

Multifunctional switches based on *bis*-imidazole derivative

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Abstract. A multifunctional *bis*-imidazole derived from piperonal was prepared and found to have photo, thermo, solvato and piezochromism with colour changes from pale green to deep blue. The multifunctionality colour changes and stability of the coloured species make the derivative candidates for various applications such as optical data storage. The photochromic properties and performance were found to be affected remarkably upon changing the solvent.

Keywords. Imidazole; free radical equilibrium; piezochromism; thermochromism; photochromism; solvatochromism.

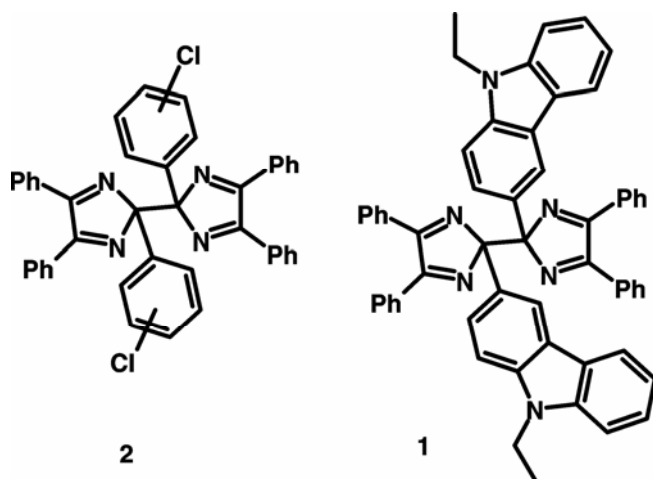
1. Introduction

Many organic molecules which exhibit reversible conversion between two states when stimulated by an external input have been proposed and investigated. Based on those the, monomolecular photochromic switches,^{1–4} fluorescence switches,^{5–8} chiral switches,^{9–12} redox switches^{13–18} and pH switches,^{19–21} metal functionalize switch,²² protonation switch,²³ morphological switch²⁴ have been successfully reported. But the information processed by these two-state molecular switches is limited. In this context, the chemical systems which integrate several switchable functions into one single molecule have recently become the focus of research and will meet the requirement in the field of high density information process. To reach this multi-switchable goal, it is essential that the organic molecule can reversibly change its structures between more states in response to the combination of external signals such as photonic, chemical, electrochemical, or magnetic stimuli and generate readable outputs such as electronic or optical signals those reflect the molecular states. In this paper, we report a single molecule which is capable of integrating the effects of multiple stimuli and producing three switchable functions. It

is known that certain dimeric nitrogen-containing heterocyclic compounds such as dimeric NAD (*N*-benzylidihydronicotinamide) are involved in some biological redox processes.²⁵ On the other hand, triphenylimidazole dimers have also attracted attention because of the sensitivity of these compounds to light, heat and pressure. Hayashi and Maeda observed that upon oxidation with potassium ferricyanide in ethanolic solution, triphenylimidazole dimer 1 gave rise to violet colour which disappeared rapidly. The oxidation product was obtained as a pale violet-coloured powder, which turned deep violet in solution under UV irradiation.²⁶ It has been suggested that the coloured species is a free radical, and EPR evidence for the existence of the radical was presented.²⁷ It is now known that the oxidation product is a piezochromic dimer, which transforms to the photochromic dimer on dissolution in a solvent. In solution, the photochromic dimer exists in a photo-stationary equilibrium with its radical form.

Radical stability in these systems has been investigated by a number of workers with respect to the influence of substituents.²⁸ It has been found that an electron-donating group on the phenyl ring will shift the photostationary state to the radical form. In continuation of some of our previous work,^{29,30} we synthesized multifunctional systems from carbazole (1) and chlorosubstituted benzaldehyde (2).

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Compound **4** is a derivative of *bis*-imidazole, namely the derivative of *bis*-imidazole functionalized with piperonal.

2. Experimental

Melting points were determined on a Thomas-Hoover capillary melting apparatus and are uncorrected. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR spectrometer. ^1H NMR were recorded in CDCl_3 on a Bruker DPX 400 spectrometer using TMS as internal standard. UV-Vis spectra were recorded on a Shimadzu 260 spectrometer for solutions.

2.1 Preparation of 2-benzo[1,3]dioxol-5-yl-4,5-diphenyl-1H-imidazole (**3**)

In a round bottom flask fitted with a magnetic stirrer, benzil (0.05 mol), Piperonal aldehyde (7.5 g, 50.0 mmol) and ammonium acetate (12.3 g, 150 mmol) were dissolved in acetic acid (100 ml). The mixture was heated under reflux in an oil bath for 1 h with stirring. After this time, the mixture was cooled to room temperature and filtered to remove any precipitate. Water (500 ml) was added to the filtrate and the precipitate formed was collected. Recrystallization from ethanol afforded the imidazole **3**.

White powder; yield 96.9%; m.p.: 256.2°C; IR ν (cm^{-1}): 3026.3 ($\text{CH}_{\text{aromatic}}$ stretch), 1598.2 ($\text{C}=\text{N}$), 1480 ($\text{C}=\text{C}$), 1338.7 ($\text{C}-\text{O}$) and 1239.1 ($\text{C}-\text{N}$). ^1H -NMR (CDCl_3) δ : 10.63 (s, NH), 8.13 (d, $\text{CH}_{\text{aromatic}}$), 7.91 (d, 4 $\text{CH}_{\text{aromatic}}$), 7.55 (s, $\text{CH}_{\text{aromatic}}$), 7.36 (dd, 4 $\text{CH}_{\text{aromatic}}$), 7.24 (dd, $\text{CH}_{\text{aromatic}}$), 6.70 (d, $\text{CH}_{\text{aromatic}}$) and 6.01 (s, CH_2).

2.2 Preparation of 2,2'-bis-benzo [1,3] dioxol-5-yl-4, 5,4', 5'-tetraphenyl-1H, 2'H- [1,2'] bisimidazolyl (**4**)

In a 1 L beaker, KOH (0.82 g, 14.7 mmol) was dissolved in 50 ml of 95% ethanol. Imidazole **3** (5.0 g, 14.7 mmol) was added into the beaker. After the complete dissolution of imidazole **3**, the reaction solution was placed in an ice bath and allowed it to cool to 5°C. A freshly prepared solution of $\text{K}_3\text{Fe}(\text{CN})_6$ (4.84 g, 14.7 mmol) was added dropwise to the stirring solution of the imidazole. The solution temperature was maintained below 10°C. The solution turned violet and then produced a precipitate. The precipitate was collected by filtration and washed with 3 \times 25 mL of water and dried, to give the bis-imidazole **4** as a yellow powder; yield 11.7%; m.p.: 192.8°C; IR ν (cm^{-1}): 3026 ($\text{CH}_{\text{aromatic}}$ stretch), 1601.9 ($\text{C}=\text{N}$), 1481.1 ($\text{C}=\text{C}$), 1247.6 ($\text{C}-\text{O}$) and 1039 ($\text{C}-\text{N}$). ^1H -NMR (CDCl_3) δ : 8.14 (d, 2 $\text{CH}_{\text{aromatic}}$), 8.03 (d, 2 $\text{CH}_{\text{aromatic}}$), 7.99 (d, $\text{CH}_{\text{aromatic}}$), 7.93 (d, 4 $\text{CH}_{\text{aromatic}}$), 7.88 (d, $\text{CH}_{\text{aromatic}}$), 7.81 (s, $\text{CH}_{\text{aromatic}}$), 7.64 (dd, 2 $\text{CH}_{\text{aromatic}}$), 7.45 (dd, 2 $\text{CH}_{\text{aromatic}}$), 7.33 (s, $\text{CH}_{\text{aromatic}}$), 7.34 (dd, 2 $\text{CH}_{\text{aromatic}}$), 7.28 (dd, 5 $\text{CH}_{\text{aromatic}}$), 7.25 (d, $\text{CH}_{\text{aromatic}}$), 7.24 (dd, $\text{CH}_{\text{aromatic}}$), 6.93 (d, $\text{CH}_{\text{aromatic}}$), 6.01 (s, 2 CH_2) and 5.94 (s, 2 CH_2). ^{13}C -NMR (CDCl_3) 168.0, 148.26, 148.2, 147.56, 147.46, 146.6, 145.9, 137.6, 134.9, 134.3, 132.9, 132.7, 131.9, 131.6, 131.1, 129.9, 129.3, 129.0, 128.9, 128.7, 128.5, 128.3, 128.0, 127.9, 127.7, 126.6, 127.2, 127.1, 126.2, 124.4, 122.7, 119.1, 111.9, 110.8, 109.1, 108.6, 108.3, 107.5, 107.2, 106.2, 101.7, 101.3, 101.0, 100.9.

3. Results and discussion

3.1 Synthesis of 2,2'-bis-benzo[1,3]dioxol-5-yl-4, 5,4',5'-tetraphenyl-1H,2'H-[1,2'] bisimidazolyl (**4**)

The preparation of 2,2'-bis-benzo [1,3] dioxol-5-yl-4, 5,4', 5'-tetraphenyl-1H, 2'H-[1,2'] bisimidazolyl **4** carried out by refluxing a solution of benzil, piperonal and ammonium acetate in acetic acid to give the 2-benzo [1,3] dioxol-5-yl-4, 5-diphenyl-1H-imidazole **3**. The oxidative dimerization was carried out using potassium ferricyanide to give the products **4**, as shown in scheme 1.

3.2 Photochromism

Irradiation of the solution of compound **4** in toluene and acetonitrile at 366 nm (medium pressure Mer-

cury lamp) gave colour change from yellow to green. This colour change is due to the dissociation of the dimer **4** to form the free radical **5** as shown in scheme 2.

Figure 1 shows the UV-Visible spectral changes of compound **4** in toluene before and after irradiation with UV light (366 nm) at different intervals of times table 1.

3.3 Thermochromism

In toluene, the compound **4**, was found to mainly in the radical form **5**, which is colour. Upon heating, the colour disappeared due to the recombination of the radical to form the original dimer (scheme 3).

The compound **4** in acetonitrile showed no thermochromic properties. Figure 2 shows the UV-Vis spectral changes of compound **4** in toluene before and after heating at different intervals of times. Table 1 summarizes the maximum wavelength of the

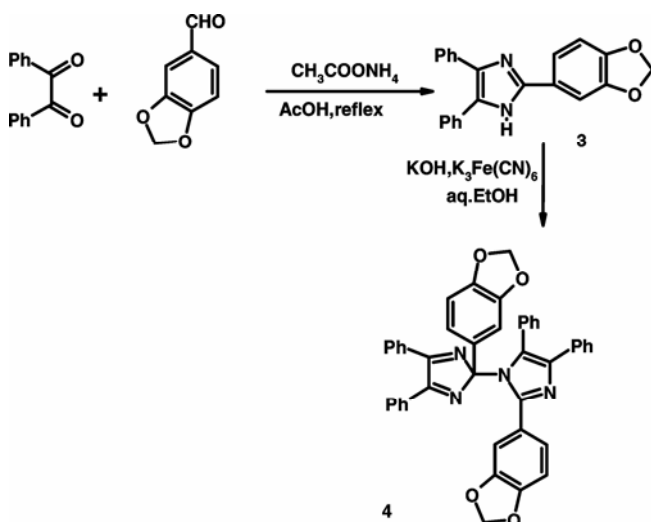
radical **5** in two different solvents namely toluene and acetonitrile.

3.4 Piezochromism

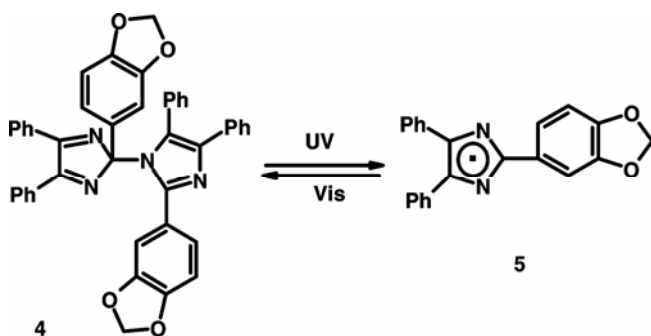
Upon grinding of **4** in the solid state change of colour from pale-green to blue was observed due to the formation of the radical **5**. When the coloured solid was kept in the dark, the colour disappeared as a result of the recombination of the radical as shown in scheme 4.

3.5 Solvatochromism

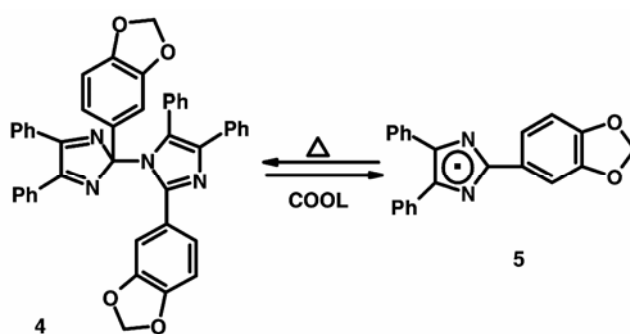
The photochromic and thermochromic behaviour of compound **4** was recorded in two solvents of different polarity, i.e. toluene and acetonitrile (table 1).



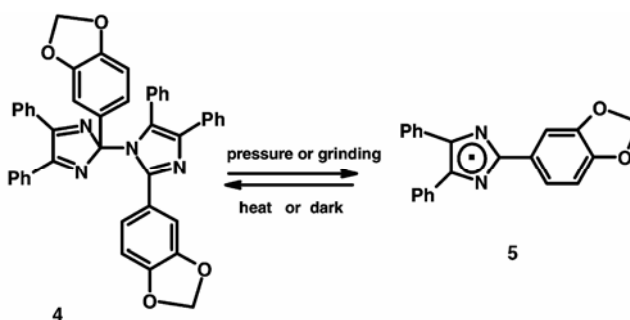
Scheme 1.



Scheme 2.



Scheme 3.



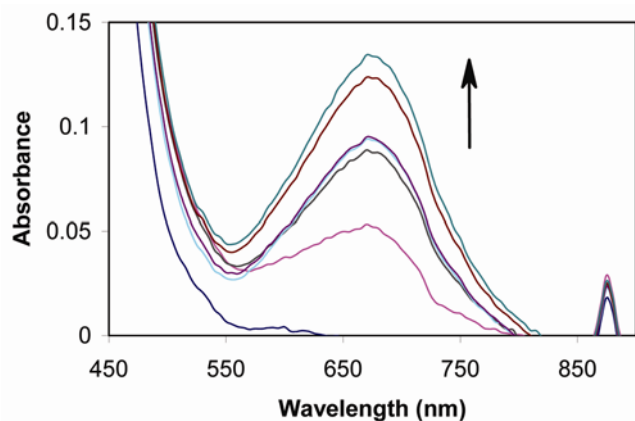
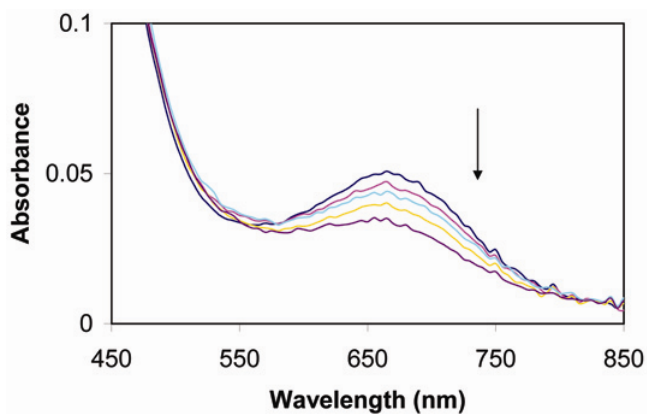
Scheme 4.

Table 1. Absorption wavelength of the coloured compound **5** after irradiation and heating.

Compound	λ_{\max} (nm)			
	Toluene		Acetonitrile	
	UV	Heating	UV	Heating
5	675	670	675	–

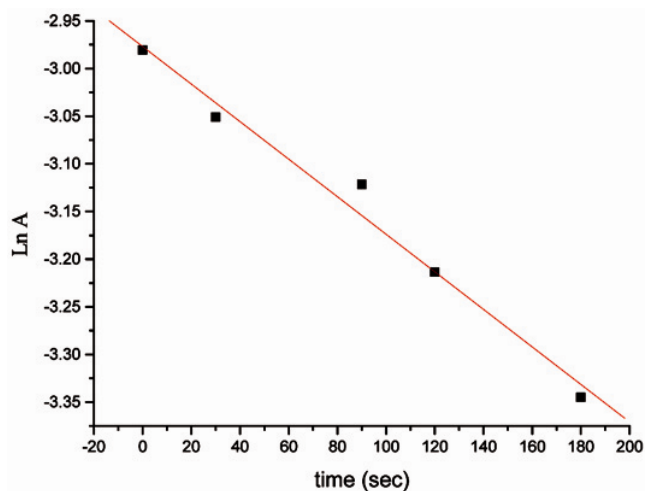
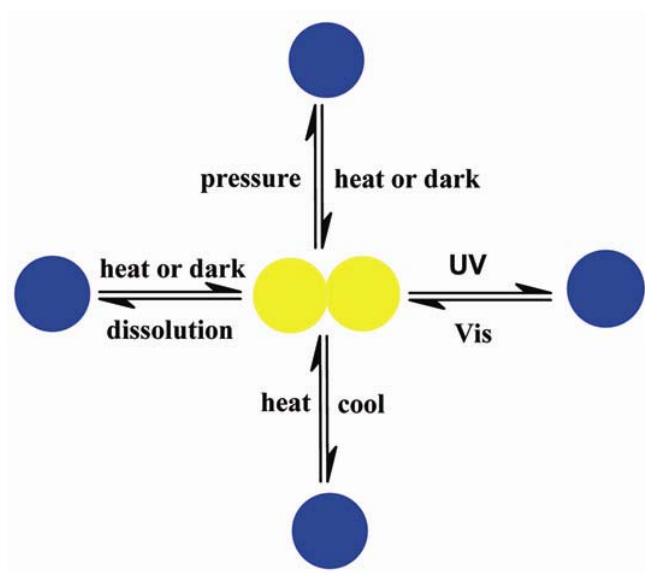
Table 2. Kinetic data for photocolouration and heating of compound **4** in various solvent.

Compound	$t_{1/2}$ (min)				K (s^{-1})			
	Toluene		Acetonitrile		Toluene		Acetonitrile	
	UV	Heat	UV	Heat	UV	Heat	UV	Heat
4	4.12	5.77	0.37	–	0.0028	–0.002	0.031	–

**Figure 1.** UV-Visible spectra of compound **4** before and after irradiation in toluene.**Figure 2.** UV-Visible spectra of compound **4** before and after heating in toluene.

3.6 Colouration kinetics

A plot of $\ln A$ vs time of irradiation or heating time gave a straight line indicating that both UV colouration and thermochromic behaviour obey first order rate equation. The colouration and bleaching data are summarized in table 2.

**Figure 3.** Plot of $\ln A$ vs time of compound **4** upon heating in toluene.**Figure 4.** Representation of multifunctionality bis-imidazol **4**.

4. Conclusion

A multifunctional *bis*-imidazole derived from piperonal was prepared and found to exhibit photo,

thermo, solvato and piezochromism with colour changes from pale green to deep blue (figure 4). The multifunctionality colour changes and stability of the coloured species make the derivative a candidate for applications in optical data storage.

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