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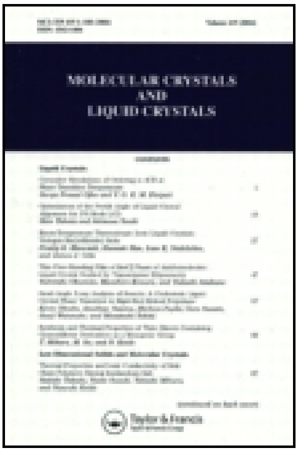

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Chemionics Study of Newly Synthesized Photochromic Schiff Base Compound

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A new Schiff base compound 4((o-tolylimino)methyl)-3-methyl-1-phenyl-1H-pyrazol-5-ol(4TM-MPP) was synthesized and characterized by elemental analyses, LC-MS, FTIR, and ^{1}*H-NMR spectra. The compound exhibits photochromic property under 365 nm UV-light irradiation, which can be observed with solid state reflectance spectra. It suggests that the photoisomerization is due to photoinduced intermolecular hydrogen bond, which results in enol to keto transformation. The chemionics study is carried out using (*Ni^{+2}*,* H^+*), (*Ag^+*,* H^+*), and (*Na^+*,* H^+*, and* OH^-*) using the UV absorption spectra in solution, which shows logic behavior of INHIBIT, NOR, and XOR, respectively.*

Keywords Chemionics study; logic gates; photochromic; photoisomerization

1. Introduction

The miniaturization of components for the construction of silicon-based electric computers is currently pursued by using the top-down approach. The top-down approach is subjected to drastic limitations for dimensions smaller than 100 nm because of cost issues [1–4]. Chemists are in an ideal position to develop bottom-up strategies for the construction of nanoscale devices since they are able to manipulate molecules, the smallest entities of the matter with distinct shapes and properties [5,6]. In an attempt to develop bottom-up electronics (molecular electronics) [7,8] in the last few years there has been an increasing interest in using molecules to construct miniaturized electric circuits that would be much smaller than the corresponding micrometer-scale digital logic circuits fabricated on conventional solid state semiconductor chips [9]. Instead of electrons or photons, molecules and ions can be used as input/output signals to process information by using solution system. Chemical processes occur at the molecular level by their own nature and usually take place in solution. The fundamental features in chemionics information systems are molecular recognition and changes in the molecular structure. In artificial systems, the most common reagents to process signal are acids and base, but metal ions

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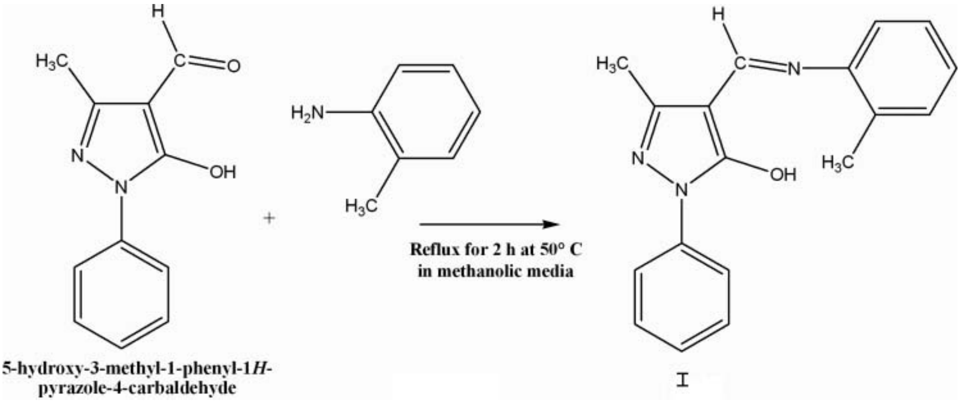
and molecules can also be used. For the perspective of futuristic applications, the development of a set of components for information processing by chemionics is an interesting challenge [10].

Photochromism in organic system is a phenomenon entailing the reversible change of a selected chemical species from one molecular conformation to another [11,12]. The development of photochromic materials has been an area of intense research in recent years because of their potential applications, such as high-density optical storage media, nonlinear-optical materials and molecular switching device etc. [13–15]. Many Schiff bases derived from pyrazolone and thiosemicarbazones were studied by Dian-Zeng Jia et al. [16–18], it was suggested that photochromic mechanism is due to intermolecular proton transfer.

In this article, chemionics study of newly Schiff base compound with different stimuli are shown. To construct logic gate, different stimuli like H^+, OH^-, Na^+, Ni^{+2}, and Ag^+ were used. The response shows different logic gates like INHIBIT, NOR, and XOR. The present Schiff base is prepared by reaction of pyrazolo and aromatic amine. The characterization is done by different instrumental techniques. The present compound (I) shows photochromic properties under 365 nm UV light irradiation (Scheme 1).



Scheme 1.

2. Experimental Section

2.1 Materials

3-methyl-1-phenyl-1*H*-pyrazol-5-one, N,N-dimethyl formamide, and 2-Amino-1-methyl benzene were purchased from the Sigma Aldrich company. 5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (hmppc) was synthesized according to the literature (yield: 81.36%; m.p. 175.3°C–176.2°C) [19]. All other reagents were of AR grade and used without further purification.

For chemionic study, Ni^{+2}, H^+, Ag^+, Na^+, and OH^- ion solutions were prepared in water having concentration 0.01 mol L^{-1}. The methanolic solution of (4TM-MPP) having 1×10^{-5} mol L^{-1} was used.

2.2 Synthesis

4((o-tolylimino)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol(4TM-MPP) was prepared by mixing 5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazole-4-carbaldehyde (5 mmol) and 2-Amino-1-methyl benzene (5 mmol) and refluxed in 40 ml of methanol in presence of glacial acetic acid (1 ml) at 50°C for 2 hours under magnetic stirring. After cooling down to room temperature in the dark, a yellow solid was obtained. The solid was filtered and washed with methanol. The solid was purified and checked for single spot on TLC. The compound was crystallized in acetone. The compound was stored in dark to protect from light interaction.

2.3 Characterization

The compound (I) yield: 87.08%; m.p. 168.1°C–169.5 °C. The ^{1}H NMR (400 MHz, DMSO-$d_{6,}$ 25°C) (δ, ppm): (after irradiation) 2.304 (m,3H, Pz-CH_3), 2.385 (m,3H, phenyl-CH_3), 7.997–7.128 (s, 12 H, Phenylring), 11.596 (s,1H, Pz-NH). FTIR (v cm^{-1}): (after irradiation) 3345 v (N–H), 3320–2560 v (O–H), 1664 v (C=O), 1629 v (C=N), 1550, 1491 v (phenyl), 1410, 1362 v (pyrazolonring). The LC-MS: (M^+) = 290.0 (formula weight: 291.35 g/mol). The elemental analysis ($C_{18}H_{17}N_3O$): found (%); C, 74.4; H, 5.8; N, 14.6; calculated (%) C, 74.2; H, 5.9; N, 14.7.

2.4 Measurements

Melting point was measured with TECH XT-5 melting point apparatus. The elemental analyses were determined on Perkin-Elmer-2400series (II). The FTIR spectrum was recorded using KBr pellet on ThermoNicolet IS10. ^{1}H NMR (DMSO-d_6) was run on BRUKER NMR Spectrometer. LC-MS was carried out on quadrupole LC-MS API-3000. UV-VIS reflection spectra were monitored on Hitachi UV-3010 Spectrometer. Irradiation of sample was carried out using 365 nm light. The absorption spectrums were recorded on Thermo Evolution 300. All measurements were performed at ambient temperature.

3. Results and Discussion

3.1 Solid-State IR

With the aim to get an idea of the mechanism of the photochromic reaction of 4((o-tolylimino)methyl)-3-methyl-1-phenyl-1*H*-pyrazol-5-ol(4TM-MPP), the IR spectra of compound before and after irradiation with 365 nm light is shown in Fig. 1. The structural differences between their enol form and keto form resulted in spectra changes in the range of 3100–3400 cm^{-1} clearly. After irradiation of 365 nm light, a new sharp band ascribed to the N–H stretching vibration appears at 3345 cm^{-1} for the formation of Keto form(II) along with relative intensity decrease of a smooth band at 3205 cm^{-1}. The band of 3205 cm^{-1} can be ascribed to O–H vibration due to the red shift induced by the strong hydrogen bonds in solid state. The intensity of 1680 cm^{-1} band is increased after irradiation, which can be attributed to the typical absorption of C=O stretching vibration. Similar type of phenomena has been observed in pyrazolone compound [20,21], which suggests the formation of the Keto form(II) isomer was occurred after UV light irradiation. Therefore, the photochromism of the compound is mainly due to proton transfer, which isomerizes from the enol-form to the keto-form isomer.

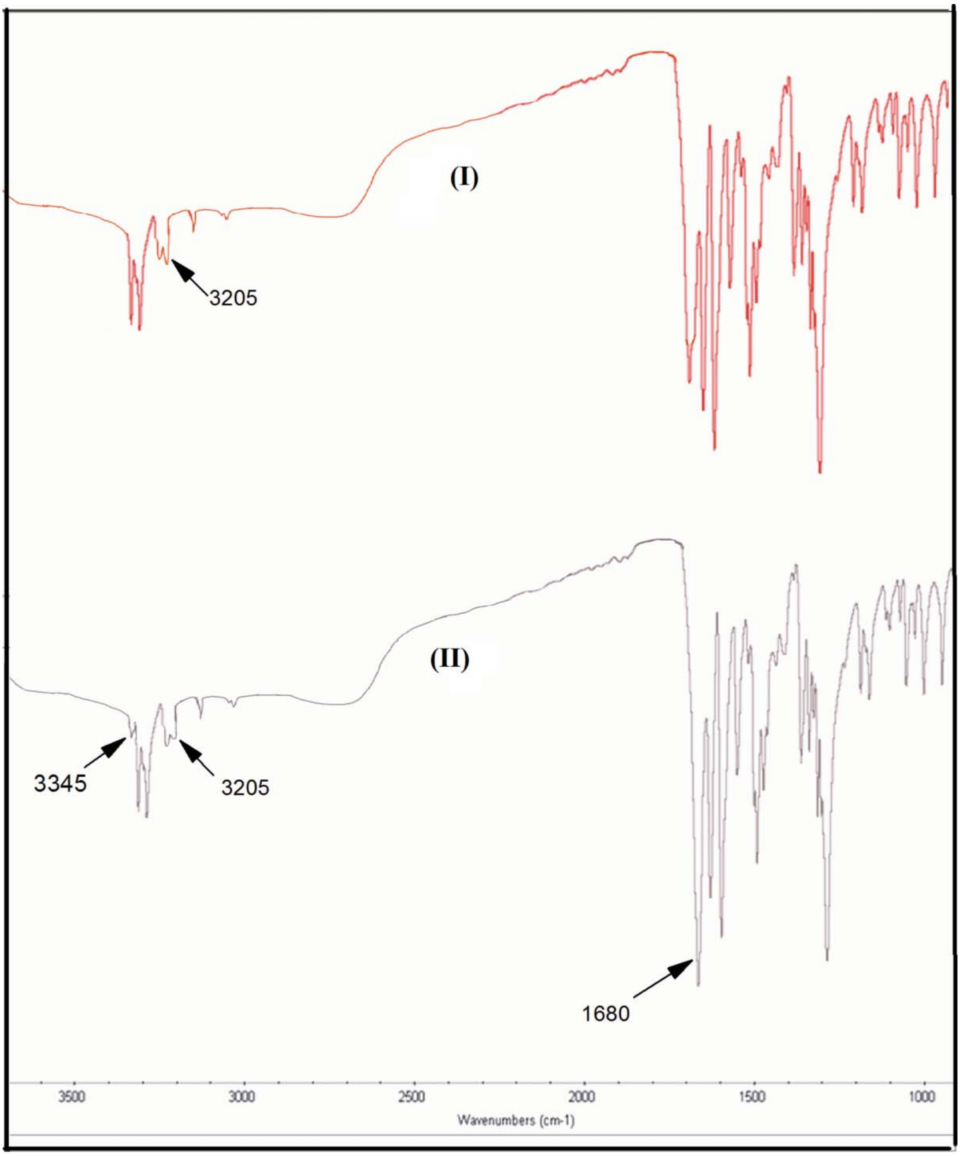


Figure 1. IR spectra of (4TM-MPP): Before irradiation (red line); after irradiation with 365 nm light (black line).

3.2 *Time-Dependent UV-Vis Spectra*

Figure 2 shows the time dependent UV-Vis. reflectance spectra of (4TM-MPP). When the compound was irradiated by ultraviolet light of 365 nm at room temperature; its color changed from yellow to reddish, which indicates a conversion of the enol in to the keto form. The reflectance spectra were recorded at different time intervals until spectral variation was no longer evident. Upon irradiation, as seen from spectra, a new reflectance band appeared in range of 425 nm to 525 nm and its intensity increased as

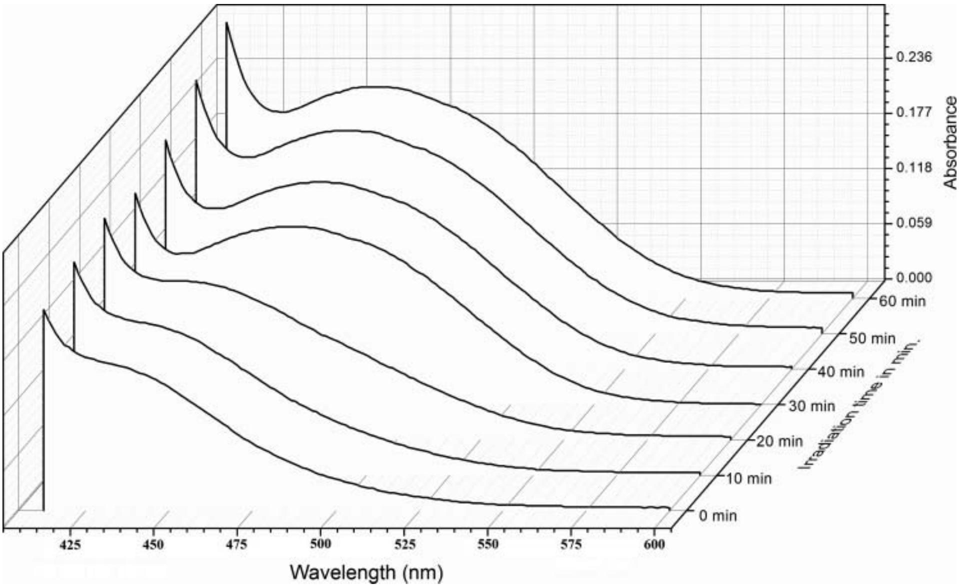


Figure 2. UV-Vis. Spectral change of (4TM-MPP) irradiated by 365 nm UV light in solid state at room temperature for different irradiation time: 0,10, 20, 30, 40, 50, and 60 min.

measurement continued. The red shift is due to the destabilization of the π-system, which mainly results in an increase of the HOMO level and smaller perturbations of LUMO [22]. The finding emphasizes the importance of electronic effects on the visible absorption spectrum.

3.3 Kinetic Measurements and Mechanism of Photochromism

The first order rate constant (k_1) was obtained essentially as described in the literature [23]. The experimental data were treated with the standard integrated expression

$$K_1t = \frac{\ln(A\infty - A0)}{A\infty - At} \tag{1}$$

The second order rate constant (k_2) was obtained through the following equation:

$$K_2t = \frac{At}{A\infty(A\infty - At)}, \tag{2}$$

where A_0, A_∞, and A_t were the observed reflectance data measured at the beginning, at the end of the reaction, and at time *t*, respectively. All reflectance data were acquired from Fig. 2 at 440 nm.

The first order and second order kinetic curves (Fig. 3) were plotted according to Eqs. (1) and (2), respectively. A good liner fit ($k_1 = 6.04 \times 10^{-4}\ s^{-1}$), $R^2 = 0.9971$, Eqs. (3) and (4) was found in the first order kinetic plot, and therefore, the photochromic reaction

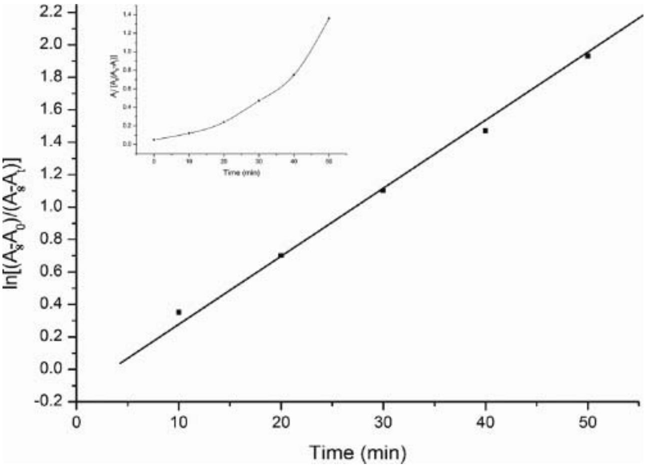


Figure 3. First order kinetic plot of photoisomerization reaction of (4TM-MPP) induced by 365 nm light (in inset the second order kinetic plot).

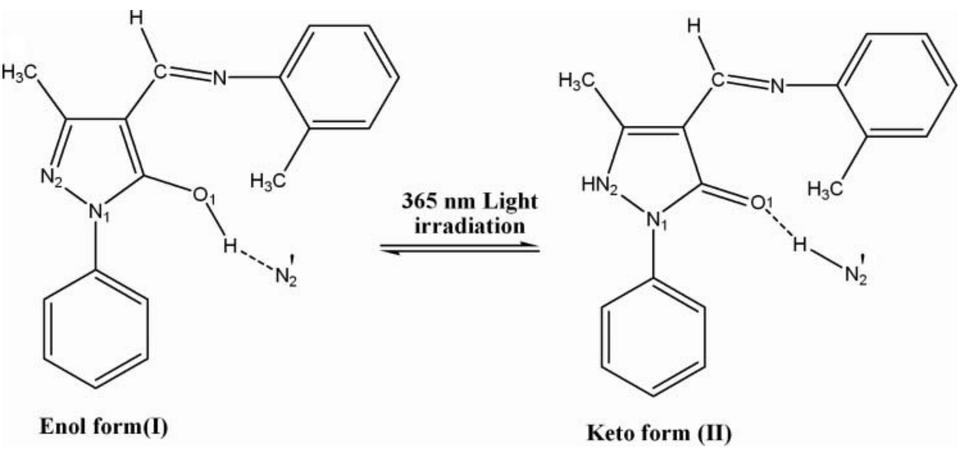
is of first order.

$$y = a + bx \tag{3}$$

$$R = \frac{S_{xy}}{\sqrt{S_{xx}\,S_{xy}}} \tag{4}$$

In Eqs. (3) and (4), $a = \bar{y} - b\bar{x}$, $b = S_{xy}/S_{xx}$, $S_{xx} = \Sigma x^2 - (\Sigma x)^2/n$, $S_{yy} = \Sigma y^2 - (\Sigma y)^2/n$, $S_{xy} = \Sigma xy - (\Sigma x \Sigma y)/n$, where the x is time (t), y is ln [(A_0–A_t) – (A_∞–A_t)]. The result of a is the intercept of the straight line which is -0.069, b the first order rate constant (k_1) and R the correlation co-efficient.

Scheme 2 shows the molecular structure with numbering. The proposed photochromic mechanism is due to inter molecular hydrogen bonding. This suggests that the change of



Scheme 2.

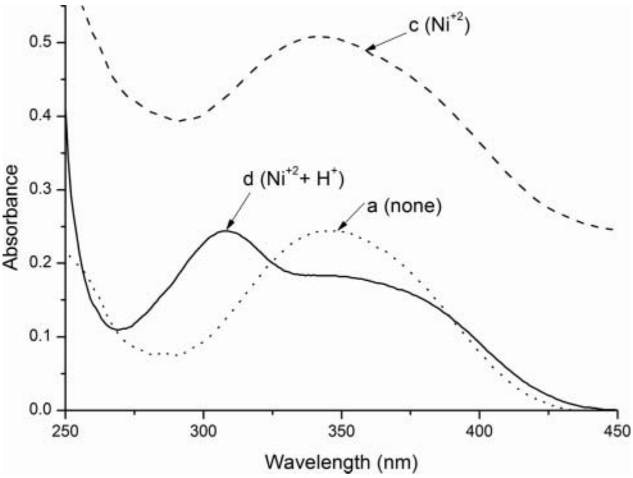


Figure 4. Absorption spectra of (4TM-MPP) in methanolic solution (1×10^{-5} mol L^{-1}) before (dot line) and after addition of 0.01 M Ni^{+2} (dash line) and combined effect of Ni^{+2} and H^{+} (solid line).

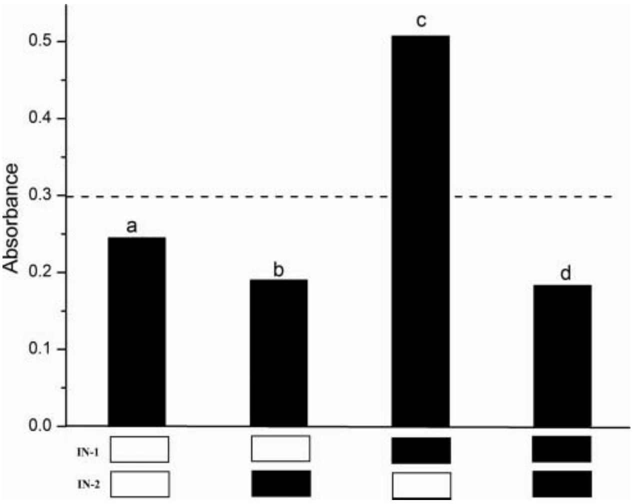


Figure 5. Under the stimulation of Ni^{+2} (IN-1) and H^{+} (IN-2) (IN-1 and IN-2 in the sequence of [a(0,0), b(0,1), c(1,0), d(1,1)]), the changes of absorbance intensity at 345 nm (☐ represents inputs that are 0, ■ represents inputs that are 1).

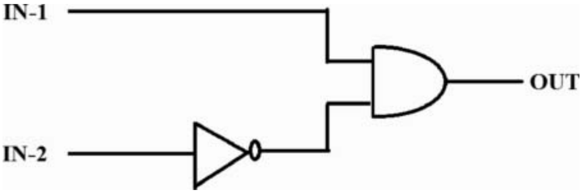


Figure 6. INHIBIT logic circuit of present compound with IN-1(Ni^{+2}) and IN-2(H^{+}).

Table 1. Truth table of INHIBIT logic gate for Ni^{+2} and H^+ system

Input			
IN-1 (Ni^{+2})	IN-2 (H^+)	H^+ Inverted	Output at 345 nm
0	0	1	0
0	1	0	0
1	0	1	1
1	1	0	0

color is due to photoisomerization from the enol-form to keto-form. The hydrogen bond between O_1 atom and N'_2 atom of neighboring molecule is form $N'_2 \ldots H–O_1$ (I) before irradiation, and after irradiation of UV light, the molecule absorbs the energy and the proton in O_1 atom transfer to N'_2 atom of the neighboring molecule to form the new hydrogen bond of $N'_2–H \cdots O_1$ (II), which results the conversion of enol form to keto form [24].

3.4 Chemionics Study

The current interest in molecular systems capable for performing logic operations is largely due to likely application of these systems as molecular devices in information processing and computation [25]. A logic gate is a switch whose output signal equal to 0 or 1 depends on the input signal, which also can take two values, 0 or 1. A logic gate with two inputs and one output has four states corresponding to four combinations of the input signals, namely,

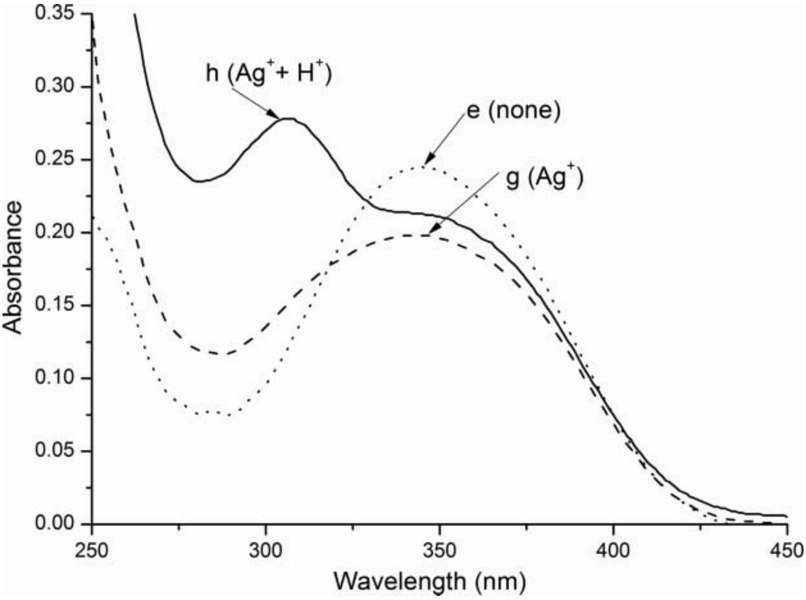


Figure 7. Absorption spectra of (4TM-MPP) in methanolic solution ($1 \times 10–^5$ mol L^{-1}) before (dot line) and after addition of 0.01 mol L^{-1} Ag^+ solution (dash line); solid line shows combined effect of Ag^+ and H^+.

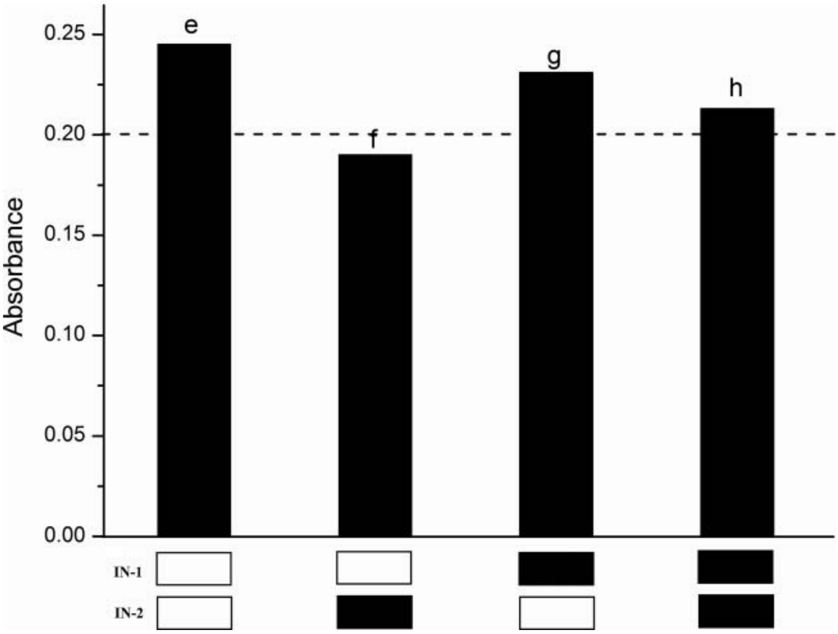


Figure 8. Under the stimulation of Ag^+ (IN-1), H^+ (IN-2) (IN-1 and IN-2 in the sequence of [e(0,0), f(0,1),g(1,0),h(1,1)]), the changes of absorbance intensity at 345 nm (☐ represents inputs that are 0, ■ represents inputs that are 1).

(0,0), (0,1), (1,0), (1,1). Similarly, when three inputs and one output system is observed it corresponds to eight possible combinations. In each case, the values of the output signal (0 or 1) depends on the type of the logic gates and is determined by a truth table in which each combination of output signals (logical variables) is assigned a desired value of the output signal [26]. The present compound shows opportunities for INHIBIT, NOR and XOR logic gates based on absorption spectral changes due to addition of (Ni^{+2} & H^+), (Ag^+ & H^+), and (Na^+, H^+, & OH^-).

3.4.1 INHIBIT Logic Gate for Ni^{+2} and H^+ Inputs. The present compound is sensitive for acid, base, and metal ions. To construct the logic gate with Ni^{+2} and H^+ (two input system) the methanolic solution of 1×10^{-5} mol L^{-1} is used. Initially, the first input (0,0), where no stimuli is added, the absorption maxima at 345 nm is obtained. The H^+ (0,1) is added as second individual input, by its effect, λ_{max} 345 nm blue shifted to 329 nm. When Ni^{+2} (1,0) is added in to the system as third input, the absorbance is increases but the absorption maxima remains same. The combined effect of Ni^{+2} and H^+ can be observed in Fig. 4.

Figure 9. NOR logic circuit of present compound with IN-1 (Ag^+) and IN-2 (H^+).

Table 2. Truth table of NOR logic gate for Ag^+ and H^+ system

Input			
IN-1 (Ag^+)	IN-2 (H^+)	H^+ Inverted	Output at 345 nm
0	0	1	1
0	1	0	0
1	0	1	1
1	1	0	1

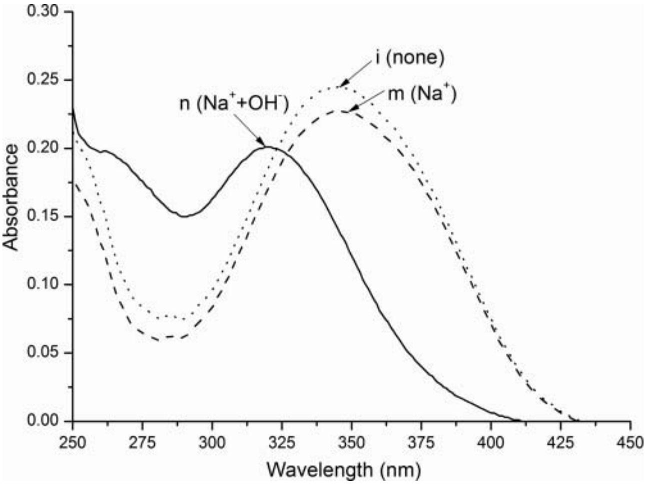


Figure 10. Absorption spectra showing simultaneous effect of Na^+(IN-1) and OH^- (IN-3).

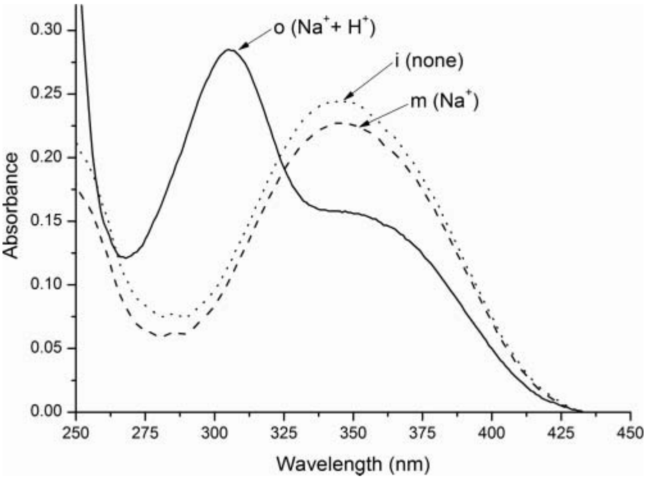


Figure 11. Absorption spectra showing simultaneous effect of Na^+(IN-1) and H^+(IN-2).

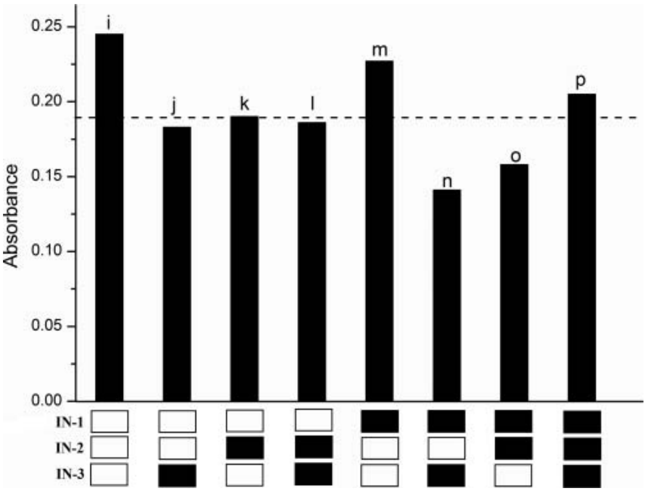


Figure 12. Under the stimulation of Na+ (IN-1), H+ (IN-2), and OH− (IN-3). (IN-1), (IN-2), and (IN-3) in the sequence of i(0,0,0), j(0,0,1), k(0,1,0), l(0,1,1), m(1,0,0), n(1,0,1), o(1,1,0), p(1,1,1).

When Ni^{+2} is added in acidic media; the new band at 309 nm appeared and the band at 345 nm vanished, gradually.

The communication between the input signals, Ni^{+2} (IN-1) and H^+(IN-2) and the output signals, the absorbance value at 345 nm (OUT), can be described with the binary logic. The absence of inputs values below a predefined threshold level (absorbance value of 0.3) are translated in to binary “0,” while above threshold corresponds to binary “1,” in accordance with the positive logic convention.

According to histogram in Fig. 5, the truth table (Table 1) can be obtained; from which we can see that this chemical system responds to an input sequence of two binary digits (IN-1, IN-2) producing an output sequence of one binary digit (OUT). Consequently, the logic behavior of the molecular switch corresponds to an INHIBIT logic gate by combining a NOT and an AND gate (Fig. 6).

3.4.2 NOR Logic Gate for Ag^+ and H^+ Inputs. For Ag^+ and H^+ system, the input sequence (0,0) and (0,1) is same as above. When Ag^+ is added in the system, the absorbance is decreased but no change in λ_{max} can be observed. Further, combined effect of Ag^+ and H^+ is observed, the new band appeared at 308 nm and the band at 345 nm disappeared gradually (Fig. 7).

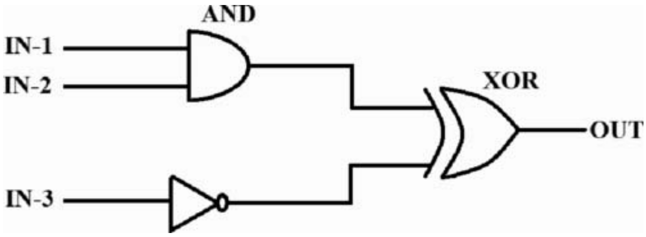


Figure 13. XOR logic circuit which is initially treated with AND (IN-1 and IN-2) and NOT (IN-3).

Table 3. Truth table of XOR logic gate for Na^+, H^+, and OH^- system

Input					
IN-1 (Na^+)	IN-2 (H^+)	IN-3 (OH^-)	OH^- Inverted	AND of IN-1 and IN-2	Output at 345 nm
0	0	0	1	0	1
0	0	1	0	0	0
0	1	0	1	0	1
0	1	1	0	0	0
1	0	0	1	0	1
1	0	1	0	0	0
1	1	0	1	1	0
1	1	1	0	1	1

In this system, the threshold value is 0.2, which can be observed by Fig. 8, and for this threshold value only one OUT signal is "0" (Table 2), which correspond to NOR logic gate (Fig. 9).

3.4.3 XOR Logic Gate for Na^+, H^+, and OH^- Inputs. The effect of Na^+, H^+, and OH^- is also studied for the present system. When the OH^- is used as input it show significant shift from 345 nm to 267 nm. Further individual effect of Na^+ input signal is checked, the absorbance value is decreased but no change in λ_{max} is observed in the system. When Na^+ and OH^- both are inserted in the system, the band at 345 nm blue shifted to 321 nm (Fig. 10). The combined effect of Na^+ and H^+ can also show considerable change, the λ_{max} at 345 nm gradually change to 305 nm (Fig. 11).

For three input systems of Na^+, H^+, and OH^-, the histogram is shown in Fig. 12. The threshold value is 0.19 for this system, which gives four on and four off communications (Table 3). The logic circuit is constructed using XOR gate, which is preliminary treated with AND and NOT for (IN-1, IN-2) and (IN-3), respectively (Fig. 13).

4. Conclusion

A new photochromic Schiff base compound containing pyrazolone-ring was prepared, whose photochromic behavior has been studied by UV-VIS reflectance spectra. The photochromism of (4TM-MPP) could be responsible for the result of isomerization from enol form to keto form. In solution, the chemionic performance of (Ni^{+2}, H^+), (Ag^+, H^+), and (Na^+, H^+, and OH^-) stimulated inputs were studied, which is executed by INHIBIT, NOR, and XOR logic circuit. This contribution can be useful in future to construct molecular switches as well as high-density optical storage devices.

Acknowledgment

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