# Photomodulation of Lewis basicity in a pyridine-functionalized 1,2-dithienylcyclopentene†

**Hema D. Samachetty and Neil R. Branda***

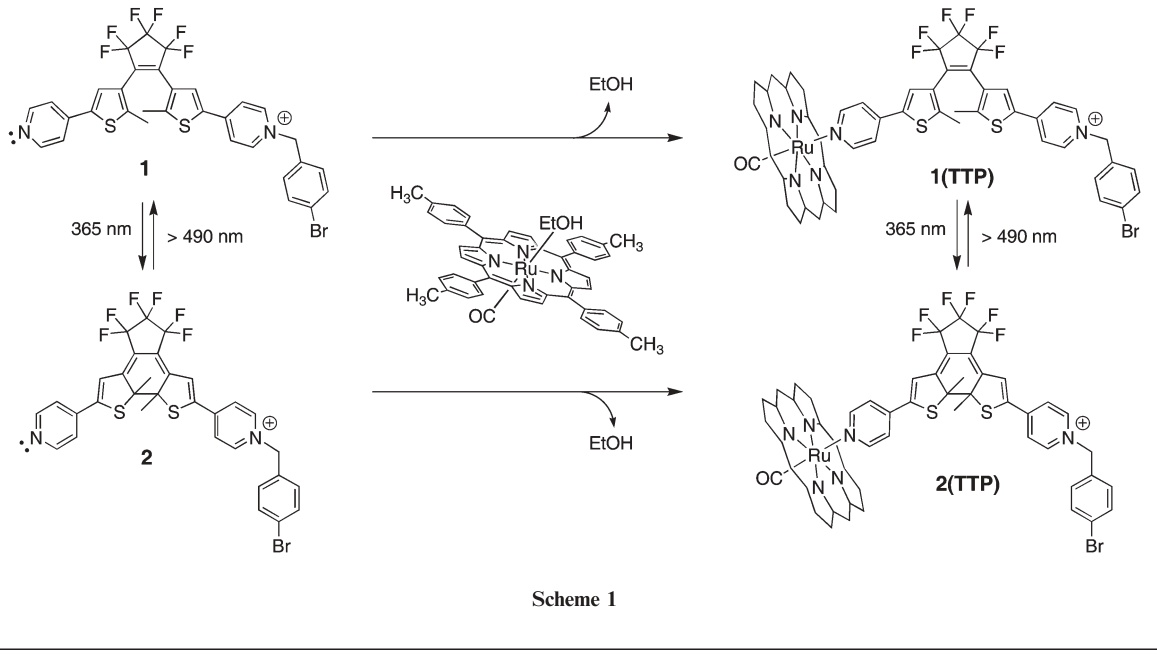
*Received (in Cambridge, UK) 3rd February 2005, Accepted 6th April 2005*
*First published as an Advance Article on the web 21st April 2005*
**DOI: 10.1039/b501779c**

**The ability of a pyridine ligand on the photoresponsive 1,2-dithienylethene backbone to coordinate to a ruthenium porphyrin is modulated by interconverting the compound between its electronically insulated ring-open and electronically connected ring-closed form.**

The development of molecular systems that respond to light by undergoing reversible changes in their structures and properties is an important goal as it has the potential to significantly impact numerous technologies related to materials science and structural biology.[1] This bold statement is based on the fact that some well-chosen photoresponsive compounds can be toggled between two thermally stable, geometrically distinct forms, each displaying unique steric and electronic properties. Photoresponsive compounds containing the dithienylethene (DTE) backbone are particularly well suited to take on the role as switching elements because they undergo thermally irreversible cyclization reactions when stimulated with UV and visible light (isomers **1** and **2** in Scheme 1, for example).[2] Due to the significant differences in the extent of linear π-conjugation between the two DTE isomers, these photoresponsive systems offer many choices of variations in physical properties such as absorbance, luminescence, magnetism, refractive index and charge transfer, all of which are useful in photo-optical and photo-electronic device applications.[3]

The synthetic and supramolecular chemist would argue that electronic differences are most dramatically manifested by how molecules react or interact with others. Despite this fact, there are few examples[4–6] of molecular systems that take advantage of the changes in electronic communication between the two heterocycles on the DTE backbone to modulate chemical reactivity even though the importance of this concept in regulating drug delivery, sensing and catalysis is obvious. It is this concept that is the focus of this study.

The photoregulation of reactivity is illustrated by the ring-open (**1**) and ring-closed (**2**) DTE isomers of the mono-alkylated bis(pyridine) shown in Scheme 1. Due to the lack of coplanarity and linear π-conjugation in the ring-open isomer **1**, the two pendant pyridine rings are electronically insulated from each other and the nucleophilic pyridine will not sense the electronic pull of the electron-deficient pyridinium cation. Photocyclization creates a linear π-conjugated pathway running along the molecular backbone in **2**. The two formerly independent pyridine rings are now electronically coupled and it is reasonable to expect that the free pyridine will sense the effects of the electron-deficient pyridinium cation residing at the other end of the conjugated system. In this communication, we show that the outcome is a lowering of the nucleophilicity as is observed when electron-withdrawing groups are appropriately placed on nitrogen ligands.



Scheme 1

---

† Electronic supplementary information (ESI) available: details of all $^1$H NMR and IR spectroscopic studies. See http://www.rsc.org/suppdata/cc/b5/b501779c/
*nbranda@sfu.ca

We chose to demonstrate the difference in Lewis basicity of the pyridine ligands in **1** and **2** by monitoring a supramolecular event. The axial coordination of the pyridine to a ruthenium porphyrin as shown in Scheme 1 is a convenient way to assess the differences in coordination behaviour because the N–Ru binding is slow on the NMR time scale,[7] and sharp, unchanging peaks for the statistical mixture of 'free' (**1** and **2**) and 'bound' (**1(TTP)** and **2(TTP)**) pyridines are clearly visible when less than one molar equivalent of Ru(TTP)(CO)(EtOH) is added to $CD_2Cl_2$ solutions of the compounds. This provides a means to instantaneously measure the relative ratios of all compounds in a single NMR experiment and assess the binding behaviour of the ring-open and ring-closed DTE isomers.

The ring-open isomer **1** is prepared in one step by mono-alkylating the known bis(pyridine)[8] with 4-bromobenzyl bromide.

The changes that occur in the UV-vis absorption spectra when a $CH_2Cl_2$ solution of **1** ($2.5 \times 10^{-5}$ M) is irradiated with 365 nm light‡ to convert it to the ring-closed isomer **2** are shown in Fig. 1. The ring-open isomer is regenerated upon irradiation with visible light and alternate irradiation with 365 nm light and wavelengths greater than 490 nm show no apparent signs of photodegradation after 10 cycles (Fig. 1). Similar cycling experiments can be analyzed using $^1H$ NMR spectroscopy, which also shows no degradation even after prolonged irradiation (365 nm for over 2 h) nor formation of the photostable side-products that are occasionally observed for DTE compounds lacking substituents at the C-4 position of the thiophene rings.[9,10]

A $CD_2Cl_2$ solution of **1** ($1.1 \times 10^{-3}$ M) can be irradiated with 365 nm light until a 50 : 50 mixture of ring-open and ring-closed isomers is generated as monitored by measuring the relative integrals of the corresponding pairs of signals for the two isomers (Fig. 2).† Partial axial coordination is then accomplished by simply treating this 50 : 50 mixture with slightly less than 1 molar equivalent of Ru(TTP)(CO)(EtOH) (**TTP**).§ The $^1H$ NMR spectra of both complexes **1(TTP)** and **2(TTP)** show significant upfield shifts for all hydrogen atoms of the DTE ligand as anticipated for protons lying within the shielding cone of the porphyrin (Fig. 2). As expected, the protons immediately adjacent to the pyridine nitrogen of the core unit are the most dramatically affected and are seen to move as much as 7.1 ppm upfield upon complexation.†

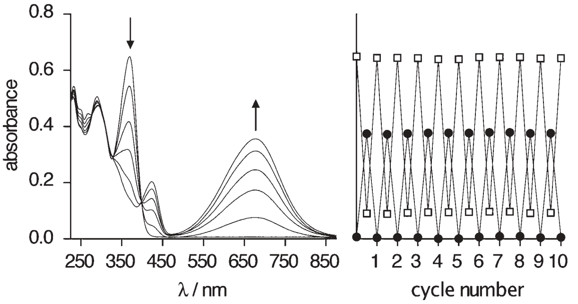


**Fig. 1** Changes in the UV-vis absorption spectra of a $CH_2Cl_2$ solution ($2.5 \times 10^{-5}$ M) of **1** when irradiated with 365 nm light for a total of 30 s (left). Modulated absorptions at 370 nm (□) and 679 nm (●) during alternating irradiation at 365 nm and >490 nm (right).

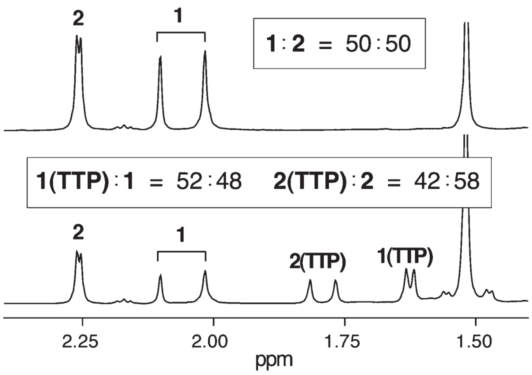
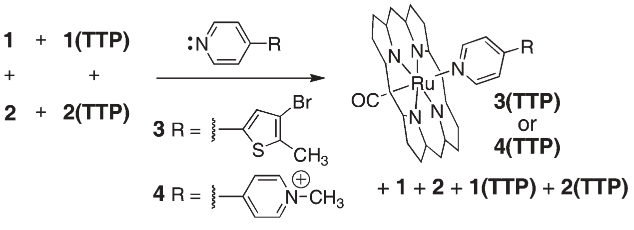


**Fig. 2** Partial $^1H$ NMR (600 MHz, $CD_2Cl_2$) spectra showing the peaks corresponding to the $CH_3$ protons in a 50 : 50 mixture of ring-open isomer **1** and ring-closed isomer **2** (top trace) and when slightly less than 1 molar equivalent of Ru(TTP)(CO)(EtOH) is added (bottom trace). The 50 : 50 mixture was obtained by irradiating a solution of **1** with 365 nm light until the appropriate ratio was achieved.

The $^1H$ NMR spectrum reveals that there is slightly less than 1.5 times more of the ring-open isomer axially coordinated to the metalloporphyrin than its ring-closed counterpart (only the signals corresponding to the thiophene methyl protons are shown in Fig. 2). This is deduced by comparing the relative ratios of the peak integrals for the 'bound' to 'free' ligands, which is measured to be 52 : 48 in the case of **1(TTP)** : **1** and 42 : 58 in the case of **2(TTP)** : **2**. Although the changes are small, they are significant and imply that the ring-open isomer is the more effective ligand.[11] The magnitude of the differences may be ascribed to the fact that the 'free' pyridine ring is twisted 20–30° out of coplanarity from the π-conjugated backbone in the ring-closed isomer **2** as predicted by molecular modeling.¶

In a competition study, 0.79 molar equivalents of 3-bromo-2-methyl-5-pyridylthiophene (compound **3** in Scheme 2) were added to the above NMR sample. This pyridine provides a competing Lewis basic nitrogen to axially coordinate to the metalloporphyrin and monitoring its coordination behaviour is a convenient way to provide additional support to the first findings. By measuring the difference in the ratios of 'bound' to 'free' **3**, the effect that the monocation has on this coordination can be assessed when it is in its all-ring-open form as opposed to its all-ring-closed form. Irradiating the NMR sample using light greater than 490 nm results in the complete ring-opening of **2** and **2(TTP)**. The $^1H$ NMR spectrum shows that half of the added pyridine is axially coordinated and the ratio of the peak integrals for the signals corresponding to **3(TTP)** : **3** is measured to be 33 : 67. The amount of axially coordinated additive increases (**3(TTP)** : **3** = 39 : 61) when the same NMR sample is irradiated with 365 nm light to



| | TTP | 1(TTP) | 2(TTP) | 3(TTP) | 4(TTP) |
|---|---|---|---|---|---|
| $\bar{\nu}_{CO}$ (cm$^{-1}$) | 1946 | 1949 | 1954 | 1951 | 1956 |

**Scheme 2**

induce the ring-cyclization and quantitatively produce **2** and **2(TTP)**. This observation reveals that the ring-closed form of the DTE is a weaker ligand than its ring-open counterpart and supports the results obtained in the first set of NMR experiments.

The final tool we used to diagnose the ability of the DTE compound to act as a Lewis base is infrared spectroscopy because monitoring the changes in the C=O stretching frequency is another convenient means to illustrate the electronic differences between the two forms of the nitrogen base (**1** and **2**). These results are shown in Scheme 2.

The metalloporphyrin reagent, Ru(TTP)(CO)(EtOH), has its C=O stretch at 1946 cm$^{-1}$ in the IR spectrum (cast in KBr pellet).† The coordination compound formed when this metalloporphyrin is complexed to the pyridylthiophene additive (**3(TTP)**) has its C=O stretch at 1951 cm$^{-1}$ due to the decrease in Ru → C=O backbonding by the presence of the pyridyl π-acid. Compound **3** is a good representative of the DTE ring-open isomer **1** and **1(TTP)** has its C=O stretch at a similar frequency, 1949 cm$^{-1}$. Monomethylbipyridine **4** is an appropriate analogue for the ring-closed isomer **2** and the coordination compound prepared when the metalloporphyrin is treated with **4** has its C=O stretch at 1956 cm$^{-1}$ as expected for the stronger π-acid. Samples prepared from all-ring-closed **2(TTP)** have the C=O stretching frequency at 1954 cm$^{-1}$ as predicted from the model compound **4(TTP)**.

Irradiating the KBr pellet of **1(TTP)** with 365 nm light results in the shifting of the C=O stretch to higher energy (1952 cm$^{-1}$) albeit very slowly (over 2 h) and not completely to the frequency corresponding to the ring-closed isomer. The fact that the photocyclization appears to be hindered in the pellet can be ascribed to the environmental constraints imposed on the ring-open form by the solid KBr matrix. It is well-documented that two equal energy conformers of DTE derivatives coexist and that only one of them is free to undergo the ring-closing reaction.[2] The close packing in the solid KBr pellet likely prevents the free rotation and renders the mixture partially inactive. Similar constraints of the medium on DTE derivatives have been described.[12,13] This limitation can be overcome in a similar manner as previously described[12] by commencing the IR studies with the pellet prepared from the all-ring-closed isomer **2(TTP)**. Exposure of this pellet (C=O stretch at 1954 cm$^{-1}$) to light of wavelengths greater than 490 nm (1 h) results in the shifting of the stretching frequency to 1949 cm$^{-1}$ corresponding to the C=O stretch of the ring-open complex **1(TTP)**. Re-irradiation of the pellet sends the C=O stretch back to the higher energy value (1954 cm$^{-1}$) corresponding to the ring-closed isomer.

We have shown here that there is a difference in the reactivity (*via* a supramolecular event) between the ring-open and ring-closed isomers of a DTE switch due to the reversible interconversion of an electronically insulating and conducting backbone. We are currently exploring the use of this technology in catalysis and reactivity.

This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Canada Research Chair Program and Simon Fraser University. We thank Nippon Zeon Corporation for supplying the octafluorocyclopentene needed to prepare the photochromic compounds.

**Hema D. Samachetty and Neil R. Branda***
*Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada V5A 1S6. E-mail: nbranda@sfu.ca*

## Notes and references

‡ Standard lamps used for visualizing TLC plates (Spectroline E-series, 470 μW cm$^{-2}$) were used to carry out the ring-closing reaction of **1** to **2** and **1(TTP)** to **2(TTP)**. The ring-opening reactions were carried out using the light of a 150 W tungsten source that was passed through a 490 nm cutoff filter to eliminate higher energy light.

§ The titration was carried out by slowly adding small portions (as a solid) of an approximately weighed amount of the metalloporphyrin.

¶ Semi-empirical calculations (AM1 and PM3) were performed using Spartan '02 from Wavefuntion, Inc.

1 (*a*) *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, Germany, 2001; (*b*) *Organic Photochromic and Thermochromic Compounds*, ed. J. C. Crano and R. J. Gugliemetti, Plenum, New York, 1999, vol. 1 and 2.

2 (*a*) M. Irie, in *Organic Photochromic and Thermochromic Compounds*, ed. J. C. Crano and R. J. Gugliemetti, Plenum, New York, 1999, vol. 1, p. 207; (*b*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (*c*) M. Irie, in *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, Germany, 2001, p. 37.

3 H. Tian and S. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85.

4 (*a*) For an example where the acidity of a phenol –OH increases due to the creation of linear π-conjugation between the phenol and a pyridinium across a DTE backbone, see: S. H. Kawai, S. L. Gilat and J.-M. Lehn, *Eur. J. Org. Chem.*, 1999, 2359; (*b*) For an example where the coordination geometry around a copper(II) ion is photoregulated using the bis(pyridine) version of the DTE, see: K. Matsuda, K. Takayama and M. Irie, *Inorg. Chem.*, 2004, **43**, 482. Although this study demonstrates that there is a difference in the π-acceptor character of the pyridyl ligand in the two forms of the DTE, the authors only suggest it is due to variations in electronics in the pyridine of the closed form and do not attribute it to electronic communication between the free pyridine and the one that is electron poor owing to the coordination. In fact they later state that the distance between the two metal centres is too far for them to be effectively coupled.

5 For examples where azobenzene has been used to regulate reactivity based on the geometric changes, see: (*a*) A. Ueno, K. Takahashi and T. Osa, *J. Chem. Soc. Chem. Commun.*, 1981, 94; (*b*) R. Cacciapaglia, S. Di Stefano and L. Mandolini, *J. Am. Chem. Soc.*, 2003, **125**, 2224; (*c*) F. Würthner and J. Rebek, Jr., *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 446; (*d*) F. Würthner and J. Rebek, Jr., *J. Chem. Soc., Perkin Trans. 2*, 1995, 1727.

6 For an example where DTE has been used to regulate reactivity based on geometric changes, see: D. Sud, T. B. Norsten and N. R. Branda, *Angew. Chem., Int. Ed.*, 2005, **44**, 2019.

7 (*a*) S. S. Eaton and G. R. Eaton, *Inorg. Chem.*, 1977, **16**, 72; (*b*) J. W. Faller, C. C. Chen and C. J. Malerich, *J. Inorg. Biochem.*, 1979, **11**, 151; (*c*) K. Chichak and N. R. Branda, *Chem. Commun.*, 2000, 1211; (*d*) K. Chichak, M. C. Walsh and N. R. Branda, *Chem. Commun.*, 2000, 847.

8 S. L. Gilat, S. H. Kawai and J.-M. Lehn, *J. Chem. Soc., Chem. Commun.*, 1993, 1439.

9 M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, *Chem. Commun.*, 1999, 747.

10 A. Peters, R. McDonald and N. R. Branda, *Adv. Mater. Opt. Electron.*, 2000, **10**, 245.

11 For an example where photochemical fragmentation of a malachite green dye leads to complete decomplexation of a cation/aza-crown ether, see: K. Kimura, R. Mizutani, M. Yokoyama, M. Okamoto and H. Doe, *J. Am. Chem. Soc.*, 1997, **119**, 2062.

12 A. Takata, M. Saito, A. Murakami, S. Nakamura, M. Irie and K. Uchida, *Adv. Funct. Mater.*, 2003, **13**, 755.

13 T. J. Wigglesworth, A. J. Myles and N. R. Branda, *Eur. J. Org. Chem.*, 2005, 1233.