and **2**, quenching of the emission intensity was only observed with CN^-. The degree of quenching depends on the number of hydrogen bonding sites, presence of a positive charge, and number of positive charges available for ionic

interaction, cavity size, and preorganization of the molecule/probe. In the case of a neutral probe **1** (i.e., with two hydrogen bonding sites, namely (i) sulfonamide N-H, and (ii) imidazole C2-H), quenching of the emission intensity obtained with CN^- was found to be 14%; other anions induced no changes in the fluorescence emission intensity (Figs. SI 3 - 4).

In the case of probe **2** bearing two positive charges and four hydrogen bonding sites (namely, two sulfonamide N-H and two imidazolium C2-H groups), quenching of the green emission intensity at 494 nm with CN^- increased to 84%; other anions induced no significant changes (Fig. 2, and Figs. SI 5 - 6). The "switch off" behavior of the green emission intensity, i.e., excimer emission with CN^-, clearly showed that in the presence of CN^-, intramolecular π-π interactions between the pyrene rings do not occur because of flipping/unlocking of this system. Thus, in order to further explore the complexation mode, fluorescence titrations of probes **1** and **2** with the CN^- ion were carried out.

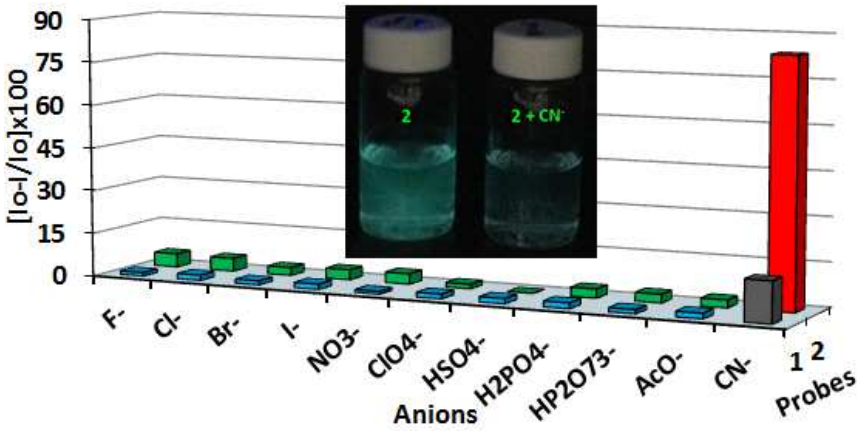


Fig. 2: Fluorescence relative-intensity bar diagram of probes **1** and **2** (1 µM, PBS -EtOH (5:95), pH = 7.4) with different anions; λ_{ex} = 336 nm for **1** and **2**; λ_{em} = 379 nm for **1**; λ_{em} = 495 nm for **2** (slit width 3, 3).

Upon excitation at 336 nm, probe **1** exhibited the largest emission maxima at 379 nm. Gradual addition of aliquots of a TBACN solution to probe **1** slowly decreased the emission intensity until a saturation level was reached. The fitting of these fluorescence titration data showed the formation of a 1:1 complex with a small association constant (K_a = 1.71 x 10^3 M^{-1}) (Table 1, Figs. SI 7 - 8). The formation of the 1:1 complex of probe **1** with CN^- was also observed with Job's plot.

Upon excitation at 336 nm, probe **2** exhibited green fluorescence emission at 495 nm due to an excimer formation, i.e., the intramolecular π-π interaction between the pyrene rings, and monomer emission at 379 nm. Gradual addition of aliquots of a TBACN solution caused a slow decrease in the monomer emission intensity at 379 nm and excimer emission at 495, until the excimer emission was completely quenched and monomer emission was saturated. The fitting of these titration data showed the formation of a 1:2 complex with a large association constant (K_a = 2.32 x 10^5 M^{-1}) (Table 1, Fig. 3, and Figs. SI 9 - 10). The formation of the 1:2 complex of probe **2** with CN^- was confirmed with Job's plot. The complete quenching of the green emission of probe **2** with CN^- suggested that the π-π interaction between the pyrene rings (which causes locking, i.e., the pyrene rings are on the same side) is completely unlocked by CN^-, i.e., the pyrene rings are on opposite sides/flipped away from each other. The lowest detection limit for the estimation of CN^- with probe **2** was found to be 0.5 µM (13 ppb), which is lower than the permissible limit for drinking water established by the WHO.[3]

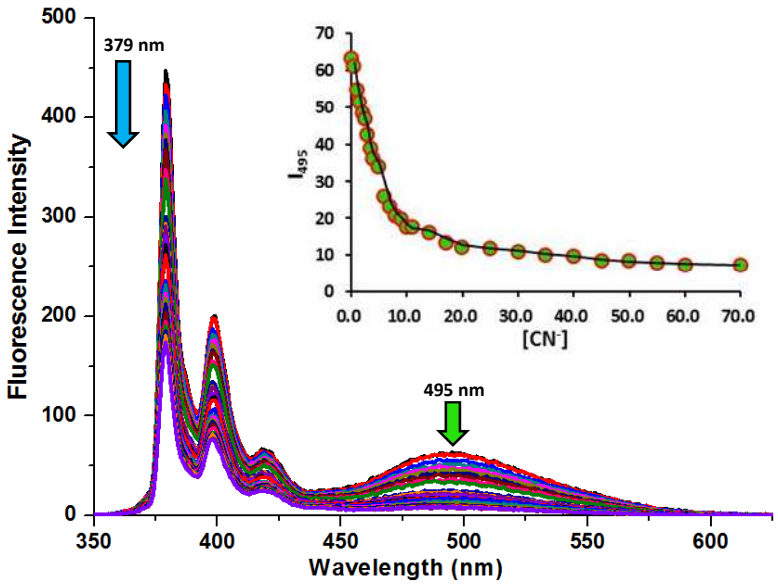


Fig. 3: Fluorescence titration of probe **2** (1 µM, PBS -EtOH (5:95), pH = 7.4) with TBACN; λ_{ex} = 336 nm, slit width 3, 3. The inset shows the curve fitting; points and lines represent the experimental values and curve fitting at I_{495} vs [CN^- µM]), respectively.

Table 1: Association constants K_a (M^{-1}) of probes **1** and **2** titrated with a solution of PBS-EtOH (5:95, pH = 7.4) containing TBACN.

	Association constant K_a (M^{-1}) with probes **1** and **2**	
	1	**2**
CN^-	1.71×10^3	2.32×10^5

Table 1 clearly shows that in the case of probe **2**, the π-π interaction between the pyrene rings, in addition to the two positive charges and four hydrogen bonding sites (two sulfonamide N-H and two imidazolium C2-H groups), leads to an association constant with CN^- that is 135 times larger than the corresponding value for the neutral probe **1**.

To further investigate the nature of these interactions and the complexation mode of CN^- with probes **1** and **2**, ^1H NMR studies with TBACN were carried out. The ^1H NMR spectra of probe **2** in D_2O-CD_3CD_2OD (1:6), showed that imidazole C2-H i.e. H_a get exchanged with deuterium, due to its more active nature whereas other imidazole protons H_b and H_c appears as two different signals as while other protons of pyrene and benzene rings of probe **2** observed as more clear as compared to its ^1H NMR spectra in DMSO-d_6.

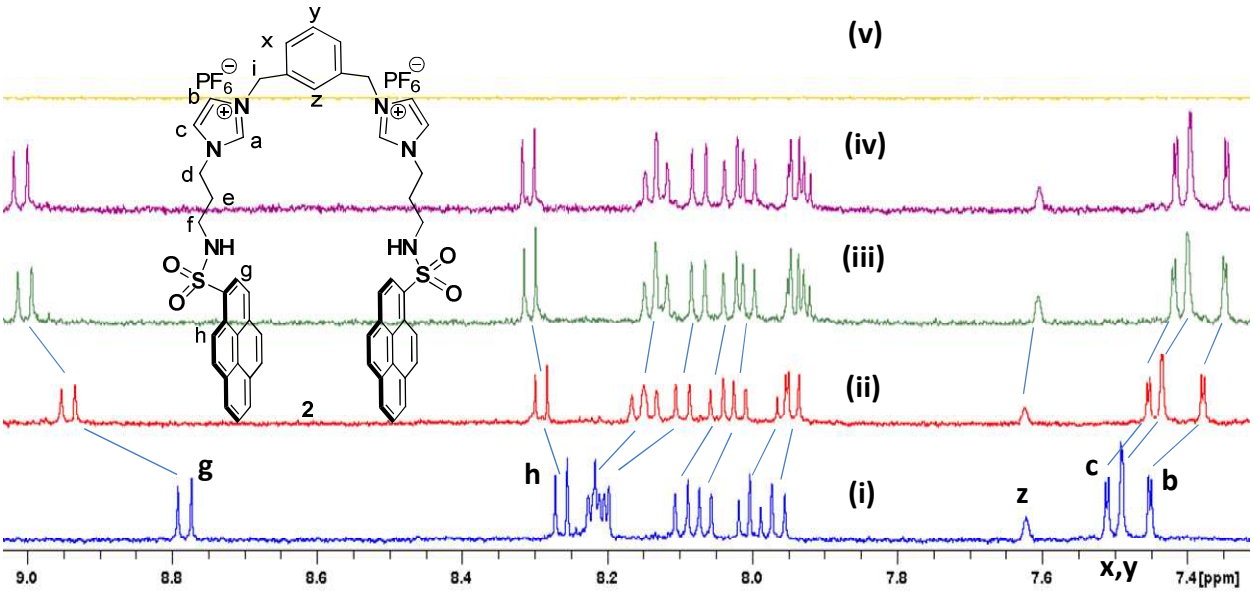


Fig. 4: (i) Partial ^1H NMR spectra of probe **2**; and (ii) upon addition of 1 eq. of TBACN; (iii) 2 eq. of TBACN; (iv) 3 eq. of TBACN; and (v) only TBACN in D_2O-CD_3CD_2OD (1:6).

Addition of 1 equiv of TBACN to the solution of probe **2** in D_2O-CD_3CD_2OD (1:6) leads to a significant downfield shift of the proton at α-position to the sulfonyl group (labeled as H_g) and proton H_g from δ 8.780 to 8.940 and from δ 8.260 to 8.290, respectively. Other protons of the

pyrene ring shifted upfield; while imidazole protons H_b and H_c shifted upfield from δ 7.450 to 7.378 and from δ 7.510 to 7.453, respectively. In addition, the H_x, H_y protons of the benzene ring shifted upfield, while the aliphatic protons H_i, H_d, H_e and H_f shifted upfield. After adding 2 equiv of TBACN, the H_g and H_h protons further shifted downfield, from δ 8.940 to 9.010 and from 8.290 to 8.307, respectively and H_b and H_c protons of the imidazole ring shifted further upfield from δ 7.378 to 7.348 and from δ 7.453 to 7.418, respectively. Other protons showed a similar behavior, i.e., they further shifted upfield. Addition of 3 equiv of TBACN caused no further shift, indicating the formation of a 1:2 complex between probe **2** and CN^- ions (Fig. 4, and Figs. SI 11).

In order to know the role of imidazole C2H, ^{1}H NMR study of probe **2** with TBACN was also done in DMSO-d_6, in this case imidzolium C2H i.e. H_a appeared at δ 9.16 which is exchanged with deuterium in D_2O-CD_3CD_2OD (1:6), whereas other imidazole protons H_b and H_c appears as merged together to appear as singlet for four protons at δ 7.68 in DMSO-d_6 (Figs. SI 12 - 13), and on addition of 1-3 equiv of TBACN to probe **2** in DMSO-d_6 the interaction behavior was found to be similar as in D_2O-CD_3CD_2OD (1:6). In this case, significant downfield shift of the imidazole C2H i.e. H_a proton on addition of TBACN clearly shows the formation of hydrogen bonding with CN^- ion. A full set of chemical shift differences is listed in Table 2. The chemical shift behavior with TBACN of probe **2** found to be nearly same in D_2O-CD_3CD_2OD (1:6) and DMSO-d_6. So, due to good solubility of probe **1** in DMSO-d_6, its ^{1}H NMR study with TBACN was carried out in DMSO-d_6.

Addition of 1 equiv of TBACN to the solution of probe **1** in DMSO-d_6 led to a significant downfield shift of the H_g protons from δ 8.977 to 9.037; other protons of the pyrene ring shifted upfield. Similarly, the H_a, H_b, and H_c protons of the imidazole ring shifted upfield, from δ 7.356 to 7.338, from 6.722 to 6.707, and from 6.882 to 6.868, respectively. In addition, the aliphatic protons H_d, H_e, and H_f shifted upfield, from δ 2.736 to 2.726, from 1.694 to 1.671, and from 3.831 to 3.827, respectively. After adding 2 equiv of TBACN, no further shift changes were observed, confirming the formation of a 1:1 complex between probe **1** and CN^- (Table 2 and Figs. SI 14 - 16).

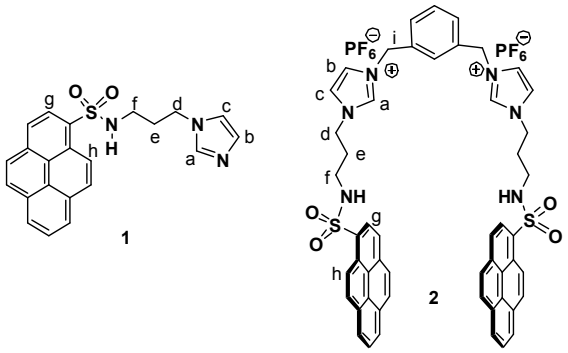


Table 2: Chemical shift differences (Δ δ) of each proton upon addition of TBACN to a solution of D_2O-CD_3CD_2OD (1:6) containing probes **1** and **2**.[a]

Protons	2 (Δ δ)	2 (Δ δ)[b]	1 (Δ δ)[b]
a	-----	0.118	-0.018
b	-0.102	-0.012	-0.015
c	-0.092	0.018	-0.014
d	-0.047	-0.043	-0.010
e	-0.133	-0.078	-0.023
f	-0.059	0.020	-0.004
g	0.230	0.180	0.060

h	0.047	-0.033	-0.012
i	-0.098	-0.002	------

[a]Positive and negative values indicate downfield and upfield shifts of the protons in the ^{1}H NMR spectra respectively, [b]chemical shifts observed in DMSO-d_6.

To understand the mode of complexation between CN^- ions and probes **1** or **2**, we have carried out the energy minimization calculations using B3LYP/6-31G* level by Spartan 04 software.[15] The optimized structures of probes **1** and **2** and their complexes with CN^- ions are presented in Fig. 5. The molecular calculation of the **1**•CN^- complex showed that the sulfonamide NH and imidazole C2H form hydrogen bonds with CN^- ion i.e. a = 1.783, b = 2.542 Å. In probe **2**, the calculated distance between the two pyrene moieties was found to be 3.764 Å, which is similar to that of many other π-π interacting systems.[16] In case of **2**•2(CN^-) complex the hydrogen bond distances of sulfonamide NH and imidazole C2H with CN^- ion found to be as: a = 2.007, b = 1.750, a' = 2.041, b' = 1.899 Å. The decreased hydrogen bond distance between imidazole C2H and CN^- ion (i.e. b and b') in probe **2** as compared to that of probe **1** (i.e. b) clearly showed that after the development of positive charge on imidazole nitrogen, CN^- ion binds more strongly with imidazole C2H whereas the electron density repulsion between two CN^- ions lead to the unlocking π-π interaction of pyrene rings in probe **2** (Fig. 5). Using B3LYP/6-31G* we obtained HOMO and LUMO of probes **1** and **2** and their CN^- ion complexes that also support the mechanism of CN^- ion interaction with probes **1** and **2**. Electronic transitions are predominantly characterized by HOMO → LUMO at the excited state geometry and it is found that on binding of CN^- ion with probe **1** the HOMO-LUMO energy difference decreased while in

case of probe **2** due to the unlocking of the π-π interactions between pyrene rings the HOMO-LUMO energy difference increased in spite of CN^- ion binding (Fig.'s SI 17- SI 18).

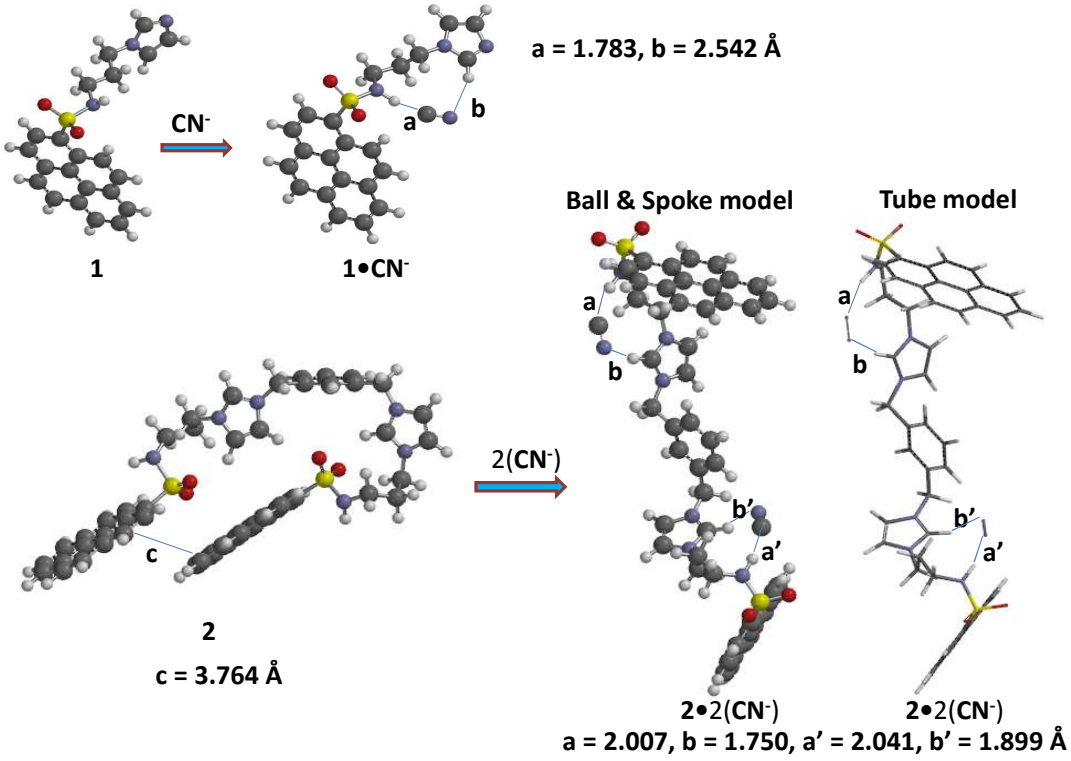


Fig. 5: Energy minimized geometries of probe **1** and **2** and their CN^- ion complexes by using B3LYP/6-31G* respectively.

The ^1H NMR, fluorescence titrations and Job's plot of probe **2** with TBACN clearly showed the formation of a 1:2 complex between probe **2** and CN^-; in addition, the quenching of the green excimer emission clearly indicated the unlocking of the π-π interaction between the pyrene rings. Moreover, our data showed that the electrostatic repulsions between the two CN^- ions on the same side of the complex reduce its stability. Thus, in order to achieve stability, probe **2**

adopts a flip-up/open-up configuration, which is characterized by no green emission. This is also evident from molecular modeling (Fig. 5) The maximum downfield shift of the imidazolium C2-H protons (H_a and H_g protons in the α-position to the sulfonamide group) confirmed that the sulfonamide N-H and imidazolium C2-H form hydrogen bonds with CN^-. The proposed mechanism of CN^- ion sensing with probe **2** is shown in Fig. 6. Therefore, the synergistic effects of the hydrogen bonding, ionic interactions between opposite charges, and π-π interactions between pyrene moieties of probe **2** lead to strong binding affinity toward CN^- ions in aqueous solution.

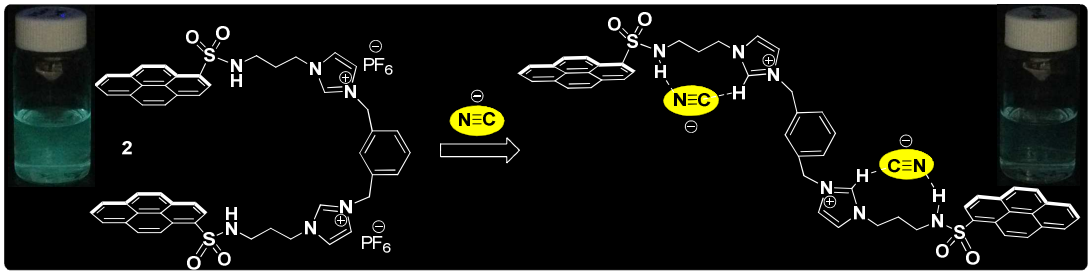


Fig. 6: Proposed complexation mechanism of probe **2** with CN^-.

Ratiometric sensing provides the additional opportunity to detect a particular analyte independent of the concentration of chemosensor. In case of probe **2**, the dissociation of excimer induced by CN^- ions favor the monomer formation, while CN^- ions also triggered the decrease of monomer emission (in case of probe **1**), whereas the different decrease rates for monomer emission and excimer emission band observed. Therefore, the ratiometric CN^- ion sensing ability of probe **2** is proposed and lead to CN^- ion detection between 0.5-60 µM (Fig. SI 19-SI 20).

Probe **2** act as a unique selective, sensitive and ratiometric CN^- ion sensor through synergic effects of π-π interaction, ionic interaction, and hydrogen bonding in aqueous solution as compared to other CN^- ion sensors such as chemodosimeter reaction/ nucleophilic attack [5, 6, 7] in which the sensing behavior was observed through addition reaction that was irreversible and also temperature, time dependent whereas response of probe **2** towards CN^- ion is quick. In case of metal coordination for CN^- ion sensing there are two different approaches: (a) metal ion displacement reactions,[11, 17] and (b) metal complexes as receptors.[18] Both these cases are two step processes, first the preparation of metal complex and then CN^- ion sensing with more often low detection limit, in comparison to these sensors our probe **2** act as single step sensor for CN^- ion with good detection limit 0.5 µM (13 ppb).

Conclusions

In conclusion, our data showed that the visual detection of CN^- under illumination at 365 nm is mainly facilitated by a combination of π-π interaction, hydrogen bonding, and ionic interaction between opposite charges in probe **2**. The repulsion between the two CN^- ions induces flipping of the pyrene rings of probe **2**, which results in unlocking of the system in aqueous solution. This is the first report for selective CN^- sensing in aqueous systems having hybrid pyrenesulfonamide and imidazolium salts through hydrogen bonding due to *"switch of"* green emission. Finally, the lowest detection limit for CN^- estimation was determined to be 0.5 µM (13 ppb), which is lower than the permissible limit for drinking water established by the WHO.

Experimental section

General

Melting points were determined using a Thomas-Hoover capillary melting-point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer using Me_4Si as the internal standard. FAB mass was determined at the KBSI Daegu branch. UV–Vis absorption spectra were determined using a Shimadzu UV-1650PC spectrophotometer. Fluorescence spectra were measured on a Shimadzu RF-5301 fluorescence spectrometer equipped with a xenon discharge lamp using quartz cells (1 cm, with slit 3). All the measurements were performed at 298 K. Analytical-grade ethanol was purchased from Merck. All other materials were purchased from Aldrich Chemical Co. and used as received. Quantum yield (Φ) was calculated using a procedure previously reported.[19]

Synthesis of probes 1 and 2

Pyrene-1-(3-imidazol-1-yl-propyl)-sulfonamide probe 1

To a solution of pyrenesulfonic acid (500 mg, 1.8 mmol) in dimethylformamide (10 mL) was added thionyl chloride (0.79 mL, 6.0 mmol), and the solution stirred at 0 °C under argon atmosphere for 3 h. After the reaction was complete, the reaction mixture was poured into ice. The yellow precipitate was filtered and washed with water. The solid was dried overnight for 12 h at 50 °C. The required pyrenesulfonyl chloride was further purified by column chromatography using CH_2Cl_2 as the eluent (R_f = 0.85), with a yield of 70% (373 mg); m.p. 169 ^{o}C.[14] A solution of pyrenesulfonyl chloride (373 mg, 1.24 mmol) in CH_2Cl_2 (22 mL) was added dropwise to the stirred solution of 1(3-aminopropyl)imidazole (250 mg, 2.0 mmol) in CH_2Cl_2 (5

mL) at 0 °C under argon atmosphere. After the addition was complete, the reaction mixture was further stirred at room temperature for 2 h. The CH_2Cl_2 layer was washed with H_2O (2 x 50 mL) and 5% aqueous NaCl (100 mL), then dried over anhydrous sodium sulfate, and finally filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography with CH_2Cl_2: CH_3OH (9:1) as the eluent (R_f = 0.15) to give a light yellow solid **1** (344 mg, 71% yield). m.p. 200°C (CH_2Cl_2-hexane); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.68-1.72 (m, 2H, CH_2), 2.74 (t, *J* = 6.8 Hz, 2H, CH_2), 3.84 (t, *J* = 6.8 Hz, 2H, CH_2), 6.72 (s, 1H, ArH), 6.85 (s, 1H, ArH), 7.36 (s, 1H, ArH), 8.23 (t, *J* = 7.6 Hz, 1H, ArH), 8.31 (d, *J* = 9.1 Hz, 1H, ArH), 8.41 (d, *J* = 8.8 Hz, 1H, ArH), 8.44 (d, *J* = 8.3 Hz, 1H, ArH), 8.48-8.51 (m, 3H, 3 x ArH), 8.57 (d, *J* = 8.1 Hz, 1H, ArH), 8.99 (d, *J* = 9.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 31.07 (CH_2), (one CH_2 merged with DMSO-d_6 signal), 43.38 (CH_2), 119.43, 123.54, 123.63, 124.64, 124.66, 127.14, 127.26, 127.46, 127.49, 127.57, 128.62, 129.97, 130.04, 130.39, 130.90, 132.52, 134.39, 137.40; HR-FAB mass calcd for: $C_{22}H_{19}N_3O_2S$ $(M+H)^+$: 390.1276; Found: *m/z* 390.1273.

Pyrenesulfonyl imidazolium probe 2.

To a solution of pyrenesulfonamide imidazole (**1**, 195 mg, 0.5 mmol) in CH_3CN (20 mL) was added 1,3-bis(bromomethyl)benzene (65 mg, 0.25 mmol), and the mixture was stirred at 90 °C under argon atmosphere for 30 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was dissolved in MeOH and stirred at room temperature. An aqueous solution of KPF_6 (184 mg, 1.0 mmol) was then added dropwise to the methanolic solution and stirred for 3 h. The solid was filtered, washed with distilled water and methanol, and finally dried to give a light yellow solid **2** (180 mg, 61% yield). m.p. 130 °C

(CH_2Cl_2-hexane); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.86-1.93 (m, 4H, 2 x CH_2), 2.76-2.81 (m, 4H, 2 x CH_2), 4.15 (t, *J* = 7.2 Hz, 4H, 2 x CH_2), 5.36 (s, 4H, 2 x CH_2), 7.33 (d, *J* = 7.2 Hz, 2H, 2 x ArH), 7.40-7.44 (m, 2H, 2 x ArH), 7.68 (s, 4H, 4 x ArH), 8.19-8.27 (m, 4H, 4 x ArH), 8.39 (d, *J* = 8.8 Hz, 4H, 4 x ArH), 8.45-8.49 (m, 6H, 6 x ArH), 8.51 (d, *J* = 8.4 Hz, 2H, 2 x ArH), 8.94 (d, *J* = 9.2 Hz, 2H, 2 x ArH), 9.16 (s, 2H, 2 x ArH i.e imidazolum C2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 28.34, (one signal for two CH_2 merged with DMSO-d_6 signal), 45.30, 50.53, 121.43, 121.60, 122.01, 123.07, 123.17, 125.49, 125.77, 125.94, 125.97, 126.02, 126.11, 127.13, 127.35, 128.52, 128.61, 128.95, 129.39, 130.76, 132.91, 134.21, 135.27; HR-FAB mass calcd for: $C_{52}H_{46}F_6N_6O_4PS_2$ $(M + PF_6)^+$: 1027.2658; Found: *m/z* 1027.2667.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT and Future Planning (2013R1A1A2006777), and by the Kyungpook National University Research Fund, 2014.

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