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Enhanced photochromism of 1,2-dithienylcyclopentene complexes with metal ion

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A new bis(5-pyridyl-2-methylthien-3-yl)cyclopentene, as a photochromic bridging ligand, has been synthesized and the photocyclization quantum yield was found to increase in the presence of a metal ion.

Introduction

Considerable attention has been paid to photochromic compounds including diarylethenes, fulguides, spiropyrans, which show reversible photoisomerization upon irradiation with light of appropriate wavelength.[1–4] In particular, studies on the 1,2-bisthienylethene derivatives (BTEs) are of interest for potential applications as erasable-memory media, photo-optical switching, display and photo-drive actuators owing to their excellent thermal-stability and fatigue-resistance.[5] Although 1,2-bisthienylethene derivatives are the most promising compounds for applications in photonic devices such as erasable data storage systems and optical switches, several additional properties need to be improved, such as cyclization quantum yield and non-destructive readout capability.[1,2] The property changes of BTEs during the photochromic process, such as the refractive index, relative permittivity, oxidation/reduction potential, photoluminescence are the basis of such applications.[3–14] Among them, reversible changes of luminescence are interesting from the viewpoint of applications for erasable memory media, optical switches and fluorescence probes. Most recently, Irie *et al.*[15] have shown that digital switching of the fluorescence of diarylethene molecules can be controlled by irradiation with UV and visible light at the single-molecular level. Branda's group[16] also described BTE-porphyrin system switches to achieve non-destructive readout using the luminescent changes. A novel family of photochromic BTE-based tetraazaporphyrin or phthalocyanine hybrids was developed in our lab.[2] The changes of near infrared luminescence of this family of compounds along with photochromism provided a wonderful non-destructive readout method and optical switches.

Also the use of a diarylethene as a photoswitching ligand has attracted much attention because of its potential in photonic switching devices. The interaction between metal ions located at both ends of pyridyl groups of the diarylethene can be switched by irradiation, because the π-conjugated bond structures between the two aryl groups in the two isomers are different.[6,7] A linear chain polymer complex, bridged by pyridyl groups, of 1,2-bis [2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene and Zn(hfac)$_2$ has been reported.[3] The complex underwent a photochromic reaction in the single-crystalline state and the absorption maximum showed a 10 nm bathochromic shift. Furthermore, the opened ring form of diarylethene has parallel and anti-parallel conformations. The balance between the two conformations limits the maximum cyclization quantum yield to 0.5.[1] The existence of the parallel conformation limits the quantum yield for the ring-closure reaction.[17] If the ratio of anti-parallel conformation can be increased, the cyclization quantum yield is expected to increase accordingly.[7,8] Takeshita *et al.*[10] has reported the enhancement of photocyclization yield by the inclusion of a photochromic diarylethene in a cyclodextrin cavity.

Diarylfluorocyclopentenes, which displayed excellent photochromic properties and marked resistance to photofatigue, have been widely investigated. In particular, the closed form of the perfluorocyclopentene switches have been shown to be stable up to temperatures well above 100 °C.[17–20] Although 1,2-bisaryl-substituted perfluorocyclopentenes have been reported with excellent photochromic behavior, there are disadvantages with these compounds such as expense and the volatile (bp 26–28 °C)[21] starting material octafluorocyclopentene. Comparatively, the synthesis of dithienylcyclopentene could be performed on a large scale and the starting materials are easily accessible. Dithienylcyclopentene also showed excellent thermal stability.[21] 1,2-Bis (5-chloro-2-methyl-3-thienyl)cyclopentene is a highly versatile starting material for a variety of dithienyl-cyclopentene-based compounds. It can be synthesized from rather cheap starting materials and the synthesis route is rather simple as described previously.[12]

In the present work we report on the synthesis, characterization, and photochromic properties of a pyridine-tethered BTE, namely, bis(5-pyridyl-2-methyl-3-thienyl)cyclopentene shown in Scheme 1. To enhance the cyclization quantum yield, the optical properties of the pyridine-tethered BTE in solution with metal ions have also been investigated. Improved ring-closing quantum yields were observed in THF in the presence of zinc ion compared with a solution without metal ions. Nevertheless, it would be useful to design new photochromic materials for information data processing.

Results and discussion

Absorption spectra of compound **2** upon UV irradiation and the addition of various amounts of Zn^{2+} in THF are shown in Fig. 1. In THF, there is almost no difference between the compound **2** (free ligand) and the zinc complex. In both cases the open isomer exhibits a UV absorption that has a maximum around 295 nm. Upon irradiation with 254 nm light the colorless solution of the open-ring form **2a** turns purple and an immediate increase in the absorption intensity is observed in the visible spectral region (λ = 558 nm). The purple color is due to the transformation of **2a** to **2b** by photocyclization. The open isomer **2a** can be photochemically regenerated by irradiation with light of 570 nm wavelength and its characteristic purple color disappeared again. Similar spectral changes are observed for **2a** upon the addition of various amounts of Zn^{2+} in THF under identical conditions as shown in Fig. 1.

After several minutes of continuous irradiation on compound **2** (4 × 10^{-4} M in CDCl$_3$), the photostationary state was reached with the isosbestic point in the absorption spectra. A second set of peaks appeared in its proton NMR spectra which are slightly shifted (upfield shifts for the thiophene C–H signals and downfield shifts for the methyl thiophene signals) with

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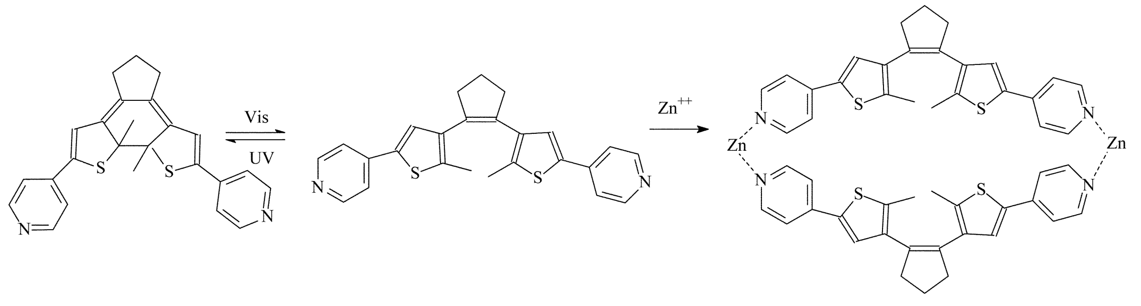
Table 1 Selected ^{1}H NMR data (500 MHz) of open and closed forms of compound **2** in $CDCl_3$ and in $CDCl_3$ with Zn^{2+}

	δ for protons(ppm)			
Compound	Thiophene C–H	Pyridine α-H	$–CH_2$	Thiophene CH_3
2 only (open)[a]	7.22	8.52(doublet)	2.85	2.01
2 only (closed)[b]	6.59	8.59	2.52	2.02
2 + 4 eq. Zn^{2+}(open)[a]	7.23	8.53(doublet)	2.85	2.02
2 + 4 eq. Zn^{2+}(closed)[b]	6.60	8.60	2.53	2.06

[a] 4×10^{-4} M in $CDCl_3$. [b] The closed form refers to the photostationary state.



2b **2a** **2a + Zn^{2+}**

Scheme 1 Photochromism and metal-complex of compound **2**.

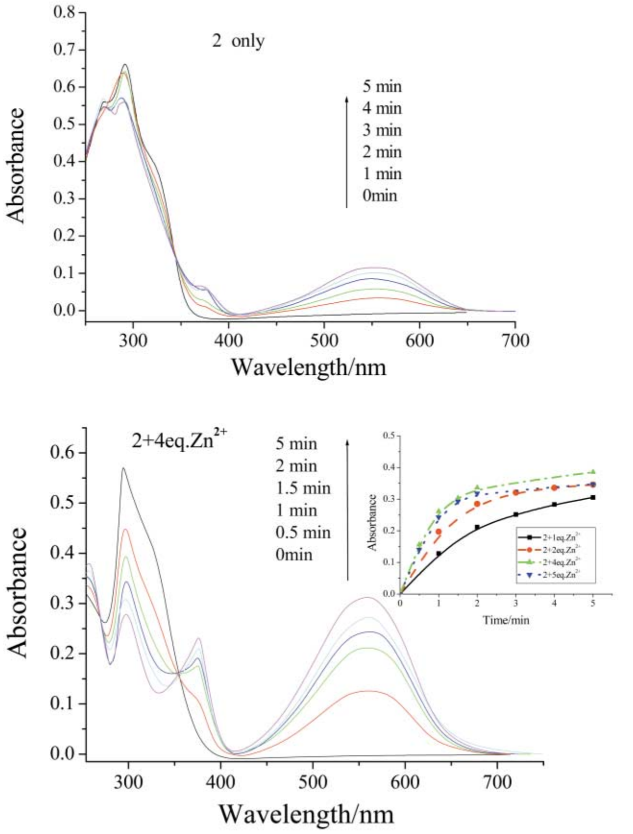


Fig. 1 UV–Vis absorption spectra of compound **2** (2×10^{-5} M) upon the addition of various amounts of Zn^{2+} in THF and the changes in absorption under different irradiation time by light of 254 nm. Insert figure: relationship between the changes in absorbance at the peak of 556 nm and time of photocyclization by irradiation with 254 nm.

respect to those of the open form and this indicates that a photochemical reaction has occurred.[20,21] The proton NMR spectral trends of compound **2** are listed Table 1. For the α-protons of the pyridine, the NMR signal feature remains the sharp doublet after complexation with Zn^{2+}. This means that the conformation of the zinc complex is as shown in Scheme 1.

The two conformations with the two rings in mirror symmetry and in C_2 symmetry of bisthienylethene determine that only the anti-parallel conformation is allowed in the photocyclization reaction. The two conformations expected are in dynamic equilibrium. In general, the population ratio of the two conformations is 1 : 1. Therefore, when the ratio of the anti-parallel conformation is increased, the photocyclization quantum yield is also expected to increase.[1] The absorption maxima of **2b** upon the addition of various amounts of Zn^{2+} in THF are all found to be in the range 554–558 nm and are shown in Table 2. It is worthwhile to note the different absorption maxima values in the photostationary state (A_{ps}) of compound **2** in THF and in the presence of Zn^{2+} and the indication of the conversion between the two states. A higher A_{ps} indicates a preferred switching process to the closed form, *i.e.* enhanced photochromism.[23] The A_{ps} values are shown in Table 2. The results for compound **2** upon the addition of various amounts of Zn^{2+} in THF was surprising and indicate that the quantum efficiency of interconversion into the photostationary state is nearly three times higher for compound **2** in the presence of Zn^{2+} than without zinc ion. The photocyclization quantum yield calculated by the comparable method[24] is also almost three times higher for compound **2** in the presence of Zn^{2+} as shown in Table 2. The ring-closure coloration quantum yield increases from 15.5% to 44.6% upon the addition of varying amounts of Zn^{2+}. It may be ascribed to the influence of the zinc ion. It plays an important role in directing the steric course of the photocyclization reaction. Although it is difficult to predict the mechanism of how the pyridyl units orient themselves around a metal ion in solution, it clearly increases the photocyclization quantum yield as shown by the values in Table 2. The salts of transition metals group (II) are well known as good complex agents. Zinc complexes with the coordination number varying from 2 to 6, and especially 4, are most favored.[25,26] In our work $ZnCl_2$ was chosen as the metal source, the two pyridyl groups of two molecules of compound **2** possibly coordinate with the zinc ion with a coordination number of four in a crablike configuration in solution as shown in Scheme 1. Because of the high binding affinity of pyridyl with metal ions,[27] the interconversion efficiency from the parallel to the anti-parallel configuration is strongly enhanced by Zn^{2+} complex and this allows the thiophene ring to rotate more freely. The possible crablike

Table 2 Absorption behavior of **2a** upon the addition of various amounts of Zn^{2+} in THF irradiated with 254 nm light[a]

Compound[b]	λ_{max}/nm (open form)	λ_{max}/nm (closed form)	A_{ps} [23] ($\Phi_{O\text{-}C}$ [24])
2 only	290	551	0.114 (15.5%)
2 + 1 eq. Zn^{2+}	292, 263	554	0.296 (36.2%)
2 + 2 eq. Zn^{2+}	295, 255	555	0.333 (39.2%)
2 + 4 eq. Zn^{2+}	296, 256	556	0.355 (44.6%)
2 + 5 eq. Zn^{2+}	295, 257	558	0.332 (42.4%)

[a] Absorption maximum obtained at the photostationary state under irradiation with 254 nm light.[23] $\Phi_{O\text{-}C}$ is the quantum yield for the photocyclization from the open form to the closed form calculated by the comparable method.[24] [b] 2×10^{-5} M upon the addition of various amounts of Zn^{2+} in THF.

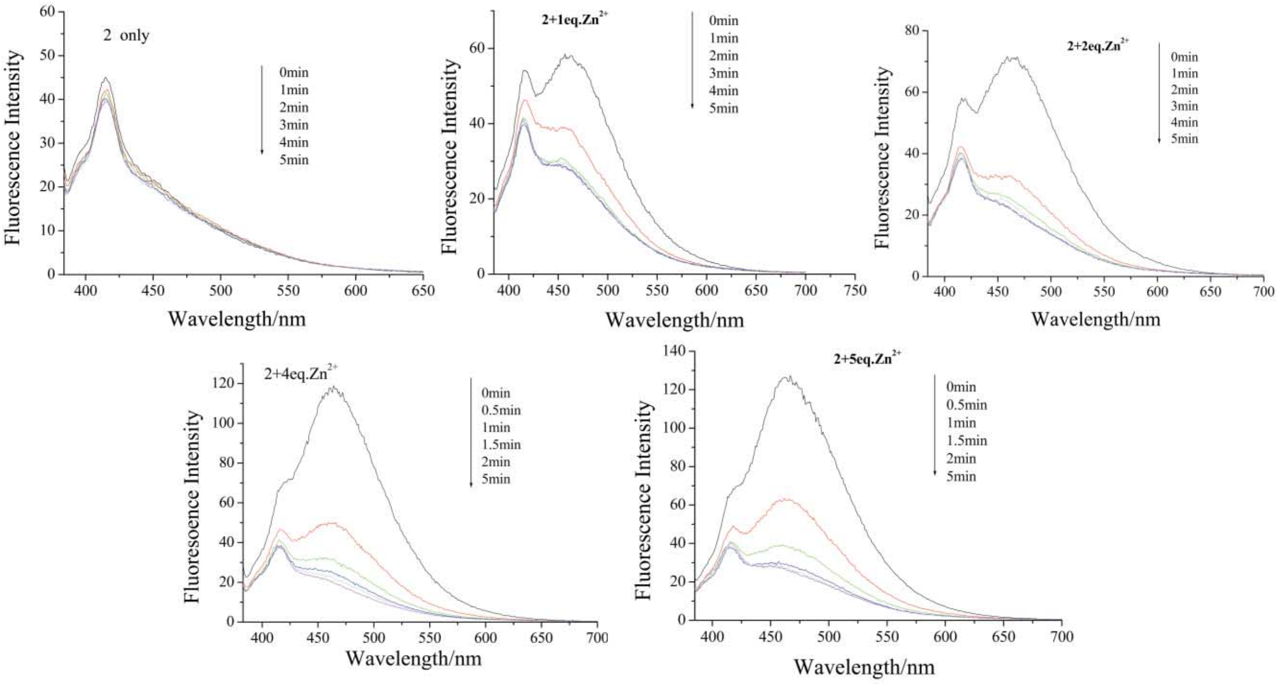
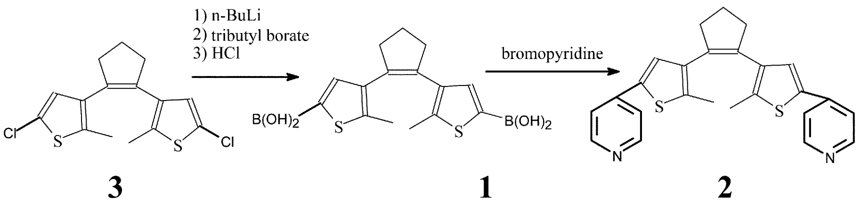


Fig. 2 Fluorescence emission spectra of compound **2** (2×10^{-5}M, excited at 370 nm) upon the addition of various amounts of Zn^{2+} in THF and their changes when **2a** was transformed to the closed form with different irradiation time by 254 nm light.

configuration shown in Scheme 1 may favor the anti-parallel conformation and this may explain why the interconversion efficiency to the photostationary state of compound **2** in the presence of Zn^{2+} is obviously higher than that in the solution without zinc ion.

In fact, the zinc coordination number in the complexes in this study can be determined by the experimental data listed in Table 2. After normalization of absorbance at 295 nm (the characteristic absorption of the free ligand **2a**), the A_{ps} values for various amounts of Zn^{2+} in THF at the photostationary state under irradiation with 254 nm are almost the same as that 1 : 1 molar ratio between compound **2** and zinc ion. This means that the coordination in the complexes dominates the configuration shown in Scheme 1, despite the variation of zinc ion concentration in THF.

Recording the change of luminescence provides another method to assess the process of storage of information, which can minimize the extent of erased information during the signal detection. An important condition must be met additionally. That is, the emission wavelengths being measured in readout process must reside far enough outside the spectral regions where the photochromic reactions are induced.[11,21] Fig. 2 shows the fluorescence intensity changes of **2a** in THF upon the addition of various amounts of Zn^{2+}. In the case of **2a** in THF, it fluoresces with a peak at 415 nm when excited by 370 nm, where the BTE photochromic unit has no absorption. The fluorescence intensity change is observed under different irradiation times. The open form **2a** in THF has relatively low fluorescence, whereas the mixture solution of **2a** and Zn^{2+} shows medium fluorescence. Initial addition of Zn^{2+} ion to the solution of compound **2** in THF leads to an increase in the fluorescence intensity and a new peak at 463 nm appears in the fluorescence spectra, which is characteristic of the zinc complex. Further addition of various amounts of Zn^{2+} increases the fluorescence intensity only at 463 nm, as shown in Fig. 2. The ratios ($I_{463\ nm}$ / $I_{415\ nm}$) of the initial fluorescent intensity between the peak at 463 nm and that at 415 nm, which is characteristic of compound **2a** alone, increase with the increase in concentration of zinc ion in the system. That is, ($I_{463\ nm}$ / $I_{415\ nm}$) is 1.09 for one equal molar of Zn^{2+}, 1.21 for two equal molars of Zn^{2+}, 1.71 for four equal molars of Zn^{2+}, 1.79 for five equal molars of Zn^{2+}, respectively. This trend implies that the conformation of the zinc complex shown in Scheme 1 is reasonable. Since the crablike conformation shown in Scheme 1 for the metal complex is a rigid structure, it would enhance fluorescence. In addition, an increase of zinc concentration in the system would convert the parallel conformation of thiophene ring of compound **2** into the anti-parallel conformation, which has been confirmed by the data listed in Table 2 and the three times enhancement in A_{ps} values. The new and strong fluorescence intensity at 463 nm is ascribed to the fluorescence of the Zn^{2+} complex. When the photocyclization reaction was carried out by irradiation on the Zn^{2+} complex with UV-light (254 nm), the intensity of the new emission at 463 nm was strongly quenched. Several minutes of irradiation later the emission at 463 nm was quenched completely and the fluorescent spectra of the systems with different concentrations of zinc ion became similar to each other. The intensity of the residual emission after UV



Scheme 2 Synthetic route of the compound **2** in the study.

irradiation for compound **2** in the presence of Zn^{2+} became similar to the fluorescence spectra of compound **2** in THF without zinc ion. The results indicate that the zinc complex favors the interconversion to the anti-parallel conformation, however, the crablike configuration of the complex shown in Scheme 1 is destroyed by 254 nm light irradiation and the zinc ion is cleaved. The residual emission observed in the solution of **2a** upon the addition of Zn^{2+} is considered to be the emission from compound **2b** (shown in Fig. 2). It should be pointed out that the zinc complex is photostable following excitation by 370 nm light, as shown in Fig. 2.

In the presence of Zn^{2+}, the complex emitted at 463 nm, which is an inactive wavelength for photo-recyclization despite the slight overlap with the UV–Vis absorption spectrum of **2a**. The photochromic compound **2** in the presence of metal ion as optical switch exhibits a light-triggered fluorescence on excitation of absorption bands that have only a minimal effect on the switching process itself. In the presence of Zn^{2+} the emission intensity of the complex can be modulated by photochemically switching between **2a** and **2b**, which provided a non-destructive readout method. Irradiation with 570 nm regenerated the open ring form and restored the luminescence to near its original value. A very important property of the dithienylcyclopentene switches is the thermal irreversibility of the photochemical cyclization.[1,21] For compound **2** in this work it was found that the closed form shows excellent thermal stability up to 80 °C for several hours.

Conclusion

In summary, the photochromic processes of a typical pyridine-tethered 1,2-bisthienylethene (BTE) with or without zinc ion were observed. The photochromism was strongly enhanced by the addition of Zn^{2+} and the photochromic reaction proceeded effectively from the open to the closed-ring form. The change of luminescence of the pyridine-tethered BTE upon the addition of metal ion holds promise for the application to non-destructive readout of optical memory media and optical switching.

Experimental

The synthesis of 1,2-bis(5-chloro-2-methyl-3-thienyl)cyclopentene (compound **3** shown in Scheme 2) was based on the literature method.[21] The synthesis of the 1,2-bis[2-methyl-5-(4-pydidyl)-3-thienyl]cyclopentene is shown in Scheme 2, the starting material 1,2-bis(5-chloro-2-methyl-3-thienyl)cyclopentene was lithiated with *n*-BuLi in THF at −78°C, then treated with $B(OBu)_3$ to provide the bis(boronic acid) **1**. The bis(boronic acid) **1** was used in Suzuki coupling reaction[22] with 4-bromopyridinium hydrochloride to provide compound **2** shown in Scheme 2. ^1H NMR spectra were recorded on a Bruker AM-500 spectrometer. UV–Vis spectra were recorded on Varian Cary 500. IR spectra were recorded on a Nicolet FT-IR20SX. photoluminescent spectra were recorded on a Varian Cary Eclipse. Elemental analysis data were obtained on a Perkin Elmer 240c instrument. Mass spectra and TOF-mass spectra were obtained at 70 eV on a VG 12–250 (VG Mass lab) and Mariner API TOF spectrometers (time of flight, TIS ion source, PE Corp.). All solvents were purified and dried. All reactions were performed in flame-dried glassware under Ar.

1,2-Bis(5-boronic acid-2-methyl-3-thienyl)cyclopentene (1)

To a stirred solution of compound **3** (2 g, 6 mmol) in THF (20 ml) at −78 °C under Ar in the absence of light was added dropwise 1.6 M n-BuLi in hexane (0.78 g, 12 mmol), and the reaction mixture was stirred at −70 °C for a further 30 min. To the reaction mixture was quickly added tributyl borate (2.76 g, 12 mmol) by syringe, and the reaction mixture was stirred at room temperature for 15 h. To the reaction mixture was added CH_2Cl_2 (30 ml) and HCl (15 ml, 3 M). The phases were separated and the organic phase was extracted with 15 ml of 10% NaOH aqueous solution three times. The combined aqueous phase was acidified with 10% HCl. The gray precipitate was collected by filtration and washed with water. Drying of the white powder in vacuum gave 1.34 g of compound **1** in yield of 63.8%. ^1H NMR (500 MHz, $CDCl_3$, ppm): 8.02(s, 4H, –OH), 7.42(s, 2H, thienyl C–H), 2.75(t, 4H, $–CH_2–$), 2.02(m, 2H, $–CH_2–$), 1.76(s, 6H, $–CH_3$).

1,2-Bis[2-methyl-5-(4-pyridyl)-3-thienyl]cyclopentene (2)

To solid 4-bromopyridinium hydrochloride (0.5 g, 1.45 mmol) in dioxane under Ar was added a 1 M aqueous Na_2CO_3 solution (8 ml). The mixture was stirred and heated to 55 °C. The catalyst $Pd(PPh_3)_4$ was added followed by the addition of a solution of compound **1** (0.62 g, 3.19 mmol) in dioxane by cannula. After being stirred at 60 °C for 6 h, the mixture was hydrolyzed with water and extracted with CH_2Cl_2. The combined extracts were washed with water twice, dried with $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel with hexane–EtOAc (1 : 1) to yield 140 mg (23%) of compound **2** as a white powder. ^1H NMR (500 MHz, $CDCl_3$, ppm): 8.52(d, 4H, pyridyl α-H), 7.33(d, 4H, pyridyl β-H), 7.22(s, 2H, thienyl C–H), 2.85(t, 4H, $–CH_2–$), 2.12(m, 2H, $–CH_2–$), 2.02(s, 6H, $–CH_3$). HR-MS: calculated for ($C_{25}H_{22}N_2S_2$) 414.58, found: 414.1. Element analysis: Calc. for $C_{25}H_{22}N_2S_2$: C 72.46, H 5.31, N 6.76; Found: C 72.38, H 5.28, N 6.72%.

Acknowledgements

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