Contents lists available at ScienceDirect



Journal of Photochemistry & Photobiology, A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

# Photo-switchable iron-terpyridine complexes functionalized with styrylbenzene unit





### Shruti Mukherjee, Poulami Pal, Anik Sahoo, Sujoy Baitalik\*

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

#### ARTICLE INFO

Terpyridine-styrylbenzene

Photo-isomerization

Emission switching

DFT and TD-DFT

Keywords:

Iron

ABSTRACT

The manuscript deals with synthesis, characterization, photophysics, and reversible *trans-cis* photoisomerization behaviours of three homoleptic Fe(II)-terpyridine complexes,  $([Fe(tpy-pvp-X)_2]^{2+}$  where X=H, Me, and NO<sub>2</sub>) covalently coupled with photo-active styrylbeneze moiety. The complexes underwent *trans-trans* to *cis-cis* isomerization upon the action of both visible and UV light with remarkable change in their absorption and emission spectral profiles. The isomerization studies were performed in four different solvents, viz. DCM, MeCN, MeOH and DMSO with both UV and visible light sources. The reversal from *cis-cis* to *trans-trans* isomerization also proceeds, albeit very slowly, on keeping and can be accelerated upon heating. The rate, rate constant and quantum yield of photoisomerization were determined in all the solvents. The rate and quantum yield of isomerization to be much higher in presence of visible light source in all solvents than that of UV light. To better understand the electronic structures and correctly assign the experimental optical spectral bands, DFT and TD-DFT computational studied were also carried out in their *trans-trans. trans-cis* and *cis-cis* forms. Reasonably good correlation between the experimental and calculated bands could lead us to assign the main absorption spectral bands of the compounds.

#### 1. Introduction

Functional molecules with switchable spectral properties induced by light have received great attention due to their crucial roles in the design of optical materials, photoswitches and memory devices [1-6]. To this end, photoisomerization behaviours of a wide variety of compounds such as azobenzenes, stilbenes, diarylethenes, spiropyrans, and spirooxazines were thoroughly studied [7-12]. Transition metal based compounds are very attractive in this regard over their organic counterparts as the complexes possess additional features in the context of better tunability of their electronic properties by varying both inorganic and organic components [13-24]. For coordination complexes, modulation of their properties by inducing conformational changes on the photo-responsive component appended on ligands has received most of the attentions. Majority of studies in this regard are mainly centered on noble metals which are very expensive and their synthetic procedures often required very drastic conditions [13-24]. Our aim in this work is to design suitable base-metal complexes which could exhibit similar behavior and can lead to the development of a new class of low-cost and easily synthesizable photo-switches.

In order to fulfill our objective, we report herein the synthesis, characterization, photophysics, and reversible trans-cis photoisomerization behaviours of three homoleptic Fe(II)-terpyridine complexes ([Fe(tpy-pvp-X)<sub>2</sub>]<sup>2+</sup>, where X=H, Me, and NO<sub>2</sub>) covalently coupled with photo-active styrylbeneze moiety (Chart 1). Iron is the most abundant low cost element in Earth's crust and also plays crucial role in transport and storage of oxygen and in electron transport in diverse metalloenzymes of living organisms [25-27]. Compared to their low spin  $d^6$  analogues (such as  $Ru^{2+}$  and  $Os^{2+}$ ), Fe(II)-polypyridine complexes usually don't function as effective sensitizers because of low lying <sup>3/5</sup>MC states localized on Fe(II) induces very fast non-radiative deactivation leading to remarkable lowering of excited state lifetime [28-35]. Although the Fe(II)-terpyridine complexes don't exhibit Fe (II)-centred emission but they exhibit strong <sup>1</sup>MLCT absorption at longer wavelength region (~575 nm) compared with both Ru(II)- and Os(II)-terpyridine motif [37,32–34]. Photoinduced isomerization studies of styrylbenzene appended heavier transition metal complexes (particularly Re, Ru, Ir and Pt) have been performed by several research groups in recent times [36-43]. These studies contribute significantly for designing of photochemical molecular devices [44–52]. On the other

\* Corresponding author. *E-mail address:* sujoy.baitalik@jadavpuruniversity.in (S. Baitalik).

https://doi.org/10.1016/j.jphotochem.2020.113059

Received 14 October 2020; Received in revised form 24 November 2020; Accepted 28 November 2020 Available online 2 December 2020 1010-6030/© 2020 Elsevier B.V. All rights reserved.



Chart 1. Chemical structures of the complexes.

hand, related studies incorporating styrylbenzene appended terpyridine ligands and 3d metals are relatively sparse in literature. Photo-isomerization behaviours of selected Fe(II) complexes based on terpyridine-azobene conjugate were reported by Nishihara and co-workers [53-53-54]. Prior to this work, only a single report on photo-isomerization behaviour of one Fe(II)-terpyridine complex covalently coupled with styrylbenzene moiety was reported by Araki and co-workers [55]. But to our knowledge, no detailed discussions on optical switching behaviours of Fe(II)-terpyridine complexes covalently coupled with photo-active styrylbeneze moiety were reported in the literature. In the present work, we thoroughly studied the effect of solvents and influence of both electron donating and electron withdrawing substituent (X) on the photophysics as well as thermodynamic and kinetic aspects of isomerization process of complexes. Effect of excitation wavelength on thermodynamic and kinetic aspects of photoisomerization process were also addressed in this work. Recently, we reported photophysics and photoisomerization behaviours of a homoleptic ([Ru(tpy-pvp-X)<sub>2</sub>]<sup>2+</sup>) as well as a heteroleptic series ([(tpy-PhCH<sub>3</sub>)Ru(tpy-pvp-X)]<sup>2+</sup>) of Ru-terpyridine complexes with same styrylbenzene-terpyridine ligands [56-56-57]. In this study, we will also be interested to compare the photo-isomerization behaviours of present Fe(II) complexes with previously reported analogous complexes of Ru(II). Finally, DFT and TD-DFT calculations were also performed on various forms of the complexes (trans-trans, trans-cis and cis-cis) to get insight about the electronic structures as well as for appropriate assignment of their optical spectral band.

#### 2. Experimental

#### 2.1. Materials

Chemicals and solvents were procured either from Sigma or from local vendors. Synthesis and characterisation of tpy-pvp-X (X = H, Me, and NO<sub>2</sub>) were accomplished by our reported procedure [56]. Detailed procedure for synthesis, purification and characterization of Fe(II) complexes are provided in electronic supplementary information.

#### 2.2. Physical measurements

## 2.2.1. Determination of trans-cis photoisomerization rate constant and quantum yields

In the photoisomerization measurements, a 1-cm light path length quartz cell was used. The concentration of solution was within the range of  $1\times 10^{-5}$  M -  $2\times 10^{-5}$  M and thoroughly degassed with  $N_2$  before the experiments. The whole isomerization processes were carried out in Lelesil photocatalytic reactor which was designed by Lelesil Innovative Systems. Here we used both ultraviolet and visible light sources. The wave length used for UV source was 334 nm and for visible it was 436 nm.

The rate constant of isomerization process in all solvents were assessed from absorption titration data by following Eq. 1 [58,59].

$$\ln\{(\mathbf{A}_0 - \mathbf{A}_\infty)/(\mathbf{A}_t - \mathbf{A}_\infty)\} = k_{iso} \mathbf{t}$$
(1)

where  $A_0$ ,  $A_t$ , and  $A_\infty$  show the absorbance at time t = 0, t, and  $\infty$ , respectively.  $k_{iso}$  is rate constant of isomerization and t is the time required for execution of isomerization process. Both rate constant ( $k_{iso}$ ) and absorption at  $\infty$  time ( $A_\infty$ ) were estimated by nonlinear least-square method. The light source intensity of the lamp was 0.11 W. Quantum yields ( $\varphi$ ) of isomerization process were derived by using the Eq. 2 [60],

$$\nu = (\phi I_0 / V) (1 - 10^{-Abs})$$
<sup>(2)</sup>

where  $\nu$  is the rate of *trans*-to-*cis* isomerization,  $I_0$  is the photon flux at the front of the cell, V is the volume of the solution, and Abs is the initial absorbance at the irradiation wavelength. We have estimated the photo-isomerization quantum yield of complexes by a relative method using azobenzene which was extensively studied in literature. We performed photoisomerization experiments of azobenzene in our experimental setup and upon considering quantum yield of *trans* to *cis* photoisomerization of azobenzene in MeOH as 0.15 according to literature report (wavelength of irradiation is 334 nm) [61–62], we have calculated the quantum flux. Then by using quantum flux, we have calculated the quantum yield of photoisomerization of the present complexes by using Eq. 2.

#### 2.3. Computational investigation

Computational details were also provided in the electronic supplementary information.

#### 3. Results and discussions

#### 3.1. Synthesis and characterization

The ligands, tpy-pvp-X (X = H, Me and NO<sub>2</sub>) were prepared upon treating 4'-(2,2':6',2"-terpyrididyl-4)-benzyltriphenyl phosphonium bromide (tpyPhCH<sub>2</sub>PPh<sub>3</sub>Br) with 4-substituted benzaldehyde in dichloromethane within the temperature range of 0-5 °C under argon protection and characterized by our reported procedure [56–57,63]. The complexes were synthesized by reacting tpy-pvp-X (X = H, Me and NO<sub>2</sub>) with Fe(ClO<sub>4</sub>)<sub>2</sub> (1:2 ratio) in CHCl<sub>3</sub>-MeOH (1:1, v/v) mixture at room temperature. Purification of the complexes were carried out by alumina column chromatography {1:10 (v/v) PhCH<sub>3</sub>-MeCN mixture} followed by recrystallization from CHCl<sub>3</sub>-MeOH (1:2, v/v) mixture. All complexes were characterized by elemental (C, H and N) analyses, high resolution mass and NMR spectral measurements and characterization data were presented in electronic supplementary information (Fig. S1-S6, Supplementary information).

#### 3.1.1. NMR spectra

<sup>1</sup>H NMR spectra of **1–3** were acquired in CD<sub>3</sub>CN and displayed in Fig. 1. Tentative assignments of all peaks were done with the help of their COSY spectra together with by comparing the spectra of structurally similar complexes. The singlet at ~2.31 ppm (Fig. S5, Supplementary information) counting three protons for **2** is clearly due to  $-CH_3$  group of coordinated tpy-PhCH<sub>3</sub> moiety. Another singlet which appears within 9.17–9.24 ppm corresponds to H3' proton. A pair of doublets within 7.16–7.90 ppm is assignable as the protons of ethylenic double bond (H<sub>9</sub> and H<sub>10</sub>) and corresponds to *trans-trans* conformation. In some cases, they appeared within the broad multiplet because of the coincidence of other protons.

#### 3.2. Computational investigations

Geometry optimization of the complexes was carried out with the aid



**Fig. 1.** <sup>1</sup>H NMR (400 MHz) spectra of  $[Fe(tpy-pvp-H)_2]^{2+}$  (a),  $[Fe(tpy-pvp-Me)_2]^{2+}$  (b) and  $[Fe(tpy-pvp-NO_2)_2]^{2+}$  (c) in CD<sub>3</sub>CN.

of Gaussian 09 program in acetonitrile medium (Fig. S7, Supplementary information). Selected bond distances and angles are given in Tables S1-S4 (Supplementary information). In all complexes, Fe(II) is coordinated in bis-tridentate manner with distorted octahedral geometry. Frontier molecular orbital sketch are presented in Figs. S8-S10 (Supplementary information). Among four HOMOs, the first two (HOMO and HOMO-1) are mainly composed of vinyl phenyl and *p*-substituted phenyl group, while the other two HOMOs (HOMO-2 and HOMO-3) are mainly localized on Fe(II) centre on all of their *trans-trans, trans-cis* and *cis-cis* forms. On the other hand, all four LUMOs are composed predominantly of tpy moiety with small contribution of vinyl phenyl group with the exception of  $[Fe(tpy-pvp-NO_2)_2]^{2+}$ , where LUMOs are mainly localized either on nitrobenzyl group or on tpy moiety (Table S5 and Fig. S10, Supplementary information).

TD-DFT calculated results of the complexes in their *trans-trans, transcis* and *cis-cis* forms are summarized in Table S6-S8 (Supplementary information) and the involvement of FMOs in their lowest energy band are displayed in Fig. S11 (Supplementary information). The lowest energy band for Fe(II) complexes is an admixture of  $Fe^{II}(d\pi) \rightarrow \pi^*(tpy-pvp-X)$  metal-to-ligand charge transfer (MLCT) and phenyl-vinyl- $\rightarrow$ terpyridine charge transfer (LLCT) transitions in the visible region. The next higher energy band is found to be an admixture of both LLCT and  $\pi$ - $\pi$ \* transitions with the exception of the nitro-derivative (**3**), where substantial MLCT character is also observed.

#### 3.3. Absorption and emission spectra

Comparison between the calculated and experimental absorption spectra of the complexes in acetonitrile are presented in Fig. 2. All complexes show a very intense band at ~575 nm due to Fe<sup>II</sup>( $d\pi$ ) $\rightarrow \pi^*$  (tpy-pvp-X) MLCT transition. TD-DFT calculations also indicate finite contribution of phenyl-vinyl $\rightarrow$ terpyridine charge transfer (LLCT) character to the said MLCT band. The band is shifted to lower energy region compared with the parent [Fe(tpy)<sub>2</sub>]<sup>2+</sup> (551 nm) complex probably because of charge delocalization induced by additional phenyl-vinyl group at 4'-position of terpyridine moiety [51–56]. The next higher

energy band(s) spanning with 368-376 nm is due to phenylvinyl→terpyridine charge transfer transitions. Multiple very intense peaks within UV region arise from ligand centred  $\pi$ - $\pi$ \* transitions. It is observed that maximum of MLCT and LLCT band in the complexes varies to a small extent depending upon electronic nature of the substituent, X. A large disagreement between experimental and theoretical absorption spectra is noticed in Fig. 2. In particular, the presence of a large band within the spectral domain of 400–600 nm in the computed spectra is not reflected in the experimental spectra. This disagreement gives an indication of an inappropriate level of calculations for 1st row transition metal complexes. Our method is based on very limited basis sets leading to very localized Kohn-Sham orbitals that do not necessary reflect the real electronic densities in play.

On excitation at the lowest energy absorption band (~575 nm), complexes do not exhibit any luminescence. The photophysics of Fe(II)-polypyridine complexes gets complicated by the presence of low-lying metal-centered ( $^{3/5}$ MC) excited states which get populated upon surface crossing from MLCT state within ultrafast time domain [28–35]. This phenomenon is frequently happened in Fe(II)-polypyridine complexes which is responsible for their non-emitting characteristics [28–35]. Upon excitation at the LLCT or  $\pi$ - $\pi$ \* band, the complexes display an intense emission band in spectral domain of 463–503 nm, probably due to LLCT transition (Fig. S12, Supplementary information). It is to be mentioned here that the free ligands, upon excitation at their LLCT band (spanning within the range of 325–361 nm), display intense emission band in the wavelength range of 398–420 nm. Thus, coordinating influence of Fe<sup>2+</sup> leads to red-shift of ligand-centered emission in the Fe(II)-terpyridine complexes.

In-situ formation of Fe(II) complexes were also monitored through absorption and emission spectroscopy (Fig. 3. and Fig. S13-S14, Supplementary information). It is observed that a new band is evolved at ~575 nm and intensity of the band increases linearly with Fe<sup>2+</sup> addition till the [Fe<sup>2+</sup>]/[tpy-pvp-X] ration reaches 0.5. Addition of Fe<sup>2+</sup> beyond 0.5 equiv does not produce any further change (Fig. 3a and Fig. S13a-S14a, Supplementary information). The titration profile based on absorbance at 575 nm and several clean isosbestic points imply single



**Fig. 2.** Overlay of the calculated (dotted lines) and experimental (solid lines) UV–vis absorption spectra of *trans*- $[Fe(tpy-pvp-X)_2]^{2+}$  with X= H (1), Me (2), and NO<sub>2</sub> (3) in acetonitrile. Calculated results are also presented in the sticks form.

conversion of free tpy-pvp-X to  $[Fe(tpy-pvp-X])_2]^{2+}$ . The composition of the complexes was also confirmed by high resolution mass spectra. The change of emission intensity of the LLCT band on gradual addition of Fe<sup>2+</sup> is delineated in Fig. 3b and Fig. S13b-S14b (Supplementary information) and the insets show that complete quenching of emission occurs upon addition of 0.5 equiv of Fe<sup>2+</sup> ion.

#### 3.4. Photo-isomerization behaviours

All three complexes possess two isomerizable strylbenzene units. We are thus interested to investigate their spectral behaviours upon action of light. We carried out photoisomerization studies of the complexes in few selected solvents, viz. dichloromethane, acetonitrile, methanol and dimethysulfoxide at room temperature (25 °C). In addition, both UV (334 nm) and visible (436 nm) light source were used for irradiating the solutions of the complexes. At first, isomerization studies are carried out in dichloromethane in presence of UV light. The intensity of both MLCT band at ~575 nm and LLCT at ~375 nm was found to decrease to a small extent for 1 and 2, whereas increase for the nitro-derivative (3) (Fig. 4a-c.). In the emission side, photo-irradiation induces remarkable decrease of ligand-centred emission band intensity at ~500 nm with the exception of nitro-derivative (3) where small enhancement is noticed (Fig. 4d-f).

It is observed that prolonged irradiation leads to gradual decrease of both MLCT and LLCT bands in all three complexes with concomitant increase of  $\pi$ - $\pi$ \* band intensities in the UV region and eventually the MLCT band is completely removed which is indicative of decoordination of  $Fe^{2+}$  centre from the complex backbone (Fig. S15-S17, Supplementary information). The final spectrum in each case looks very similar to that of the photolyzed product (cis-form) of free ligand [63]. Continued photo-irradiation, also leads to gradual increase of emission intensity in the second step and finally reaches at saturation at the end of photolysis (Fig. S15b-S17b, Supplementary information). Enhancement of emission intensity in the second step is again indicative of de-coordination of  $\bar{Fe}^{2+}$  from complex architecture. In presence of visible light source, we observed almost similar trend (with small variation of spectral profile) but the rate is much faster than with UV light (Fig. S18-S19, Supplementary information). Thus, in dichloromethane, the first-step change is due to  $trans \rightarrow cis$  isomerization while the second-step change corresponds to de-coordination Fe<sup>2+</sup> from complex architecture.

As photo-irradiation, irrespective of irradiation wavelength, of DCM solution of the complexes leads to de-coordination, we are interested to see the behaviours of the complexes in other solvents. To this end, we have taken a representative complex,  $[Fe(tpy-pvp-H)_2]^{2+}$  and carried out isomerization experiments in three additional solvents, *viz*. aceto-nitrile, methanol and dimethysulfoxide. Absorption and emission spectral changes of  $[Fe(tpy-pvp-H)_2]^{2+}$  upon action of visible light are presented in Fig. 5–7, while in presence of UV light are displayed in Fig. S20-S22 (Supplementary information). In contrast to the behaviours in DCM, all the three complexes exhibit a distinct one-step spectral change in presence of both UV and visible light source and no signature of Fe<sup>2+</sup> de-coordination is observed even after photolysis of more than three hours. One-step spectral change is observed in all three solvents, although the pattern and extent of change differ slightly from each



**Fig. 3.** UV–vis absorption (a) and emission ( $\lambda_{ex}$  =330 nm) (b) spectral changes of tpy-pvp-H in dichloromethane upon incremental addition of Fe<sup>2+</sup>. Inset to figure (a) shows the change of absorbance at 575 nm, while inset to figure b indicates the change in emission intensity at 398 nm *vs.* equivalent of Fe<sup>2+</sup>.



**Fig. 4.** Absorption and emission  $(\lambda_{ex} = 330 \text{ nm})$  spectral change of  $[Fe(tpy-pvp-H)_2]^{2+}$  (a and d, respectively),  $[Fe(tpy-pvp-Me)_2]^{2+}$  (b and e, respectively) and  $[Fe(tpy-pvp-NO_2)_2]^{2+}$  (c and f, respectively) in dichloromethane upon irradiation with UV light. Insets to the figures a-f indicate the irradiation time.



**Fig. 5.** UV–vis absorption (a) and emission ( $\lambda_{ex} = 330 \text{ nm}$ ) (b) spectral changes of [Fe(tpy-pvp-H)<sub>2</sub>]<sup>2+</sup> (1) in acetonitrile upon irradiation with visible light. Inset to figure (a) indicates the irradiation time.



Fig. 6. UV–vis absorption (a) and emission ( $\lambda_{ex} = 330 \text{ nm}$ ) (b) spectral changes of  $[Fe(tpy-pvp-H)_2]^{2+}$  (1) in dimethysulfoxide upon irradiation with visible light. Inset to figure (a) indicates the irradiation time.



Fig. 7. UV–vis absorption (a) and emission ( $\lambda_{ex} = 330 \text{ nm}$ ) (b) spectral changes of [Fe(tpy-pvp-H)<sub>2</sub>]<sup>2+</sup> (1) in methanol upon irradiation with visible light. Inset to figure (a) indicates the irradiation time.

other. Furthermore, the extent of change is much greater with visible light than that of UV light. The spectral change in MeCN and DMSO is very neat and well defined compared with MeOH in presence of visible light. Gradual decrease in intensities for MLCT and LLCT band occurred and at their expense concomitant increase of  $\pi$ - $\pi$ \* band intensities are observed in both solvents. Well defined isosbestic points are observed in each case. By contrast, the extent of change in MeOH is much less. The intensity of the ligand-centred emission band at ~400 nm for [Fe(tpy-pvp-H)<sub>2</sub>]<sup>2+</sup> in MeCN gradually quenched and at the end of photolysis, the band is substantially red-shifted to ~500 nm. In DMSO, similar quenching of emission takes place but no red-shift of the band is noticed. The emission spectrum in MeOH is different from both MeCN and DMSO. Instead of quenching, substantial emission enhancement is observed in MeOH in presence of both UV and visible light source.

Well-defined spectral changes (both absorption and emission) clearly indicate the occurrence of isomerization across the double bond. But we are not very sure whether isomerization taking place from *trans-trans* to *trans-cis* or to *cis-cis* form. In spite of our low level of calculations, TD-DFT results indicate that the MLCT band of *trans-cis* form is red-shifted compared with their *trans-trans* form, while blue-shifted in case of *ciscis* forms. In the final form of our experimental absorption spectra, the MLCT band also gets blue shifted Fig. 8 and Fig. S23 (Supplementary information). That's why we speculate that *trans-trans* to *cis-cis* conversion are occurring for these complexes upon photo-irradiation. While going from *trans-trans* to *cis-cis* form of the complexes, obviously there is an intermediate *trans-cis* state. But we are unable to locate *trans-cis* form



**Fig. 8.** Overlay of the calculated (dotted lines) and experimental (solid lines) absorption spectra of *trans-trans* (black), *trans-cis* (blue) and *cis-cis* (red) form of  $[Fe(tpy-pvp-Me)_2]^{2+}$  in acetonitrile.

during the course of isomerization. The reverse process that is isomerization from *cis-cis* to *trans-trans* form also proceeds very slowly on keeping and accelerated upon heating the solution of the complexes. The complexes are heated around 40 °C in each of three solvents. The reversible changes are very prominent and we got cis-*cis* to *trans-trans* form of the complexes (Fig. 9, Fig. S24-S26, Supplementary information).

It would be better if we could also monitor the isomerization process



Fig. 9. UV-vis absorption (a) and emission ( $\lambda$ ex =330 nm) (b) spectral changes of [Fe(tpy-pvp-H)<sub>2</sub>]<sup>2+</sup> (1) in acetonitrile upon keeping heating for times. Inset to figure (a) and (b) indicates the heating time at 40 °C.

through NMR spectroscopy. To this end, we attempted isomerization studies in the said solvents. Unfortunately, the rate of isomerization process is extremely slow and we are unable to see any observable change even after photolysis for about 12 h. Concentration of the complexes for NMR experiments were  $10^{-3}$  M compared with  $10^{-5}$  M used for absorption and emission spectral studies.

The rate constant ( $k_{iso}$ ) and quantum yield ( $\Phi$ ) of isomerization were calculated for both forward and backward process (thermal) in all solvents (Table 1). It is noticed that  $k_{iso}$  as well as  $\Phi$  are dependent upon irradiation wavelength as well as nature of the solvents. First of all, both  $k_{\rm iso}$  and  $\Phi$  was found to be much higher in presence of visible light source in all solvents than that of UV light (Table 1).  $k_{iso}$  is also dependent on polarity as well as bulk viscosity of the solvents; found to be highest in DCM and least in MeOH. The dependence of  $k_{iso}$  and  $\Phi$  with different solvent parameters (viz. polarity index, dielectric constant, and dipole moment) is displayed in Fig. 10 and Fig. S27-S28 (Supplementary information). The correlation is reasonably well with the exception of MeOH. Lesser value of  $k_{iso}$  in more polar solvents is probably because of greater degree of solvation leading to increase of effective rotor volume of the complex cations. Free energy of activation ( $\Delta G^{\neq}$ ) of the isomerization processes (both forward and backward) were also calculated from  $k_{iso}$  values and by the use of Eyring's theory. Calculated  $\Delta G^{\neq}$  values are presented in Table 1.

$$\Delta G^{\neq}_{298k} = 298R\{\ln(k_{\rm B}298/h.k_{iso})\}$$
(3)

We have previously reported photoisomerization behaviours of free tpy-pvp-X ligands in presence of UV light [63]. We found that the lowest energy LLCT absorption band within the spectral domain of 330–361 nm gradually decreases with concomitant increase of a band ~355–390 nm upon irradiation. Free ligands exhibit strong emission band within 389–420 nm which quenched substantially upon isomerization. The rate constant of trans→cis isomerization was found to vary between 1.61 and  $11.7 \times 10^{-3} \text{ s}^{-1}$ . In the present study, we observed that photophysics and photo-isomerization of tpy-pvp-X unit gets dramatically affected upon coordination with Fe<sup>2+</sup>. Coordination of Fe<sup>2+</sup> leads

to evolution of a strong band in the visible (~575 nm due to Fe(II) $\rightarrow$ tpy MLCT transition) and induces significant quenching of ligand-centered emission in [Fe(tpy-pvp-X)<sub>2</sub>]. Photo-isomerization rate constants of Fe (II) complexes retarded dramatically (varying between 0.8 and  $32.4 \times 10^{-4} \text{ s}^{-1}$ , depending upon irradiating wavelength and nature of solvents). This is a consequence of the presence of a low lying MLCT electronic excited state that efficiently quenches the higher energy phantom p\* state. In addition, presences of several low energy vibrational states that are created upon complexation, restrict the molecule from reaching the crossing point for isomerization.

It would be appropriate to give some insight about the isomerization process. Light-induced ligand substitution of otherwise photochemically inert complexes is not very unusual in DCM. Although  $[Ru(bpy)_3]^{2+}$  is photochemically inert, there is evidence that it undergoes photosubstitution in chlorinated solvent (such as DCM). While  $[Ru(bpy)_3]^{2+}$  as the PF<sub>6</sub> salt is photo-inert in water but in DCM, the photochemistry of  $[Ru(bpy)_3]X_2$ , (X = Cl<sup>-</sup>, Br<sup>-</sup>, NCS<sup>-</sup>) is well behaved [64-65], giving rise to Ru(bpy)\_2X\_2 with  $\phi$  lying between  $10^{-1}$  and  $10^{-2}$ . A crucial difference between water and DCM solutions is that salts of  $[Ru(bpy)_3]^{2+}$  are fully ion-paired in the latter medium. The probable reason for photo-substitution is thermally activated formation of a <sup>3</sup>MC excited state which induces large metal-ligand displacement in the excited state leading to the cleavage of Ru-N bond.

Proper understanding of photo-reactivity and photophysics of firstrow transition metal complexes is still a challenge for both experimentalists and theoreticians. Indeed the high density of excited states of mixed characters with important contribution of metal-centered (MC) states lead to a rich and extremely complicated photochemistry with various competing channels of deacativation such as luminescence, nonradiative processes, dissociation and isomerization. Due to lack of our expertise, we are unable to calculate appropriately the low-lying triplet and quintet MC states which is crucial for understanding the photophysics of Fe(II)-polypyridine complexes. Usually the pure triplet IL state localized on the isomerizable ligand plays a central role in the photoisomerization processes. It should be accessible via  ${}^{1}MLCT/{}^{1}LLCT$ 

Table 1

Rate constants, quantum yield and free energy of activation of trans $\rightarrow$  cis and cis $\rightarrow$  trans in isomerization process of [Fe(tpy-pvp-H)<sub>2</sub>]<sup>2+</sup> in different solvents.

Solvents	Monit-oring λ/nm	<i>trans→cis</i> (visible light)			$cis \rightarrow trans$ (thermal)		<i>trans→cis</i> (UV light)			$cis \rightarrow trans$ (thermal)	
		$\substack{k_{iso}\times 10^4\\/s^{-1}}$	$\Phi{\times}10^2$	$\begin{array}{c} \Delta G^{\pm} / \\ k J M^{-1} \end{array}$	$\frac{k_{iso} \times 10^5}{/s^{-1}}$	$\Delta G^{\pm}/kJM^{-1}$	$\substack{k_{iso}\times 10^4 / \\ s^{-1}}$	$\Phi{ imes}10^2$	$\begin{array}{c} \Delta G^{\pm} / \\ kJM^{-1} \end{array}$	$\substack{k_{iso}\times 10^5/\\s^{-1}}$	$\Delta G^{\pm}/kJM^{-1}$
DCM	365	32.4	11.9	87.2	12.9	95.2	14.1	5.2	89.2	9.2	96.0
MeCN	361	9.1	3.8	90.9	8.4	96.2	2.6	1.1	100.2	1.7	100.3
DMSO	375	5.3	2.3	91.7	5.5	103.0	2.8	1.2	98.9	3.1	98.7
MeOH	365	4.3	1.3	92.2	2.5	99.2	0.8	0.5	96.2	0.5	103.2



Fig. 10. Plot of rate constant (k<sub>iso</sub>) and quantum yield (Φ) vs. dielectric constant of solvents (a and b respectively) with linear least-squares fit to the data.

to <sup>3</sup>MLCT/<sup>3</sup>LLCT ISC and/or <sup>3</sup>MLCT/<sup>3</sup>LLCT-<sup>3</sup>IL vibronic coupling. This could help at deciphering the competition between luminescence /isomerization/dissociation and at understanding why solvent effects are very important. The present data are not at maturity for pushing too far for mechanistic interpretation for the isomerization process of present Fe(II)-terpyridine complexes. We are still working on this and several fundamental issues which we are unable to address presently are open for further investigation for understanding the complete picture.

#### 4. Conclusions

With regard to our aim for designing suitable base-metal complexes for the development of new class of low-cost easily synthesizable photoswitches, we designed in this work a new class of homoleptic Fe(II)terpyridine complexes by incorporating styrylbenzene moiety as the photo-switchable unit and thoroughly investigated their photoisomerization behaviours through absorption and emission spectroscopic techniques. The complexes underwent trans-trans to cis-cis isomerization upon the action of both visible and UV light with remarkable change in their absorption and emission spectral profiles. The isomerization studies were performed in four different solvents, viz. DCM, MeCN, MeOH and DMSO with both UV and visible light sources. Apart from DCM, where de-coordination of Fe<sup>2+</sup> takes place from the complex backbone upon prolonged light exposure, isomerization process proceeds smoothly in all the other solvents. The reversal from *cis-cis* to trans-trans isomerization also proceeds, albeit very slowly, on keeping and can be accelerated upon heating. The rate, rate constant and quantum yield of isomerization were determined in all the solvents in presence of both UV and visible light source. The  $k_{iso}$  as well as  $\Phi$  is found to be much higher in presence of visible light source in all solvents than that of UV light.  $k_{iso}$  and  $\Phi$  is also dependent on polarity as well as bulk viscosity of the solvents and a linear correlation is found between either  $k_{iso}$  or  $\Phi$  and different solvent parameters (viz. polarity index, dielectric constant, and dipole moment). The present data are not sufficient for complete understanding of the mechanistic aspects for isomerization process of Fe(II)-terpyridine complexes. Close proximity of several excited states with mixed characters together with sizeable contribution of metal-centered (MC) states complicate the photochemistry with various competitive process of relaxation, viz. emission, nonradiative processes, dissociation and isomerization. We are still working on this and several fundamental issues which we are unable to address presently are open for further investigation for understanding the complete picture. Although we are unable to present proper mechanistic details for photoisomerization process, present Fe(II)-terpyridine complexes could be useful for the construction low-cost molecular photoswitches which in turn could be potential building blocks for information processing and at the molecular level.

#### Authors statement

I am submitting the revised manuscript on behalf of all the coauthors. All the authors are aware of the submission and no one have any objection.

#### **Declaration of Competing Interest**

The authors declare no conflict of interest.

#### Acknowledgements

Financial assistance received from SERB [Grant No. CRG/2020/ 001233] and CSIR [Grant No. 01(7619)/18/EMR-II], New Delhi, India are gratefully acknowledged. P. Pal and A. Sahoo acknowledge CSIR for their research fellowship.

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jphotochem.2020. 113059.

#### References

- M. Irie, Diarylethenes for memories and switches, Chem. Rev. 100 (2000) 1685–1716.
- [2] B.L. Feringa, R.A. van Delden, M.K.J. ter Wiel, Chiroptical Molecular Switches, Wiley-VCH, 2001.
- [3] H. Tian, S. Yang, Recent progresses on diarylethene based photochromic switches, Chem. Soc. Rev. 33 (2004) 85–97.
- [4] S. Kawata, Y. Kawata, Three-dimensional optical data storage using photochromic materials, Chem. Rev. 100 (2000) 1777–1788.
- [5] H. Rau, H. Dürr, H.B. Eds Laurent, Photochromism: Molecules and Systems, Elsevier, Amsterdam, The Netherlands, 1990, pp. 165–192.
   [6] K. Ichimura, S.K. Oh, M. Nakagawa, Light-driven motion of liquids on a
- photoresponsive surface, Science. 288 (2000) 1624–1626.
- [7] H. Tian, J.Eds. Zhang, Photochromic Materials: Preparation, Properties and Applications, Wiley-VCH, Weinheim, Germany, 2016.
- [8] J.C. Crano, R.Eds. Guglielmetti, Organic Photochromic and Thermochromic Compounds, Vol 1: Main Photochromic Families, Plenum Press, New York, 1999.
   [9] J.C. Crano, R.Eds. Guglielmetti, Organic Photochromic and Thermochromic
- [5] J.C. Grano, K.Eds. Gighenmetti, Organic Photochronic and Thermochronic Compounds, Vol 2, Physicochemical Studies, Biological Applications and Thermochromism, Plenum Press, New York, 1999.
- [10] D.H. Waldeck, Photoisomerization dynamics of stilbenes, Chem. Rev. 91 (1991) 415–436.

#### S. Mukherjee et al.

- [11] T. Ikeda, O. Tsutsumi, Optical switching and image storage by means of azobenzene liquid-crystal films, Science. 268 (1995) 1873–1875.
- [12] K. Matsuda, M. Irie, Diarylethene as a photoswitching unit, J. Photochem. Photobiol. C 5 (2004) 169–182.
- [13] S. Kume, H. Nishihara, Photochrome-coupled metal complexes: molecular processing of photon stimuli, Dalton Trans. (2008) 3260–3271.
- [14] C.-C. Ko, V.W.-W. Yam, Coordination compounds with photochromic ligands: ready tunability and visible light-sensitized photochromism, Acc. Chem. Res. 51 (2018) 149–159.
- [15] M. Kurihara, H. Nishihara, Azo-and quinone-conjugated redox complexes photoand proton-coupled intramolecular reactions based on d-π interaction, Coord. Chem. Rev. 226 (2002) 125–135.
- [16] H. Nishihara, Multi-mode molecular switching properties and functions of azo conjugated metal complexes, Bull. Chem. Soc. Jpn. 77 (2004) 407–428.
- [17] H. Nishihara, in: Y.F. Kodansha (Ed.), Inorganic Photochromism, Springer, 2007, pp. 239–257.
- [18] S. Kume, H. Nishihara, Metal-based photoswitches derived from photoisomerization, Struct. Bonding, (Berlin, Ger.) 123 (2006) 79–112.
  [19] C.-C. Ko, V.W.-W. Yam, Transition metal complexes with photochromic
- [19] C.-C. KO, V.W.-W. rain, transition metal complexes with photochronnic ligands–Photosensitization and photoswitchable properties, J. Mater. Chem. 20 (2010) 2063–2070.
- [20] C.-C. Ko, L.-X. Wu, K.M.-C. Wong, N. Zhu, V.W.-W. Yam, Synthesis, characterization and photochromic studies of spirooxazine- containing 2,2'bipyridine ligands and their rhenium(I) tricarbonyl complexes, Chem.-Eur. J. 10 (2004) 766–776.
- [21] Y. Li, A.Y.-Y. Tam, K.M.-C. Wong, W. Li, L. Wu, V.W.-W. Yam, Synthesis, characterization, and the photochromic, luminescence, metallogelation and liquidcrystalline properties of multifunctional platinum(II) bipyridine complexes, Chem.-Eur. J. 17 (2011) 8048–8059.
- [22] C.-C. Ko, W.-M. Kwok, V.W.-W. Yam, D.L. Phillips, Triplet MLCT Photosensitization of the Ring-closing Reaction of Diarylethenes by Design and Synthesis of a Photochromic Rhenium(I) Complex of a Diarylethene-Containing 1,10-Phenanthroline Ligand, Chem.-Eur. J. 12 (2006) 5840–5848.
- [23] P.H.-M. Lee, C.-C. Ko, N. Zhu, V.W.-W. Yam, Metal coordination- assisted nearinfrared photochromic behavior: a large perturbation on absorption wavelength properties of N,N-donor ligands containing diarylethene derivatives by coordination to the rhenium(I) metal center, J. Am. Chem. Soc. 129 (2007) 6058–6059.
- [24] J.C.-H. Chan, W.H. Lam, H.-L. Wong, N. Zhu, W.-T. Wong, V.W.-W. Yam, Diarylethene-containing cyclometalated platinum- (II) complexes: tunable photochromism via metal coordination and rational ligand design, J. Am. Chem. Soc. 133 (2011) 12690–12705.
- [25] E.M. Nolan, S.J. Lippard, Chem. Rev. 108 (2008) 3443.
- [26] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th ed., Wiley Interscience Publi cation, John-Wiley & Sons, 1988.
- [27] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements: Maxwell Macmillan International Edn, 1989.
- [28] C. Creutz, M. Chou, T.L. Netzel, M. Okumura, N. Sutin, J. Am. Chem. Soc. 102 (1980) 1309.
- [29] H. Cho, M.L. Strader, K. Hong, L. Jamula, E.M. Gullikson, T.K. Kim, F.M.F. deGroot, J.K. McCusker, R.W. Schoenlein, N. Huse, Ligand-field symmetry effects in Fe(II) polypyridyl compounds probed by transient X-ray absorption spectroscopy, Faraday Discuss. 157 (2012) 463–474.
- [30] J.K. McCusker, K.N. Walda, R.C. Dunn, J.D. Simon, D. Magde, D.N. Hendrickson, Subpicosecond <sup>1</sup>MLCT → <sup>5</sup>T<sub>2</sub> intersystem crossing of low-spin polypyridyl ferrous complexes, J. Am. Chem. Soc. 115 (1993) 298–307.
- [31] A.T. Yeh, C.V. Shank, J.K. McCusker, Ultrafast Electron localization dynamics following photo-induced charge transfer, Science. 289 (2000) 935–938.
- [32] S. Baitalik, X. Wang, R.H. Schmehl, A trimetallic mixed Ru(II)/Fe(II) terpyridyl complex with a long-lived excited state in solution at room temperature, J. Am. Chem. Soc. 126 (2004) 16304.
- [33] X. Wang, A.D. Guerzo, S. Baitalik, G. Simon, G.B. Shaw, L.X. Chen, R.H. Schmehl, The influence of bridging ligand electronic structure on the photophysical properties of noble metal diimine and triimine light harvesting systems, Photosynth. Res. 87 (2006) 83.
- [34] A. Paul, M. Bar, S. Deb, S. Baitalik, Long-lived trimetallic complexes of Fe(II), Ru (II), and Os(II) based on a heteroditopic bipyridine–Terpyridine bridge:synthesis, photophysics, and electronic energy transfer, Inorg. Chem. 58 (2019) 10065–10077.
- [35] D. Maity, C. Bhaumik, S. Mardanya, S. Karmakar, S. Baitalik, Light harvesting and directional energy transfer in long-lived Homo- and heterotrimetallic complexes of FeII, RuII, and OsII, Chem. Eur. J. 20 (2014) 13242–13252.
- [36] V.W.-W. Yam, Y. Yang, J. Zhang, B.W.-K. Chu, N. Zhu, Synthesis, characterization, and photoisomerization studies of azo- and stilbene- containing surfactant rhenium (I) complexes, Organometallics. 20 (2001) 4911–4918.
- [37] M.S. Wrighton, D.L. Morse, L. Pdungsap, Intraligand lowest excited states in tricarbonylhalobis(styrylpyridine)rhenium(I) complexes, J. Am. Chem. Soc. 97 (1975) 2073–2079.
- [38] V.W.W. Yam, V.C.Y. Lau, L.X. Wu, Synthesis, photophysical, photochemical and electrochemical properties of rhenium(I) diimine complexes with photoisomerizable pyridyl-azo, -ethenyl or -ethyl ligands, J. Chem. Soc. Dalton Trans. (1998) 1461–1468.
- [39] S.S. Sun, A.J. Lees, Organometallics, Synthesis, Photophysical Properties, and Photoinduced Luminescence Switching of Trinuclear Diimine Rhenium(I)

#### Journal of Photochemistry & Photobiology, A: Chemistry 407 (2021) 113059

Tricarbonyl Complexes Linked by an Isomerizable Stilbene-like Ligand, Organometallics 21 (2002) 39–49.

- [40] A.S. Polo, M.K. Itokazu, K.M. Frin, A.O.T. Patrocinio, N.Y.M. Iha, Light driven transto- cis isomerization of stilbene-like ligands in fac- [Re(CO)3(NN)(trans-L)]+ and luminescence of their photoproducts, Coord. Chem. Rev. 250 (2006) 1669–1680.
- [41] L.S. Matos, R.C. Amaral, N.Y.M. Iha, Visible photosensitization of transstyrylpyridine coordinated to fac-[Re(CO)<sub>3</sub>(dcbH<sub>2</sub>)]<sup>+</sup>: new insights, Inorg. Chem. 57 (2018) 9316–9326.
- [43] M. Busby, F. Hartl, P. Matousek, M. Towrie, A.J. Vlcek, Ultrafast Excited State Dynamics Controlling Photochemical Isomerization of N-methyl-4-[trans-2-(4pyridyl) Ethenyl]pyridinium Coordinated to a {ReI(CO)<sub>3</sub>(2,2'-bipyridine) Chromophores, Chem. Eur. J. 14 (2008) 6912–6923.
- [44] A.J. Vlcek, M. Busby, Ultrafast ligand-to-Ligand Electron and energy transfer in the complexes fac-[ReI(L)(CO)<sub>3</sub>(bpy)]<sup>n+</sup>, Coord. Chem. Rev. 250 (2006) 1755–1762.
- [45] V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, Photophysics and photochemistry of novel luminescent rhenium(I) photoswitchable materials, J. Chem. Soc. Chem. Commun. (1995) 259–261.
- [46] R.C. Amaral, L.S. Matos, K.P.S. Zanoni, N.Y.M. Iha, Photoreversible molecular motion of stpyCN coordinated to fac-[Re(CO)<sub>3</sub>(NN)]<sup>+</sup> complexes, J. Phys. Chem. A 122 (2018) 6071–6080.
- [47] J. Bossert, C. Daniel, Trans-cis photoisomerization of the styrylpyridine ligand in [Re(CO)<sub>3</sub>(2,2'-bipyridine)(t-4-styrylpyridine)]<sup>+</sup>: role of the metal- to-ligand charge transfer excited states, Chem. Eur. J. 12 (2006) 4835–4843.
- [48] O.S. Wenger, L.M. Henling, M.W. Day, J.R. Winkler, H.B. Gray, Photoswitchable luminescence of rhenium(I) tricarbonyl diimines, Inorg. Chem. 43 (2004) 2043–2048.
- [49] J.D. Lewis, R.N. Perutz, J.N. Moore, Proton-controlled photoisomerization: rhenium (I) tricarbonyl bipyridine linked to Amine or azacrown ether groups by a styryl pyridine bridging ligand, Chem. Commun. (2000) 1865–1866.
- [50] H. Zhang, C.S. Rajesh, P.K. Dutta, Visible-Light-Driven Photoreactions of [(bpy)<sub>2</sub>Ru (II)L]Cl<sub>2</sub> in Aqueous Solutions (bpy = bipyridine, L= 1,2-bis(4-(4'-methyl)-2,2'bipyridyl)ethene), J. Phys. Chem. A 112 (2008) 808–817.
- [51] D.M. Dattelbaum, M.K. Itokazu, N.Y.M. Iha, T.J. Meyer, Mechanism of Metal-to Ligand Charge Transfer Sensitization of Olefin Trans-to-cis Isomerization in the*fac*-[ReI(phen)(CO)<sub>3</sub>(1,2-bpe)]+ cation, J. Phys. Chem. A 107 (2003) 4092–4095.
- [52] P. Pal, T. Ganguly, D. Maity, S. Baitalik, 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, J. Photochem. Photobiol. A Chem. 392 (2020) 112409.
- [53] T. Yutaka, I. Mori, M. Kurihara, N. Tamai, H. Nishihara, Photochemical behavior of azobenzene-conjugated Co<sup>II</sup>, Co<sup>III</sup>, and Fe<sup>II</sup> bis(terpyridine) complexes, Inorg. Chem. 42 (2003) 6306–6313.
- [54] Y. Hasegawa, K. Takahashi, S. Kume, H. Nishihara, Complete solid state photoisomerization of bis(dipyrazolylstyrylpyridine)iron(II) to change magnetic properties, Chem. Commun. 47 (2011) 6846–6848.
  [55] J.J. Santos, S.H. Toma, P.M. Lalli, M.F. Riccio, M.N. Eberlin, H.E. Tomaa, K. Araki,
- [55] J.J. Santos, S.H. Toma, P.M. Lalli, M.F. Riccio, M.N. Eberlin, H.E. Tomaa, K. Araki, Exploring the coordination chemistry of isomerizable terpyridine derivatives for successful analyses of Cis and trans isomers by travelling wave ion mobility mass spectrometry, Analyst. 137 (2012) 4045.
- [56] P. Pal, S. Mukherjee, D. Maity, S. Baitalik, Synthesis, structural characterization, and luminescence switching of diarylethene-conjugated Ru(II)-Terpyridine complexes by trans-cis photoisomerization: experimental and DFT/TD-DFT investigation, Inorg. Chem. 57 (2018) 5743–5753.
  [57] P. Pal, S. Mukherjee, D. Maity, S. Baitalik, Synthesis, photophysics, and switchable
- [57] P. Pal, S. Mukherjee, D. Maity, S. Baitalik, Synthesis, photophysics, and switchable luminescence properties of a new class of ruthenium(II)–Terpyridine complexes containing photoisomerizable styrylbenzene units, ACS Omega 3 (2018) 14526–14537.
- [58] K. Gille, H. Knoll, K. Quitzsch, Rate constants of the thermal cis-trans isomerization of azobenzene dyes in solvents, acetone/water mixtures, and in microheterogeneous surfactant solutions, Int. J. Chem. Kinet. 31 (1999) 337–350.
- [59] T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, K. Kubo, S. Furusho, K. Matsumra, N. Tamai, H. Nishihara, Synthesis, characterization, and photochemical properties of azobenzene-conjugated Ru(II) and Rh(III) bis(terpyridine) complexes, Inorg. Chem. 40 (2001) 4986–4995.
- [60] J. Otsuki, K. Suwa, K. Narutaki, C. Sinha, I. Yoshikawa, Photochromism of 2-(phenylazo)imidazoles, K. Araki, J. Phys. Chem. A 109 (2005) 8064–8069.
- [61] G. Gauglitz, S. Hubig, Chemical actinometry in the UV by azobenzene in concentrated-solution - A convenient method, J. Photochem. 30 (1985) 121–125.
- [62] V. Ladanyi, P. Dvorak, J.A. b Anshori, L. Vetrakova, J. Wirz, D. Heger, Azobenzene photoisomerization quantum yields in methanol redetermined, Photochem. Photobiol. Sci. 16 (2017) 1757–1761.
- [63] S. Mukherjee, P. Pal, D. Maity, S. Baitalik, Photophysics and luminescence switching properties of a series of photochromic styrylbenzene-terpyridine conjugate: experimental and DFT/ TD-DFT investigation, J. Photochem. Photobiol. A Chem. 378 (2019) 94–104.
- [64] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, von A. Zelewsky, Coord. Chem. Rev. 84 (1988) 85–277.
- [65] B. Durham, J.V. Casper, J.K. Nagle, T.J. Meyer, J. Am. Chem. Soc. 104 (1982) 4803–4810.