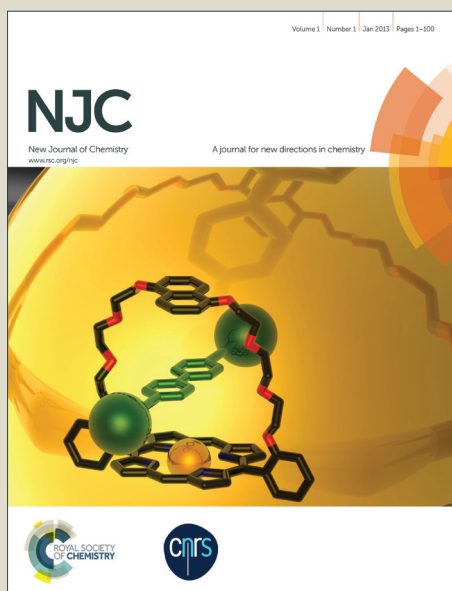


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PAPER

Fe-terpyridyl complex based multiple switches for application in molecular logic gate and circuit†

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Molecular logic gate and circuits are constructed using the optical and electrochemical addressable-reversible-multiple switching event of Fe(II)-4²-pyridyl terpyridyl complex (**1**) using multiple analytes. The process involves oxidation-reduction of Fe²⁺ as well as successive quarternization-dequarternization of the free pendant pyridyl group monitored optically. The whole switching process could also be visualized with naked eye as colour changes upon switching are quite apparent and instant.

1 Introduction

Molecular logic has seen exponential growth in the recent times.¹⁻³ Chemical approach towards molecular logic is inherently viable, since molecules are the smallest entities which have discrete shape and properties.⁴⁻⁶ Molecular manipulation by chemists through bottom-up approach could probably result in more efficient nanoscale devices, unlike the top-down approach, which has its own intrinsic limitations.⁷⁻⁸ Generally, molecules which could switch between at least two stable states, upon specific external input(s) have found practical applications in constructing molecular logic gate and circuits. Such intelligent use of inorganic/organic molecules and their interplay with varying input(s) have resulted in the development of information technology at molecular level.⁹ In this context, chemists have utilized and fine-tuned the redox, photophysical and photochemical properties of polypyridyl complexes of transition metal ions such as Fe(II), Ru(II), Ir(III), Os(II) and Re(I) in the overall development of material science.¹⁰⁻¹¹ Interestingly, these properties/states could easily be set/reset through external triggers/inputs, viz. light, electric field, magnetic field or chemicals, while keeping the molecule stable in different states and often leading to visible colour changes or similar easy to recognize properties as outputs.¹² This fine relationship between molecular properties in different yet stable and identifiable states leads to molecular multiple switches. Such molecule based switches have gained a lot of interest from scientific community for the development of molecular logic in solution as well as on surface.¹³⁻¹⁹

Our group has been engaged in exploring the tremendous potential of terpyridyl-transition metal complexes both in solution as well as on solid surfaces.²⁰⁻²² Functionalized terpyridyl and its derivatives offer several synthetic and structural advantages due to its excellent structure-properties correlations. For example, (i) it has strong “chelate effect” towards the transition metal ions, (ii) facile synthetic route, (iii) versatile coordination modes and (iv) the strong π - electron accepting nature of the ligand stabilize the

metal ions in lower oxidation states. In the present work, an optically rich and redox-active Fe(II)-terpyridyl complex (**1**) (Fig. 1) has been utilized for successful demonstration of multiple switching events with chemical(s) and electric potential as input and the process is monitored optically using an off-the-shelf UV-Vis spectrophotometer under transmission mode. These triggered, reversible events prompted us to construct related molecular-integrated molecular logic gates and circuits. To the best of our knowledge, this is the first report on reversible multiple state-switching of **1** via both chemically and electrochemically. The optical read-out is fast and non-destructive, while electrochemical aspects demonstrate redox stability and electro-chromic reversibility of **1**. This study could possibly be an addition in the further development of solution based molecular logic gates.

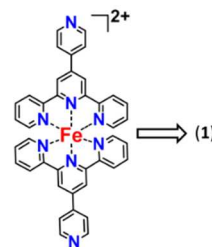


Fig. 1: Structure of Fe-terpyridyl complex (**1**).

2 Experimental

2.1 Materials

2-acetyl pyridine, pyridine-4-carboxaldehyde, FeCl₂, NH₄PF₆, NOBF₄, CD₃CN, CDCl₃ were purchased from Sigma-Aldrich and used as received. Hydrochloric acid (HCl), triethyl amine (Et₃N) were purchased from s. d. fine chemicals (Mumbai, India). Tetra-n-butyl ammonium hexafluorophosphate (TBAPF₆) was purchased from Alfa-Aesar and it was further recrystallized and dried under vacuum before use. All other chemicals were used as received without any further purification. All Solvents (AR grade) were purchased from Merck (Mumbai, India), s. d. fine

chemicals (Mumbai, India) and were purified using literature procedures so as to make them moisture free and further degassed using N_2 and kept in N_2 filled glove box ($O_2 < 2$ ppm).

2.2 Physical Measurements

UV-Vis spectra were recorded at room temperature on a double beam JASCO (Model V-670) spectrophotometer. One cm path length quartz cuvette having Teflon stopper was used for data collection. Suitable baselines were recorded for preliminary adjustments. 1H NMR spectra were recorded on JEOL 400 NMR (JNMEX 400P) using suitable deuterated solvent. ESI-TOF (electrospray-ionization, time-of-flight) mass spectra were recorded on a microTOF QII from BrukerDaltonik (Germany). Electrochemical experiments were performed using a CH Instrument (Model 660D) electrochemical Workstation equipped with BASi bulk electrolysis three electrode cell. Cyclic voltammograms (CV) of the complex **1** was recorded in dry acetonitrile with tetra-n-butyl ammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte using a glassy carbon as working electrode (WE, ~ 0.2 cm²), a Pt wire as counter electrode and Ag/AgCl (in 1 M KCl) as the reference electrode (RE). For bulk electrolysis with coulometry experiments similar procedure was followed except that porous glassy carbon (coil) was used as working electrode (50 mm high, 5 mm thick, 40 mm diameter; surface area = 10.5 cm²/cm²). The TBAPF₆ was dried at 100 °C for 30 min before use. The solution was degassed by bubbling N_2 bubbling for at least 15 min before the experiment. All the experiments were performed at room temperature unless mentioned otherwise.

2.3 Methods

Synthesis of 4'-pyridyl-2,2':6',2''-terpyridine(pytpy) (Scheme S1). pytpy was synthesized following a published procedure²³ resulting in needle shaped white crystals. 1H NMR (400 MHz, CDCl₃): δ /ppm (Fig. S1) 8.76 (s, 2H), 8.78 (d, 2H), 8.68 (d, 2H), 7.8 (d, 2H), 7.89 (t, 2H), 8.75 (d, 2H), 7.39 (t, 2H); ESI-MS: m/z 310 [M⁺]; UV-Vis in CHCl₃ (λ_{max}): 316, 278 and 245 nm.

Synthesis of **1 (Scheme S2).** **1** was prepared according to a reported procedure.¹⁶ In brief, 4'-pyridyl-terpyridine (98 mg; 0.316 mmol) was dissolved in 10 mL hot methanol and then FeCl₂ (21 mg; 0.158 mmol) in 10 mL methanol was added dropwise. The reaction mixture was refluxed with stirring for 4h under N_2 atmosphere. Subsequently, the reaction mixture was slowly cooled to room temperature and **1** was precipitated out by addition of an excess of a saturated methanolic solution of NH₄PF₆, which was then filtered off. The residue was washed with an excess amount of water followed by diethyl ether. Recrystallized using acetonitrile and acetone mixture (1:1, v/v) resulting in purple colour microcrystalline solid. 1H NMR (400 MHz, CD₃CN): δ /ppm (Fig. S2): 9.20 (s, 4H, Ar H), 9.02 (d, J = 8.0 Hz, 4H), 8.61 (d, J = 11 Hz, 4H), 8.23 (d, J = 10.2 Hz, 4H), 7.90 (t, J = 8.2 Hz, 4H), 7.15 (d, J = 5.8 Hz, 4H), 7.10 (t, J = 7 Hz, 4H). ^{13}C NMR (400 MHz, CD₃CN, δ): 118.29, 122.58, 122.98, 125.04, 128.36, 139.82, 148.75, 152.08, 154.22, 158.77, 161.84. IR, (KBr): ν = 838 (vs), 1408 (m) 1598 cm⁻¹ (m). UV-Vis (CH₃CN): λ_{max} (ϵ) = 569 nm (23,000); ESI-TOF m/z (%): 338 (90) [M-2PF₆]²⁺, 339 (46) [(M-2PF₆) + H]²⁺, 821(30) [(M-PF₆)]⁺, Anal. Calcd. for C₄₀H₂₈N₈FeP₂F₁₂: C, 45.47; H, 3.63; N, 10.61. Found: C, 45.16; H, 3.34; N, 9.96%.

2.4 Preparation of solutions of **1** and other chemical reagents

A 10 μ M solution of **1** was prepared in CH₃CN (purple coloured solution) and kept inside N_2 glove box and is pipetted out as and when required. The complex solution was sufficiently stable in presence of air/light within experimental time-frame. 100 ppm of fresh NOBF₄ (source of NO⁺) solution in dry CH₃CN was prepared, as per requirement, for further dilution to one and two eqv solutions with respect to **1**. Conc. HCl and Et₃N were diluted to one and two eqv with respect to **1**, using deionized water.

2.5 Chemical induced optical switching

Optical changes in **1 by NO⁺ and H⁺.** At first, the UV-Vis spectrum of 2 mL of 10 μ M solution of **1** was recorded in transmission mode with 200-800 nm range with CH₃CN for baseline correction. (Note: Any external chemical added afterwards was added to both sample and reference side so as to measure optical changes occurring for **1** only). One eqv of freshly prepared NO⁺ solution was then added using a 0 to 200 μ L pipette and corresponding UV-Vis spectrum was recorded. Then another equivalent of NO⁺ was added and UV-Vis spectrum was recorded thereafter. Further, in a separate experiment, an excess of NO⁺ (> 2 eqv) was added and corresponding changes in UV-Vis spectrum were recorded. Similar procedure was followed for addition of HCl solution. All additions and recording optical absorption was performed under standard conditions.

For switching back optical changes in **1.** To the **1** + NO⁺ (excess) solution, were added 5 μ L of deionized water and two equivalents of Et₃N in a stepwise manner with recording of UV-Vis spectrum at each step. To the **1** + H⁺ solution was added two equivalent of Et₃N and its UV-Vis spectrum was recorded.

2.6 Spectro-Electrochemical switching

At first, cyclic voltammogram of 10 μ M of **1** in dry CH₃CN was recorded with 20 mM TBAPF₆ as supporting electrolyte. Fe(II)/Fe(III) couple was observed at $\Delta E_{pa} = 1.24$ V and $\Delta E_{pc} = 1.17$ V with $E_{1/2} = 1.20$ V at a scan rate of 0.3 V s⁻¹. Now, with similar concentration of **1** bulk electrolysis with coulometry was performed at initial potential of 1.4 V, so as to oxidise **1**. At an interval of 500 s, 2 mL of solution was drawn from the electrolytic cell and its optical absorption was recorded and the process was continued till there is no further alteration in the optical absorption or when the increase in charge saturates with respect to time. For Fe(III) to Fe(II) conversion, a potential of 1.0 V and similar procedure was followed thereafter. UV-Vis was recorded after considering TBAPF₆ solution in CH₃CN as baseline for preliminary adjustments.

2.7 Molecular computational studies

The ground state geometry optimizations of 1²⁺, 2³⁺, 3⁴⁺ and 4⁵⁺ were carried out in the gas phase using B3LYP method LANL2DZ²⁴⁻²⁵ basis set with effective core potential was used for iron atom. The 6-31G*²⁶ basis set was used for all other atoms except iron. The initial geometry was obtained from the standard geometrical parameters. All calculation was performed using Gaussian 03 program package.²⁷

3 Results and Discussions

3.1 Optical Monitoring of switching events

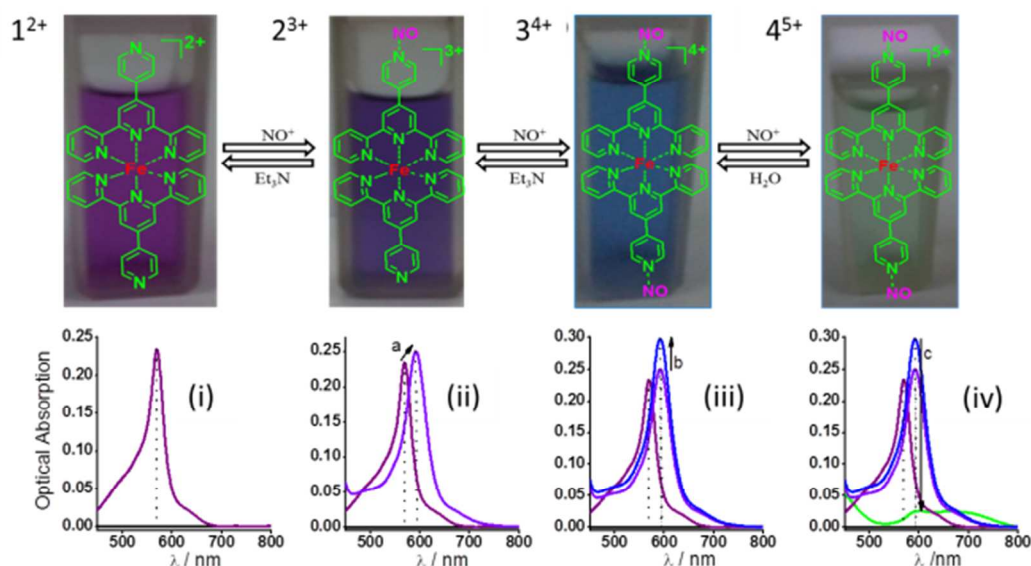


Fig. 2: (i) Native colour of **1** in CH₃CN and (below) corresponding UV-Vis spectrum (¹MLCT) with $\lambda_{\text{max}} = 569$ nm; (ii) Addition of 1 eqv of NO⁺ to **1** with colour changing from purple to blue and (below) 'a' represents bathochromic shift of ~17 nm to 586 nm and increase in molar absorptivity in ¹MLCT of **1**; (iii) Addition of another eqv of NO⁺ to **1** changed colour to light blue and (below) 'b' represents changes in the UV-Vis spectrum; (iv) Excess of NO⁺ results in green colour and (below) 'c' represents vanishing of ¹MLCT and leading to Fe³⁺ formation. Successive use of H₂O and Et₃N leads to original state of **1**. Black line in the UV-Vis spectra represent baseline with dry CH₃CN.

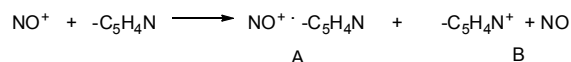
Fe(II)-terpyridyl complexes characteristically exhibit ¹MLCT band in the visible region of the spectrum, whose peak position is obviously dependent on ligand environment, while Fe(III) analogues generally lack this characteristic.²¹ Moreover, inter-conversion of the two oxidation states could be performed using suitable oxidizing/reducing agents. Particularly, addition of water could easily convert Fe(III) to Fe(II). In case of **1**, MLCT band appeared at $\lambda_{\text{max}} \sim 569$ nm in dry CH₃CN. Additionally, the free pendant pyridyl groups of **1** could potentially interact or form adducts with several cationic species, including NO⁺ and H⁺, due to the presence of non-bonding electrons on N-atom.²⁸

Chemical inputs induced optical changes. The above optical and structural attributes of state-switching of **1** using carefully chosen chemical input(s) applied at different stages of switching experiment, viz. NO⁺, H⁺, H₂O and Et₃N. Addition of one eqv of NO⁺ to **1** shifted the ¹MLCT band peak position to ~586 nm (~+17 nm shift) along with a visible, instant colour change to light purple/blue (Fig. 2(2³⁺)). Another eqv of NO⁺ further shifted the ¹MLCT band to ~590 nm (~+4 nm shift) and colour of the solution changed to blue (Fig. 2(3⁴⁺)). Moreover, optical absorption of the ¹MLCT band increased with each addition step as signified by 13% and 34% increase in molar absorptivity (' ϵ ') for each addition, respectively. Excess of NO⁺ (> 2 eqv) addition to **1** produced remarkable deviation from above behaviour. With each further aliquot (1 eqv each), the ¹MLCT band centred at $\lambda_{\text{max}} \sim 590$ nm, started to diminish in intensity, finally resulting in a broad band in the range ~600-800 nm and concomitant blue to green colour change (Fig. 2(4⁵⁺)).

Explanation and verification of observed changes. The most plausible explanation for observed bathochromic and hyperchromic shifts in optical absorption spectra of **1** upon NO⁺ addition could potentially be the sequential quaternization of pendant pyridyl N-atoms. Induced electron deficiency in terpyridyl unit forces it to withdraw electronic charge from the

metal centre. This perhaps resulted in lowering of band gap between metal and ligand centred molecular orbitals and hence bathochromism is observed.²¹ Hyperchromic effects at fixed concentrations, generally relates to increase in ' ϵ '. Formation of different species from **1** could only bring about changes in ' ϵ '. The concept of quaternization is based on the fact that ionization energy of appended pyridine unit is slightly greater than that of NO and consequently charge transfer process (pyridyl N-atom to NO⁺ or Fe(II) to NO⁺) gets inhibited to a large extent and adduct formation prevails.²⁸⁻³⁰ The probable absence of quaternization sites for further added aliquots of NO⁺ makes the charge transfer from metal centre Fe(II) to NO⁺ the most reasonable conclusion, ably supported by diminishing ¹MLCT band, appearance of a broad band in the range ~600-800 nm and visible colour change. This potentially signifies the oxidation of Fe(II) to Fe(III).³¹ Moreover, absence of H₂O and O₂ in CH₃CN rules out the probable formation of acid (HBF₄) and protonation of pyridyl N-atoms on reaction with HBF₄. To further verify that adduct formation governs the process and for this purpose, dil. HCl was added to solution of **1** and UV-Vis spectrum was recorded (Fig. S3). Upon adding one eqv of dil. HCl, the colour changed to light purple and ¹MLCT band peak position shifted to ~582 nm (~+13 nm shift) and enhancement of ' ϵ ' by 10% (Fig. S3(2)). Two equivalent of dil. HCl produced blue colour and ¹MLCT band peak position shifted to $\lambda_{\text{max}} \sim 590$ nm with net 26% increase in ' ϵ ' (Fig. S3(3)). Further addition of equivalent of dil HCl could not induce any further spectral or colour changes in **1**. These spectral changes could well be ascribed to the protonation of pendant pyridyl N-atoms.³² We observed a significant difference in NO⁺ and H⁺ addition to **1**: Changes in molar absorptivity, ' $\Delta\epsilon$ ' with addition of NO⁺ are greater than H⁺. ' ϵ ' is the intrinsic property of a specie. If there had been no adduct formation between **1** and NO⁺ (A; see below), the specie generated in both cases would probably have been same (-C₅H₄N⁺) (B; see below)

and $\Delta\epsilon$ values similar, which is not the case. Thus, it is tentatively stated that NO^+ leads to adduct formation, while H^+ promotes charge transfer.



5

Reverting to original optical signal. In continuation, addition of only 5 μL deionized H_2O to NO^+ saturated solution of **1** resulted in quick reappearance of $^1\text{MLCT}$ band at $\lambda_{\text{max}} = \sim 590$ nm and change of colour to blue from green (Fig. S4(1)). Further addition of H_2O was neither able to reposition $^1\text{MLCT}$ band to original value of $\lambda_{\text{max}} = \sim 569$ nm nor able to produce any colour change or change in ' ϵ ' value. This suggested that addition of H_2O induced possible reduction of Fe(III) to Fe(II) , which is actually a well-known phenomenon, but failed to dequaternize the adduct forming pyridyl N-atoms as proposed earlier (dicationic specie). Moreover, the dicationic specie (adduct) could be considered as a weak lewis acid and it was presumed that action of a mild lewis base such as Et_3N would neutralize as well as dequaternize the pyridyl N-atoms. This is indeed what we observed after adding two eqv of Et_3N solution to the solution of dicationic specie. $^1\text{MLCT}$ band reverted to $\lambda_{\text{max}} = \sim 569$ nm along with instant change in colour from blue to purple (Fig. S4(2)). Addition of water to **1** + H^+ solution produced no effect, while addition of 2 eqv of Et_3N restored the $^1\text{MLCT}$ peak position. To check the effect of direct addition of either H_2O or Et_3N to **1**, control experiments were performed. 2 eqv each of H_2O and Et_3N were added either individually or together to solution of **1**, but no noticeable change was observed even after 30 min of reaction time.

Thus, **1** could exist in stepwise formed four stable states, viz. monocationic, dicationic, dicationic-oxidized and **1** itself, upon careful sequential addition of NO^+ . Additionally, monoprotonated, bisprotonated states were observed for addition of H^+ . Moreover, facile switching between different states could be achieved by addition of selected chemical reagents as input. This behaviour of **1** prompted its use as a molecular switch, for different molecular states were inter-convertible as well as stable within experimental time-frame. Moreover, the whole exercise was repeated for at least ~ 4 times to confirm the switching behaviour using the same solution of **1**. Fig.4, left panel demonstrates effect of set-reset events on optical absorption at $\lambda_{\text{max}} = 590$ nm for NO^+ addition to **1**. It does not include the action of Et_3N . With each cycle, there was only ~ 5 -8% signal loss (change in optical absorption) at each step of switching from **1** to dicationic-oxidized state and back, which could be termed as reasonable performance in terms of efficiency. Similar signal losses were observed for H^+ addition. Moreover, signal deviation from three independent switching experiments with different solutions of **1** (10 μM each) was only ~ 3 -6%, (Fig. 4; right panel) which potentially relates to sufficient accuracy of the multiple switching events.

3.2 Molecular Orbitals properties

DFT studies revealed that highest occupied molecular orbital (HOMO) of 1^{2+} and 2^{3+} is dominated by pyridyl moiety of pytpy (see S5a-5d for optimized structures and Table S1-S2 for selected

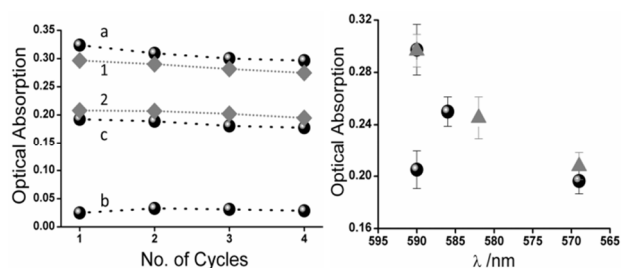


Fig. 3: Black spheres represents addition of NO^+ and grey squares addition of H^+ . (Left) represents same solution optical switching of **1** across four cycles. 'a' indicates changes in absorbance of dicationic state for a single solution in four cycles. Similarly 'b' and 'c' indicates changes absorbance of in oxidized and original state after regeneration respectively. '1' and '2' indicates changes in absorbance of bisprotonated and original state after regeneration respectively. Overall, ~ 5 -8% signal losses were observed after four cycles. (Right) ~ 3 -6% deviation in absorbance of **1** at different wavelengths under study, after addition of either NO^+ or H^+ in three separate experiments. Dotted lines are guide to eyes.

bond length and angles). On the other hand, in the HOMO of 3^{4+} and of 4^{5+} electronic charge density is mainly distributed over metal d orbitals and pyridyl unit. It is observed that, all molecules lowest unoccupied molecular orbitals (LUMO's), electron densities are predominantly residing on pytpy moiety. In order to corroboration of experimentally observed results, calculation of HOMO-LUMO energy gap was performed (1^{2+} for 3.39 eV, 2^{3+} for 0.9 eV, 3^{4+} for 2.08 eV and 4^{5+} for 3.63 eV), which is in general agreement with the changes observed in the $^1\text{MLCT}$ band of **1** upon addition of NO^+ .

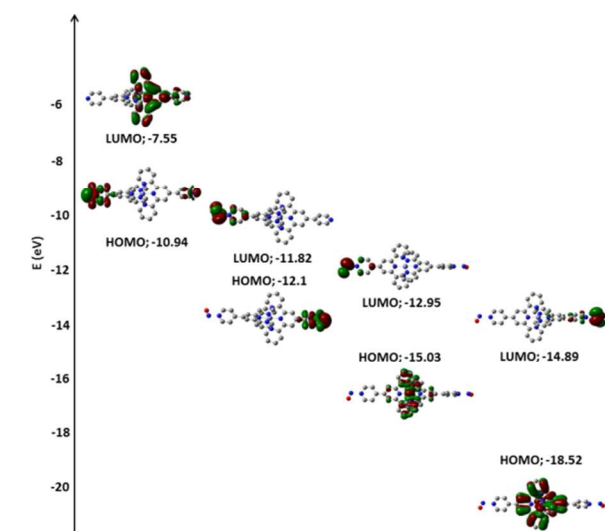


Fig. 4: Molecular orbital pictures (HOMO and LUMO) of 1^{2+} , 2^{3+} , 3^{4+} and 4^{5+} in gas phase.

3.3 Spectro-electrochemical switching events

During bulk electrolysis with coulometry, applied potential of 1.4 V produced significant visible change in the colour of the solution which was confirmed by reduction in optical absorption at ~ 569 nm. The purple colour of the solution became colourless within ~ 3000 s and changes in the optical absorption became stagnant at ~ 6000 s. This observation was in sync with saturation of charge with respect to time and is presented in Fig. 5. At this point, applied potential was changed to 1.0 V and the experiment was re-run. Within ~ 2500 s, the colour changed to purple from

colourless and optical absorption was restored almost to original level (Fig. S6).

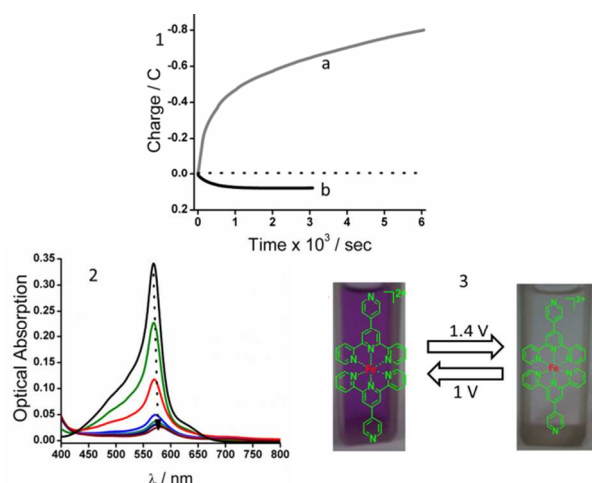


Fig. 5: (1) represents the bulk electrolysis with coulometry of **1** in CH_3CN . 'a' represents oxidation of **1** at an applied potential of 1.4 V while 'b' signifies reduction of **1** from oxidized state at an applied potential of 1.0 V; (2) corresponding changes in the UV-Vis spectrum of **1** during electrochemical oxidation and (3) shows visual colour changes upon application of potential.

The colour changes upon applied potential and as verified through UV-Vis spectroscopy could easily be attributed to Fe(II)/Fe(III) conversion based reversible and oxidation state dependent electrochromic effect. Moreover, upon performing similar experiment for at least five times with the same solution, a ~5 % signal loss was observed (Fig. 6, left panel). Further, it was also observed that there was only ~4-6% signal deviation from three independent reversibility experiments each performed for at least five cycles (Fig. 6, right panel). In addition, cyclic voltammograms of **1** was recorded for 300 cycles at a scan rate of 0.3 V/s and no degradation of **1** was noticed under experimental conditions (Fig. S7). These experiments suggest that electrochemical switching events are sufficiently efficient and accurate along with satisfactory stability of different oxidation states of **1**.

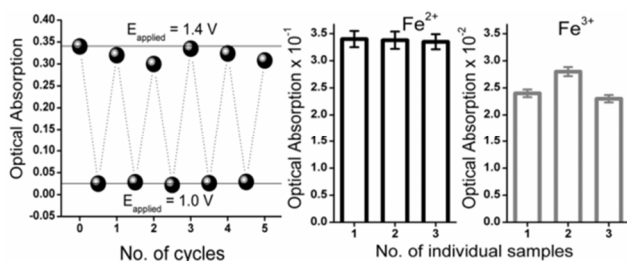


Fig. 6: (Left) Changes in absorbance of **1** in CH_3CN with application of potential across five cycles for a single sample resulting in ~5% signal losses. Top sphere to bottom sphere: $E_{\text{applied}} = 1.4 \text{ V}$; bottom to top sphere: $E_{\text{applied}} = 1.0 \text{ V}$. (Right) Signal deviation of ~4-6% (in terms of absorbance) were observed in three separate spectro-electrochemical switching events. Fe^{2+} represent reduced state (presence of ¹MLCT) and Fe^{3+} oxidized state (absence of ¹MLCT). Dotted lines are guide to eyes.

3.4 Construction of logic gate and circuits

Based on the experimental results, we constructed two and three input molecular logic gates and circuit using **1** and the chemical inputs at molecular level. For designing logic gates, addition of NO^+ or H^+ was considered as Input = 1, else Input = 0. Similarly, when the significant optical changes were observed considered as Output = 1, else Output = 0. In presence of H^+ , the MLCT transition of **1** showed a red shift, while addition of Et_3N reconfigured the MLCT transition. To accomplish logic gate, addition of H^+ was considered as Input1 = 1, while addition of Et_3N as Input2 = 1, while the shifting of MLCT band to $\lambda_{\text{max}} = 590 \text{ nm}$ was considered as Output = 1. When both the chemical inputs (H^+ and Et_3N) were added (Input1 and Input2 = 1) simultaneously, Output = 0 was obtained. Interestingly, when Input1 was applied, Output was observed but no Output was observed upon exclusive application of Input2. This result is presented in Fig. 7 as INHIBIT molecular logic gate along with truth table.

Input 1 (H^+)	Input 2 (Et_3N)	Output ($\lambda_{\text{max}} = 590 \text{ nm}$)
0	0	0
1	0	1
0	1	0
1	1	0

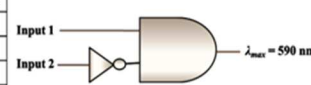


Fig. 7: Representation of the INHIBIT logic gate constructed using two inputs (H^+ and Et_3N) applied on (**1**). Given alongside is the associated truth table.

Molecular logic circuits using three chemical inputs and two outputs have also been designed using **1**. Three chemical inputs used were NO^+ (excess), Et_3N and H_2O as Input1, Input2 and Input3, respectively. Absorbance ("1" for above the threshold value, "0" for below the threshold value) and the red shift of MLCT band to $\lambda_{\text{max}} = 590 \text{ nm}$ were considered as Output1 and Output2 respectively (Fig. 8). The truth table for multiple chemical inputs and multiple outputs has been presented. The Output1 was obtained for all combinations except when Input1 = 1, Input2 = 0 and Input3 = 0, while Output2 was observed ("1") exclusively when Input1 and Input3 were applied and Input2 was absent. The observation afforded the three inputs logic circuits as presented in Fig. 9.

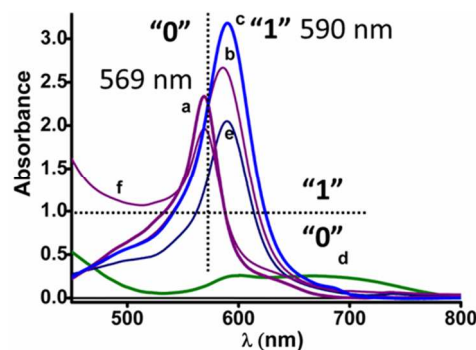


Figure 8: Combined UV/Vis spectra of **1** undergoing switching between different reversible stable states upon external chemical stimulus. a) MLCT band of **1** with $\lambda_{\text{max}} = 569 \text{ nm}$; b) 1 eq. of NO^+ , c) 2 eq. of NO^+ , d) excess of NO^+ ; (e) 5 μL of DI H_2O ; (f) addition of Et_3N . Black line represents baseline with dry acetonitrile. Threshold criteria are clearly indicated.

Input 1 (NO ⁺)	Input 2 (Et ₃ N)	Input 3 (H ₂ O)	Output 1 (Absorbance)	Output 2 (λ _{max} 590 nm)
0	0	0	1	0
0	0	1	1	0
0	1	0	1	0
0	1	1	1	0
1	0	0	0	0
1	0	1	1	1
1	1	0	1	0
1	1	1	1	0

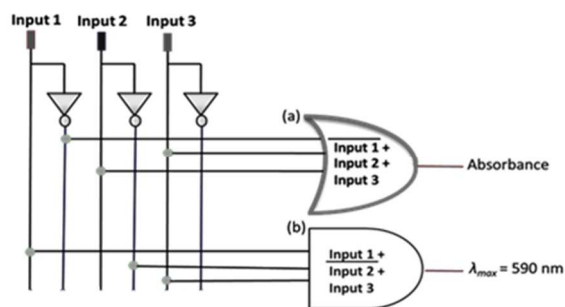


Fig. 9: Representation of molecular logic circuit constructed using three (NO⁺, Et₃N, H₂O) inputs and resulting in two outputs. Given alongside is the associated truth table.

In summary, it has been demonstrated that **1** based molecular building block possesses controllable multiple switching characteristic and is able to generate logic gates and circuits. The operation mechanism has also been proposed and justified. The complex showed up as a multiple switching event and NO⁺ plays dual role i.e., quaternization at lower concentration and oxidation at higher concentration. The molecular switch in response to the external chemical inputs is capable of executing multiple binary Boolean logics at the molecular level. These attractive features makes **1** a smart candidate for the development of hybrid materials³³⁻³⁴ and it could potentially be used for chemically addressable information processing devices at the molecular level.³⁵ Notably, the above complex showed reversible color change by applying potential so; it could potentially find an application as an electrochromic material,³⁶⁻³⁷ and molecular memory devices.³⁸⁻³⁹

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5 Notes and references

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† Dedicated to Late Dr. Tarkeshwar Gupta

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