

Fluorescence Modulation and Photochromism in Azobismaleimide Derivatives

Nicusor Fifere · Anton Airinei · Constantin Gaina · Viorica Gaina · Mircea Grigoras

Received: 18 March 2013 / Accepted: 10 September 2013 / Published online: 19 September 2013
© Springer Science+Business Media New York 2013

Abstract A fluorophore-photochrome system incorporating an aryleneimine type fluorophore and an azobismaleimide photochrome was developed and the photochemical properties of this system were investigated. The photoisomerization of trans-azoaromatic chromophore leads to the increase of the fluorescence intensity of fluorophore. The cis azobismaleimide isomers revert photochemically to the trans form and the emission intensity decreases. The fluorescence intensity of the imine fluorophore can be modulated under irradiation with UV and visible (436 nm) light due to reversible trans-cis-trans photoisomerization of azobismaleimide partner. The photoisomerization kinetics was obeyed a first-order relationship with a rate constant of $1.95 \times 10^{-2} \text{ s}^{-1}$ for azobismaleimide/imine fluorophore system and for polyazothioetherimide/imine derivative the kinetics was described by a biexponential equation.

Keywords Azobismaleimide · Photoisomerization · Fluorescence modulation · UV–vis absorption spectra · Photoswitching

Introduction

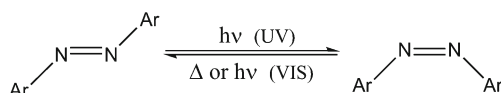
Organic photochromic molecules and fluorescent compounds attracted a growing attention due to their different potential applications for example, as optical information storage, photoswitchable devices, organic light emitting devices, sensors or actuators [1–11]. The modification in fluorescence

intensity of a luminescent compound represents an important feature for photoswitching devices. There are usually three kinds of photochromic-fluorescent systems: the photochromic unit and fluorescent partner are located in the same molecule, multicomponent systems (dyads, triads, hybrid systems) where the energy or electron transfer can be reversibly modified by the photochromic unit and the fluorescent component can be doped into photochromic compounds or in polymer matrices where fluorescence is reversibly quenched by the photochromic unit by energy transfer or shielding [12–18].

Several families of photoisomerizable molecules can be utilized to develop photomodulation phenomena. Among them, azobenzene derivatives are considered as promising components in molecular switches because of the reversibility between their trans and cis states. The pronounced changes upon light-induced isomerization in molecular shape between extended coplanar and bent forms of azobenzene, C4–C4' distance being reduced from 9.0 Å to 5.5 Å and in dipole moment value from 0.5 D to 3.1 D, determine substantial modifications in optical and free volume properties, morphology of materials containing azobenzene chromophores [19, 20]. At thermal equilibrium under UV irradiation a fraction of trans isomer converts to the cis form (Scheme 1). The reverse reaction to the more stable trans isomer can be induced thermally or photochemically (at 430 nm). The thermal relaxation is a slow process on time scale (hour-to-day) while the photochemical recovery is much faster. Thus, the azobenzene derivatives exhibit a clean photoreaction with photostability, fast and reversible isomerization processes which can be exploited to control their photoswitching and photoresponsive behaviour.

The photoinduced interconversion of the states of the photochromic compound can be utilized to control the emission intensity of a fluorophore from a photochrome-fluorophore system. The transformation of one state of the photochromic partner in the other can either activate or prevent emission quenching of the fluorophore.

N. Fifere · A. Airinei (✉) · C. Gaina · V. Gaina · M. Grigoras
“Petru Poni” Institute of Macromolecular Chemistry,
41A Aleea Grigore Ghica Voda, 700487 Iasi, Romania
e-mail: airineia@icmpp.ro



Scheme 1 Photochromism of azobenzene derivatives

The UV irradiation of fluorophore-photochrome construct can activate an electron or energy transfer between one of the chromophore states (trans or cis isomers) and the fluorescent component, which is responsible for quenching. The photochemical recovery to the initial form of the chromophore can suppress the quenching process and switch the fluorophore emission again [3, 4, 21]. The emission of the fluorophore-photochrome construct can be repeatedly quenched and recovered by only switching photochromic partner between its interconversion states under light irradiation. In order to obtain an efficient modulation of the emission intensity of fluorescent partner with a photochromic switch, a high degree of overlap between the emission band of fluorophore and the absorption band of photochrome is necessary [3, 13, 17].

The concomitant association of the photochromic and fluorescent moieties can also be performed in polymer matrices. The main advantage of these materials is that the photochromic properties of photosensitive compounds and the emission intensity of fluorophore will be more or less affected on the photoinduced electron transfer or energy transfer in the ground or excited state between the two partners [11, 16].

Although a large variety of azobenzene derivatives were used in order to develop photochromic transformations switchable at high speed, the azobismaleimide derivatives [22–24] were not yet exploited to modulate the emission intensity of a fluorophore.

Herein, we describe a photoswitchable system in which a fluorescent compound, N,N'-bis(2-naphthalenethylene)-1,4-diaminobenzene was blended with a photochromic azobismaleimide derivative in solution. The fluorescence intensity of fluorophore can be modulated by the photoisomerization process of the photochromic azobismaleimide partner. The influence of photoisomerization of azobismaleimide derivative on the behavior of the photoswitchable system was discussed. Trans-cis-trans photoisomerization kinetics was investigated and the rate constants were determined.

Experimental

Materials

Spectroscopic grade solvents (Aldrich) were utilized to prepare solutions for spectral measurements. Azobismaleimide (AZM) was synthesized by the condensation reaction of 2,4-amino-4'-methylazobenzene with

maleic anhydride in acetone by a two-step method according to previously reported procedure [22, 23, 25]. Polyazothioetherimide was obtained by the reaction of azobismaleimide and bis-2-mercaptoethylether [22, 23]. The fluorescent dopant, N,N'-bis(2-naphthalenethylene)-1,4-diaminobenzene (BNDB) was prepared in previous papers reported [26, 27]. The synthesis procedure for azobismaleimide (AZM), polyazothioetherimide (PATEI) and fluorescent component (BNDB) structure are presented in Scheme 2.

Methods

Electronic absorption spectra were recorded on Shimadzu UV-3600 spectrophotometer with 1 cm quartz cells. Fluorescence spectra were obtained using a Perkin Elmer LS55 luminescence spectrometer using 10 mm optical path quartz cells. All measurements were made at room temperature. The emission intensities were corrected for absorption of exciting light in order to decrease the inner filter effect using the following equation [28, 29]:

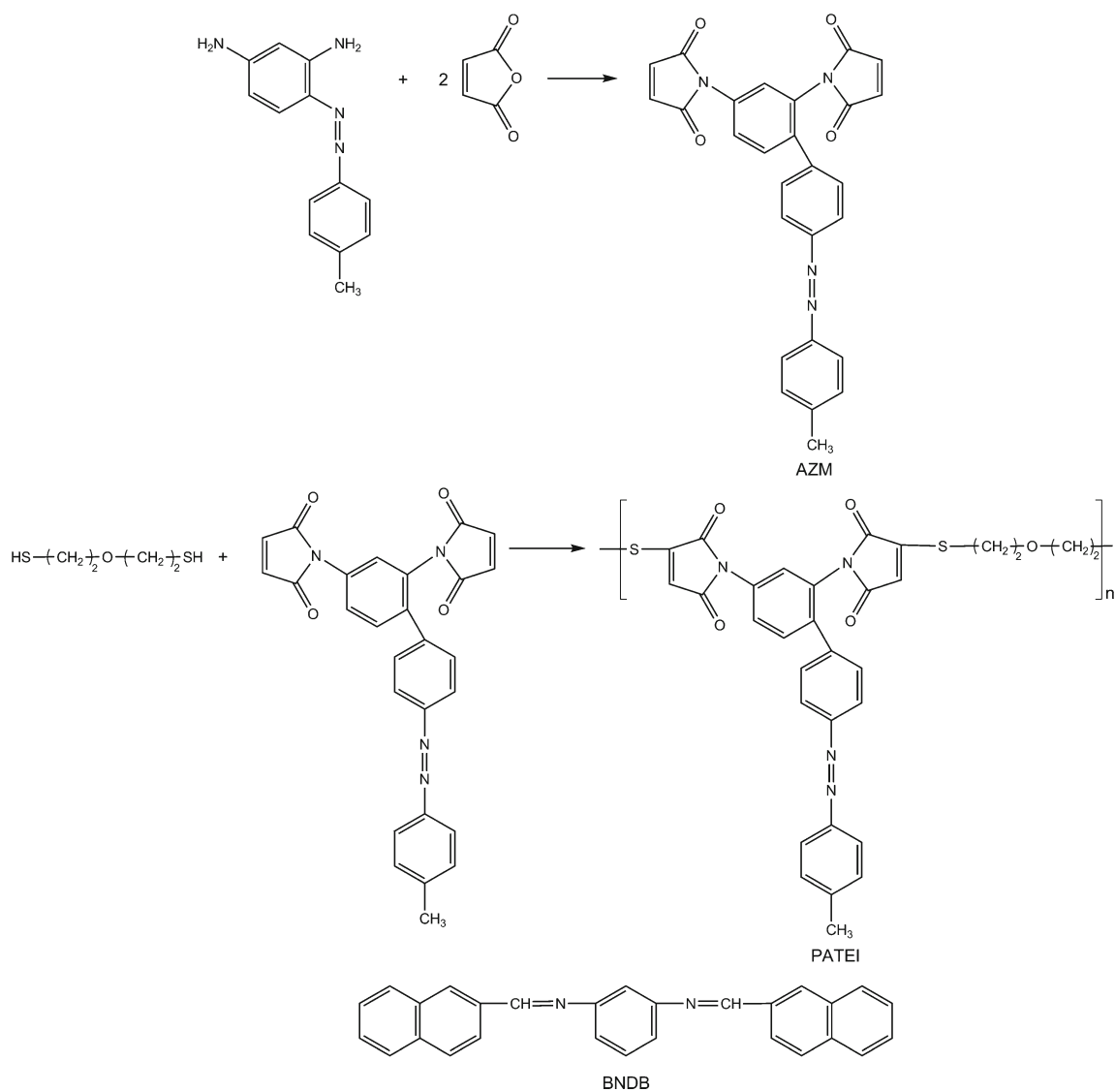
$$I_{corr} = I_{obs} e^{\frac{1}{2}(A_{ex} + A_{em})}$$

where I_{corr} and I_{obs} denotes the fluorescence intensities corrected and observed, respectively; A_{ex} ($\lambda_{ex}=370$ nm) and A_{em} ($\lambda_{em}=452$ nm) are the absorbances at the excitation and emission wavelengths, respectively. The photoisomerization of azochromophores was carried out using a 500 W high-pressure mercury lamp (OSRAM HBO) equipped with adequate filters for UV (365 nm) or visible (436 nm) light irradiation.

Results and Discussion

The electronic absorption spectra of trans and cis isomers of azobismaleimide (AZM) and emission spectrum of fluorophore (BNDB) in dimethylformamide (DMF) solution are shown in Fig. 1. The emission maximum for BNDB was observed at 452 nm and the absorption band of fluorophore was located at 370 nm. No significant changes in the absorption spectra under UV irradiation were observed, resulting that BNDB is photostable under UV irradiation. The UV–VIS absorption spectra of azobismaleimide (AZM) show an intense band at about 345.5 nm ($\epsilon=21,740$ mol⁻¹ L cm⁻¹) attributed to a $\pi \rightarrow \pi^*$ transition of trans azobenzene and a weak band in the visible region at about 442 nm ($\epsilon=1,270$ mol⁻¹ L cm⁻¹) ascribed to the lowest singlet state of $n \rightarrow \pi^*$ transition [20, 22].

The fluorescence switch was constructed with BNDB donor and polyazothioetherimide (PATEI) photochrome acceptor components. Compound BNDB displays a strong



Scheme 2 Synthetic route of azobismaleimide derivatives and chemical structure of imine monomer (BNDB)

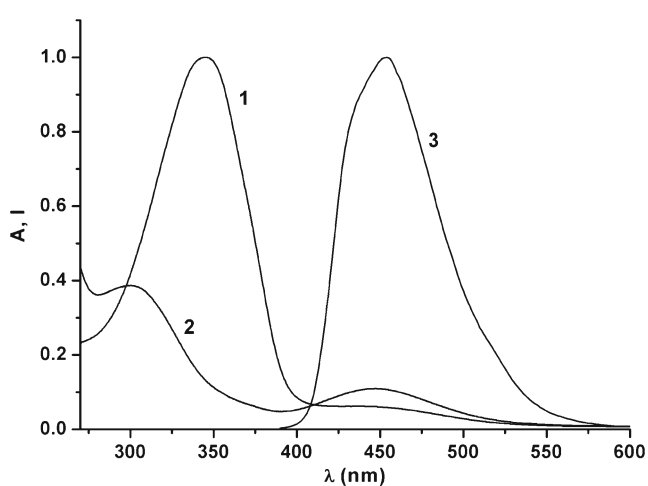


Fig. 1 Absorption and emission (excitation of 370 nm) spectra in DMF solution of AZM: trans form – 1; cis form – 2; and BNDB – 3

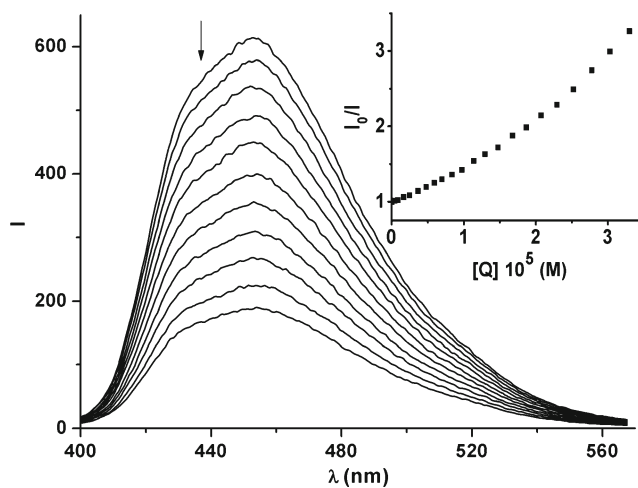


Fig. 2 Fluorescence spectra of BNDB in DMF as a function of quencher (PATEI) concentration. Inset shows Stern-Volmer analysis of quenching data

fluorescence in DMF solution ($\lambda_{em}=452$) when excited at 370 nm. The fluorescence spectral changes of fluorophore solution (7.74×10^{-7} mol/L) under increasing concentrations of PATEI (9.19×10^{-5} mol/L, trans PATEI) are presented in Fig. 2. The fluorescence quenching of fluorophore BNDB using PATEI as quencher was performed to the moment when the emission intensity of fluorophore-quencher system was represented about 30 % of that of starting value. The fluorescence quenching data of PATEI/BNDB system (Fig. 2) were analyzed using Stern-Volmer equation [30].

$$\frac{I_0}{I} = 1 + k_{SV}[Q]$$

where I_0 and I is the fluorescence intensity in absence and presence of quencher, k_{SV} is the Stern-Volmer constant and $[Q]$ is the quencher concentration. The Stern-Volmer plot is found to be nonlinear showing a positive deviation from linearity at higher concentration of the quencher (Fig. 2 inset). The deviation from linearity in the Stern-Volmer plot upon curving upwards towards the y-axis is an indication of the presence of both static and dynamic quenching [30]. As can be seen the plot of $\ln(I_0/I)$ against quencher concentration in Fig. 3 follows a linear relationship on the whole domain of concentrations, showing that the experimental points fit very well the static quenching model given by Perrin. From the slope of the Perrin plot, a radius of quenching sphere of 184.4 Å was obtained. This value is too large and thus a specific quenching mechanism was not identified in this case.

The above-mentioned quenched fluorophore-photochrome solution was irradiated with a wavelength of 365 nm at room temperature. The changes in the UV–VIS absorption spectra under 365 nm light irradiation confirmed the trans-cis photoisomerization of azo chromophores. The absorption band at 343 nm ascribed to trans-azobenzene moiety

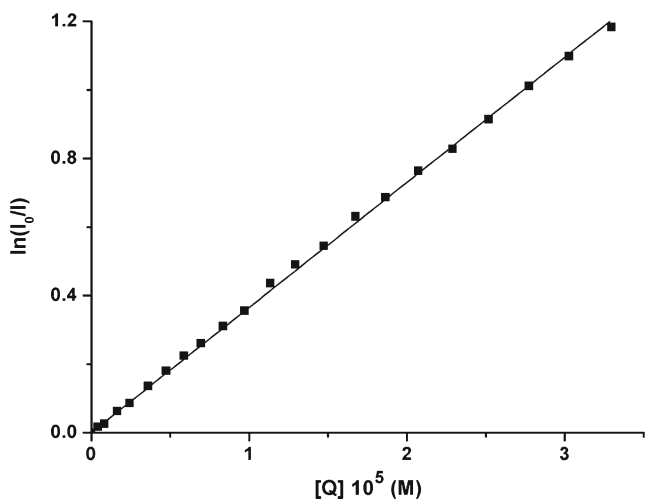


Fig. 3 Perrin plot for fluorescence quenching of PATEI/BNDB in DMF solution

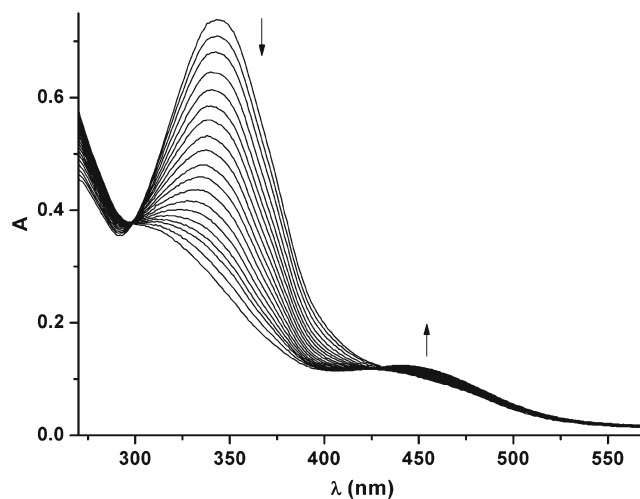


Fig. 4 Absorption spectral change of PATEI/BNDB system in DMF on UV irradiation

decreases progressively in intensity whereas the absorbance around 445 nm due to the cis-azobenzene units increases in intensity (Fig. 4). The absorbance at 343 nm in photostationary state was about 37 % of its original value, with a conversion in cis isomer of 0.63. Concomitantly, when the photostationary state was gained after 280 s, the emission intensity increased to about 55 % of the initial value (Fig. 5). The increase in fluorescence intensity together with the increase of cis isomer concentration by the trans isomer consumption in system shows that the fluorophore is selectively quenched just the trans-isomer of azobismaleimide derivative in the polymer chain.

The above solution was irradiated by visible light of 436 nm. The absorbance at 343 nm increases during blue irradiation till its initial state was almost recovered, while the emission intensity decreases with increasing irradiation time. Compared with the pattern of fluorescence intensity of the

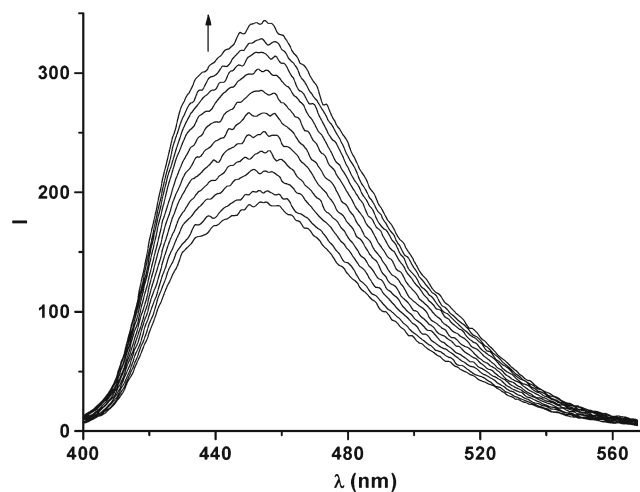


Fig. 5 Emission spectral change of PATEI/BNDB system ($\lambda_{ex}=370$ nm) in DMF on UV irradiation

AZM/BNDB system, where the emission intensity reached 47 % from the initial value [24], here the emission of fluorophore did not exceed 40 %. This process was performed many times in solution. Each cycle of UV irradiation generates trans-cis isomerization and the corresponding increase in fluorescence intensity. On the other hand each visible irradiation determines the return to trans state of azo chromophores and the decrease of emission intensity. In this way the emission intensity of BNDB can be modulated upon alternative irradiation with UV and visible light. Besides, repeated cycles were carried out under alternate UV/Visible irradiations without any modification of the switching characteristics (Fig. 6).

The modulation efficiency can be defined according to the following equation [18, 19]:

$$E_{\text{mod},fl} = 1 - \frac{I(0)}{I(\infty)}$$

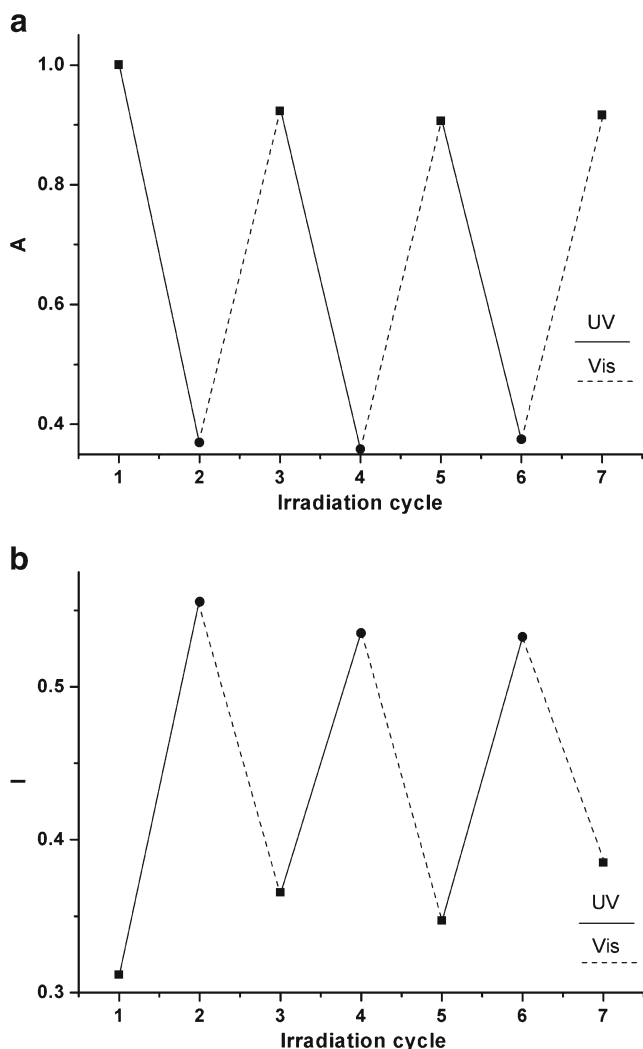


Fig. 6 Modulated absorption (a) and emission (b) signals of PATEI/BNDB system in DMF by alternate irradiation with UV (365 nm) and blue (436 nm) light

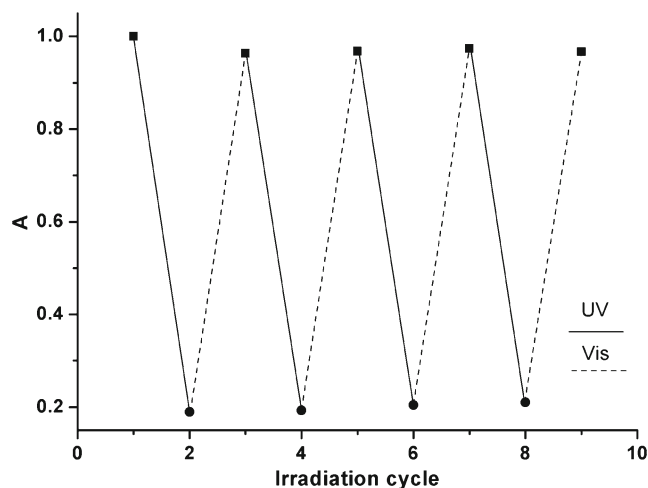


Fig. 7 Photoinduced alternation of normalized absorbance at 345.5 nm of AZM/BNDB system in DMF on UV light of 365 nm and visible light of 436 nm

Also, the modulation efficiency of trans-cis isomerization upon irradiation with 365 nm is given by the relation:

$$E_{\text{mod},abs} = 1 - \frac{A(\infty)}{A(0)}$$

where $I(0)$, $I(\infty)$, $A(0)$, $A(\infty)$ denote the fluorescence intensities and the absorbances, before irradiation and at the photostationary state, under irradiation with 365 nm light.

For the AZM/BNDB system, several switching cycles were recorded under alternating UV and visible (436 nm) irradiation with an isomerization efficiency of 80 % (Fig. 7), whereas the emission efficiency is 47 % [24]. The photoisomerization of azobenzene chromophores in AZM/BNDB solution is very stable over many cycles of irradiation (Fig. 7).

The fluorescence quenching process can be due to an energy transfer from the donor fluorescent component to the photochromic azobenzene units which act as a quencher. This transfer is well consistent with the overlap between the low intensity $n \rightarrow \pi^*$ absorption band at about 442 nm of AZM and the emission band of fluorophore (Fig. 1). The absorption band of the photochrome assigned to be $n \rightarrow \pi^*$ transition of cis-isomer is two times stronger than the absorption band of the starting trans isomer. Thus, the overlap between the absorption and emission bands is greater for cis isomer than in the case of trans-isomer. In this way the two azobenzene isomers can operate as quenching agents of fluorescence but cis isomer might present higher quenching efficiency than trans isomer.

Admitting that the mechanism of nonradiative energy transfer is of Förster type, the transfer efficiency can be estimated with the following relation [30]:

$$E = 1 - \frac{I}{I_0} = \frac{R_0}{R_0 + r^6}$$

where r is the distance between the donor-acceptor pair and R_0 indicates the Förster distance, defined as the distance where the transfer efficiency is 50 % and can be calculated by the equation:

$$R_0 = 8.88 \cdot 10^{-25} K^2 n^{-4} \phi J$$

where n is the refractive index of medium, K^2 is the orientation factor in energy transfer and assumed to be equal to 2/3, ϕ is the quantum yield of donor in the absence of acceptor, where a value of 0.07 was used, J is the spectral overlap integral between the donor emission spectrum and the acceptor absorption spectrum, which can be evaluated using the equation:

$$J = \frac{\int I(\lambda) \varepsilon(\lambda) \lambda^4 d\lambda}{\int I(\lambda) d\lambda}$$

where $I(\lambda)$ is the fluorescence intensity of fluorophore at λ , $\varepsilon(\lambda)$ is the molar absorptivity of acceptor at λ .

The overlap integral between the emission spectrum of BNDB and absorption spectrum of photochrome AZM (acting as quencher in the two isomer forms) has the value of $4.73 \times 10^{-15} \text{ cm}^3 \text{ M}^{-1}$ for trans isomer of AZM and $7.86 \times 10^{-15} \text{ cm}^3 \text{ M}^{-1}$ for cis isomer, respectively. Given the values as listed above, R_0 is estimated to be 18.95 Å for trans isomer and 20.64 Å for cis isomer, respectively. These values agree very well with the reported literature values [31]. The only aspect that should be noticed is that the difference between the values of the two isomers is lower in our fluorophore-azophotochrome system because the ratio of the two integrals ($J_{\text{trans}}/J_{\text{cis}}$) is 1.66, therefore the radii difference between the two isomers will be lower. Knowing the above values the quenching efficiency for AZM was estimated. Also, the quenching efficiency was represented as a function of fluorophore-quencher distance (Fig. 8). For a donor-acceptor distance of 20 Å, the difference between the quenching efficiency of the two isomers is 12 %; as a result the radiative modulation efficiency of the fluorescence might not be higher. However, the modulation efficiency was experimentally found to be 47 % and moreover the efficiency of fluorescence quenching is higher for trans isomer as compared to cis isomer. Since the difference between the overlap integrals as well as between the Förster radii of the two isomers is low enough, we can conclude that the radiative modulation of fluorescence can be caused by other molecular characteristics which determine the difference between the two isomers taking into account the quenching process. As is known the trans isomer of AZM is planar and this isomer quenches the fluorescence of BNDB more efficiently than the cis isomer. In this case the planarity of trans isomer favors the energy transfer between azochromophore AZM and fluorophore

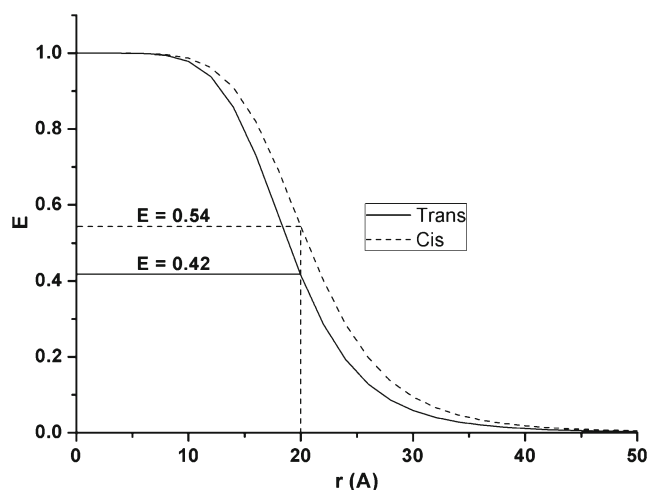


Fig. 8 Energy transfer efficiency for trans- and cis-azobismaleimide acceptors

BNDB. The nonplanar structure of cis isomer for the aromatic rings linked to the azo nitrogen atoms diminishes the conjugation of nitrogen lone pair of electrons with the π electrons of donor occurring thus the inhibition of energy transfer [32]. When the overlap integrals and the Förster radii of the two isomers have close enough values the planarity of photochromic molecule plays a prominent part in the fluorescence quenching of AZM/BNDB system.

In the PATEI/BNDB system the modulation efficiency of fluorescence is about 34 % due to the lower conversion degree in the photoisomerization process (Fig. 9), whereas the modulation efficiency of isomerization is 62 %. When the photostationary state was reached the system was irradiated with 436 nm light and the intensity of $\pi \rightarrow \pi^*$ transition band at 343 nm is increased with irradiation time which evidence that the cis-trans isomerization of cis isomers operates as a process of fluorescence quenching followed by the decrease of fluorescence intensity of the PATEI/BNDB system with increasing irradiation time till reaching the photostationary state. The recovery of trans isomers in solution by visible irradiation in the PATEI/BNDB system is similar to the AZM/BNDB system.

In order to establish the effect of fluorophore (BNAB) on the rate of the trans-cis-trans isomerization process of azo chromophores in AZM and PATEI from fluorophore-photochrome constructs, the isomerization kinetics under irradiation by 365 nm and back photoreaction under irradiation by light of 436 nm were studied. The photoisomerization of azo chromophores in AZM/BNDB system proceeds as a first-order reaction according to the equation [33, 34]:

$$\ln \frac{A(0) - A(\infty)}{A(t) - A(\infty)} = k_{ir} f(t)$$

where $A(0)$, $A(t)$, $A(\infty)$ are the absorbances of trans azoaromatic derivative at time 0, t and at the photostationary

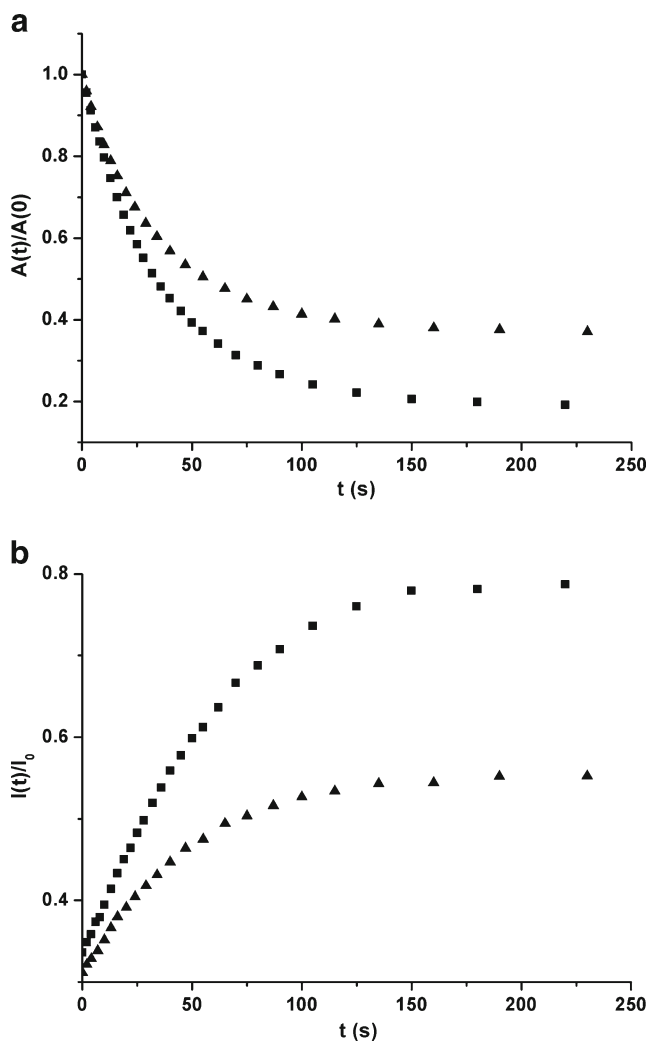


Fig. 9 Relative absorption and emission intensity as a function of UV irradiation time at 365 nm in DMF for the photoisomerization process (a) and the fluorescence recovery of BNDB (b) for AZM (■) for PATEI (▲)

state, respectively and k_{ir} is the photoisomerization rate constant. The photokinetic factor $F(t)$ has the expression [35, 36]:

$$F(t) = \frac{1 - 10^{-A'(t)}}{A'(t)}; \quad f(t) = \int_0^{t_\infty} F(t) dt$$

where A' is the absorbance at irradiation wavelength and t_∞ denotes the time when the photostationary state was reached.

First-order plot of $\ln[(A(0) - A(\infty))/(A(t) - A(\infty))]$ as against $f(t)$ in the AZM/BNDB system in DMF shows a fast photoisomerization process with rate constant of $1.95 \times 10^{-2} \text{ s}^{-1}$ (Fig. 10). Note that this value is close to that found for AZM in DMF solution ($2.11 \times 10^{-2} \text{ s}^{-1}$) [37].

The photoisomerization reaction for PATEI/BNDB system exhibits a deviation from the first-order kinetics

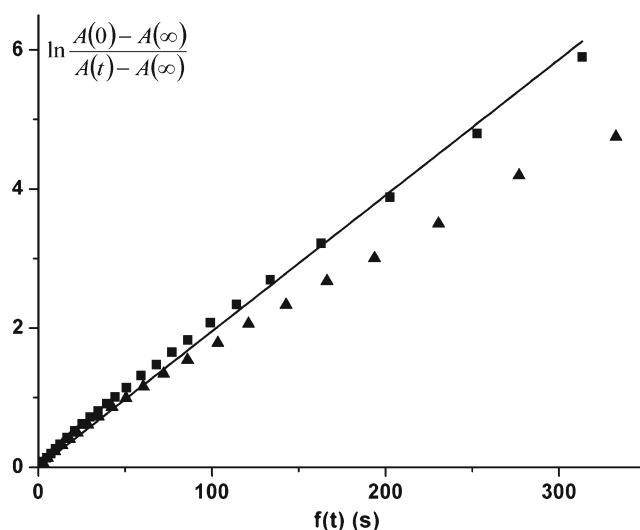


Fig. 10 First-order plots for trans-cis photoisomerization for AZM/BNDB (■) and PATEI/BNDB (▲) in DMF

(Fig. 10) and the kinetics can be described by a biexponential equation [33, 34, 38]:

$$\frac{A(t) - A(\infty)}{A(0) - A(\infty)} = \alpha \exp(-k_{ir,f} f(t)) + (1 - \alpha) \exp(-k_{ir,s} f(t))$$

where: $k_{ir,f}$ and $k_{ir,s}$ are the rate constants for the fast and slow photoprocesses, respectively and α represents the fraction of the fast species (Fig. 11).

The rate constants of the photoisomerization for PATEI/BNDB and AZM/BNDB systems are the same order of magnitude as in the case of azochromophore photoisomerization in the absence of fluorophore, suggesting that the trans-cis photoisomerization was not sensitized by the energy transfer from fluorophore to photochrome.

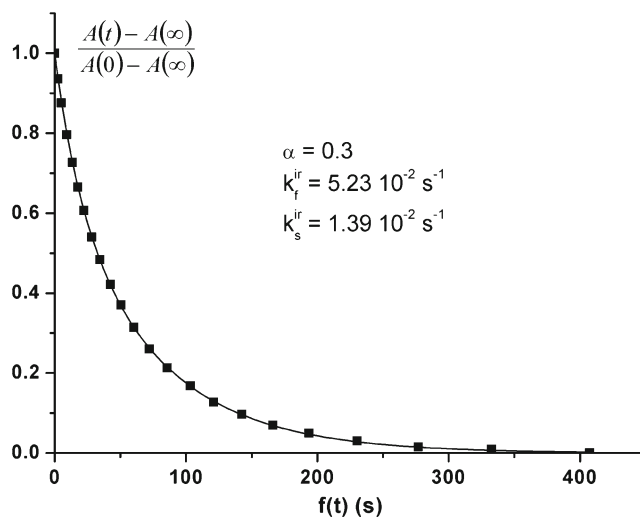


Fig. 11 Biexponential function for trans-cis photoisomerization of azo chromophores in PATEI/BNDB system

The photochemical reversion from cis to trans isomer using visible light (436 nm) obeys to a first order kinetics for AZM and PATEI incorporating fluorophore.

$$\ln \frac{A(\infty) - A(0)}{A(\infty) - A(t)} = k_{ir,c} f(t)$$

in which $k_{ir,c}$ is the rate constant of cis-trans photoisomerization. From the slopes of the straight lines in Fig. 12, the rate constants were estimated to be 6.10×10^{-2} for AZM/BNDB and $4.23 \times 10^{-2} \text{ s}^{-1}$ for PATEI/BNDB systems. The obtained values of rate constants were not different from the systems which not containing BNDB, the rate constant ratio being 1.1 from AZM and 0.95 for PATEI. Therefore, a no photosensitization effect was evidenced in the case of cis-trans photoisomerization for these fluorophore-photochrome systems.

The studies on the radiative modulation of fluorescence reveal a certain degree of photosensitization of cis-trans photoisomerization regardless of the fact if the quenching is selective to cis isomer or to trans isomer [18, 39]. The selectivity of isomerization depends on the spectral overlap degree between the absorption spectra of the two isomers and the fluorescence spectrum of donor whatever the isomer which determine the modulation process. However, in our fluorophore-photochrome system the isomerization selectivity is due especially to geometry of isomer acting as quenching agent. The trans isomer becomes an efficient quencher because of its planar geometry. In this instance the photosensitization of one of two isomers is determined by a certain orientation of the azochromophore molecule relating to the fluorophore.

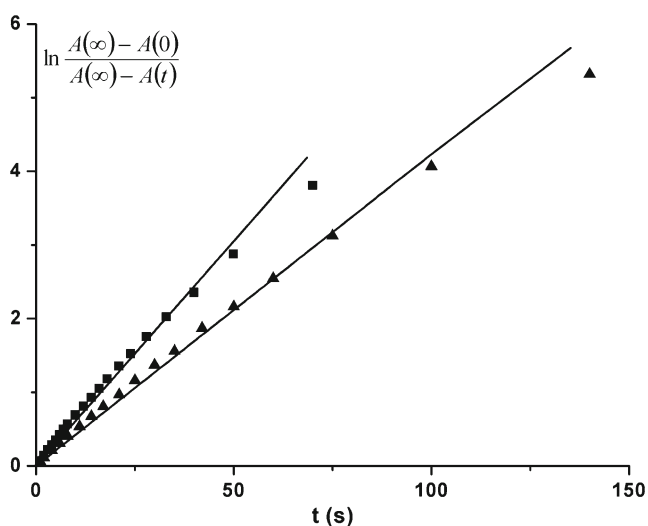


Fig. 12 Kinetics of photochemical recovery during irradiation with 436 nm light in DMF for AZM/BNDB (■) and PATEI/BNDB (▲) systems

Conclusions

A fluorescence switch based on fluorescent N,N'-bis(2-naphthalenethylene)-1,4-diaminobenzene and polyazothioetherimide as photochromic component was investigated. The control of emission intensity could be performed by alternate irradiation of light at 365 nm and 436 nm, respectively. In this way the emission intensity of aryleneimine partner can be modulated synchronously under irradiation of azobismaleimide chromophore. The emission modulation efficiency with polyazothioetherimide is comparable to that found out for the simple azobismaleimide derivative.

Acknowledgments Financial support from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° 264115—STREAM is gratefully acknowledged.

References

- Russev MM, Hecht S (2010) Photoswitches: from molecules to materials. *Adv Mater* 22:3348–3360
- Liu LH, Nakatani K, Ishow E (2009) Synthesis and photophysical properties of a highly fluorescent azo derivative. *New J Chem* 33: 1402–1408
- Ercole F, Davis TP, Evans RA (2010) Photo-responsive systems and biomaterials: photochromic polymers, light-triggered self-assembly, surface modification, fluorescence modulation and beyond. *Polym Chem* 1:37–54
- Yildiz I, Deniz E, Raymo FM (2009) Fluorescence modulation with photochromic switches in nanostructured constructs. *Chem Soc Rev* 38:1859–1867
- Berkovic G, Kongrauz V, Weiss V (2000) Spiropyrans and spirooxazines for memories and switches. *Chem Rev* 100:1741–1754
- Evans SD, Johnson SR, Ringsdorf H, Williams LM, Wolf H (1998) Photoswitching of azobenzene derivatives formed on planar and colloidal gold surfaces. *Langmuir* 14:6436–6440
- Wang S, Qi Q, Li C, Ding G, Kim SM (2011) Organic dyes incorporating low-band-gap chromophores based on p-extended benzothiadiazole for dye-sensitized solar cells. *Dyes Pigm* 89:188–192
- Feringa BL (2001) *Molecular switches*. Wiley-VCH, Weinheim
- Raymo FM, Tomasulo M (2005) Electron and energy transfer modulation with photochromic switches. *Chem Soc Rev* 34:327–336
- Tian H, Yang SJ (2004) Recent progresses on diarylethene based photochromic switches. *Chem Soc Rev* 33:85–97
- Chen Y, Xie N (2005) Modulation of a fluorescent switch based on a controllable photochromic diarylethene shutter. *J Mater Chem* 15: 3229–3232
- Piard J, Metivier R, Giraud M, Leautic A, Yu P, Nakatani K (2009) Photoswitching in diarylethene nanoparticles, a trade-off between bulk solid and solution: towards balanced photochromic and fluorescent properties. *New J Chem* 33:1420–1426
- Metivier R, Badre S, Meallet-Renault R, Yu P, Pansu RB, Nakatani K (2009) Fluorescence photoswitching in polymer matrix: mutual influence between photochromic and fluorescent molecules by energy transfer processes. *J Phys Chem C* 113:11916–11926
- Folling MJ, Polyakova S, Belov V, Blaadern A, Rossi ML, Hell SW (2008) Synthesis and characterization of photoswitchable fluorescent silica nanoparticles. *Small* 4:134–142

15. Sheepwash MAL, Mitchell RH, Bohne C (2002) Mechanistic insights into the photochromism of trans-10b,10c-dimethyl-10b,10c-dihydropyrene derivatives. *J Am Chem Soc* 124:4693–4700
16. Chen L, Wang G, Zhao X (2011) A fluorescence switch based on a controllable photochromic naphthopyran group. *J Luminesc* 131: 1617–1620
17. Tomasulo M, Giordani S, Raymo FM (2005) Fluorescence modulation in polymer bilayers containing fluorescent and photochromic dopants. *Adv Funct Mater* 15:787–794
18. Lewis SM, Harbron EJ (2007) Photomodulated PPV emission in a photochromic polymer film. *J Phys Chem C* 111:4425–4430
19. Kumar G, Neckers D (1989) Photochemistry of azobenzene-containing polymers. *Chem Rev* 89:1915–1925
20. Rau H (1990) Photoisomerization of azobenzenes. In: Rabek JF (ed) *Photochemistry and photophysics*, vol. 2. CRC Press, Boca Raton, pp 119–141
21. Deniz E, Tomasulo M, Cusido J, Sortino S, Raymo FM (2011) Fast and stable photochromic oxazines for fluorescence switching. *Langmuir* 27:11773–11783
22. Airinei A, Fifere N, Homocianu M, Gaina C, Gaina V, Simionescu BC (2011) Optical properties of some new azo photoisomerizable bismaleimide derivatives. *Int J Mol Sci* 12:6176–6193
23. Airinei A, Homocianu M, Fifere N, Gaina C, Gaina V (2011) Optical properties of some bismaleimide derivatives. *Optoelectr Adv Mater—Rapid Commun* 5:655–660
24. Fifere N, Airinei A, Gaina C, Gaina V, Grigoras M, Simionescu BC (2012) Isomerization characteristics of some azobismaleimides. *Rev Roum Chim* 57:599–607
25. Dix LR, Ebdon JR, Flint NJ, O'Dell R (1995) Chain extension and crosslinking of telechelic oligomers I. Michael additions of bisamines to bismaleimides and bis(acetylene ketone)s. *Eur Polym J* 31:647–652
26. Grigoras M, Cianga I, Farcas A, Nastase G, Ivanoiu M (2000) Fully conjugated and soluble polyazomethines containing 1,1'-binaphthyl groups. *Rev Roum Chim* 45:703–708
27. Grigoras M, Catanescu CO, Colotin G (2001) Poly(Schiff base)s containing 1,1'-binaphthyl moieties: synthesis and characterization. *Macromol Chem Phys* 202:2262–2266
28. Ding F, Zhao G, Chen S, Liu F, Zhang L (2009) Chloramphenicol binding to human serum albumin: determination of binding constants and binding sites by steady-state fluorescence. *J Mol Struct* 929:159–166
29. Gayen A, Chatterjee C, Mukhopadhyay C (2008) GM1-induced structural changes of bovine serum albumin after chemical and thermal disruption of the secondary structure: a Spectroscopic comparison. *Biomacromolecules* 9:974–983
30. Lakowicz JR (2006) *Principles of fluorescence spectroscopy*, 3rd edn. Springer, New York
31. Grimes AF, Call SE, Vicente DA, English DE, Harbron EJ (2006) Toward efficient photomodulation of conjugated polymer emission: optimizing differential energy transfer in azobenzene-substituted PPV derivatives. *J Phys Chem B* 110: 19183–19190
32. Smitha P, Asha SK (2007) Structure control for fine tuning fluorescence emission from side-chain azobenzene polymers. *J Phys Chem B* 111:6364–6373
33. Shen YQ, Rau H (1991) The environmentally controlled photoisomerization of probe molecules containing azobenzene moieties in solid poly(methyl methacrylate). *Makromol Chem* 192:945–957
34. Ruslim C, Ichimura K (1999) Comparative studies on isomerization behavior and photocontrol of nematic liquid crystals using polymethacrylates with 3,3'- and 4,4'-dihexyloxyazobenzenes in side chains. *Macromolecules* 32:4254–4263
35. Malkin S, Fischer E (1962) Temperature dependence of photoisomerisation. II. Quantum yields of cis-trans isomerization in azo-compounds. *J Phys Chem* 66:2482–2486
36. Zimmerman G, Chow LY, Paik UJ (1958) The photochemical isomerization of azobenzene. *J Am Chem Soc* 80:3528–3531
37. Fifere N, Airinei A, Homocianu M, Gaina C, Gaina V, Simionescu BC (2012) Effect of trans-cis photoisomerisation of azobismaleimide derivatives on the emission intensity of an aryleneimine fluorophore. *Rev Roum Chim* 57:609–614
38. Suzuki I, Ishizaki T, Hoshi T, Anzai J (2002) Fully reversible isomerization of azobenzene chromophores in polyelectrolyte layered assemblies. *Macromolecules* 35:577–580
39. Abdallah D, Whelan J, Dust JM, Hoz S, Buncel E (2009) Energy transfer in the azobenzene-naphthalene light harvesting system. *J Phys Chem A* 113:6640–6647