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Synthesis and chemosensitivity of a new iminium salt toward a cyanide anion

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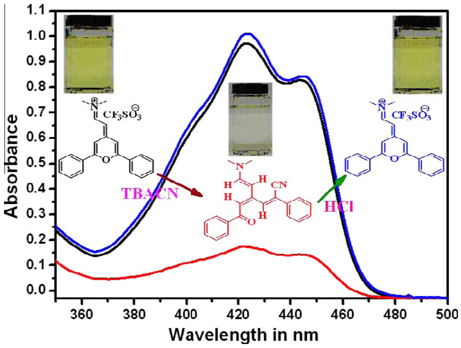
HIGHLIGHTS

- Synthesis of a new pyranylidene iminium (**Imi**) salt in high yields (92%).
- Pyranylidene iminium (**Imi**) salt can be used to determine CN^- ion with high selectivity.
- **Imi** salt attracts the nucleophilic CN^- ion to form the cyano-enone structure.
- Selective binding leads to ~171 nm [423–252 nm] hypsochromic (blue) shift.
- The binding mechanism and product identity were confirmed using FT-IR studies.

GRAPHICAL ABSTRACT



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ABSTRACT

A short, high-yielding route to pyranylidene Iminium (**Imi**) salts using a new pyrylium salt reaction between N,N-Dimethylformamide (DMF) and acetic anhydride is reported. The **Imi** salt-sensing behavior toward various anions has been investigated using UV–Visible spectroscopy. The **Imi** salt demonstrates high selectively for CN^- when various other anions, such as CN^-, Cl^-, Br^-, I^-, SCN^-, ClO_4^-, NO_3^-, HSO_4^-, PF_6^- and N_3^-, are present because it is highly reactive towards nucleophiles. The selective detection of CN^- with the **Imi** unit gave rise to a significant hypochromic shift in the CH_3CN solution at λ_{max} = 444 nm and 423 nm and creation of new peak at 252 nm. These studies indicated that CN^- had high affinity toward **Imi**, forming a 1:1 complex; this observation agrees with the current understanding of these materials.

Introduction

The first pyrylium and pyranylideneiminium (**Imi**) salts were synthesized nearly 100 years ago. During the first half of the present century, interest in these compounds was reasonable [1]. Among the six membered heterocycles containing one heteroatom, the pyrylium cation is the most strongly perturbed benzenoid system with a low aromaticity [2,3]; however, pyrylium salts are good synthons for numerous chemical reactions and a nodal point for many synthetic routes. They may function as intermediates for various synthetic applications [4]. Pyrylium rings are able to react with different nucleophiles according to the steric or electronic effects caused by the substituents; the nucleophile may also selectively add in either the α- or γ-position to create 2H- or 4H-pyrans, respectively, Unless the γ-position is unsubstituted or the nucleophile is small or unselective (e.g., hydrides, Grignard reagents), addition to the α-position is preferred because the α-position is more electron deficient than the γ-position. Both positions may undergo subsequent reactions to generate acyclic end products

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that may be converted into other ring systems [5]. One of the more important pyrylium ring transformation reactions is the generation of **Imi** salts. Pyrylium salts containing active methyl groups produce mono-iminium salts with DMF in acetic anhydride using the Vilsmeier complex. Donor–acceptor (D–A) **Imi** salt derivatives are interesting because they have interesting optical properties. Therefore, **Imi** salt derivatives are well-known laser dyes, and many of these derivatives are also useful red dopants for organic light-emitting diodes (OLED) [6]. In most cases, the pyranylidene moiety is incorporated into the π-spacer, generating either one-dimensional (1D) or two-dimensional (2D, also called V-shaped) [7] nonlinear optical (NLO) D–A and D–A–D type chromophores, respectively [8–10]. We have synthesized new 4-methyl 2,6-diphenyl pyrylium trifluoromethanesulfonate and **Imi** salts. These salts were described previously with different counter anions. The reported method used to synthesize **Imi** salts involved 4-methyl 2,6-diphenyl pyrylium perchlorate and DMF reacting within acetic anhydride [11,12].

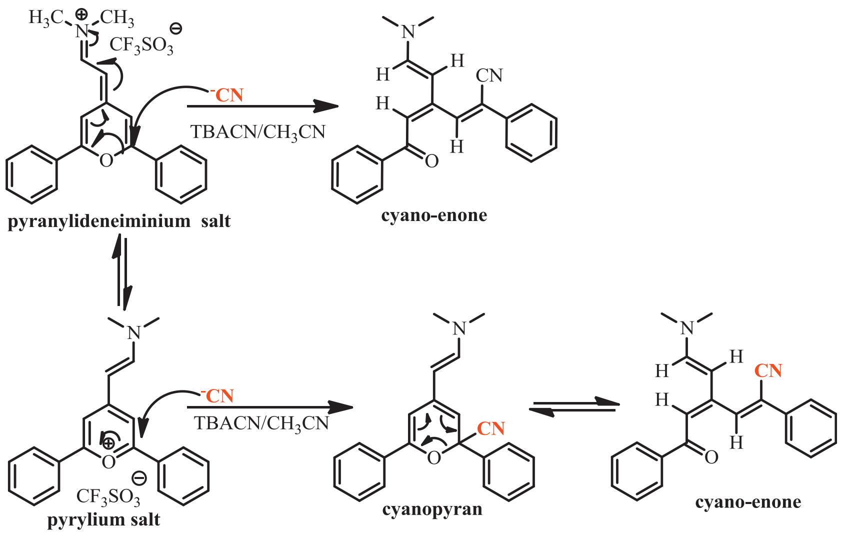
Anion sensors are important in biological, environmental, and industrial processes. Cyanide (CN^-) is the most toxic inorganic anion; it is acutely toxic to mammals when administered through any route, causing death in minutes [13]. CN^- strongly interacts with the cytochrome a_3 active sites and inhibits cellular respiration in mammalian cells [14,15]. Cyanide fishing [16] also pollutes waters in areas used for fishing for exotic fish, such as the coral reefs, and is a component of tabun, which is a chemical warfare agent [17]. Currently, various analytical methods have been developed to determine cyanide ion content, such as chromatographic [18], fluorometric [19], flow injection [20] and electrochemical [21] analyses. Many analytical techniques, such as potentiometry, chromatography and flow injection have been developed to detect cyanide [22,23]. Recently, nucleophilic addition of cyanide to pyrylium salt derivatives has also been adopted to sense CN^- [24]. This type of recognition exploits the nucleophilicity of the cyanide ion and enables the construction of a system that recognizes the characteristic features of CN^-, generating a specific response. C—C bond formation was observed with the pyrylium salt and its derivatives when used as colorimetric sensors for cyanide ions. The pyran's electrophilicity and CN^-'s nucleophilicity combine to form cyano-enone derivatives in CH_3CN solution [25,26]. Consequently, this reaction-based method might be developed to create a platform for discovering new **Imi** salts resembling sensors that may be potentially useful to detect CN^- in industrial, environmental, and biological capacities. Based on earlier reports, we propose the binding mechanism between **Imi** and CN^- ions, as displayed in Scheme 1.

Based on this hypothesis, we designed and synthesized a new small molecular sensor pyranylidene iminium (**Imi**) salt based on a pyrylium salt derivative and a suitable chromogenic organic group to develop a new chromogenic with enhanced sensing properties. We describe the synthesis and the binding properties of **Imi** salt chemosensor that display highly selective absorption changes with cyanide in the presence of various anions. We have explored a new one-pot synthesis to prepare the 4-methyl 2,6-diphenyl pyrylium trifluoromethanesulfonate salt using benzoyl chloride, anhydrous *t*-butyl alcohol and trifluoromethanesulfonic acid in high yields (>90%) for the primary step. Finally, reacting the pyrylium salt with DMF and acetic anhydride produces the **Imi** salt in high yields (>92%), as presented in Scheme 2. The sensor performance was not affected by other ions, demonstrating the high selectivity of this sensor toward cyanide. Therefore, in this paper we wish to report the design and synthesis of an **Imi** salt and its unique interaction with cyanide ion.

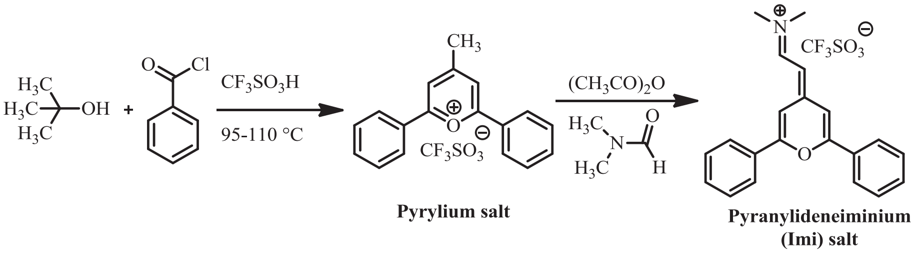
Materials and methods

Materials and apparatus

All solvents and reagents (analytical grade and spectroscopic grade) were obtained commercially and used as received unless otherwise noted. AVANCE III 600 Magnet: Ascend™ series, 14.1 T, ^1H resonance frequency 600 MHz, ^{13}C resonance frequency 150 MHz, Top Spin 3.1 (software), Germany and JNM-AL400, 9.4 T, ^1H resonance frequency 400 MHz, ^{13}C resonance frequency 100 MHz, Alice 4.0 (software), Akishima, Japan spectrometers respectively, in CF_3COOD, DMSO-d_6 and $CDCl_3$ solvents were purchased from Sigma–Aldrich. The chemical shifts (δ values) were reported in ppm down field from an internal standard (Me_4Si) (^1H and ^{13}C NMR). The mass spectra were recorded with a JEOL MStation [JMS-700] mass spectrometer. FTIR spectra were recorded with a FTS-175C spectrometer (Bio-laboratories, Cambridge, USA). Melting points were recorded with a Bamstead electrothermal (UK) apparatus and are reported uncorrected. Elemental analyses were performed with a Carlo Elba Model 1106 analyzer. UV–Visible absorption spectra were recorded with an Agilent 8453 spectrophotometer. HOMO/LUMO (Highest Occupied Molecular Orbital/Lowest Unoccupied Molecular Orbital) calculations



Scheme 1. A plausible mechanism for the formation of the pyranylidene iminium salt (**Imi** salt) and its cyano-enone derivatives.



Scheme 2. Synthesis of the pyranylidene iminium salt (**Imi** salt).

and modeling simulations were conducted with $DMol^3$ in the *Material Studio 4.3 suite*. The anions were introduced as tetra-butyl ammonium (TBA) salts and were purchased from Sigma–Aldrich and Alfa–Aesar Chemical Reagent Co.

General spectroscopic methods

TBA salts and **Imi** salt were dissolved in CH_3CN to obtain 1×10^{-3} M stock solutions. Before the spectroscopic measurements, samples were freshly prepared by diluting the concentrated stock solution to the required concentration. All of the experiments were conducted at ambient pressure and room temperature.

Synthesis of 4-methyl 2,6-di-phenyl-pyrylium trifluoromethanesulfonate

A 500 mL three neck round bottom flask was equipped with a temperature probe, a magnetic stir bar and a nitrogen inlet adaptor with a dry ice condenser. Next, 24 g (0.2 mol) of benzoyl chloride and 3.7 g (0.05 mol) of anhydrous *t*-butyl alcohol was loaded into the round bottom flask and the condenser was filled with acetone-dry ice. The reaction mixture was heated to 95 °C with stirring. Subsequently, 15 g (0.1 mol) of trifluoromethanesulfonic acid was added with stirring over 2–3 min. After the addition was complete, the temperature was raised to 105–115 °C and the mixture was allowed to react for 20 min. Later, the reaction mixture color changed to brown, and it was allowed to cool to 50 °C before being cooled to −10 °C in an ice-salt bath. A precipitate formed while adding the 100 mL of cold diethyl ether to the reaction mixture. After precipitation, the mixture was filtered using a Buchner funnel; the collected solid was washed with diethyl ether (3 × 100 mL) and dried over P_2O_5 to give 17.86 g of the title compound (Yield 90.32%).

M.P = 283–285 °C; IR (KBr): 3072, 1629, 1518, 1271, 1148, 1030, 635 cm^{-1}; ^1H NMR (600 MHz, CF_3COOD): δ 3.26 (s, 3H), 8.08 (t, 4H, J = 7.34 Hz), 8.19 (t, 2H, J = 7.34 Hz), 8.59 (d, 4H, J = 3.76 Hz), 8.61 (s, 2H) ppm; ^{13}C NMR (150 MHz, CF_3COOD): δ 25.1, 121.1, 130.1, 130.4, 132.7, 138.6, 174.2, 176.4 ppm; ESI-MS (m/z): 247.3 $[M]^+$ (100) for the pyrylium cation and 148.9 $[M]^+$ (100) for the trifluoromethanesulfonate anion; Elemental Analysis calcd (%) for $C_{19}H_{15}F_3O_4S$: C, 57.57; H, 3.81; F, 14.38; O, 16.15; S, 8.09; found: C, 57.43; H, 3.85; O, 16.43; S, 7.98.

*Synthesis of pyranylidene iminium (**Imi**) salt*

A mixture of 3.96 g (0.01 mol) of 4-methyl 2,6-diphenyl pyrylium trifluoromethanesulfonate salt, 2.3 mL (0.03 mol) of DMF and 80 mL of acetic anhydride was refluxed for 15 min and allowed to cool. If no product separated, ether (100 mL) was added to the solution to initiate precipitation. The precipitate was collected via filtration, recrystallized from methanol and dried to produce 4.15 g of the desired compound with a 92.1% yield.

M.P = 223–225 °C; IR (KBr): 3074, 2917, 1594, 1528, 1488, 1454, 1405, 1148, 1028, 926, 724 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ + DMSO-d_6): δ 3.22 (s, 3H), 3.48 (s, 3H), 5.79 (d, 1H, J = 12.19 Hz), 7.29 (s, 1H), 7.52 (d, 6H, J = 7.07 Hz), 7.90 (d, 2H, J = 7.07 Hz), 7.94 (s, 1H), 8.03 (d, 2H, J = 7.07 Hz), 8.79 (d, 1H, J = 12.19 Hz) ppm; ^{13}C NMR (150 MHz, $CDCl_3$ + DMSO-d_6): δ 37.78, 45.98, 99.0, 103.17, 109.03, 125.14, 128.39, 129.42, 131.22, 155.63, 158.49, 159.96 ppm; ESI-MS (m/z): 302.4 $[M]^+$ (100) for the iminium cation and 148.9 $[M]^+$ (100) for the trifluoromethanesulfonate anion; Elemental Analysis calcd (%) for $C_{22}H_{20}F_3NO_4S$: C, 58.53; H, 4.47; F, 12.62; N, 3.10; O, 14.18; S, 7.10; found: C, 58.43; H, 4.45; N, 3.03; O, 15.51; S, 6.92.

Results and discussion

Photophysical properties

The sensing activity was investigated by adding various anions using TBA salts (CN^-, Cl^-, Br^-, I^-, SCN^-, ClO_4^-, NO_3^-, HSO_4^-, PF_6^- and N_3^-) to the **Imi** salt in CH_3CN. When one equivalent (equiv.) of CN^- ion (2×10^{-5} M) relative to the **Imi** salt (2×10^{-5} M) was added, color changes were identifiable with the naked eye. Excitingly, the **Imi** salt demonstrated sensing behavior using color changes from yellow to colorless, as presented in Fig. 1. Other experiments demonstrated that the complex formed between the **Imi** salt and the cyanide ion was highly selective. We report the experimental results in detail.

UV–Visible spectroscopic studies

The UV–Vis absorption changes in the **Imi** salt solution (2×10^{-5} M) after adding various anions (CN^-, Cl^-, Br^-, I^-, SCN^-, ClO_4^-, NO_3^-, HSO_4^-, PF_6^- and N_3^- (1 equiv. each)) were also explored. After adding 1.0 equiv. of CN^- ion to an **Imi** salt solution, the original absorption bands at 444 nm and 423 nm greatly decreased (see Fig. 2). However, the addition of other anions (1 equiv.) did not cause any apparent color or spectral change. One characteristic property of the **Imi** salt pyran ring is its vulnerability toward nucleophilic addition; additionally the selectivity of **Imi** salt for CN^- in CH_3CN validates the high nucleophilicity of cyanide.

To study the binding properties of the sensing **Imi** salt with CN^-, we measured the UV–Vis spectra of the **Imi** salt (2×10^{-5} M) with various concentrations of CN^- (0–2.5 equiv.), as presented in Fig. 3. During the photometric titrations of **Imi** using CN^- (0–2.5 equiv.), a gradual decrease in the absorbance's at 444 nm and 423 nm were observed, indicating only one CN^- complex had formed. In addition a new peak at 252 nm is shown in Fig. 3 inset absorption spectra along by isosbestic point through 331 nm. The absorption spectrum remained at a plateau when more CN^- (>1.0 equiv) was added, implicating a 1:1 complex between the sensor and the CN^- ion, and a color change from yellow to colorless was observed. The color change of the **Imi** salt after CN^- was added may be caused by cyanopyran formation during the first step; this compound is readily converted into a cyano-enone derivative through tautomerization (see Scheme 1).

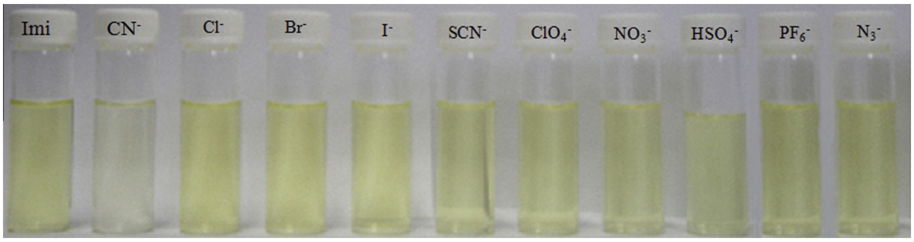


Fig. 1. Photograph (naked eye) of solutions containing various anions (2×10^{-5} M) and **Imi** (2×10^{-5} M) in CH_3CN: **Imi**, CN^-, Cl^-, Br^-, I^-, SCN^-, ClO_4^-, NO_3^-, HSO_4^-, PF_6^- and N_3^- (from left to right).

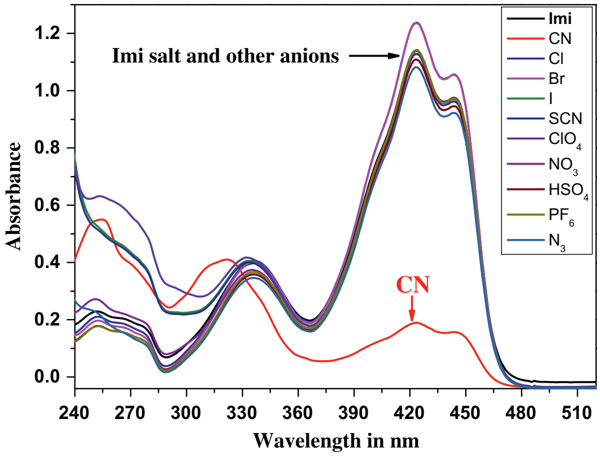


Fig. 2. Absorption spectra of the **Imi** salt (2×10^{-5} M) combined with different anions (2×10^{-5} M) in CH_3CN.

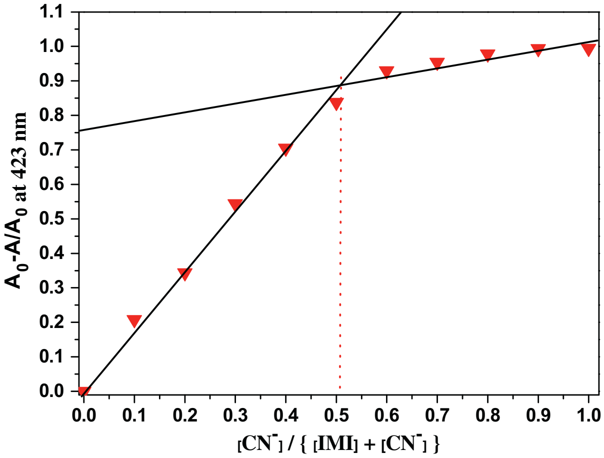


Fig. 4. Job plot for **Imi** salt absorbance at 423 nm ($A_0 - A/A_0$) *Vs* mole fraction of the CN^- in CH_3CN solution.

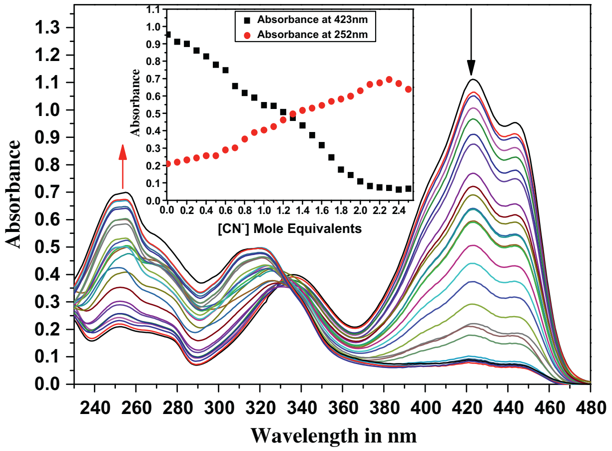


Fig. 3. Absorption spectra of the **Imi** salt (2×10^{-5} M) combined with various concentrations of CN^- (0–2.5 equiv.) for titration in CH_3CN. Insert: absorbance at 423 nm and 252 nm.

In addition, binding stoichiometry experiments were carried out to explore the interference abilities of CN^-. The binding stoichiometry between the **Imi** salt (2×10^{-5} M) and CN^- (2×10^{-5} M) was essential to the sensing properties. A Job's plot also indicated that a 1:1 stoichiometric ratio was necessary for **Imi** salt and CN^- complex formation, as indicated by the absorption spectra at 423 nm in CH_3CN (Fig. 4). The $(A_0 - A)/A_0$ absorption at 423 nm were plotted against different molar fractions of the **Imi** salt and CN^-, demonstrating that their maximum intensity occurred at a 0.5 stoichiometric ratio. Suitable to the binding nature of **Imi** salt with CN^- ion absorbance after 0.5 ratio is almost constant. These results also meet the requirements for complex formation in a 1:1 ratio. Therefore, the oxygen atom in the pyran ring of the **Imi** salt attracts the nucleophilic CN^- ion (1 equiv.) to form the cyano-enone structure.

To become a highly selective probe for the target analyte, a good tolerance for disturbance is required. Therefore, competition experiments were examined using absorption spectra. The high sensitization of the **Imi** salt toward the CN^- ion was demonstrated during extreme competition. Of the 10 different anions surveyed under identical conditions, including Cl^-, Br^-, I^-, SCN^-, ClO_4^-, NO_3^-,HSO_4^-,PF_6^- and N_3^-, the absorption response of the **Imi** salt works exclusively for CN^- ion with an intense and consistent hypochromic shift at 423 nm (as shown in Fig. 5). An **Imi** salt solution was treated with all 10 different anions combined and exhibited only a weak background signal in absorption intensity at 423 nm. The **Imi** salt's absorption turn-off detection by CN^- relies on a clean and rapid C—C bond formation under ambient conditions (see Scheme 1). These results demonstrate **Imi**'s exclusive selectivity toward CN^-.

The CN^- ion's reactivity with the pyran ring of the **Imi** salt is reversible; in the presence of an acidic solution, the **Imi** salt derivative might be retrieved. Therefore, the possibility of attaining a reusable colorimetric **Imi** salt was tested by regenerating the **Imi** salt by reacting the cyano-enone derivative with acid to obtain the original **Imi** salt. An **Imi** salt saturated with CN^- was added to aqueous hydrochloric acid (2×10^{-5} M), and the original color of the **Imi** salt solution was recovered and observed in the absorption spectrum (see Fig. 6). This acidic treatment also reversed the ring-opening caused by the HCl conditioning. When the absorption for the pure **Imi** salt was observed at 423 nm and 444 nm, a hypochromic shift occurred after adding CN^-. Addition of hydrochloric acid to the **Imi**-CN^- complex (saturated) solution, regenerated

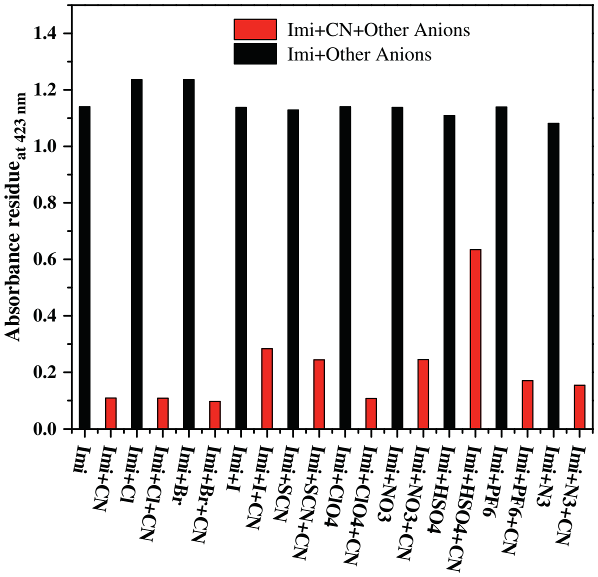


Fig. 5. Sensitization competition between CN$^-$ and other anions, such as Cl$^-$, Br$^-$, I$^-$, SCN$^-$, ClO$_4^-$, NO$_3^-$, HSO$_4^-$, PF$_6^-$ and N$_3^-$. The black bars represent the absorption of the **Imi** salt when combined with 1 equiv. of an anion. The red bars indicate the change in the absorption (423 nm) that occurs when 1 equiv. of CN$^-$ ion is added to a solution containing **Imi** and the anion of interest.

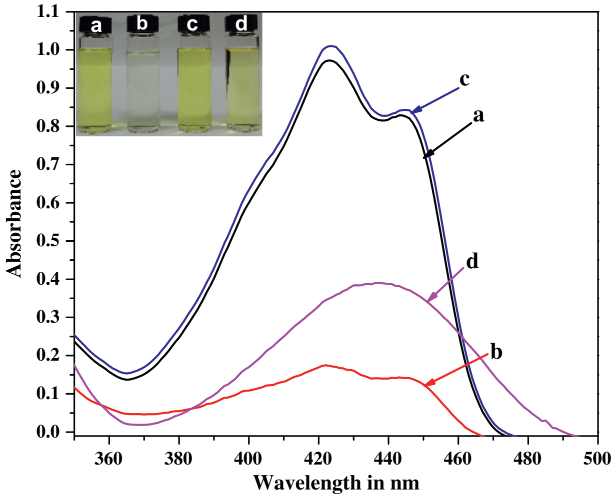


Fig. 6. Absorption spectra of the pure **Imi** salt (2×10^{-5} M) with CN$^-$ (2×10^{-5} M) during the ion turn-off/turn-on sensitization method using aqueous HCl (2×10^{-5} M) and another equivalent of CN$^-$ (2×10^{-5} M) ion turn-off absorption at 440 nm.

the original absorbance profile of the **Imi** salt. Finally, after a second equivalent of CN$^-$ ion was added to the HCl-treated solution, the absorbance of the **Imi** salt was not eliminated. The trifluoromethanesulfonic acid (Triflic acid, super acid) [27,28] that formed when the HCl solution was added might not be neutralized by the second equivalent of CN$^-$ ion. Therefore, the hypochromic shift was not observed after that addition of a second equivalent of the CN$^-$ ion (shown in Scheme 1). These studies resolved the regeneration of the **Imi** salt using hydrochloric acid to treat the **Imi**-CN$^-$ complex (saturated) solution.

Fourier transform infrared spectroscopy (FTIR) studies for complexation between ***Imi*** *salt and CN$^-$ ion*

The involvement of the pyran ring in the **Imi** salt during the complexation was confirmed by analyzing the FTIR data for the **Imi** salt in the presence and absence of CN$^-$. The FTIR spectra of the **Imi** salt displays a characteristic strong absorption peak at approximately 1594 cm^{-1} from the C=C stretching vibration of the pyran ring. These data suggest that extensive bond delocalization of π-electrons in the pyran ring of **Imi** salt occurs and that the characteristic carbonyl stretching frequencies in the **Imi** salt were absent. Interestingly, when 1 equiv. of CN$^-$ was added to the **Imi** salt, we observed a strong C=O stretching vibration at 1707 cm^{-1}, as displayed in Fig. 7. However, the —C≡N stretching vibrations were observed at 2153 cm^{-1} and underwent a domino effect during the pyran ring-opening of the **Imi** salt. Finally, an unsaturated cyano-enone derivative was formed and confirmed by the strong C=C—H stretching vibrations at 2967 cm^{-1}. The anion bonds with the pyran ring, forming the C—C of the cyanopyran in the first step, which is voluntarily changed into a cyano-enone derivative through tautomerism.

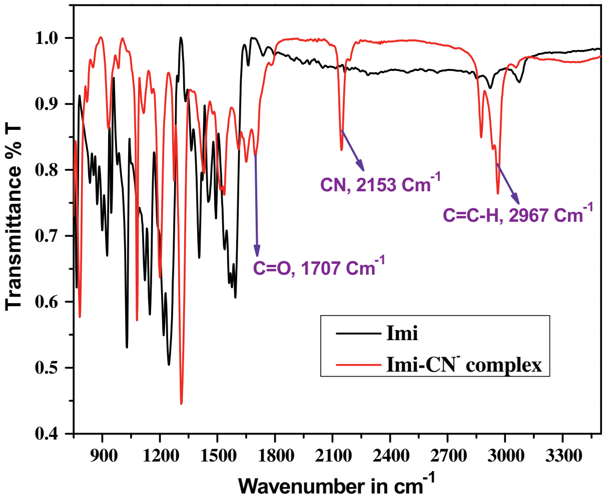


Fig. 7. Fourier Transform Infrared (FTIR) spectra of the **Imi** salt and the **Imi**-CN$^-$ ion complex in the solid state.

Computational studies

Finally, computational calculations were carried out to investigate the binding mechanism and the HOMO/LUMO energy levels of the **Imi** salt and the **Imi**-CN$^-$ complex (Fig. 8). These simulations utilized *Material Studio 4.3 suite*, which is a quantum mechanical

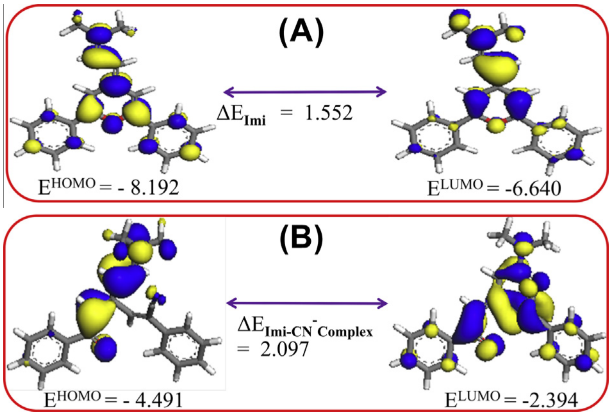


Fig. 8. Electron distributions in the HOMO and LUMO energy levels: [**A**] the pure **Imi** salt and [**B**] the **Imi**-CN$^-$ complex using electronic distributions in the *Material Studio 4.3 suite*.

program using density functional theory (DFT). Perdew–Burke–Ernzerhof (PBE) functions of the generalized gradient approximation (GGA) levels with double numeric polarization basis sets were used to calculate the energy level of the frontier molecular orbitals (MOs) [29–32]. Comparing the electron distributions of the HOMO and LUMO states in the **Imi** salt and the **Imi**-CN^- complex revealed that the electron density decreased in the LUMO levels relative to the HOMO levels in the **Imi** salt structure, as displayed in Fig. 8A and B. The energy gap between the HOMO and LUMO levels of the **Imi** salt is 1.552 eV and 2.097 eV with **Imi**-CN^- complex. According to the experimental results, the hypsochromic (blue) shift in the absorbance leads to ~171 nm [423–252 nm] displayed by the **Imi**-CN^- complex was attributable to the decreased HOMO–LUMO gap from **Imi** salt to the **Imi**-CN^- complex. The most unique property of the pyran ring in **Imi** salt is its vulnerability toward nucleophilic addition reactions. Therefore, the clean and rapid C—C bond formation and subsequent ring-opened product were able to form. This addition results in the opening of the pyran ring of the **Imi** salt and generates the cyano-pyran moiety in equilibrium with the corresponding cyano-enone tautomer.

Conclusion

In conclusion, we have synthesized **Imi** and demonstrated its utility as a molecular sensor for detection of CN^- in CH_3CN solutions. A small molecular sensor with the ability to detect the CN^- ion by quenching absorption intensity has been successfully developed. Additionally, the color of the solution changed from yellow to colorless and was then recovered. The optical properties of this **Imi** salt were investigated using various anions, such as CN^-, Cl^-, Br^-, I^-, SCN^-, ClO_4^-, NO_3^-, HSO_4^-, PF_6^- and N_3^-. **Imi** exhibited enhanced sensitivity and the significant selectivity for recognizing CN^- over other anions. The UV–visible spectra revealed a hypochromic shifts at 423 nm and 444 nm after CN^- was added to the **Imi** salt. In addition a new peak at 252 nm is shown in absorption spectra along with isosbestic point with 331 nm. In this pattern selective binding leads to ~171 nm [423–252 nm] hypsochromic (blue) shift. The complex between the **Imi** salt and CN^- had a 1:1 stoichiometry. The feasibility of reusable colorimetric **Imi** salt was tested by recuperating the sensing **Imi** salt by exposing the cyano-enone derivative to an acidic solution to regenerate the **Imi** salt. The reaction used was reversible, and the **Imi** salt sensor may be recovered using aqueous hydrochloric acid. FTIR studies indicated that a carbonyl compound derivative formed during the binding mechanism. In this study, we summarized the theoretical properties of an **Imi** salt and the **Imi**-CN^- complex to further understand the electronic distribution in HOMO and LUMO. Using these findings, the theoretical approaches were compared to elucidate more detailed characteristics of the **Imi** salt and **Imi**-CN^- complex formation. Further studies are in progress to understand the effects of various substituent during the recognition process and to develop **Imi** salt-based sensors for anions.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.02.052.

References

[1] A.T. Balaban, W. Schroth, G. Fischer, Pyrylium salts. Part I. Syntheses, Adv. Heterocycl. Chem. vol. 10, Springer, Berlin, 1969, pp. 241–326.

[2] A.T. Balaban, The pyrylium cation as a synthon in organic chemistry, in: R.B. Mitra, N.R. Ayyangar, V. N Gogte, R.M. Acheson, N. Cromwell (Eds.), New Trends in Heterocyclic Chemistry, Elsevier, Amsterdam, 1979, pp. 79–111.

[3] T.S. Balaban, A.T. Balaban, Science of synthesis: Pyrylium salts-Hetarenes and related ring systems, six-membered hetarenes with one chalcogen, Houben-Weyl Methods of Molecular Transformations, Stuttgart: Georg Thieme Verlag, 14, 2003, pp. 11–200.

[4] A.T. Balaban, A. Dinculescu, G.N. Dorofeenko, G.W. Fischer, A.V. Koblik, V.V. Mezheritskii, W. Schroth, in: A.R. Katritzky (Ed.), Pyrylium Salts: Syntheses, Reactions and Physical Properties, vol. 2, Academic Press, New York, 1982, p. 454.

[5] A.T. Balaban, Pyrylium salts as useful synthons, in: O. Chizov (Ed.), Organic Synthesis: Modern Trends, Proc. 6th IUPAC Internat. Symp. On Organic Synthesis, Moscow, 1987, pp. 263–274.

[6] Y.S. Yao, Q.X. Zhou, X.S. Wang, Y. Wang, B.W. Zhang, A DCM-type red-fluorescent dopant for high-performance organic electroluminescent devices, Adv. Funct. Mater. 17 (2007) 93–100.

[7] J.J. Wolff, R. Wortmann, Organic materials for non-linear optics: the 2D approach, J. Prakt. Chem. 340 (1998) 99–111.

[8] S. Alias, R. Andreu, M.J. Blesa, M.A. Cerdan, S. Franco, J. Garin, C. Lopez, J. Orduna, J. Sanz, R. Alicante, B. Villacampa, M.J. Allain, Iminium salts of ω-dithiafulvenylpolyenals: an easy entry to the corresponding aldehydes and doubly proaromatic nonlinear optic-phores, J. Org. Chem. 73 (2008) 5890–5898.

[9] R. Andreu, L. Carrasquer, S. Franco, J. Garın, J. Orduna, N. Martinez de Baroja, R. Alicante, B. Villacampa, M. Allain, 4H-Pyran-4-ylidenes: strong proaromatic donors for organic nonlinear optical chromophores, J. Org. Chem. 74 (2009) 6647–6657.

[10] R. Andreu, E. Galan, J. Garin, V. Herrero, E. Lacarra, J. Orduna, R. Alicante, B. Villacampa, Linear and V-shaped nonlinear optical chromophores with multiple 4H-pyran-4-ylidene moieties, J. Org. Chem. 75 (2010) 1684–1692.

[11] G.A. Reynolds, J.A. VanAllan, Pyranylidene iminium salts. I. Iminium salts derived from alkyl-substituted pyrylium salts and their hydrolysis products, J. Org. Chem. 34 (1969) 2736–2741.

[12] J.A. Van Allan, G.A. Reynolds, D.P. Maier, S. Chie Chang, The reactions of some pyranylideneiminium salts with amines. Part 1, J. Heterocycl. Chem. 9 (1972) 1229–1233.

[13] K.W. Kulig, B. Ballantyne, Cyanide toxicity, vol. 15, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, 1991.

[14] B. Vennesland, E.E. Comm, C.J. Knownles, J. Westly, F. Wissing, Cyanide in Biology, Academic Press, London, 1981.

[15] G.D. Muir, Hazards in the Chemical Laboratory, 2nd edition., The Chemical Society, London, 1977.

[16] K.K.W. Mak, H. Yanase, R. Renneberg, Cyanide fishing and cyanide detection in coral reef fish using chemical tests and biosensors, Biosens. Bioelectron. 20 (2005) 2581–2593.

[17] K. Kim, O.G. Tsay, D.A. Atwood, D.G. Churchill, Destruction and detection of chemical warfare agents, Chem. Rev. 111 (2011) 5345–5403.

[18] P.B. Vaello, E. Jover, J. Llorens, J.M. Bayona, Determination of cyanide and volatile alkylnitriles in whole blood by headspace solid-phase microextraction and gas chromatography with nitrogen phosphorus detection, J. Chromatogr. B 870 (2008) 17–21.

[19] Y. Sun, Y. Liu, M. Chen, W. Guo, A novel fluorescent and chromogenic probe for cyanide detection in water based on the nucleophilic addition of cyanide to imine group, Talanta 80 (2009) 996–1000.

[20] D.G. Themelis, S.C. Karastogianni, P.D. Tzanavaras, Selective determination of cyanides by gas diffusion-stopped flow-sequential injection analysis and an on-line standard addition approach, Anal. Chim. Acta 632 (2009) 93–100.

[21] A. Taheri, M. Noroozifar, M.K. Motlagh, Investigation of a new electrochemical cyanide sensor based on Ag nanoparticles embedded in a three-dimensional sol-gel, J. Electroanal. Chem. 628 (2009) 48–54.

[22] B.V. Pecharroman, M.D.L. de Castro, Determination of cyanide by a pervaporation–UV photodissociation–potentiometric detection approach, Analyst 127 (2002) 267–270.

[23] C. Giuriati, S. Cavalli, A. Gorni, D. Badocco, P. Pastore, Ion chromatographic determination of sulfide and cyanide in real matrices by using pulsed amperometic detection on a silver electrode, J. Chromatogr. A 1023 (2004) 105–112.

[24] F. Heidarizadeh, F. Abadast, Reactions of some nucleophiles with pyrylium salts, Oriental J. Chem. 27 (2011) 1421–1436.

[25] A. Mouradzadegun, F. Abadast, Thermally-induced ring contraction as a novel and straightforward route for the synthesis of 2-furyl acetonitrile derivatives, Tetrahedron Lett. 54 (2013) 2641–2644.

[26] A. Mouradzadegun, F. Abadast, An improved, safe, and efficient conversion of triarylpyrylium perchlorates to corresponding cyanodienones using Amberlite IRA 910[CN], Monatsh. Chem. 144 (2013) 375–379.

[27] L. Fabes, T.W. Swaddle, Reagents for high temperature aqueous chemistry: trifluoromethanesulfonic Acid and its Salts, Can. J. Chem. 53 (1975) 3053–3059.

[28] T. Gramstad, R.N. Haszeld, Perfluoroalkyl derivatives of sulphur. Part VII. Alkyl trifluoromethanesulphonates as alkylating agents, trifluoromethanesulphonic anhydride as a promoter for esterification, and some reactions of trifluoromethanesulphonic acid, J. Chem. Soc. (1957) 4069–4079.

[29] P. Dev, S. Agrawal, N.J. English, Determining the appropriate exchange–correlation functional for time-dependent density functional theory studies of charge-transfer excitations in organic dyes, J. Chem. Phys. 136 (2012) 224301–224311.

[30] A.D. Boese, N.C. Handy, A new parametrization of exchange–correlation generalized gradient approximation functionals, J. Chem. Phys. 114 (2001) 5497–5503.

[31] B. Delley, From molecules to solids with the DMol3 approach, J. Chem. Phys. 113 (2000) 7756–7764.

[32] B. Delley, An all-electron numerical method for solving the local density functional for polyatomic molecules, J. Chem. Phys. 92 (1990) 508–517.