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New photo-responsive unit of biindenylidene with TEMPO radical substituents

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Abstract—Incorporation of organic radical TEMPO into photochromic biindenylidene system leads to the synthesis of a novel dual functional compound **4**. Its photochromism, structure, magnetic properties as well as ESR spectroscopy were deliberately investigated. Remarkable changes of the ESR spectra were observed for **4** upon photoirradiation with different light sources. The intermolecular interactions were interpreted with regard to its crystal structure.

The development of novel magnetic material, which responds to light, heat, pressure or other stimuli, is of significance from the viewpoints of both basic science and new technology emergence.[1] Currently, there is much interest in the preparation of organic photochromic and photomagnetic materials, in which color and magnetic properties can be controlled by light. Such an optically induced tuning of color and magnetic behaviors may have potential applications in molecular photoswitching devices for memory and information processing.[2] Up to date, several types of organic photochromic and photomagnetic compounds such as azobenzene, diarylethene, spiropyran, terphenoquinone, anthracene, naphthopyran, and hexaarylbiimidazole have been discovered, and their properties have been extensively investigated.[3] Aminoxyl radical moieties have been widely adopted in these compounds, because of their versatility and good stability in the field of material chemistry as building blocks for molecule-based magnetic materials.[4] As disclosed in recent reports from our group and others,[5] the biindenylidene derivatives are a unique class of photochromic organic compounds, which undergo photochromism and simultaneously generate radicals in the crystalline state. If the stable aminoxyl radical moiety is incorporated into such a photochromic compound like biindenylidene, a new multifunctional molecule could be designed with two kinds of magnetic moieties. This new photochromic compound could serve as a good candidate to investigate inter- or intra-molecular magnetic interaction, which could be controlled by irradiation with light.

With this idea in mind, we have successfully synthesized a new dual-functional biindenylidene derivative **4** by introducing a nitroxide radical (TEMPO) to the biindenylidene system (Scheme 1). The structure of **4** was confirmed by single crystal X-ray diffraction, and its photochromic and photomagnetic properties were investigated, and characterized with UV–vis absorption and ESR techniques. For the purpose of comparison, the precursor **3** was investigated accordingly as well. Herein, we report the results from these investigations.

The photocolor reaction of **3** and **4** was monitored by UV–vis absorption. As expected, the precursor **3** shows photochromic property. Yellow powder **3** turns to brown, when exposed to sunlight for a few minutes, and the brown powder returns slowly to yellow solid in the dark or upon heating. The new radical compound **4** shows photochromism in a crystalline state, Scheme 2 shows the supposed photochromic interconversion between **4a** and **4b**. The yellow crystals of **4a** turn to

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Keywords: Photochromism; Magnetic; Biindenylidene; Radicals.

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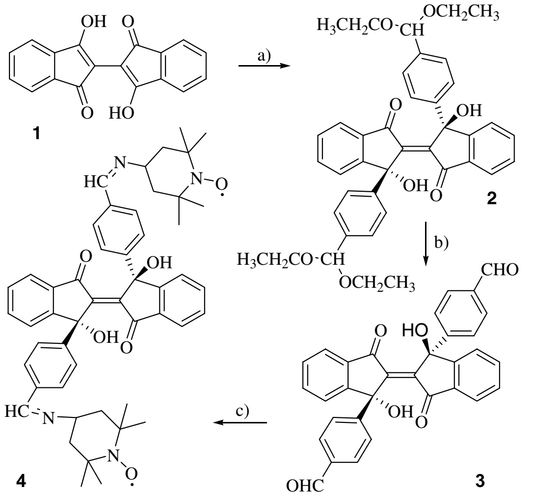
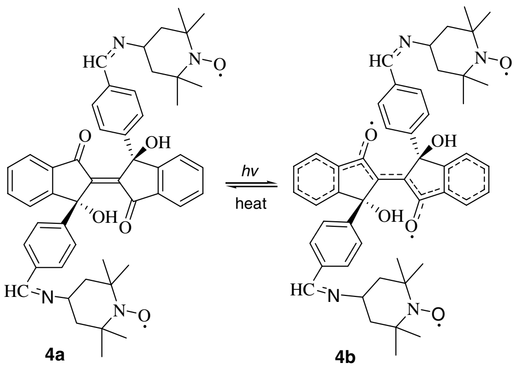


Scheme 1. Synthetic route of the radical biindenylidene **4**. (a) *p*-benzaldehyde diethyl acetal magnesium bromide in dry THF, then air oxidation H^+, 46%; (b) *p*-toluenesulfonic acid in chloroform, 90%; (c) 4-amino-TEMPO and AcOH in dichloromethane, 60%.



Scheme 2. Photochromic reaction of **4**.

reddish brown **4b**, when exposed to sunlight for a few minutes. Compound **4b** is thermally labile, and the reddish brown crystals fade and return to the original yellow gradually in the dark or quickly upon heating under nitrogen atmosphere. Also, UV–vis absorption of **4** considerably increases in the range of 500–800 nm wavelength after irradiation (Fig. 1). This result is consistent with the proposed photochromism mechanism (Scheme 2).

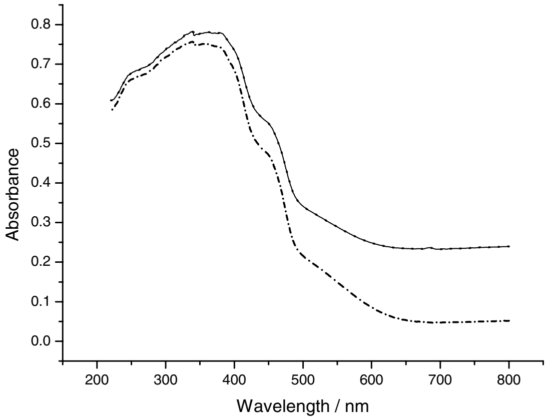
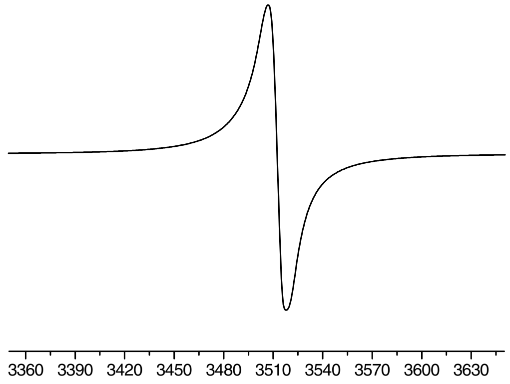


Figure 1. UV spectral changes of **4** (···) before and (—) after irradiation.

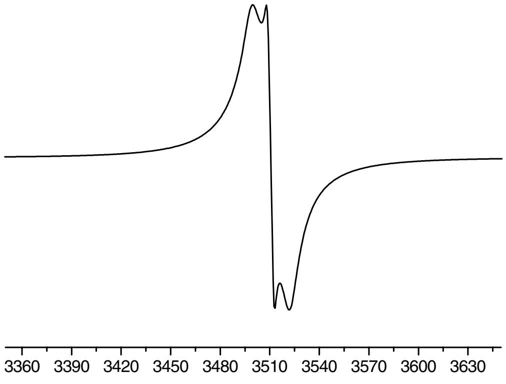
The significant changes of the ESR spectra of **4** were observed along with the photochromism in solid state after irradiation with different light source. For the comparison with compound **4**, the precursor **3** was tested by ESR technique before and after irradiation, respectively. The unirradiated yellow **3** does not show ESR signals at room temperature, and the irradiated brown **3** shows ESR signals. While the irradiated brown **3** is dissolved in dichloromethane, the resultant solution does not show any ESR signals. The results clearly indicate that the radicals generated from two indanione moieties are quenched in the solution. In the ESR measurement, **4** was irradiated with UV or visible light, and its ESR changes were recorded at room temperature. Figure 2a–c show the corresponding ESR spectra of **4** in different states upon unirradiation and upon irradiation with different light source in solid state.[6] The ESR spectrum of the unirradiated **4** shows just one ESR signal—that of the TEMPO ($g = 2.0055$, Fig. 2a). When **4** is exposed to sunlight for several minutes, the ESR spectrum changes apparently, and a new radical signal ($g = 2.0056$, Fig. 2b) appears besides that of TEMPO. Apparently, there exist two different kinds of radicals in the irradiated compound **4**, one kind of radical generated from two indanione moieties,[5b] as expected in Scheme 1, the other originated from the stable TEMPOs, and the former kind of radicals is photo-responsive, so the photochromism and radical behaviors of compound **4** can be controlled by light. It is worthy to note that the two expected ESR signals merge, forming a broad pattern, when **4** is irradiated with a high pressure Hg lamp for 10 min ($g = 2.0075$, Fig. 2c), which may be explained by the interactions existing between the two kinds of radicals.

When the irradiated reddish brown **4** was dissolved in dichloromethane, there is only a typical TEMPO signal (Fig. 2d) in the ESR spectrum of the resultant solution,[7] and the ESR spectra of compound **4** did not change in solution under irradiation, which also means that the radicals originated from the indanione moieties are also quenched in the solution. Further research discovered that the family compounds in this work display photochromism and simultaneously generate radicals in solid or crystalline state; however, the radicals generated from the two indanione moieties can be easily quenched in solution and the photochromism also does not appear in solution.

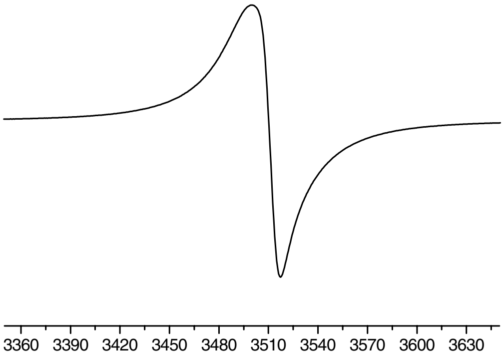
The magnetic susceptibility of the photochromic compound **4** was measured by SQUID susceptometer within the temperature range of 2–300 K (Fig. 3). A Curies–Weiss plot of $1/\chi$ versus T yields Curies constant of 0.62 emu K mol^{-1} and a Weiss constant of −9.38 K. The data have been deduced after calibration. According to Curie–Weiss law, both constants are in favor of antiferromagnetic interaction.[8]



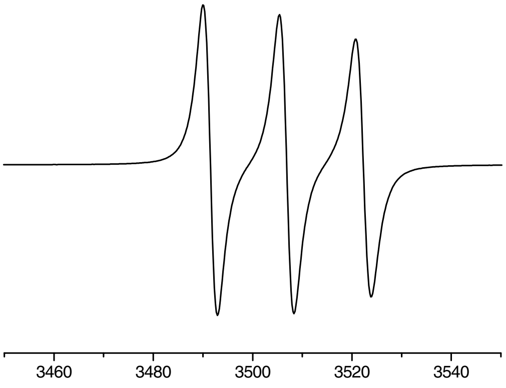
a Magnetic Field / G



b Magnetic Field / G



c Magnetic Field / G



d Magnetic Field / G

Figure 2. ESR spectra of **4** at different states at room temperature.

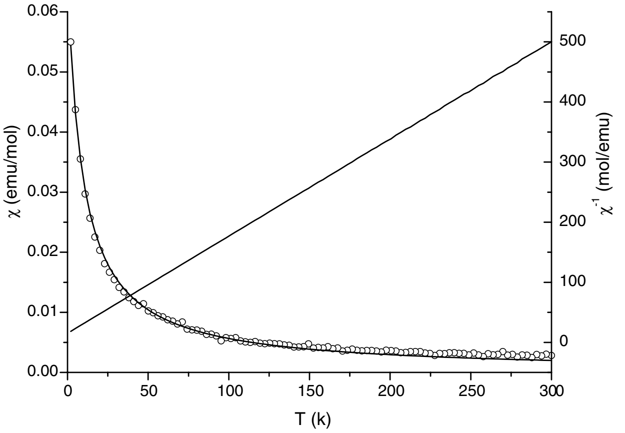


Figure 3. Temperature dependence of the magnetic susceptibility (χ) and 1/χ for **4** is shown in the solid line.

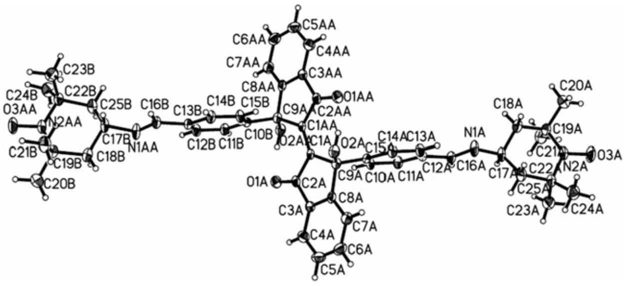


Figure 4. Molecular structure of isomer **4**.

In order to investigate the relationship between the photoreactivity and the structure, X-ray crystal structure analysis was carried out on **4** (Fig. 4).[9] Compound **4** has a central symmetry with two indanione moieties linked by a double bond C1A–C1AA (1.342(6) Å). Two loops of indanione are almost perfectly parallel in very short perpendicular distance (0.2321 Å), hence the double bond has little distortion. This kind of conformation could be crucial to its photochromic and photomagnetic properties. There is also intermolecular hydrogen bonding among the molecules, which could stabilize the radicals (Fig. 5). The shortest distance between the neighboring TEMPO radical molecules is

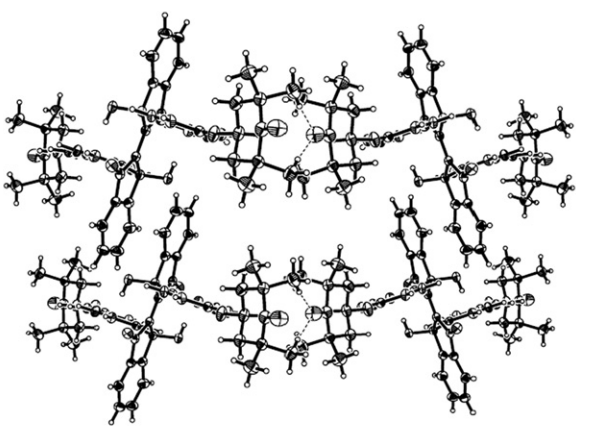


Figure 5. Stacking of compound **4**, the dotted line means the H-bonding interaction.

found to be 5.391 Å for oxygen–oxygen, which is a fair distance as to allow only weak antiferromagnetic interaction between the spins.[10] According to the McConnell mechanism,[11] the relative signs of the spin densities on those oxygen atoms are opposite to each other, which leads to the intermolecular antiferromagnetic result. On the other hand, the shortest distance between the adjacent molecular carbonyl oxygen atoms is 6.923 Å, which is too long for any possible interaction.

In conclusion, we have first synthesized a novel biindenylidene derivative having two TEMPO radicals in the molecule, and studied its photochromism and photomagnetism in the crystalline state. ESR results clearly show that two kinds of radicals exist in the crystalline molecule **4**, and the radical generated from two indanione moieties is photo-responsive. Incorporation of organic photochromism into magnetic system may not only lead to interesting photochromic behaviors, but may also provide a new strategy to develop photo-control magnetic materials. Herein we have made a small step in the direction. Further detailed studies of the mechanism of photomagnetism of **4** are in progress in our laboratory.

Acknowledgement

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.067.

References and notes

1. Nakatsuji, S. *Adv. Mater.* **2001**, *13*, 1719–1724.
2. (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716; (b) Matsuda, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 383–392; (c) Matsuda, K.; Matsuo, M.; Mizoguti, S.; Higashiguchi, K.; Irie, M. *J. Phys. Chem. B* **2002**, *106*, 11218–11225; (d) Benard, S.; Riviere, E.; Yu, P. *Chem. Mater.* **2001**, *13*, 159–162; (e) Tanifuji, M.; Irie, M.; Matsuda, K. *J. Am. Chem. Soc.* **2005**, *127*, 13344–13353.
3. (a) Hamachi, K.; Matsuda, K.; Itoh, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2937–2943; (b) Matsuda, K.; Matsuo, M.; Irie, M. *Chem. Lett.* **2001**, 436–437; (c) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195–7201; (d) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 8309–8310; (e) Kaneko, T.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Org. Lett.* **2003**, *5*, 2127–2129; (f) Kikuchi, A.; Iyoda, T. J. Abe *Chem. Commun.* **2002**, 1484–1485; (g) Teki, Y.; Miyamoto, S.; Nakatsuji, M.; Miura, Y. *J. Am. Chem. Soc.* **2001**, *123*, 294–305; (h) Kurata, H.; Takehara, Y.; Kawase, T.; Oda, M. *Chem. Lett.* **2003**, 538–539.
4. (a) Frank, N. L.; Clerac, R.; Sutter, J.-P.; Daro, N.; Kahn, O.; Coulon, C.; Green, M. T.; Golhen, S.; Ouahab, L. *J. Am. Chem. Soc.* **2000**, *122*, 2053–2061; (b) Nakatsuji, S.; Ikemoto, H.; Akutsu, H.; Yamada, J.-I.; Mori, A. *J. Org. Chem.* **2003**, *68*, 1708–1714; (c) Greve, S.; Nather, C.; Friedrichsen, W. *Org. Lett.* **2000**, *2*, 2269–2270.
5. (a) Xu, L.-L.; Huang, H.-M.; Song, Z.-Y.; Meng, J.-B.; Matsuura, T. *Tetrahedron Lett.* **2002**, *43*, 7435–7439; (b) Xu, L.-L.; Sugiyama, T.; Huang, H.-M.; Song, Z.-Y.; Meng, J.-B.; Matsuura, T. *Chem. Commun.* **2002**, 2328–2329; (c) Li, X.; Xu, L.-L.; Han, J.; Pang, M.-L.; Ma, H.; Meng, J.-B. *Tetrahedron* **2005**, *61*, 5373–5377; (d) Li, X.; Song, Z.-Y.; Chen, Y.; Meng, J.-B. *J. Mol. Struct.* **2005**, *748*, 161–164; (e) Xu, L.-L.; Meng, J.-B.; Wang, H.; Li, P.; Sugiyama, T.; Wang, Y. M.; Matsuura, T. *Mol. Cryst. Liq. Cryst.* **2002**, *389*, 33–37; (f) Chen, Y.; Pang, M.-L.; Cheng, K.-G.; Wang, Y.; Han, J.; He, Z.-J.; Meng, J.-B. *Tetrahedron* **2007**, *63*, 4319–4327; (g) Han, J.; Li, Y.-X.; Pang, M.-L.; Cheng, K.-G.; Wang, Y.-M.; Ma, Y.-X.; Meng, J.-B. *New J. Chem.* **2007**, *31*, 543–548; (h) Tanaka, K.; Toda, F.; Higuchi, T. *Mol. Cryst. Liq. Cryst.* **1992**, *219*, 135–137; (i) Tanaka, K.; Toda, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 873–874.
6. The ESR test was carried out on a Bruker EMX-6/1 EPR Spectrometer. The g value was calculated by the known parameters of g_3 and g_4 of Mn-mark. X-band EPR spectra were obtained at room temperature. Measurement conditions: center field 3510.000 G, sweep width 600.000 G, modulation frequency 100.00 kHz, modulation amplitude 0.50 G, and microwave frequency 9.854 GHz.
7. Measurement conditions: center field 3510.000 G, sweep width 200.000 G, modulation frequency 100.00 kHz, modulation amplitude, 0.50 G, and microwave frequency 9.854 GHz.
8. Kaneko, T.; Akutusu, H.; Yamada, J.-I.; Nakatsuji, S. *Org. Lett.* **2003**, *5*, 2127–2129.
9. *Crystal data for* **4**: $C_{26}H_{29}C_{12}N_2O_3$, $M = 488.41$, monoclinic, space group $P2(1)/c$, $a = 8.5321(13)$, $b = 29.469(5)$, $c = 10.2948(16)$ Å, $\beta = 105.032(3)°$, $T = 294(2)$ K, $D_c = 1.298$ g cm^{-3}, $V = 2499.9(7)$ Å^3, crystal size = 0.22 × 0.18 × 0.14 mm, $Z = 4$, $F(000) = 1028$, $\mu = 0.290$ mm^{-1}, 12,693 Reflections collected, 4401 unique ($R_{int} = 0.0678$), The final $R_1 = 0.0545$, $wR_2 = 0.1201$ and for all data $R_1 = 0.1316$, $wR_2 = 0.1592$, CCDC 287993.
10. Nakatsuji, S.; Ojima, T.; Akutsu, H.; Yamada, J.-I. *J. Org. Chem.* **2002**, *67*, 916–921.
11. McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910–1923.