Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2019, **29**, 285–287

Mendeleev
Communications

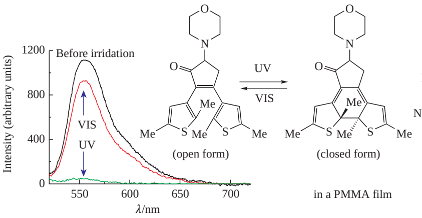
Fluorescence modulation of eosin Y in a PMMA film by diarylethene switching

Sofia K. Lazareva,[a,b] Evgeni M. Glebov,*[a,b] Danil A. Nevostruev,[a] Dmitry V. Lonshakov,[c] Andrey G. Lvov,[c] Valerii Z. Shirinian,[c] Vladimir A. Zinovyev[d] and Artem B. Smolentsev[a]

[a] *V. V. Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: glebov@kinetics.nsc.ru*
[b] *Novosibirsk State University, 630090 Novosibirsk, Russian Federation*
[c] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[d] *A. V. Rzhanov Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation*

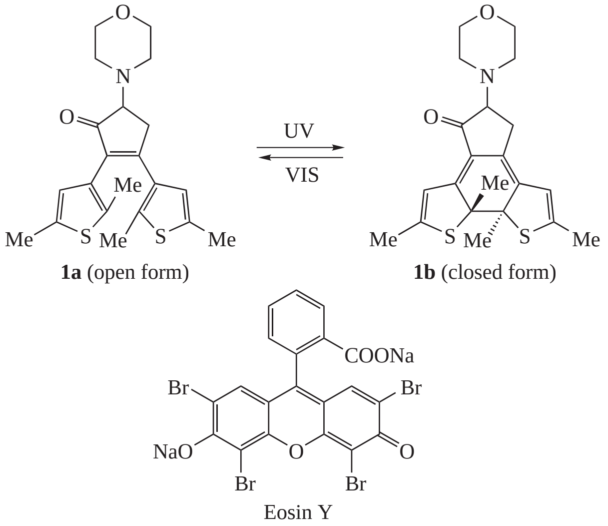
DOI: 10.1016/j.mencom.2019.05.014

A switchable fluorescence system has been prepared based on an eosin Y fluorophore and a photochromic diarylethene. The fluorescence emission was switched between the ‘on’ and ‘off’ states *via* photochromic isomerization. Fluorescence was quenched due to energy transfer from the excited eosin Y to the closed form of diarylethene.



Optical storage materials and fluorescent switchers are among the most promising materials due to their potential applications in optical data storage, as fluorescent biological markers and other molecular electronic devices.[1–8]

The fluorescence switchers should exhibit rapid response, durability, stability in both ‘on’ and ‘off’ states, and reactivity in a solid state and/or in polymers.[5] In this regard, photochromic molecules are particularly efficient as they can be reversibly switched between two different isomers upon light excitation. Among the families of photochromic compounds, diarylethenes are of particular interest due to their breadth of color, absence of thermal reversibility and good resistance to thermal and photochemical fatigue.[9–11] Here, we report a fluorescent switchable polymer material based on diarylethene **1** [2,3-bis(2,5-dimethylthiophen-3-yl)-5-morpholinocyclopent-2-enone] and fluorophore eosin Y (Scheme 1). As all the diarylethenes, compound **1** undergoes photoisomerization between open-ring and closed-ring forms upon alternating irradiation with UV and visible light. Diarylethene **1** exhibits excellent photochromic switching properties in liquid solutions remaining stable after 1500 on-off cycles in solution[12] (for convenience, photochromic properties of **1** in solution are presented in Table S1, Online Supplementary Materials). No evidence of the bistability of compound **1** caused by parallel and anti-parallel conformations was found neither in solutions nor in polymethylmethacrylate (PMMA) films (steric-hindranced ethene bridge systems were reported recently[13,14]).



1a (open form)

1b (closed form)

Eosin Y

Scheme 1

A conventional tool for modulating fluorescence is energy transfer.[15] There are two main approaches to create photochromic materials with fluorescence modulated by energy transfer.[16,17] One of them based on intramolecular transport involves combining fluorophore and photochromic units within a single molecule.[18–20] On the one hand, this ensures the most efficient energy transfer and, on the other hand, it can lead to a reduced quantum yield of photochromic reactions due to the absorption of the fluorophore. The other approach is based on intermolecular energy transfer when the photochrome and the fluorophore are mixed in a solution or a polymer.[21,22] Within this approach, the problem of the absorption of a fluorophore is solved by reducing its concentration with respect to a diarylethene.

We used the second approach to develop a fluorescence switch.† Diarylethene **1** was mixed with a fluorophore within a polymeric matrix. The fluorescence switch was achieved by effective energy

---

† Commercial polymethylmethacrylate (PMMA) was used without further purification. UV absorption spectra were recorded using a Varian Cary 50 spectrophotometer. Stationary luminescence spectra were recorded on Hitachi MPF-4 and Edinburgh Instruments FLSP-920 spectrofluorimeters. A high pressure mercury lamp with a set of glass filters (313 nm) or a XeCl excilamp (308 nm, produced by Institute of High Current Electronics SB RAS, Tomsk, Russia) were used as UV light sources. A green (530 nm) LED was used for irradiation by visible light.

© 2019 Mendeleev Communications. Published by ELSEVIER B.V. on behalf of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.

transfer from the excited fluorophore to the closed form of **1** absorbing in the region of fluorophore emission. Eosin Y (see Scheme 1) was chosen as a fluorophore due to the large overlap of its emission spectrum with the absorption spectrum of the closed form of **1**. Eosin Y is a disodium salt of 2,4,5,7-tetrabromofluorescein; it is most commonly used as an acidic red stain for highlighting cytoplasm material in samples.[23]

PMMA films of three types were used. The samples of the first type were prepared as follows. A mixture of 50 mg of PMMA and 1 to 10 ml of acetonitrile or tetrahydrofuran were stirred thoroughly, and 8 mg of compound **1** was added. Then, the mixture was further stirred to become homogenous and 0.5 ml of the solution was dropped on a quartz plate 32 mm in diameter to prepare the sample film by spin-coating at 1000–3000 rpm for 10 s using a T200 Glichn spin coater. The films were dried in a vacuum at room temperature and then kept in darkness. To measure film thickness, the surface was scratched with a thin blade; after that, the surface area was scanned by an atomic force microscope (Nt-MDT, Russia) operated in the semi-contact mode. Film thickness varied in a range of 20 nm–5 μm.

The samples of the second type were films prepared from similar starting solutions as the samples of the first type, but they contained 8 mg of diarylethene and 0.5 mg of eosin Y. The samples of the third type were films prepared from starting solutions containing only 0.5 mg of eosin Y without diarylethene.

Diarylethene **1** exhibits excellent photochromic performance in PMMA films and in solutions. The UV irradiation (308 or 313 nm) of the film results in a new absorbance band at 400–700 nm with a maximum at 570 nm, which was attributed to the closed form of **1**,[12] and this process led to the coloration of the film (Figure 1). When the UV irradiation was ceased and the film was irradiated by visible light (530 nm), the absorbance band of the closed form decreased with time and disappeared eventually without any residual. The closed isomer of **1** was thermally stable, and the optical density of its absorption (400–700 nm) band did not change after the sample was kept in dark for 24 h.

One of the main issues of diarylethenes is photostability. Photodegradation can occur with the formation of non-photochromic products causing the decrease of integral absorption.[24] Fatigue testing was performed by the following procedure: a diarylethene-containing film was irradiated consequently by UV and visible light. No photodegradation was observed after 10 cycles (Figure 2). Thus, the resistance of compound **1** to photodegradation in PMMA is comparable with the case of liquid solutions demonstrating great durable photochromic switch.

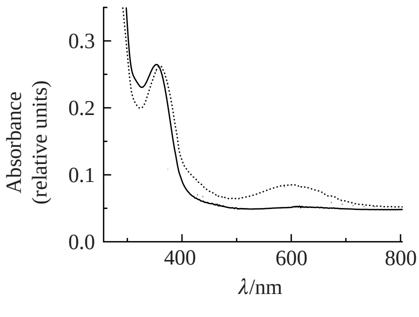


Figure 1 Spectral evolution of **1** in PMMA film (thickness, 2.5 μm). Solid and dashed lines show spectra before and after UV irradiation (313 nm), respectively. Consequent irradiation at 530 nm leads to the restoration of the initial spectrum.

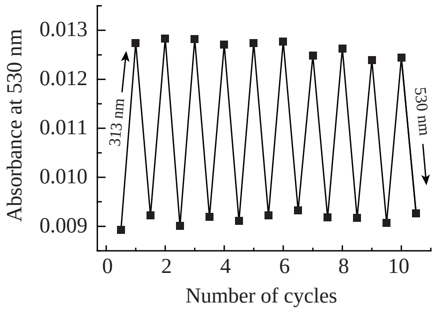


Figure 2 Changes in absorption of **1** in a PMMA film (thickness, 150 nm) caused by sequential UV and VIS irradiation.

The next step was combining together diarylethene **1** and eosin Y within a PMMA polymer. A 25-fold molar excess of **1** was used. The sample containing no eosin Y did not exhibit emission, whereas a PMMA film doped with both eosin Y and **1** exhibited fluorescence at 555 nm [Figure 3(*b*)]. Films were consequently irradiated by UV (313 nm) and visible (530 nm) light. Eosin Y has absorption in the visible region [Figure 3(*a*)] independent on irradiation. Irradiation with the UV light led to the formation of the closed isomer of **1** resulted in the growth of the film absorption at 400–700 nm [Figure 3(*a*)]. A significant change in fluorescence spectra intensity was observed. After irradiation with the UV light, the fluorescence band almost disappeared [Figure 3(*b*)]. The following irradiation by visible light transformed the closed form back to the open one, resulting in the restoration of the initial absorption spectrum.

Three reasons of changes in the fluorescence intensity were considered. First, the absorption of emitted light by the closed form of **1** (internal filter effect) was insufficient because the optical density was small (less than 0.1 at 555 nm). The second reason of the fluorescence intensity change after UV irradiation is the absorption of exciting light by the closed form. This effect is sufficient for visible excitation (518 nm) and negligible for UV (318 nm) excitation because, in the latter case, absorption at the excitation wavelength is not changed during the photochromic reaction.

The third reason for fluorescence quenching is energy transfer from the excited eosin Y to the closed form of **1**. The eosin Y emission band is completely overlapped with the absorption of the

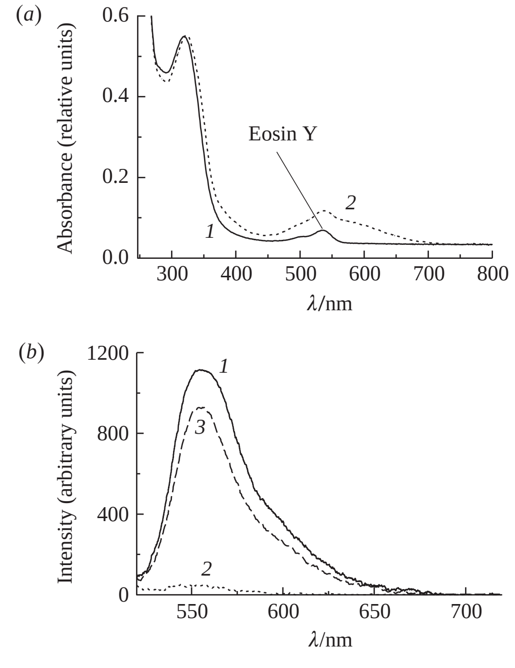


Figure 3 Spectral evolution of the PMMA film (thickness, 2.5 μm) containing **1** and eosin Y. (*a*) Absorption spectra (*1*) before irradiation and (*2*) after irradiation at 313 nm. After the consequent irradiation at 530 nm, the initial spectrum restored. (*b*) Emission spectra (*1*) before irradiation, (*2*) after irradiation at 313 nm, and (*3*) after the consequent irradiation at 530 nm. The initial emission intensity restores only partially due to eosin Y degradation. Luminescence was excited at 518 nm.

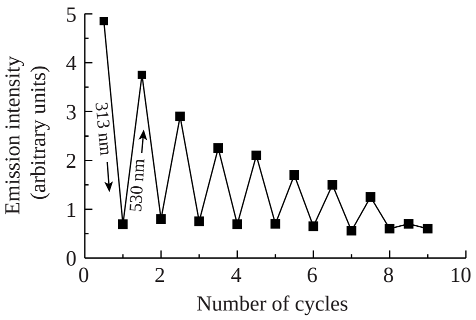


Figure 4 Changes in eosin Y emission in the PMMA film (thickness, 220 nm) containing **1** and eosin Y caused by sequential UV (308 nm, 20 min) and VIS (530 nm, 5 min) irradiation. Luminescence was excited at 518 nm.

closed form of **1** (see Figure S1, Online Supplementary Materials) but not with its open form. This allows energy transfer to occur when **1** is in its closed form.[16,17,20] In the case of excitation at 318 nm, energy transfer is the only reason of the effect.

However, the fluorescence is not restored completely after the finishing of the reverse photochromic reaction (Figure 4). The reason was the unexpectedly poor stability of eosin Y itself under irradiation by both UV and visible light. The irradiation of a pure eosin Y film containing no diarylethene revealed that the intensity of eosin Y fluorescence decreases significantly after 1-min irradiation. Thus, the usage of other types of fluorophores is required to accomplish stable and durable fluorescent photoswitch.

In conclusion, a fluorescent photoswitchable PMMA film composed of eosin Y and a photochromic diarylethene was designed and prepared. Diarylethene displayed excellent photochromic performance in the PMMA films. The fluorescent emission of the film could be modulated between ‘off’ and ‘on’ *via* diarylethene photoisomerization under alternate irradiation by UV and visible light. The polymeric materials doped with a fluorophore–diarylethene mixture can be potentially utilized for erasable optical data storage. However, the usage of more stable fluorophores is essential for practical applications.

This work was supported by the Russian Foundation for Basic Research (grant no. 18-03-00161).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.05.014.

References

1 M. Sauer, *Proc. Natl. Acad. Sci. USA*, 2005, **102**, 9433.
2 M. L. Bossi and P. F. Aramendia, *J. Photochem. Photobiol., C*, 2011, **12**, 154.
3 A. Bianco, S. Perissinotto, M. Garbugli, G. Lanzani and C. Bertarelli, *Laser Photonics Rev.*, 2011, **5**, 711.
4 J. Cusido, E. Deniz and F. M. Raymo, *Eur. J. Org. Chem.*, 2009, 2031.
5 T. Fukaminato, *J. Photochem. Photobiol., C*, 2011, **12**, 177.
6 F. M. Raymo and M. Tomasulo, *J. Phys. Chem. A*, 2005, **109**, 7343.
7 M. V. Alfimov, O. A. Fedorova and S. P. Gromov, *J. Photochem. Photobiol., A*, 2003, **158**, 183.
8 A. N. Arkhipova, P. A. Panchenko, Yu. V. Fedorov and O. A. Fedorova, *Mendeleev Commun.*, 2017, **27**, 53.
9 M. Irie, T. Fukaminato, K. Matsuda and S. Kobatake, *Chem. Rev.*, 2014, **114**, 12174.
10 M. F. Budyka, *Russ. Chem. Rev.*, 2012, **81**, 477.
11 A. G. Lvov, M. M. Khusniyarov and V. Z Shirinian, *J. Photochem. Photobiol., C*, 2018, **36**, 1.
12 V. Z. Shirinian, A. A. Shimkin, D. V. Lonshakov, A. G. Lvov and M. M. Krayushkin, *J. Photochem. Photobiol., A*, 2012, **233**, 1.
13 W. Li, C. Jiao, X. Li, Y. Xie, K. Nakatani, H. Tian and W. Zhu, *Angew. Chem., Int. Ed.*, 2014, **53**, 4603.
14 M. Li, L.-J. Chen, Y. Cai, Q. Luo, W. Li, H.-B. Yang, H. Tian and W.-H. Zhu, *Chem.*, 2019, **5**, 634.
15 F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327.
16 C. Yun, J. You, J. Kim, J. Huh and E. Kim, *J. Photochem. Photobiol., C*, 2009, **10**, 111.
17 V. Z. Shirinian, D. V. Lonshakov, A. G. Lvov and M. M. Krayushkin, *Russ. Chem. Rev.*, 2013, **82**, 511.
18 M.-S. Kim, T. Kawai, T. Sasaki and M. Irie, *Opt. Mater.*, 2002, **21**, 275.
19 M.-S. Kim, T. Kawai and M. Irie, *Opt. Mater.*, 2002, **21**, 271.
20 D. V. Lonshakov, V. Z. Shirinian, A. G. Lvov, B. V. Nabatov and M. M. Krayushkin, *Dyes Pigm.*, 2013, **97**, 311.
21 C. C. Corredor, Z.-L. Huang and K. D. Belfield, *Adv. Mater.*, 2006, **18**, 2910.
22 C. Zhang, H.-P. Zhou, L.-Y. Liao, W. Feng, W. Sun, Z.-X. Li, C.-H. Xu, C.-J. Fang, L.-D. Sun, Y.-W. Zhang and C.-H. Yan, *Adv. Mater.*, 2010, **22**, 633.
23 H. Rahman, *Int. J. Pharm. Pharm. Sci.*, 2017, **9**, 1.
24 M. Herder, B. Schmidt, L. Grubert, M. Pätzel, J. Schwarz and S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 2738.
25 F. Tian W. Huang, J. Yang and Q. Li, *Spectrochim. Acta, Part A*, 2014, **126**, 135.

Received: 22nd October 2018; Com. 18/5723