Low-cost photo-switches based on stilbene-appended Zn(II)–terpyridine complexes

Shruti Mukherjee¹ · Poulami Pal¹ · Anik Sahoo¹ · Sujoy Baitalik¹

Received: 23 April 2021 / Accepted: 30 July 2021 / Published online: 27 August 2021

© The Author(s), under exclusive licence to European Photochemistry Association, European Society for Photobiology 2021

Abstract

We report herein the synthesis, characterization, photophysics, and photo-isomerization behaviors of three Zn(II)–terpyridine complexes of the type $[Zn(tpy-pvp-X)_2]^{2+}$ ($X = H, Me, \text{ and } NO_2$) covalently tethered with stilbene moiety. The complexes exhibit absorption bands stretching up to the edge of the visible domain due to ligand $\rightarrow$ ligand charge transfer (LLCT) transitions and strong emission at room temperature in the visible due to radiative deactivation of 3LLCT state having lifetime within 1.0–3.0 ns. The stilbene motifs in the complexes undergo *trans* to *cis* isomerization upon irradiating with UV and visible light accompanied by significant alteration of their absorption, emission, and 1H NMR spectral profiles. Apart from the variation of electron donating and electron withdrawing substituent (X), the isomerization studies were also carried out in three different solvents (DCM, MeCN, and DMSO) to further tune their kinetic and thermodynamic parameters. The rate, rate constant and quantum yield of isomerization were estimated in all the solvents. The reverse process (*cis* to *trans*) also occurs very slowly on keeping but could be accelerated upon heating. *Trans* to *cis* photoisomerization leads to quenching of emission in case of **1** and **2**, whereas backward thermal *cis* to *trans* conversion leads to restoration of emission. By contrast, for the nitro-derivative (**3**) forward process induces emission enhancement, while backward process gives rise to emission quenching. In essence, “on–off” and “off–on” emission switching is feasible for **1** and **2**, whereas “off–on” and “on–off” emission switching occurs in case of **3**. Emission spectral responses upon successive action of photonic and thermal input lead to the fabrication of INHIBIT and IMPLICATION logic gates. DFT and TD-DFT computational investigations were also undertaken to visualize their electronic structures, correct assignment of the spectral bands, and mode of isomerization process.

✉ Sujoy Baitalik
sbaitalik@hotmail.com; sujoy.baitalik@jadavpuruniversity.in

¹ Inorganic Chemistry Section, Department of Chemistry,
Jadavpur University, Kolkata 700032, India

Graphic abstract

Low cost photo-switches based on stilbene-appended Zn(II)-terpyridine complexes

Keywords Zn(II)-terpyridine complexes · Trans-cis photoisomerisation · Photo-switching · Logic gate · DFT-TDDFT

1 Introduction

There is increasing interest in the fabrication of task-specific materials as a response to external stimuli, such as light, heat, mechanical effects or chemical species [1–6]. Among the different external stimuli, light is one of the most convenient source and the substances can be excited at desired wavelength of choice spanning within a wide domain (UV to IR). The interaction event can often lead to different performances, such as emission of light, electron or energy transfer, conformational changes, sensitization or chemical transformation which can laid the foundations for many applications [7–16]. An optical stimulation is also very loyal to user, and switching off the source creates an instant turn off of the optical signal. Moreover, the light sources can be remote controlled over a long distance which is beneficial for the design of optical information storage, high density optical memory, and optical switches [11–14, 17].

Stilbene and its derivatives undergo optically stimulated reversible *trans*–*cis* isomerization and constitute an important class of photo-responsive materials [18–22]. The conformational change is coupled with a significant alteration of their photophysical behaviors which in turn is useful for practical applications. Even though lots of studies were performed with purely organic stilbene derivatives, but analogous studies with their coordination complexes are comparatively limited in the literature [18–22]. Compared to organic compounds, metal complexes offer a greater variety of electronic structures, in relation to the coordination

sphere, electronic configuration and oxidation state of the metal [23–33]. To mimic the function of photochemical molecular devices (such as photo switches) in metal complexes, one of the most effective strategies is to reversibly alter their properties by inducing conformational changes on the photo-responsive component appended on the ligands. A majority of the studies to this end are primarily focused on noble metals which are very expensive and the synthetic procedures often demand very drastic conditions [23–33]. Our primary objective in this work is to design suitable base-metal complexes which could show off similar behavior and can lead to the construction of a new class of low-cost and easily synthesizable photo-switches.

For achieving our goal, we report in this work synthesis, characterization, photophysics, and reversible *trans*–*cis* photoisomerization properties of a new class of homoleptic Zn(II)-terpyridine complexes of composition $[\text{Zn}(\text{tpy-pvp-X})_2]^{2+}$ ($\text{X} = \text{H}$, Me , and NO_2) covalently attached with photo-responsive stilbene moiety (Structure 1). Among the polypyridines, 2,2':6',2''-terpyridine affords an excellent building motif for the construction of molecular systems around the photoactive metal centers [34–41]. The superiority of terpyridine over bipyridines is because of its effortless functionalization, particularly at 4'-position and competence to build up linear achiral structures [34, 35].

Low-cost zinc metal is playing progressively important role for the design of a wide variety of coordination complexes with interesting photophysical properties which in turn can be useful in nonlinear optical properties as well

Structure 1 Chemdraw structures of the complexes under present investigation

as multi-photon fluorescent probes [42–45]. Because of d^{10} electronic configuration, Zn(II) complexes do not display stereochemistry preference arising from ligand field stabilization effects and they can acquire a wide variety of geometries and coordination numbers, depending upon the electronic nature and stereochemistry of ligands. The important characteristics of zinc also allows the preparation of complexes with intense intra-ligand charge transfer (LLCT) absorption and emission at low energy [42–45]. In addition, the absence of low-energy metal-to-ligand (MLCT) or metal $d-d$ electronic transitions makes these zinc complexes generally more optically transparent than other metal d^n congeners.

Optically stimulated reversible *trans*–*cis* isomerization of stilbene appended heavier transition metal complexes (particularly Re, Ru, Ir and Pt) were thoroughly investigated by different research groups [46–56]. The results of these investigations laid the foundation for the construction of effective photo molecular switches. In contrast to noble metal analogues, similar investigations with low-cost 3d metals are much less in literature [57–59]. Although, Zn(II)–terpyridine complexes appended with one or more stilbene moiety are reported with regard to the design of efficient two-photon probes for bioimaging [60] and improvement of second-order nonlinear optical (NLO) responses [61], no report dealing with their photo-isomerization aspects are available in the literature. Herein, we address the influence of solvents and the effect of electron donating/withdrawing substituent (X) on their optical properties as well as thermodynamic and kinetic features of photoisomerization procedure. The influence of excitation wavelength on thermodynamic and kinetic features of isomerization procedure will also be maneuvered. In essence, substantial alteration of the optical properties along with switching of emission spectral characteristics of the complexes is made possible upon isomerization. Moreover, the emission spectral output as a function of photonic and thermal inputs is utilized

for the fabrication of INHIBIT and IMPLICATION logic gates. The processing of information at the molecular level is now a very active area of research and proper utilization of sequential logic functions exhibited by molecular and supramolecular species is a huge challenge in research filed of information technology [62–66]. In conjunction with experiment, theoretical studies employing DFT and TD-DFT methods are also carried out to acquire insight about the electronic structures of the complexes, correct assignment of the spectral bands, and to understand the actual mode of isomerization process.

2 Experimental section

2.1 Materials

Chemicals and solvents are procured either from Sigma or from the local vendors. Synthesis and characterization of the ligands, tpy-pvp-X (X = H, Me, and NO₂) are accomplished by our reported procedure [30]. Detailed procedure for the synthesis, purification and characterization of the Zn(II) complexes are provided in Electronic supplementary information.

2.2 Physical measurements

2.2.1 Determination of photoisomerization rate constants and quantum yields

Photoisomerization experiments are carried out in a 1-cm quartz cuvette using $\sim 10^{-5}$ M nitrogen purged solution of the complexes in a Lelesil photocatalytic reactor. UV light source of 334 nm and visible light of 405 nm are used. The rate constant of photoisomerization (k_{iso}) is determined via absorption titration data through the use of Eq. 1 [67, 68]:

$$\ln \left\{ (A_0 - A_\infty) / (A_t - A_\infty) \right\} = k_{\text{iso}} t, \quad (1)$$

where A_0 , A_t , and A_∞ corresponds to the absorbance at time $t=0$, t , and ∞ , respectively. The light source intensity of the lamp is ~ 0.11 W. The quantum yield (ϕ) of isomerization is determined using Eq. 2: [69]

$$\nu = (\phi I_0 / V) (1 - 10^{-\text{Abs}}), \quad (2)$$

where ν , I_0 , and V corresponds to the rate of *trans*-to-*cis* isomerization, the photon flux at the front of the cell, and the volume of the solution, respectively. The ϕ value of photoisomerization is determined by a relative method using azobenzene as the standard. We carried out the isomerization measurements of azobenzene in our experimental setup and upon considering the ϕ of *trans* to *cis* photoisomerization of azobenzene in MeOH as 0.15 [70, 71]. Finally, we calculated the ϕ through the use of said quantum flux via Eq. 2.

2.3 Computational studies

Computational details are given in the Electronic supplementary information.

3 Results and discussion

3.1 Synthesis and characterization

The terpyridine ligands (tpy-pvp-X with X=H, Me and NO₂) are synthesized upon reacting tpyPhCH₂PPh₃Br with 4-substituted benzaldehyde in DCM at ~ 5 °C and thoroughly characterized by adopting our reported procedure [30–32]. The Zn(II) complexes are synthesized upon treating tpy-pvp-X with [Zn(ClO₄)₂] in 2:1 molar ratio in chloroform–methanol (1:1, v/v) mixture at RT and purified through column chromatography followed by recrystallization from chloroform–methanol (1:2, v/v) mixture. The complexes are characterized by elemental (C, H and N) analyses as well as ESI mass and NMR spectroscopy.

3.2 NMR spectra

¹H NMR spectra of the complexes **1–3** in CD₃CN are presented in Fig. 1. The entire proton resonances are tentatively assigned by comparing with the ¹H NMR spectra of the related complexes.⁴³ The overall spectral pattern suggests that the two tpy-pvp-X units around the Zn²⁺ center are oriented symmetrically. The singlet at ~ 2.31 ppm (not displayed in Fig. 1) which integrates three protons is assignable as methyl protons of tpy-PhCH₃ motif in **2**. A second singlet which appears within 9.33–8.86 ppm region and integrates

four protons is due to H₃. A pair of doublets that appear within 7.25–7.84 ppm is due to ethylenic protons (H₉ and H₁₀). The spectral pattern and the values of coupling constants of H₉ and H₁₀ protons suggest the *trans–trans* conformation of the complexes.

3.3 Mass spectra

Electrospray ionization mass spectra of the complexes along with their isotopic distribution are presented in Fig. S1 (ESI). A strong peak is observed at $m/z=443.15$ for **1** and 457.13 for **2**. The agreement between the experimental and calculated pattern is quite good. The peak corresponds to the bi-positive ion of the type [Zn(tpy-pvp-X)₂]²⁺ in the complexes.

3.4 Computational investigations

Geometry optimization of the Zn(II)–terpyridine complexes in their *trans–trans* forms were performed in acetonitrile using Gaussian 09 program [72] and employing the DFT method with B3LYP/level and CAM-B3LYP level of theory [73, 74]. 6-31G* basis sets were employed for the C, H, N, and O, while LanL2DZ basis set was employed for the Zn atom [74]. The optimized structures are presented in Fig. S2 (ESI). Representative bond distances and angles are provided in Tables S1–S2 (ESI). Zn²⁺ is coordinated in bis-tridentate manner with two tpy-pvp-X units in the complexes with distorted octahedral geometry. Frontier molecular orbital plots show that with a few exception, the HOMOs are predominantly located on stilbene and *p*-substituted phenyl group (Table S3 and Fig. S3, ESI). LUMOs are mainly located on the tpy motif with small contribution of stilbene moiety with the exception of **3**, where the LUMOs are principally located on either nitrobenzene or tpy unit (Table S3 and Fig. S3, ESI).

TD-DFT calculations are performed using both B3LYP and CAM-B3LYP level to get the calculated absorption spectra of the complexes and the results are summarized in Fig. 2 and Tables S4–S5 (ESI). The participation of FMOs in their lowest energy band is also displayed in Fig. 2. The lowest energy band is principally due to stilbene to terpyridine charge transfer (LLCT) transitions, while the next higher energy band is found to be an admixture of both LLCT and $\pi-\pi^*$ transitions.

The lowest triplet states (T1) of the complexes are also optimized in the solution state by TD-DFT calculation using B3LYP/level methodology. The singly occupied molecular orbitals (SOMOs) which participate in the lowest lying triplet excited state of the complexes are presented in Fig. S4 (ESI) and the singlet–triplet excitation energies at the lowest triplet state are presented in Table S6 (ESI). Upon analysis of the dominant transition, it could be concluded

Fig. 1 ^1H NMR spectra of **1** (a), **2** (b) and **3** (c) in CD_3CN

the emission is originated mainly from radiative deactivation of $^3\text{LLCT}$ excited state featuring SOMOs located on the stilbene and tpy unit for **1** and **2**, while on stilbene and nitrobenzene moiety for **3**. In addition to TD-DFT, UKS calculations are also performed directly on the triplet state of the complexes using both B3LYP and CAM-B3LYP methods (Tables S7–S8, ESI). The emission energies of the complexes are obtained from the energy difference between the ground singlet and the excited lowest triplet state in the optimized geometry. The calculated emission maximum on the basis of TDDFT and UKS are presented in Tables S6–S8 (ESI). The spin density plots for the complexes in their triplet state derived from UKS calculations are also presented in Fig. 3 to get an idea about the nature of the emitting excited state in the complexes. In line with TD-DFT calculations, the spin density plots also suggest that the emission is originated from radiative deactivation of the $^3\text{LLCT}$.

3.5 Absorption and emission spectra

Absorption and emission spectra of the complexes are recorded in three different solvents. The overlay of the experimental and the calculated absorption spectra of the complexes in MeCN are displayed in Fig. 2, while the relevant spectral data are presented in Table 1. A broad band within the spectral domain of 341–390 nm is observed in all complexes which can be assigned with the aid of TD-DFT calculations as ligand-to-ligand charge transfer (LLCT) from phenyl–vinyl to the coordinated terpyridine moiety. Several bands within 291–236 nm region originated because of $\pi\text{--}\pi^*$ transitions. The position of LLCT band maximum varies to a small extent, depending on the nature of X in the complexes. The outcomes of the TD-DFT calculations obtained using B3LYP level of theory show a large disparity between experimental and

Fig. 2 Left panel shows the overlay of the calculated (pink lines) and experimental (blue lines) UV–Vis absorption spectra of **1** (a), **2** (b) and **3** (c) in acetonitrile. Calculated results are also presented in the

sticks form by CAM-B3LYP level of calculation. The right panel shows the frontier molecular orbitals that are involved in the lowest energy absorption band

Fig. 3 Spin density plots for the T1 state of the *trans–trans* form of **1**(a), **2**(b) and **3**(c) in MeCN

Table 1 Absorption and emission spectral data of **1–3**

Compounds	Absorption, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)			Luminescence, $\lambda_{\text{max}}/\text{nm}$		
	MeCN	DCM	DMSO	MeCN	DCM	DMSO
1	362 (28,900), 344 (31,300), 288 (27,600)	381 (25,400), 344 (sh) (20,800), 322 (25,600)	347 (22,700), 291 (19,400)	522	510	421, 518
2	363 (26,400), 342 (28,200), 285 (24,900)	390 (32,300), 322 (35,400), 287 (34,400)	347 (33,900), 288 (28,900)	518	524	435, 535
3	341 (44,900), 284 (34,880), 236 (41,680)	372 (39,500), 343 (42,400), 285 (32,200)	375 (28,000), 351 (27,100), 287 (26,100)	499	503	515

calculated spectra (Table S4, ESI). Particularly, the huge band within the spectral region of 400–500 nm in the calculated spectra is not show off in the experimental spectra. To this end, we again carried out calculations using CAM-B3LYP level of theory, keeping the basis sets unchanged (Table S5, ESI). The overlay of the experimental and calculated absorption spectra obtained by the later method is displayed in Fig. 2 which shows a good agreement between the calculated and experimental results.

Upon excitation at the LLCT or π – π^* band, all the Zn (II) complexes exhibit strong emission band within 420–535 nm, dependent on the electronic nature of the substituent (X) and the solvent used (Fig. 4). Good correlation between the experimental observations and theoretical results performed on the triplet state of the complexes also leads us to conclude that the emission arises from radiative deactivation of $^3\text{LLCT}$ state. It is to be noted from Tables S6–S8 (ESI) that as compared with the UKS approach, the calculated values of emission maxima of the complexes obtained by TDDFT method are closer to those of the experimentally observed values. Lifetime of the complexes was measured through time-correlated single photon counting and the decay profiles together with their lifetime values are presented in Fig. 4b. The complexes display mono-exponential decay profiles and the emission lifetime of the complexes in MeCN increases in the order **3** (2.4 ns) < **1** (2.8 ns) < **2** (3.0 ns).

In situ generation of Zn(II) complexes are also observed in all the three studied solvents via absorption and emission spectroscopy (Fig. 5 and Figs. S5–S8, ESI). Upon incremental addition of $\text{Zn}(\text{ClO}_4)_2$, a new band evolves in the longer wavelength region (341–390 nm), gradually intensifies and finally saturates upon addition of 0.5 equiv of Zn^{2+} indicating the formation of $[\text{Zn}(\text{tpy-pvp-X})_2]^{2+}$ (Inset of Fig. 5a and Figs. S5–S6, ESI). In the absorption spectral profiles, several clean isosbestic points (at 361, 307 and 272 nm for tpy-pvp- CH_3 in DCM) clearly suggest the transformation of the free tpy-pvp- CH_3 to $[\text{Zn}(\text{tpy-pvp-CH}_3)_2]^{2+}$ (Fig. 5a). In the emission side, gradual quenching of emission at ~410 nm is also accompanied by a distinct emission enhancement at ~524 nm upon incremental addition of Zn^{2+} (Inset of Fig. 5d and Figs. S5b–S8b, ESI).

3.6 Photo-isomerization studies of the complexes

As the complexes possess two stilbene motifs, we are interested to undertake their light-induced isomerization behaviors. We performed isomerization studies in three different solvents (DCM, MeCN and DMSO) upon the action of UV (334 nm) as well as visible (405 nm) light sources. The isomerization event was monitored through absorption, emission and time correlated single photon counting measurements. First, the isomerization studies are carried out in acetonitrile and absorption and emission spectral changes upon irradiation of UV light are presented in Fig. 6. Only one-step change is observed in their absorption and emission spectral profiles. The intensity of LLCT band (at ~345 nm) decreased gradually with simultaneous increase of the π – π^* band intensity (~285 nm). The extent of decrease varies in the range of 40–65% for the LLCT, while increases between 15 and 35% for the π – π^* band (~285 nm), depending upon the nature of X. During the process, successive absorption lines pass through several well defined isosbestic points (307 nm and 248 nm for **3**). Small blue-shift of the LLCT bands is observed during the isomerization process (Fig. 6). Almost complete quenching of emission intensity (~95%) at ~510 nm was noticed for **1–2**, whereas substantial enhancement (~56%) was observed for **3** during photo-irradiation (Fig. 6f). In spite of emission quenching, small increase in lifetime is observed during the isomerization processes (inset of Fig. 6f). The isomerization studies performed in two other solvents (DCM and DMSO) in presence of UV light also induce one-step change in all the three complexes. The absorption spectral profiles of the complexes in DMSO (Fig. S9, ESI) are similar to that of MeCN but differ considerably in DCM (Fig. 7). In DCM, the intensity of broad LLCT absorption band decreased gradually through several isosbestic points (358, 285 and 237 nm for **1**) with concomitant increase of the π – π^* band intensity at ~325 nm. In contrast to the observed behavior in MeCN and DMSO, the emission intensity gradually increases in DCM together with significant blue shift of the emission maximum (510 → 460 nm for **1**) upon isomerization (Fig. 7). In addition, a clean isoemissive point (~499 nm) is observed

in all cases except nitro derivative. By contrast, red-shift of the emission maximum is observed (500→510 nm) in the case of nitro-derivative (**3**) (Fig. 7f). To check the effect of irradiation wavelength on the thermodynamic and kinetic aspects of the isomerization process, we also monitor the spectral change in the complexes in presence of visible light ($\lambda_{\text{max}} = 405$ nm). One-step change is also observed with visible light having almost similar spectral profile as noticed with UV irradiation, although the time of irradiation and extent of spectral change differ (Figs. S10–S12, ESI). Taking into consideration the one-step change in both absorption and emission spectral profiles, irrespective of solvents and irradiating wavelengths, we surmise a possible mode of conversion could be due to *trans*–*trans* to the corresponding *trans*–*cis* form.

We also monitored the isomerization behavior through ^1H NMR spectroscopy to ascertain the probable mode of isomerization of the complexes. A representative complex (**2**) is chosen for this purpose as the signals for the isomerizable protons associated with the stilbene bond are clearly observed for this complex. ^1H NMR spectrum of **2** as a function of irradiation time with 405 nm light is shown in Fig. 8. Upon photolysis, we noticed a gradual decrease in intensity of the proton signals associated with stilbene unit (H_9 and H_{10}) as well as the adjacent protons (H_7 , H_8 , H_{11} and H_{12}). Concomitant growth along with systematic intensification of the said proton signals are observed in the up-field region with time ($\{\text{H}_7 = 8.25$ ppm, $J = 7.2$ Hz); ($\text{H}_8 = 8.01$ ppm, $J = 7.4$ Hz); ($\text{H}_9 = 6.76$ ppm, $J = 12.0$ Hz); ($\text{H}_{10} = 6.69$ ppm, $J = 12$ Hz), ($\text{H}_{11} = 7.77$ ppm, $J = 7.9$ Hz); ($\text{H}_{12} = 7.47$ ppm, $J = 8.2$ Hz)}. It is observed that H_9 and H_{10} protons experienced an up-field shift ($\{\Delta\delta(\text{H}_9) = 0.57$ ppm and $\Delta\delta(\text{H}_{10}) = 0.56$ ppm} along with remarkable decrease of J values (from ~ 16 to ~ 12 Hz). The adjoining protons (H_7 , H_8 , H_{11} and H_{12}) also experienced an up-field shift ($\{\Delta\delta(\text{H}_7) = 0.07$ ppm, $\Delta\delta(\text{H}_8, \text{H}_{11}) = 0.06$ ppm and $\Delta\delta(\text{H}_{11}, \text{H}_{12}) = 0.04$ ppm} upon photolysis for 8 h. The observed spectral change suggests the isomerization is taking place from *trans*–*trans* to the corresponding *trans*–*cis* form [43, 52, 69].

We also carried out TD-DFT calculations on the *trans*–*cis* forms of the complexes in their singlet and triplet excited states to compare the experimental spectra with the calculated results. The calculated results are summarized in Tables S9–S14 and Figs. S13–S15 (ESI). The overlay of the calculated and experimental absorption spectra of the *trans*–*trans* and *trans*–*cis* forms of the complexes is displayed in Figs. 9 and S16 (ESI). The agreement between the experimental and calculated results is remarkably good and the trend of the experimentally observed blue-shift in the lowest energy absorption and emission maxima on going from *trans*–*trans* to *trans*–*cis* isomer is reproduced in our calculation. The lowest triplet states of the *trans*–*cis*

forms are also optimized through UKS calculations using both B3LYP and CAM-B3LYP methods and the results are summarized in Tables S15–S16 (ESI). The experimentally observed emission maxima match better with the results obtained from TD-DFT calculation than that of the UKS calculation.

The backward *trans*–*cis* to *trans*–*trans* conversion proceeds very slowly at ambient condition. We tried to revert back by heating the isomerized solution at ~ 40 °C and observed slow conversion towards their initial form in all the studied solvents. But we are unable to revert back to the exact initial position. The absorption and emission spectral changes of the complexes upon heating at 40 °C are presented in Figs. 10, 11 and S17–S20 (ESI). Emission quenching and red-shifting of the respective band is observed in the reverse process and restoration of the original spectra occurs to the extent of $\sim 90\%$ in DCM. In MeCN and DMSO, the original emission was also restored up to the extent of 80% by heating at 40 °C. Thus, successive “on–off” and “off–on” emission switching processes can be achievable by alternative treatment with light and heat.

We calculated the “apparent” rate constants (k_{iso}), quantum yield (Φ) and free energy of activation ($\Delta G^\ddagger$) for both the forward and the reverse processes and the values are provided in Tables 2, 3 and 4. We used the term “apparent rate constant” as it depends on the intensity of light. The k_{iso} for the forward process varies between $1.1 \times 10^{-4} \text{ s}^{-1}$ and $38.9 \times 10^{-4} \text{ s}^{-1}$, dependent on the nature of substituent X, solvent and wavelength of light used. The rate constants of the thermal backward process, on the other hand, vary between $0.5 \times 10^{-5} \text{ s}^{-1}$ and $9.2 \times 10^{-5} \text{ s}^{-1}$.

In a previous report, we investigated the photoisomerization aspects of *tpy*-*pvp*-X ligands upon irradiating with UV light [75]. We observed that the lowest energy LLCT absorption peak lying within the range of 330–361 nm, depending upon the nature of X, gradually diminished in intensity together with simultaneous enhancement of peak in the spectral domain of 355–390 nm. The ligands which display intense emission with the maximum lying in the range of 398–420 nm, quenched remarkably upon photoisomerization. The rate constant of *trans*→*cis* isomerization varies in the range of 1.61×10^{-3} and $11.7 \times 10^{-3} \text{ s}^{-1}$. Thus, Zn^{2+} affects the photophysics and isomerization behaviors of *tpy*-*pvp*-X motif to a great extent in the present study. Coordination of Zn^{2+} induces evolution of an intense absorption band in the near-visible (~ 380 nm) region and also causes substantial quenching of ligand-centered emission in the range of 398–420 nm with simultaneous evolution of emission band in the visible spectral domain (500–524 nm). The rate constant of photo-isomerization for $\text{Zn}(\text{II})$ complexes decreases substantially (between 1.1×10^{-4} and $38.9 \times 10^{-4} \text{ s}^{-1}$). This is most probably due to the presence

Table 2 Apparent rate constants (k_{iso}) and quantum yields (Φ) for the forward photoisomerization processes of the complexes 1–3

Compound	UV light (350 nm)						Visible light (405 nm)					
	MeCN			DCM			MeCN			DCM		
	$k_{\text{iso}}/\text{s}^{-1} (\times 10^{-4})$ $t \rightarrow t$	$\Phi (\times 10^{-2})$ $t \rightarrow t$	$k_{\text{iso}}/\text{s}^{-1} (\times 10^{-4})$ $t \rightarrow t$	$k_{\text{iso}}/\text{s}^{-1} (\times 10^{-4})$ $t \rightarrow t$	$\Phi (\times 10^{-2})$ $t \rightarrow t$	$k_{\text{iso}}/\text{s}^{-1} (\times 10^{-4})$ $t \rightarrow t$	$k_{\text{iso}}/\text{s}^{-1} (\times 10^{-4})$ $t \rightarrow t$	$\Phi (\times 10^{-2})$ $t \rightarrow t$	$k_{\text{iso}}/\text{s}^{-1} (\times 10^{-4})$ $t \rightarrow t$	$\Phi (\times 10^{-2})$ $t \rightarrow t$	$k_{\text{iso}}/\text{s}^{-1} (\times 10^{-4})$ $t \rightarrow t$	$\Phi (\times 10^{-2})$ $t \rightarrow t$
1	7.6	2.7	11.2	7.4	4.5	19.7	6.9	33.4	15.1	1.5	6.5	6.5
2	13.8	5.1	15.2	4.5	5.5	26.3	9.8	38.9	14.1	2.2	9.3	9.3
3	4.0	2.0	9.2	5.6	4.4	9.5	4.7	17.6	5.6	2.2	11.1	11.1

of a low lying LLCT excited state that efficiently quenches the higher energy phantom p^* state.

It would be good to provide some insight about the mechanism of the isomerization process. In general, the pure triplet LL state located on the isomerizable ligand plays a crucial role in the photoisomerization event. It should be accessible via $^1\text{LLCT}$ to $^3\text{LLCT}$ ISC and/or $^3\text{LLCT}$ – ^3IL vibronic coupling and there will be a competition between emission and isomerization processes. Although the present data are not at maturity for pushing too far for mechanistic interpretation, we are providing a simplified and tentative energy diagram for the isomerization process of the present Zn(II) complexes (Fig. 12).

It would be of interest to compare the photoisomerization efficiencies of the present complexes with previously reported polypyridine complexes of heavier transition metals (such as Re, Ru, Rh, Ir, and Pt) appended with stilbene and azo groups. Table 5 shows representative examples of metal complexes exhibiting *trans/cis* isomerization at different irradiating wavelengths as well as solvents. It is evident that quite a large number of reports are available on stilbene-appended pyridine or bipyridine-type systems of heavier transition metal complexes but no report is available on stilbene-appended terpyridine systems. Nishihara's group reported some terpyridine complexes of Ru(II) and Rh(III) coupled with photoactive azo unit [68]. Recently, our group initiated the isomerization studies of stilbene-appended terpyridine complexes of Fe(II), Ru(II) and Os(II) metals [30, 31, 33, 59]. Photoisomerization behaviors of various heavier transition metal complexes (Re, Co, Rh, Ir, etc.) covalently coupled with stilbene-appended polypyridine complexes are reported by different research groups (Gray, Wrighton, Yam, Lees, Iha and Patricinio, to name a few) and the quantum efficiency of the isomerization process of those systems are summarized in Table 5 [22, 47, 49–51, 56, 76, 77]. It is observed that when the stilbene-appended pyridine unit is coordinated in a monodentate fashion together other co-ligand (CO and/or halide) with the heavier metals, such as Re(I), the quantum efficiency of the photoisomerization process is usually high as compared with related systems having bipyridine or phenanthroline type coordination motifs. As compared with Re(I)-carbonyl-stilbene systems, the quantum efficiency of azo-terpyridine conjugate of Ru(II) and Rh(III) is usually small, although exception is there, depending upon specific system and condition used for isomerization. They estimated higher Φ values for the Rh(III) azo-terpyridine systems compared with their Ru(II) systems probably because of the increased charge of the metal. The quantum efficiency of our stilbene-appended Ru(II)-terpyridine complexes was found to higher relative to the azo-terpyridine Ru(II) systems. In addition to other factors, the Φ value of our stilbene-appended terpyridine systems depends mainly on the nature of metal ion and follows the general trend,

Table 3 Free energies of activation ($\Delta G^\ddagger$) of the forward photoisomerization processes for **1–3**

Compound	UV light (350 nm)			Visible light (490 nm)		
	MeCN	DCM	DMSO	MeCN	DCM	DMSO
	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-t \rightarrow t-c$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-t \rightarrow t-c$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-t \rightarrow t-c$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-t \rightarrow t-c$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-t \rightarrow t-c$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-t \rightarrow t-c$
1	90.8	89.8	94.5	88.4	87.1	94.9
2	89.3	89.0	95.7	87.7	86.7	93.8
3	92.3	90.3	95.6	90.2	88.7	93.9

Table 4 Apparent rate constants (k_{iso}), free energies of activation ($\Delta G^\ddagger$) and chemical yield (Φ) for the backward thermal isomerization processes for **1–3**

Compound	Heat (40 °C)								
	MeCN			DCM			DMSO		
	$k_{\text{iso}}/\text{s}^{-1}$ ($\times 10^{-5}$) $t-c \rightarrow t-t$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-c \rightarrow t-t$	Chemical yield ($\times 10^{-3}$) $t-c \rightarrow t-t$	$k_{\text{iso}}/\text{s}^{-1}$ ($\times 10^{-5}$) $t-c \rightarrow t-t$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $t-c \rightarrow t-t$	Chemical yield ($\times 10^{-3}$) $t-c \rightarrow t-t$	$k_{\text{iso}}/\text{s}^{-1}$ ($\times 10^{-5}$) $c-c \rightarrow t-t$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$ $c-c \rightarrow t-t$	Chemical yield ($\times 10^{-3}$) $c-c \rightarrow t-t$
1	6.0	97.1	5.9	7.6	96.5	3.9	0.8	102.1	0.4
2	9.0	96.1	6.3	9.2	96.0	5.7	0.6	102.8	1.1
3	2.7	99.1	8.9	3.1	98.7	2.5	0.5	103.2	2.1

Fig. 4 Normalized emission ($\lambda_{\text{ex}}=330$ nm) spectra (a) and excited state decay profiles along with the lifetime values of the complexes in MeCN (b)

Ru(II) < Os(II) < Fe(II) < Zn(II). Among the four types, the Ru(II) and Os(II) complexes exhibit emission predominantly from their $^3\text{MLCT}$ state, while the Fe(II) complexes are non-luminescent because of presence of low-lying $^3/5\text{MC}$ state. In case of Ru(II) and Os(II) systems, the isomerization is believed to take place through combined $^3\text{MLCT}$ – $^3\text{LLCT}$

excited states and also the emission is a competitive decay pathway of isomerization. The enhanced quantum efficiency of present Zn(II)–terpyridine complexes is highest as isomerization is believed to take place through $^3\text{LLCT}$ excited states and due to absence of low-lying metal centered

Fig. 5 UV–Vis absorption and emission ($\lambda_{\text{ex}}=330$ nm) spectral change of tpy-pvp-CH₃ upon incremental addition of Zn²⁺ in DCM (**a** and **d**, respectively), MeCN (**b** and **e**, respectively) and DMSO (**c** and **f**, respectively). The inset to fig. a shows the change of absorbance at 390 nm, while the inset to **d** shows the quenching of emission at 410 nm as a function of the equivalent of Zn²⁺

excite state. Thus, the present low-cost Zn(II)–terpyridine complexes could acts as potential photoswitches.

In the previous section, we were successful in modulating the absorption and emission spectral behaviors of the Zn(II) complexes to a significant extent upon irradiating with UV and visible light sources. In case of **1** and **2**, the emission quenching upon irradiation with 334 nm and 405 nm light sources and restoration of the original emission upon heating at 40 °C gives rise to “on–off” and “off–on” emission switching. By contrast, for **3**, emission enhancement upon

exposing to the said light sources followed by restoration of emission upon heating leads to “off on” and “on–off” emission switching. We can utilize the emission responses of the complexes as function of photonic and thermal inputs to mimic the function of two-input binary logic gates.

3.7 IMPLICATION gate

The IMPLICATION logic operation was initiated by Whitehead and Russell along with three fundamental logic

Fig. 6 Absorption and emission ($\lambda_{\text{ex}}=330$ nm) spectral change of $[\text{Zn}(\text{tpy-pvp-H})_2]^{2+}$ (**a** and **d**, respectively), $[\text{Zn}(\text{tpy-pvp-Me})_2]^{2+}$ (**b** and **e**, respectively) and $[\text{Zn}(\text{tpy-pvp-NO}_2)_2]^{2+}$ (**c** and **f**, respectively)

in acetonitrile upon irradiation with UV light. Insets to the **a–f** indicate the irradiation time. Inset of **f** shows the excited state decay traces and values of the lifetimes

operations: AND, OR, and NOT. The function of IMPLICATION gate is very important as well as useful for the material implication. Molecular systems exhibiting excellent implication activity (IMP) are relatively sparse in literature. To mimic the function of an IMPLICATION gate, we have selected two stimuli (heat as input 1 and photon as input 2) and the emission maximum at 522 nm was used as the output signal (Fig. 13). The truth table in Fig. 13 shows that in absence of either of the two inputs, **1** exhibits intense

emission at 522 nm corresponding to the “ON” state (1) of the system. By contrast, input 2 (photon) induces decrease in emission intensity below the threshold corresponding to the “OFF” state (0) of the system. In addition, two other possible input combinations as shown in the truth table exhibit the value of the output signals above the threshold energy level and thus corresponds to the “ON” state (1) of the system. Thus, by monitoring the emission maximum at 522 nm by the action of heat and photon, the function of

Fig. 7 Absorption and emission ($\lambda_{\text{ex}}=330$ nm) spectral change of **1** (a and d, respectively), **2** (b and e, respectively) and **3** (c and f, respectively) in DCM upon irradiation with UV light. Insets to the a–c indicate the irradiation time

an IMPLICATION gate can be mimicked at the molecular level. Figure 13e shows the reversibility of the system upon alternative action of the two inputs (heat and photon). In absence of two inputs, the emission maximum at 522 nm lies above the threshold energy level indicating the “ON” state of the system. The stepwise interaction of “heat-photon-heat” give rise to the “ON–OFF–ON” state of the system and indicates one complete cycle of this reversible process. With increasing the number of cycles, the emission intensities of the “ON” state decreases and “OFF” state increases as simultaneous interaction of heat (Input 1) or photon (Input 2) with the solution which was already treated with both the inputs cannot fully restored the original emission in the complex.

3.8 INHIBIT gate

The term INHIBIT means the gate which produces a certain or fixed output whatever be the inputs or even the inputs are changed. An INHIBIT gate is basically an AND gate with an additional event. To construct an INHIBIT gate, we used the same two inputs (heat as input 1 and photon as input 2) and also used the emission maximum at 500 nm for complex **3** as the output signals (Fig. 14). The truth table in Fig. 14 indicates that in absence of either of the two inputs, **3** exhibits emission at 500 nm which lies below the threshold energy level and corresponds to the “OFF” state (0) of the system. Input 2 (photon) induces substantial increase in emission intensity and corresponds to the “ON” state (1) of

Fig. 8 ^1H NMR spectrum of **2** and upon 8 h of photo-irradiation with visible light of 405 nm in CD_3CN

Fig. 9 Overlay of the calculated (dotted lines) and experimental (solid lines) absorption spectra of *trans-trans* (blue) and *trans-cis* (red) form of **1** (left) and **3** (right) in acetonitrile

the system. In addition, two other possible input combinations also show the output signal below the threshold energy level indicating the “OFF” state (0) of the system. Thus, by monitoring the emission maximum at 500 nm upon the action of heat and photon inputs, an INHIBIT gate can be constructed. Figure 14e shows the reversibility of the system upon alternative addition of the two inputs (heat and photon) can be repeated many times without appreciable loss of emission intensity.

4 Conclusions

With regard to our objective to design low-cost and easily synthesizable photo-switches, we reported in this work the synthesis, characterization, photophysics, and photoisomerization behaviors of three Zn(II) -terpyridine complexes covalently tethered with stilbene moiety. The complexes exhibit absorption bands stretching up to the edge of the visible domain due to ligand–ligand charge transfer

Fig. 10 UV-Vis absorption (a) and emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) (b) spectral changes upon heating the photolyzed acetonitrile solution of **1** at 40°C . Insets show the heating time

Fig. 11 UV-Vis absorption (a) and emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) (b) spectral changes upon heating the photolyzed dichloromethane solution of **1** at 40°C . Insets show the heating time

Fig. 12 Simplified and tentative energy diagram displaying photoisomerization along with competitive photophysical processes in the complexes

(LLCT) transition and strong emission at room temperature arising out from radiative deactivation of $^3\text{LLCT}$ state having lifetime within 1.0–3.0 ns. The electron donating as well as electron withdrawing group was introduced in the complex backbone to modulate their spectral behaviors as well as the kinetic and thermodynamic aspects of the isomerization process. Taking advantage of stilbene moieties, the photo-isomerization studies of the complexes were carried out in three different solvents with both UV and visible light sources to tune the thermodynamic and kinetic aspects of the isomerization process. All the three complexes underwent *trans-trans* to *trans-cis* isomerization with substantial change in their absorption, emission and ^1H NMR spectral profiles. The reversal from *trans-cis* to *trans-trans* isomerization also occurs, albeit very slowly, on keeping and can be accelerated upon heating. The k_{iso} as well as Φ is found to be much higher in presence of visible light source in all solvents than that of UV light. The electronic nature of X

Table 5 Representative metal complexes exhibiting photo-induced *trans/cis* isomerization

Compounds	Solvent	Irradiating wavelength	Φ	ref
<p>M = Rh³⁺ or Ru²⁺ A = BF₄, PF₆, BPh₄</p>	MeCN DMSO MeCN DMSO	366 nm (<i>trans</i> → <i>cis</i>)	(di-Rhtpy.nA ⁺) 0.000016(A = BF ₄), 0.000011(A = PF ₆) 0.00058(A = BF ₄), 0.0016(A = PF ₆), 0.0033(A = BPh ₄). (di-Rhtpy.nA ⁺) 0.0057(A = BPh ₄). 0.0019(A = BF ₄), 0.0016(A = PF ₆), 0.0021(A = BPh ₄).	68
<p>[Fe(tpy-pvp-X)₂]²⁺ X = H (1), X = Me (2), and X = NO₂ (3)</p>	DCM MeCN DMSO MeOH DCM MeCN DMSO MeOH	436nm (<i>trans</i> → <i>cis</i>) 336(<i>trans</i> → <i>cis</i>)	0.0032(1) 0.0009(1) 0.0005(1) 0.0004(1) 0.0014(1) 0.0002(1) 0.0003(1) 0.00008(1)	59
<p>[Ru(tpy-pvp-X)₂]²⁺ X = H (1), Me (2), Cl (3), NO₂ (4), Ph (5)</p>	MeCN-DCM	436nm(<i>trans</i> → <i>cis</i>)	0.000036 (1) 0.000046 (2) 0.000029(3) 0.00001 (4) 0.000038 (5)	31
<p>[Os(tpy-pvp-X)₂]²⁺ X = H (1), Me (2), Cl (3), NO₂ (4), Ph (5)</p>	MeCN-DCM MeCN DMSO MeCN-DCM	490nm (<i>trans</i> → <i>cis</i>) 350nm (<i>trans</i> → <i>cis</i>)	0.00011-0.0012 0.00019-0.00062 0.00013-0.0004 0.00004-0.00010	33
<p>[(tpy-Ph-CH₂)Ru(tpy-pvp-X)]²⁺ X = H (1), Me (2), Cl (3), NO₂ (4), Ph (5)</p>	MeCN-DCM	UV light	0.00013(1) 0.00012(2) 0.00016(3) 0.0001(4) 0.00012(5)	30
<p>X = Cl, Br L = t-3-stpy or t-4-stpy</p>	CH ₂ Cl ₂	313 nm (<i>trans</i> → <i>cis</i>) 366 nm (<i>trans</i> → <i>cis</i>)	0.49 (X = Cl, L = t-4-stpy) 0.64(X = Br, L = t-4-stpy) 0.60(X = Cl, L = t-3-stpy) 0.54 (X = Cl, L = t-4-stpy) 0.51(X = Br, L = t-4-stpy) 0.51(X = Cl, L = t-3-stpy)	50
350 nm (<i>trans</i> → <i>cis</i>) 250 nm (<i>cis</i> → <i>trans</i>)	0.21 (NN = bpy) 0.23 (NN = Me ₂ bpy) 0.22 (NN = phen) 0.21 (NN = Me ₄ phen) 0.18 (NN = bpy) 0.18 (NN = Me ₂ bpy) 0.18(NN = phen) 0.16 (NN = Me ₄ phen)	56

Table 5 (continued)

<p>R = , </p>	MeCN	365nm (<i>trans</i> → <i>cis</i>) 404nm (<i>trans</i> → <i>cis</i>) 365nm (<i>trans</i> → <i>cis</i>) 404nm (<i>trans</i> → <i>cis</i>)	0.33 (R=bpe) 0.29 (R=bpe) 0.57 (R=stpe) 0.35 (R=stpe)	47
<p>Ar = (1) (2)</p>	DCM	366nm(<i>trans</i> → <i>cis</i>)	—	76
CH ₂ Cl ₂	365 nm (<i>trans</i> → <i>cis</i>)	0.49 0.43 0.42	22
<p>(NN)(CO)₃Re</p> <p>1 2 3 4</p>	MeCN	405 nm (<i>trans</i> → <i>cis</i>)	0.65 (Re-1) 0.45 (Re-1) 0.21 (Re-1) 0.19 (Re-1)	49
DCM	365nm (<i>trans</i> → <i>cis</i>)	0.003	77

Fig. 13 **a** Emission ($\lambda_{\text{ex}}=370$ nm) spectral change of **1** upon the action of heat (input 1) and photon (input 2). **b** Corresponding truth table. **c** 3D representation of the changes in emission intensities upon the action of different combinations of stimuli. **d** Schematic representation

of an IMPLICATION gate based on the emission at 522 nm for **1** and **e** diagram showing the reversibility of the system due to step-wise addition of heat and photon

imparts a dramatic influence on the emission characteristics of their Zn(II) complexes during isomerization process. In case of **1** and **2**, the emission quenching upon irradiation with 336 nm and 405 nm light sources and restoration of original emission upon heating at 40 °C gives rise to “on–off” and “off–on” emission switching. By contrast, for **3**, emission enhancement upon light irradiation followed by restoration of emission upon heating leads to “off–on” and “on–off” emission switching. Another important aspect of the present work is that the emission responses of the complexes as function of photonic and thermal inputs were successfully utilized to construct two-input IMPLICATION and INHIBIT logic gates. Thus, present Zn(II)–terpyridine complexes are quite useful for the fabrication of low-cost

molecular photo-switches which in turn could be potential building blocks for information processing at the molecular level.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s43630-021-00085-z>.

Acknowledgements Financial assistance received from SERB [Grant no. CRG/2020/001233] and CSIR [Grant no. 01(2945)/18/EMR-II], New Delhi, India are gratefully acknowledged. P. Pal and A. Sahoo acknowledge CSIR for their research fellowship.

Declarations

Conflict of interest The authors declare no conflict of interest.

Fig. 14 **a** Emission ($\lambda_{\text{ex}}=370$ nm) spectral changes of $[\text{Zn}(\text{tpy-pvp-NO}_2)_2]^{2+}$ (3) upon the action of heat (input 1) and photon (input 2). **b** Corresponding truth table. **c** 3D representation of emission intensities which changes upon addition of different combinations of stimuli. **d**

Schematic representation of an INHIBIT gate based on the emission at 500 nm for 3. **e** Diagram showing the reversibility of the system due to stepwise addition of photon and heat

References

- McConnell, A. J., Wood, C. S., Neelakandan, P. P., & Nitschke, J. R. (2015). Stimuli-responsive metal-ligand assemblies. *Chemical Reviews*, 115, 7729–7793.
- Kobatake, S., Takami, S., Muto, H., Ishikawa, T., & Irie, M. (2007). Rapid and reversible shape changes of molecular crystals on photoirradiation. *Nature*, 446, 778–781.
- Kondo, M., Uchikawa, M., Zhang, W. W., Namiki, K., Kume, S., Murata, M., Kobayashi, Y., & Nishihara, H. (2007). Protonation-induced cyclocondensation of 1-aryl ethynylantraquinones: Expanding the π conjugation. *Angewandte Chemie International Edition*, 46, 6271–6274.
- Li, Q. (Ed.). (2013). *Intelligent stimuli-responsive materials*. Wiley.
- Rommel, S. A., Sorsche, D. U., Fleischmann, M., & Rau, S. (2017). Optical sensing of anions via supramolecular recognition with biimidazole complexes. *Chemistry—A European Journal*, 23, 18101–18119.
- Kume, S., & Nishihara, H. (2008). Photochrome-coupled Metal Complexes: Molecular Processing of Photon Stimuli. *Dalton Transactions*, 25, 3260–3271.
- Valeur, B. (2002). *Molecular fluorescence: Principles and applications*. Wiley.
- Prodi, L., Bolletta, F., & Montalti, M. (2000). Luminescent chemosensors for transition metal ions. *Coordination Chemistry Reviews*, 205, 59–83.
- Mullen, K., & Scherf, U. (2006). *Organic light emitting devices—synthesis, properties and applications*. Wiley.
- Kim, H. N., Ren, W. X., Kim, J. S., & Yoon, J. (2012). Fluorescent and colorimetric sensors for detection of lead, cadmium, and mercury ions. *Chemical Society Reviews*, 41, 3210–3244.
- Irie, M. (2000). Diarylethenes for memories and switches. *Chemical Reviews*, 100, 1685–1716.
- Feringa, B. L., van Delden, R. A., & ter Wiel, M. K. J. (2001). *Chiroptical molecular switches*. Wiley.
- Tian, H., & Yang, S. (2004). Recent progresses on diarylethene based photochromic switches. *Chemical Society Reviews*, 33, 85–97.
- Kawata, S., & Kawata, Y. (2000). Three-dimensional optical data storage using photochromic materials. *Chemical Reviews*, 100, 1777–1788.
- Rau, H. (1990). In Dürr, H., Laurent, H. B., Photochromism: Molecules and systems, 1st edn. Elsevier, pp 165–192.
- Ichimura, K., Oh, S. K., & Nakagawa, M. (2000). Light-driven motion of liquids on a photoresponsive surface. *Science*, 288, 1624–1626.

17. Sakamoto, R., Kume, S., & Nishihara, H. (2008). Visible-light photochromism of triarylamine- or ferrocene-bound diethynylethenes that switches electronic communication between redox sites and luminescence. *Chemistry—A European Journal*, 14, 6978–6986.
18. Waldeck, D. H. (1991). Photoisomerization dynamics of stilbenes. *Chemical Reviews*, 91, 415–436.
19. Bossert, J., & Daniel, C. (2006). Trans-cis photoisomerization of the styrylpyridine ligand in $[\text{Re}(\text{CO})_3(2,2'\text{-bipyridine})(\text{t-4-styrylpyridine})]^+$: role of the metal-to-ligand charge transfer excited states. *Chemistry—A European Journal*, 12, 4835–4843.
20. Dattelbaum, D. M., Itokazu, M. K., Iha, N. Y. M., & Meyer, T. J. (2003). Mechanism of metal-to ligand charge transfer sensitization of olefin trans-to-cis isomerization in the *fac*- $[\text{Re}(\text{phen})(\text{CO})_3(1,2\text{-bpe})]^+$ cation. *Journal of Physical Chemistry A*, 107, 4092–4095.
21. Sun, S. S., & Lees, A. J. (2002). Synthesis, photophysical properties, and photoinduced luminescence switching of trinuclear diimine rhenium(I) tricarbonyl complexes linked by an isomerizable stilbene-like ligand. *Organometallics*, 21, 39–49.
22. Yam, V.W.-W., Yang, Y., Zhang, J., Chu, B.W.-K., & Zhu, N. (2001). Synthesis, characterization, and photoisomerization studies of azo- and stilbene-containing surfactant rhenium(I) complexes. *Organometallics*, 20, 4911–4918.
23. Ko, C.-C., & Yam, V.W.-W. (2018). Coordination compounds with photochromic ligands: Ready tunability and visible light-sensitized photochromism. *Accounts of Chemical Research*, 51, 149–159.
24. Kurihara, M., & Nishihara, H. (2002). Azo- and quinone-conjugated redox complexes—photo- and proton-coupled intramolecular reactions based on d- π interaction. *Coordination Chemistry Reviews*, 226, 125–135.
25. Nishihara, H. (2004). Multi-mode molecular switching properties and functions of azo-conjugated metal complexes. *Bulletin of the Chemical Society of Japan*, 77, 407–428.
26. Nishihara, H. (2007). In: Y. F. Kodansha, Ed. *Inorganic Photochromism*. Springer, pp 239–257.
27. Kume, S., & Nishihara, H. (2006). Metal-based photoswitches derived from photoisomerization. *Structural Bonding (Berlin, Ger.)*, 123, 79–112.
28. Ko, C.-C., & Yam, V.W.-W. (2010). Transition metal complexes with photochromic ligands—photosensitization and photoswitchable properties. *Journal of Materials Chemistry*, 20, 2063–2070.
29. Ko, C.-C., Wu, L.-X., Wong, K.M.-C., Zhu, N., & Yam, V.W.-W. (2004). Synthesis, characterization and photochromic studies of spirooxazine- containing 2,2'-bipyridine ligands and their rhenium(I) tricarbonyl complexes. *Chemistry A-European Journal*, 10, 766–776.
30. Pal, P., Mukherjee, S., Maity, D., & Baitalik, S. (2018). Synthesis, structural characterization, and luminescence switching of diarylethene-conjugated Ru(II)-terpyridine complexes by trans-cis photoisomerization: Experimental and DFT/TD-DFT investigation. *Inorganic Chemistry*, 57, 5743–5753.
31. Pal, P., Mukherjee, S., Maity, D., & Baitalik, S. (2018). Synthesis, photophysics, and switchable luminescence properties of a new class of ruthenium(II)–terpyridine complexes containing photoisomerizable styrylbenzene units. *ACS Omega*, 3, 14526–14537.
32. Pal, P., Ganguly, T., Maity, D., & Baitalik, S. (2020). Experimental and theoretical exploration of photophysics and trans-cis photoisomerization of styrylbenzene conjugated terpyridine complexes of Ru(II): strong effect of deprotonation from second coordination sphere. *Journal of Photochemistry and Photobiology A*, 392, 112409.
33. Pal, P., Ganguly, T., Sahoo, A., & Baitalik, S. (2021). Emission switching in the near-infrared by reversible trans–cis photoisomerization of styrylbenzene-conjugated osmium terpyridine complexes. *Inorganic Chemistry*, 60, 4869–4882.
34. Constable, E. C. (2007). 2,2':6',20''-Terpyridines: From chemical obscurity to common supramolecular motifs. *Chemical Society Reviews*, 33, 246–253.
35. Hofmeier, H., & Schubert, U. S. (2004). Recent developments in the supramolecular chemistry of terpyridine-metal complexes. *Chemical Society Reviews*, 33, 373–399.
36. Baranof, E., Collin, J. P., Flamigni, L., & Sauvage, J.-P. (2004). From ruthenium(II) to iridium(III): 15 years of triads based on bis-terpyridine complexes. *Chemical Society Reviews*, 33, 147.
37. Wang, X., Guerso, A., Baitalik, S., Simon, G., Shaw, G. B., Chen, L., & Schmehl, R. H. (2006). The influence of bridging ligand electronic structure on the photophysical properties of noble metal diimine and triimine light harvesting systems. *Photosynthesis Research*, 87, 83–103.
38. Breivogel, A., Kreitner, C., & Heinze, K. (2014). Redox and photochemistry of bis(terpyridine) ruthenium(II) amino acids and their amide conjugates—from understanding to applications. *European Journal of Inorganic Chemistry*, 2014, 5468–5490.
39. Harriman, A., & Ziessel, R. (1996). Making photoactive, molecular-scale wires. *Chemical Communications*, 15, 1707–1716.
40. Medlycott, E. A., & Hanan, G. S. (2006). Synthesis and properties of mono- and oligo-nuclear Ru(II) complexes of tridentate ligands: The quest for long-lived excited states at room temperature. *Coordination Chemistry Reviews*, 250, 1763.
41. Medlycott, E. A., & Hanan, G. S. (2005). Designing tridentate ligands for ruthenium(II) complexes with prolonged room temperature luminescence lifetimes. *Chemical Society Reviews*, 34, 133.
42. Chen, X., Zhou, Q., Cheng, Y., Geng, Y., Ma, D., Xie, Z., & Wang, L. (2007). Synthesis, structure and luminescence properties of zinc(II) complexes with terpyridine derivatives as ligands. *Journal of Luminescence*, 126, 81–90.
43. Tessore, F., Roberto, D., Ugo, R., & Pizzotti, M. (2005). Terpyridine Zn(II), Ru(III), and Ir(III) complexes: The relevant role of the nature of the metal ion and of the ancillary ligands on the second-order nonlinear response of terpyridines carrying electron donor or electron acceptor groups. *Inorganic Chemistry*, 44, 8967–8978.
44. Tsukamoto, T., Takada, K., Sakamoto, R., Matsuoka, R., Toyoda, R., Maeda, H., Yagi, T., Nishikawa, M., Shinjo, N., Amano, S., Iokawa, T., Ishibashi, N., Oi, T., Kanayama, K., Kinugawa, R., Koda, Y., Komura, T., Nakajima, S., Fukuyama, R., & Nishihara, H. (2017). Coordination nanosheets based on terpyridine–zinc(II) complexes: As photoactive host materials. *Journal of the American Chemical Society*, 139, 5359–5366.
45. Tsukamoto, T., Aoki, R., Sakamoto, R., Toyoda, R., Shimada, M., Hattori, Y., Kitagawa, Y., Nishibori, E., Nakano, M., & Nishihara, H. (2017). Mechano-, thermo-, solvato-, and vapochromism in bis(acetato- $k^1\text{O}$)[4'-(4-(diphenylamino)phenyl)]-2,2':6',2''-terpyridine- $k^3\text{N}$, N' , N'')-zinc(II) and its polymer. *Chemical Communications*, 53, 9805–9808.
46. Amaral, R. C., Matos, L. S., Zanoni, K. P. S., & Iha, N. Y. M. (2018). Photoreversible molecular motion of stpyCN coordinated to *fac*- $[\text{Re}(\text{CO})_3(\text{NN})]^+$ complexes. *Journal of Physical Chemistry A*, 122, 6071–6080.
47. Polo, A. S., Itokazu, M. K., Frin, K. M., Patrocínio, A. O. T., & Iha, N. Y. M. (2006). Light driven trans-to-cis isomerization of stilbene-like ligands in *fac*- $[\text{Re}(\text{CO})_3(\text{NN})(\text{trans-L})]^+$ and luminescence of their photoproducts. *Coordination Chemistry Reviews*, 250, 1669–1680.
48. Faustino, L. A., Machado, A. E. H., & Patrocínio, A. O. T. (2018). Photochemistry of *fac*- $[\text{Re}(\text{CO})_3(\text{dcbH}_2)(\text{trans-stpy})]^+$:

- New insights on the isomerization mechanism of coordinated stilbene-like ligands. *Inorganic Chemistry*, 57, 2933–2941.
49. Lin, J. L., Chen, C. W., Sun, S. S., & Lees, A. J. (2011). Photoswitching tetranuclear rhenium(I) tricarbonyl diimine complexes with a stilbene-like bridging ligand. *Chemical Communication*, 47, 6030–6032.
 50. Wrighton, M. S., Morse, D. L., & Pdungsap, L. (1975). Intraligand lowest excited states in tricarbonylhalobis(styrylpyridine)rhenium(I) complexes. *Journal of the American Chemical Society*, 97, 2073–2079.
 51. Yam, V. W. W., Lau, V. C. Y., & Wu, L. X. (1998). Synthesis, photophysical, photochemical and electrochemical properties of rhenium(I) diimine complexes with photoisomerizable pyridylazo, -ethenyl or -ethyl ligands. *Journal of the Chemical Society, Dalton Transactions*, 9, 1461–1468.
 52. Matos, L. S., Amaral, R. C., & Iha, N. Y. M. (2018). Visible photosensitization of trans-styrylpyridine coordinated to fac-[Re(CO)₃(dcbH₂)]⁺: New insights. *Inorganic Chemistry*, 57, 9316–9326.
 53. Patrocínio, A. O. T., & Iha, N. Y. M. (2008). Photoswitches and luminescent rigidity sensors based on fac-[Re(CO)₃(Me₄phen)(L)]⁺. *Inorganic Chemistry*, 47, 10851–10857.
 54. Vlcek, A. J., & Busby, M. (2006). Ultrafast ligand-to-ligand electron and energy transfer in the complexes fac-[ReI(L)(CO)₃(bpy)]ⁿ⁺. *Coordination Chemistry Reviews*, 250, 1755–1762.
 55. Kayanuma, M., Daniel, C., Koppel, H., & Gindensperger, E. (2011). Photophysics of isomerizable Re(I) complexes: A theoretical analysis. *Coordination Chemistry Reviews*, 255, 2693–2703.
 56. Wenger, O. S., Henling, L. M., Winkler, J. R., Day, M. W., & Gray, H. B. (2004). Photoswitchable luminescence of rhenium(I) tricarbonyl diimines. *Inorganic Chemistry*, 43, 2043–2048.
 57. Yutaka, T., Mori, I., Kurihara, M., Tamai, N., & Nishihara, H. (2003). Photochemical behavior of azobenzene-conjugated Co^{II}, Co^{III}, and Fe^{II} bis(terpyridine) complexes. *Inorganic Chemistry*, 42, 6306–6313.
 58. Hasegawa, Y., Takahashi, K., Kume, S., & Nishihara, H. (2011). Complete solid state photoisomerization of bis(dipyrzolylstyrylpyridine)iron(II) to change magnetic properties. *Chemical Communications*, 47, 6846–6848.
 59. Mukherjee, S., Pal, P., Sahoo, A., & Baitalik, S. (2021). Photo-switchable iron-terpyridine complexes functionalized with styrylbenzene unit. *Journal of Photochemistry and Photobiology A*, 407, 113059.
 60. Zhang, Q., Tian, X., Hu, Z., Brommesson, C., Wu, J., Zhou, H., Li, S., Yang, J., Sun, Z., Tian, Y., & Uvdal, K. (2015). A series of Zn(II) terpyridine complexes with enhanced two-photon-excited fluorescence for in vitro and in vivo bioimaging. *Journal of Materials Chemistry B*, 3, 7213–7221.
 61. Tang, Y., Kong, M., Tian, X., Wang, J., Xie, Q., Wang, A., Zhang, Q., Zhou, H., Wu, J., & Tian, Y. (2017). A series of terpyridine-based zinc(II) complexes assembled for third-order nonlinear optical responses in the near-infrared region and recognizing lipid membranes. *Journal of Materials Chemistry B*, 5, 6348–6355.
 62. De Silva, A. P., Gunaratne, H. Q. N., & McCoy, C. P. (1993). A Molecular Photoionic AND Gate Based on Fluorescent Signaling. *Nature*, 364, 42–44.
 63. De Silva, A. P., Fox, D. P., Huxley, A. J. M., & Moody, T. S. (2000). Combining Luminescence, Coordination and Electron Transfer for Signaling Purposes. *Coordination Chemistry Reviews*, 205, 41–57.
 64. Katz, E. (2012). *Molecular and supramolecular information processing: From molecular switches to logic system*. Wiley.
 65. Guliyev, R., Ozturk, S., Kostereli, Z., & Akkaya, E. U. (2011). From Virtual to Physical: Integration of Chemical Logic Gates. *Angewandte Chemie International Edition*, 50, 9826–9831.
 66. Karmakar, S., Mardanya, S., Das, S., & Baitalik, S. (2015). Efficient Deep-Blue Emittier and Molecular-Scale Memory Device Based on Dipyrityl-Phenylimidazole-Terpyridine Assembly. *Journal of Physical Chemistry C*, 119, 6793–6805.
 67. Gille, K., Knoll, H., & Quitzsch, K. (1999). Rate constants of the thermal cis-trans isomerization of azobenzene dyes in solvents, acetone/water mixtures, and in microheterogeneous surfactant solutions. *International Journal of Chemical Kinetics*, 31, 337–350.
 68. Yutaka, T., Mori, I., Kurihara, M., Mizutani, J., Kubo, K., Furusho, S., Matsumura, K., Tamai, N., & Nishihara, H. (2001). Synthesis, characterization, and photochemical properties of azobenzene-conjugated Ru(II) and Rh(III) bis(terpyridine) complexes. *Inorganic Chemistry*, 40, 4986–4995.
 69. Otsuki, J., Suwa, K., Narutaki, K., Sinha, C., Yoshikawa, I., & Araki, K. (2005). Photochromism of 2-(phenylazo)imidazoles. *The Journal of Physical Chemistry A*, 109, 8064–8069.
 70. Gauglitz, G., & Hubig, S. (1985). Chemical actinometry in the UV by azobenzene in concentrated-solution—a convenient method. *Journal of Photochemistry*, 30, 121–125.
 71. Ladanyi, V., Dvorak, P., Anshori, J. A., Vetrakova, E., Wirz, J., & Heger, D. (2017). Azobenzene photoisomerization quantum yields in methanol redetermined. *Photochemical & Photobiological Sciences*, 16, 1757–1761.
 72. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., ... Fox, D. J. (2009). *Gaussian 09, revision A.02*. Gaussian Inc.
 73. Becke, A. D. (1993). Density functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics*, 98, 5648–5652.
 74. Lee, C. T., Yang, W. T., & Parr, R. G. (1988). Development of the colle-salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*, 37, 785–789.
 75. Mukherjee, S., Pal, P., Maity, D., & Baitalik, S. (2019). Photophysics and luminescence switching properties of a series of photochromic styrylbenzene-terpyridine conjugate: Experimental and DFT/TD-DFT investigation. *Journal of Photochemistry and Photobiology A: Chemistry*, 378, 94–104.
 76. Sinha, S., Mandal, S., & Gupta, P. (2015). Cyclometalated iridium(III) complexes of (aryl) ethenyl functionalized 2,2'-bipyridine: Synthesis, photophysical properties and trans-cis isomerization behavior. *RSC Advances*, 5, 99529–99539.
 77. Nisic, F., Colombo, A., Dragonetti, C., Roberto, D., Valore, A., Malicka, J. M., Cocchi, M., Freemane, G. R., & Williams, J. A. G. (2014). Platinum(II) complexes with cyclometallated 5- π -delocalized-donor-1,3-di(2-pyridyl)benzene ligands as efficient phosphors for NIR-OLEDs. *Journal of Materials Chemistry C*, 2, 1791–1800.