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Photoassisted "Gate-Lock" Fluorescence "Turn-on" in a New Schiff Base and Coordination Ability of *E*–*Z* Isomers

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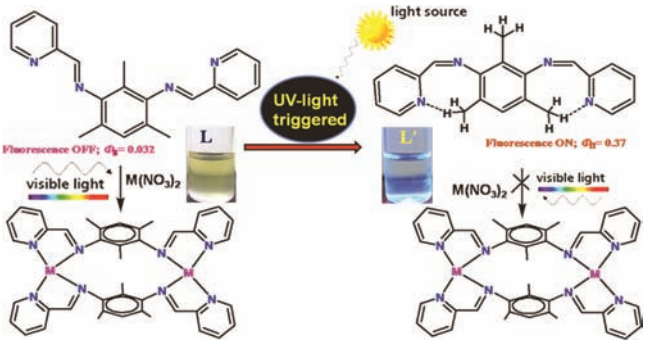
ABSTRACT



Rapid photoresponse (1.0–8.0 min) through fluorescence "turn-on" signaling displayed by a novel Schiff base (L) creating "gate lock" via intramolecular C–H···N interaction in photoisomerized product (L′) has been described. Coordination chemistry of pre- and postirradiated species demonstrated a drastic change in the reactivity which has been supported by NMR, HRMS, UV–vis, emission, electrochemical, and complexation studies.

Light-regulatable fluorescent compounds that undergo structural, conformational, and dynamic changes triggered by light excitation find wide applications as temporal probes.[1] The light-induced structural changes can be easily evaluated if they are directly related to a fluorescent readout.[2] Photoactivation of the compounds in biological systems frequently leads to fluorescence "turn-on" by release of fluorophores with reasonable photostability.[3] Considering their electrical and optical properties, some chemical, biological, gas, and UV-light sensors have been developed.[4] Among these, UV-responsive compounds are in high demand because of their potential applications in diverse areas.[5a,6] Although "off–on" UV-light switches containing ZnO, CdS quantum dots/graphene, and a few retinal-linked Schiff bases have been reported, a selective and sensitive UV-light "off–on" switch based on a free Schiff base has not been described.[5,7]

Further, metallo-supramolecular entities, metallo-hosts, and related systems have received substantial interest owing to their potential application in various fields.[8] Creation of such a system is directed by the relative position of nitrogen atoms in bis-imine Schiff bases.[9,10] To our knowledge, Schiff bases derived from the condensation

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of phenylene-1,3-diamine with pyridyl-*n*-carboxaldehydes (n = 2/3/4, Scheme S1, Supporting Information) have not been reported.[9,10] The objective of designing a selective and sensitive photoresponsive compound can be achieved by developing a conjugated π-electron system, which can assume a more stable configuration by acquiring an appropriate amount of energy. Based on our earlier results and those from other groups,[10,11] through this contribution we describe a new Schiff base 2,4,6-trimethyl[*N*,*N*′-bis-(pyridin-2-ylmethylene)]benzene-1,3-diamine (**L**) which acts as photoswitch and is blind to visible light. The UV-triggered fluorescence enhancement via structural changes and coordination chemistry of both photoisomers has not been described to the best of our knowledge.

Figure 1 summarizes the synthetic strategy for preparation of **L** and its response toward UV-light and metal ions. Schiff base **L** was synthesized by condensation of pyridine-2-carboxaldehyde with 2,4,6-trimethylbenzene-1,3-diamine (2: 1) in benzene (Scheme S1, Supporting Information) in reasonably good yield (83%).

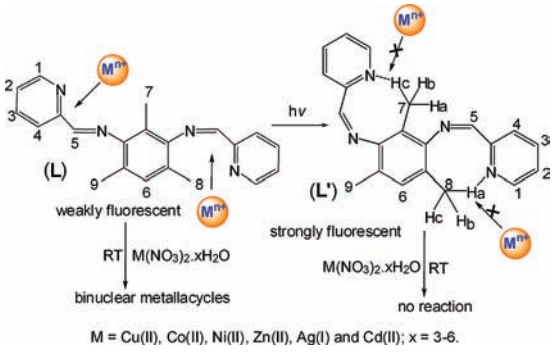

Figure 1. Structures of **L** and **L**′ and approach of metal ions toward the coordination sites of both isomers.

Details about the synthesis of **L**/ **L**′, metallacycles **1**−**6**, and their characterization data is given in the Supporting Information. The characterization of **L** has been achieved by satisfactory elemental analyses, FT-IR, NMR [^{1}H, ^{13}C, 2D COSY (^{1}H−^{1}H, ^{1}H−^{13}C), and DEPT (135°/90°)], UV−vis, fluorescence, and cyclic voltametric studies.

In the ^{1}H NMR spectrum of **L**, *H*1 and *H*4 protons resonated as doublets at δ 8.72 and 8.29 ppm (Figure S1a, Supporting Information) while *H*5 (−CH═N−) and *H*6 as singlets at δ 8.35 and 6.98 ppm. The triplets at δ 7.84 and 7.40 ppm has been assigned to *H*3 and *H*2 proton resonances. Methyl protons of the central mesitylene ring resonated at δ 2.15 (*H*8/*H*9) and 1.99 ppm, (*H*7) suggesting symmetrical orientation of the molecule. The aromatic protons (*H*1-*H*6) of **L**′ exhibited small upfield shift (Figure S2a, Supporting Information). However, the signals due to methyl protons displayed splitting and appeared at ∼δ 2.18−1.98 ppm (downfield shift) indicating some sort of interaction between methyl protons and pyridyl nitrogen (Figure 1). Further, 2D COSY and DEPT NMR spectra of **L**′ exhibited enhanced H−H and C−H coupling and the presence of $-CH_2$ and −CH aliphatic protons (Figure S4 and S5, Supporting Information). On the basis of NMR spectral studies we conclude that the intramolecular C−H···N interactions are responsible for the splitting of methyl protons. Stacked ^{1}H NMR spectra also supported UV-light induced structural changes (Figure S3, Supporting Information). The presence of molecular ion peak at m/z, 329 in the HRMS of both **L** and **L**′ with different fragmentation patterns strongly supported our scheme (Figure 2b and S6, Supporting Information).

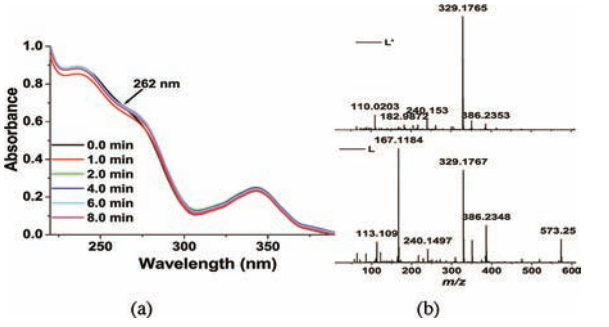

Figure 2. (a) Absorption spectra of **L** (5 μM) and after UV irradiation. (b) HRMS spectra of **L** and **L**′.

UV−vis spectrum of **L** (10 μM, Supporting Information) displayed transitions at 351, 271, and 238 nm assignable to n→π* and π→π* transitions (Table S2, Supporting Information). The absorption spectrum of **L** in methanol also exhibited a pattern analogous to that in H_2O/MeCN system (Figure S7a, Supporting Information, inset). After UV irradiation (01 min, 365 nm; 5 μM), the optical density of low energy band at 348 nm (ε, 2.29 × 10^4 M^{-1} cm^{-1}) gradually increases while that for high energy band (271 nm, ε, 6.20 × 10^4 M^{-1} cm^{-1}) decreases (ε, 6.07 × 10^4 M^{-1} cm^{-1}) (Figure 2a). Notably, irradiation up to 2.0−8.0 min leads to a considerable change in the absorption spectra wherein low energy band showed hyperchromic shift (ε, 2.51 × 10^4 M^{-1} cm^{-1}) and the high energy band a hypsochromic (ε, 7.13 × 10^4 M^{-1} cm^{-1}) with red shift of ∼3−5 nm. The isosbestic point at 275 nm (1.0 min exposure) disappeared upon increasing the

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irradiation time (2.0−8.0 min) and a new one appeared at 264 nm. Narrow spectral alterations with two consecutive isosbestic points clearly suggested the presence of more than one species.[12] Closer examination of the absorption spectra of **L** and **L′** (Figure 2) indicated some structural changes (i.e., orientation, geometry, etc.) retaining conjugation length. This can be rationalized by assuming the movement of pyridyl ring (*E,Z*) to form an eight membered cyclic ring (*Z,Z*) involving C−H···N hydrogen bonding between methyl protons and nitrogen lone pair.[13] The effect of metal ions were investigated under analogous conditions. Notably, interactions between **L′** and various metal ions led to insignificant changes (Figure S8, Supporting Information) suggesting **L** becomes inert toward the tested metal ions after UV exposure.

The Schiff base **L** fluoresces weakly at 430 nm (λ_{ex}, 350 nm; Φ_{fl}, 0.032)[14] with a Stokes shift of 5316 cm^{-1} (Figure 3 and Table S2, Supporting Information), which may be attributed to photoinduced electron transfer process.[14] To examine the photostability of **L** fluorescence spectra of the same solution was acquired repeatedly with 1 min time interval which showed gradual increase in the relative emission intensity (∼91%). The light-induced fluorescence enhancement motivated us to scrutinize the cause of photoswitching ability. Therefore, fluorescence titrations were performed using **L** as a 'host' and light as a 'guest'. After each excitation and proper mixing (Δt, 1.0 min) **L** showed gradual increase in the fluorescence intensity (Figure 3b) with insignificant change in the Stokes shift (53 cm^{-1}). The trend continued and attained saturation after 8.0 min (Figure 5, inset) with an increase in quantum yield by a factor of ∼11 (Φ_{fl}, 0.377). Time versus intensity plot gave a sigmoid curve indicating two step structural changes (Figure 3b, inset). Fluorescence "turn-on" without any significant change in Stokes shift suggested the possibility of structural changes rather than photocleavage. The interaction of solvent with **L** under influence of UV light cannot be ruled out; therefore, fluorescence behavior of **L** was investigated in MeOH, THF, DMF, DMSO, 1,4-dioxane, CH_2Cl_2, and C_6H_6. Notably, it exhibited an analogous pattern in the aforesaid solvents except a small decrease in relative intensity in C_6H_6 (Figure S7b, Supporting Information).

To understand the reversibility of structural changes in the presence and absence of UV light, **L** (MeCN, 3 mL, 100 μM) was irradiated for different durations (10 min to 24 h, 365 nm) and monitored by emission spectral studies. The spectral features were similar for a sample irradiated for short (10 min) or long (24 h) time period suggesting that ∼10 min is sufficient for the conversion of **L** to **L′**. To

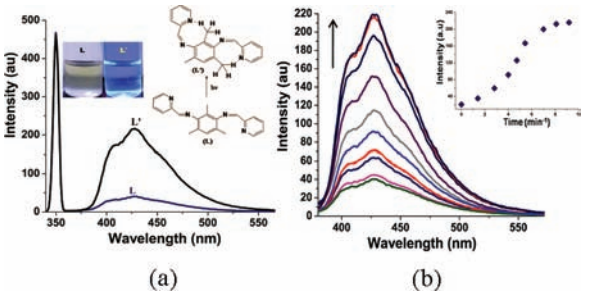

Figure 3. (a) Fluorescence spectra of **L** and **L′** (*c*, 10 μM; λ_{exc}, 350 nm). Inset shows structural and color changes upon irradiation. (b) Fluorescence titrations of **L** to **L′** (*c*, 10 μM). Inset shows fluorescence enhancement of **L** with respect to fraction of UV-light/min.

gain deep insight into wavelength triggered structural changes, **L** was irradiated at 254 nm. It showed behavior similar to that observed at 365 nm (Figure S9b, Supporting Information). Additionally, **L′** remains unchanged in dark (298 K, CH_2Cl_2, 24 h).

Based on our earlier findings,[10] the report by Ray et al.,[11] and NMR, HRMS, UV−vis, and fluorescence spectral data, we propose that light-induced structural changes in **L** retain the extent of conjugation and controlled by intramolecular C−H···N interactions.[13] The resulting eight-membered ring creates rigidity in the molecule which controls vibrational motion and in turn, fluorescence "turn-on".[15] One can speculate that **L′** would be less reactive or inert toward metal ions. To affirm our postulation, nitrate salts of various metal ions were added to a solution of **L′** (Figure S9a, Supporting Information). It was observed that the fluorescence spectrum of **L′** remains unchanged indicating inertness of **L′** toward the metal ions. In contrast, such type of ligands show good coordination ability toward transition metals.[10]

Therefore, **L** and **L′** were treated with various metal ions in the absence of UV light in methanol at room temperature. Notably, **L** reacted readily with most of the metal nitrates and afforded binuclear metallacycles $[\{M(C_{21}H_{20}N_4)\}_2\}_2]$ $(X^-)_n$, (**1**−**6**), $[Co(C_{12}H_8N_3O_2)_2]$-$PF_6 \cdot H_2O$ (**2b**), and $[\{Ni(C_{21}H_{20}N_4)(H_2O)_2\}_2]$ $(NO_3)_4$ (**3a**) (Scheme S2, Supporting Information), characterized by elemental analyses and spectral (FT-IR, NMR, absorption, and emission) and electrochemical studies (Figures S10−S12, Supporting Information). Structures of **1**, **2b**, **3a**, and **5** have been determined crystallographically (Figure 4 and Figure S13 and Table S1, Supporting Information). The crystal structure of **3a** exhibited a looped arrangement with double-stranded 12-membered metallamacrocycle cation $[\{Ni(C_{21}H_{24}N_4O_2)\}_2]^{4+}$ along with coordinated water molecules. In the cations of **3a** immediate coordination geometry about each Ni(II) is distorted octahedral with NiN_4O_2 environment[16] and N_4O_2

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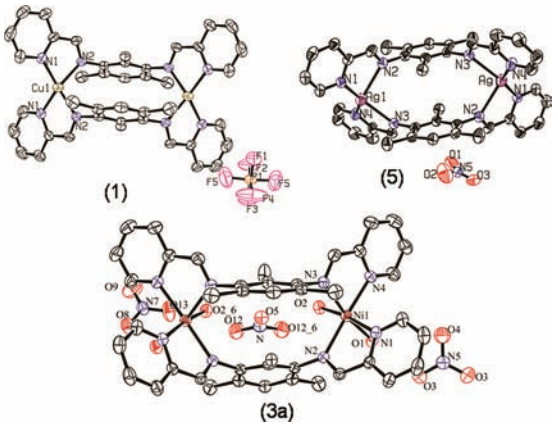

Figure 4. Crystal structures of **1**, **3a**, and **5** (30% thermal probability).

donor sites contains opposite (Δ, Λ) chirality. It represents the first Ni(II) octahedral complex containing a Schiff base derived from substituted benzene-1,3-diamine.[16]

To have a clear correlation between **L** and corresponding metallacycles, the absorption and fluorescence behaviors of **1**−**6** were investigated (Figure 5 and Figure S14 and Table S2, Supporting Information). Among these, **1**, **2b**, **3a**/**3b** are nonfluorescent, while **4**−**6** displays strong fluorescence with significant Stokes shift relative to **L**/**L**′ due to the chelation enhanced fluorescence (CHEF) process.[17]

On the other hand, the reaction between **L**′ and metal nitrates under only visible light do not yield any complex at room temperature. Further, **L**′ was extracted from the reaction mixture (96%) using dichloromethane. Marked difference in the reactivity of **L** and **L**′ supported creation of a cyclic structure after UV irradiation, wherein the approach of metal is restricted by intramolecular C−H···N interactions "gate-lock" (Figure 1).[13]

Redox behavior of **L**, **L**′ (Figure 6 and Table S2, Supporting Information) and metallacycles **1**−**6** (Figures S15−S22, Supporting Information) have been followed by cyclic voltammetry. The cyclic voltammogram of **L** displayed one irreversible wave at +1.63 V (E_{pa}) in the anodic potential window. It has been tentatively assigned to oxidation of π-conjugated Schiff base (HOMO) to mono cationic ($HOMO^{+}$) species.[18] The quasi-reversible waves at E_{pc} −1.38 and −1.97 V may be assigned to ligand based reductions.[18] Conversely, **L**′ displayed an oxidative wave at +1.72 V and two quasi-reversible reductions −1.45, and −2.43 V. High positive and negative $E_{1/2}$ values for **L**′ are consistent with its stabilization relative to **L**. The observation is consistent with the conclusions drawn from optical studies.

Light induced *E*−*Z* isomerization in **L** and the presence of C−H···N interactions in **L**′ has further been supported

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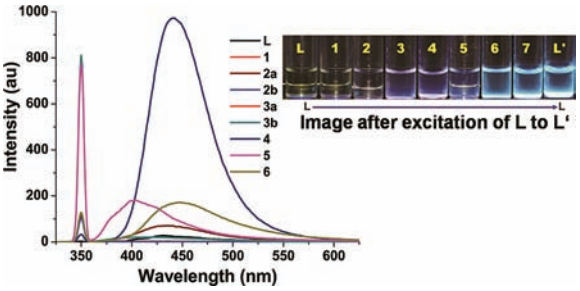

Figure 5. Fluorescence spectra of **1**−**6** (*c*, 10 μM; H_2O/MeCN, 7: 3). Inset shows fluorescence enhancements from **L** to **L**′.

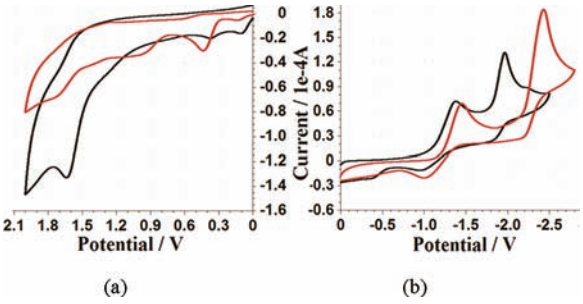

Figure 6. Cyclic voltammograms of **L** (black) and **L**′ (red) in H_2O/MeCN (7:3) in anodic (a) and cathodic (b) windows.

by comparing optical properties of **L**, **L**′ and model system **L1**. The UV−vis spectra of **L1** exhibited changes due to *E*−*Z* isomerization, while fluorescence spectra remains unaltered upon UV-irradiation (Figure S23, Supporting Information).

Through this work we have presented a new Schiff base **L** exhibiting UV-triggered fluorescence 'turn-on' due to *E*−*Z* structural changes controlled by intramolecular C−H···N interactions leading to a gate-lock for metal ion coordination. Unambiguous support has been provided by NMR, HRMS, UV−vis, emission, and electrochemical studies and complexation behavior. Both **L** and **L**′ are stable under visible light and exhibit marked difference in the reactivity toward various metal ions.

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Supporting Information Available. Schemes, NMR spectra, ORTEP view, optical plots, cyclic voltammograms, and tables. This material is available free of charge via the Internet at http://pubs.acs.org.