EFFECT OF *TRANS-CIS* PHOTOISOMERIZATION OF AZOBISMALEIMIDE DERIVATIVES ON THE EMISSION INTENSITY OF AN ARYLENEIMINE FLUOROPHORE

Nicuşor FIFERE,[a] Anton AIRINEI,[a,*] Constantin GAINĂ[a], Viorica GAINĂ[a], Mircea GRIGORAŞ[a] and Bogdan C. SIMIONESCU[a,b]

[a]"Petru Poni" Institute of Macromolecular Chemistry, Roumanian Academy, Aleea Grigore Ghica Voda, 41A, 700487 Iaşi, Roumania
[b]Department of Natural and Synthetic Polymers, "Gheorghe Asachi" Technical University, Iaşi 700050, Roumania

The fluorescence intensity of an aryleneimine monomer can be photoregulated by irradiation with UV and visible light due to reversible trans-cis-trans photoisomerization of azobenzene chromophores from azobismaleimide. The emission band appeared at 452 nm being situated of the range of n-π* transition of azobismaleimide. Reversible change of emission intensity in solution was performed by alternating irradiation with UV and visible light. This change is possible for multiple cycles, so the emission intensity can be controlled.

INTRODUCTION

Fluorescent switchable systems containing photochromic moieties have attracted extensive interest on account of their potential applications in optical memory media, switching devices, photomechanical actuators, photoresponsive biomaterials, etc.[1-9] The working principle of these devices is based on the modulation of emission intensity of a fluorescent partner being irradiated with UV and visible light together with an azobenzene chromophore which may undergo a trans-cis photoisomerization. The modifications in emission intensity can be an adequate method for manufacturing photoswitching devices taking into consideration high sensitivity and resolution of the emission fluorescence.

The photochromic fluorescent systems can be classified in several categories: 1) molecules consisting of one single unit having both photochromic and fluorescent characteristics; 2) multicomponent systems (dyads, triads, hybrids, supramolecular assemblies) containing photochromic and light-emitting units where energy or electron transfer can be controlled reversibly by the photochromic moieties; 3) polymers or related materials bearing photochromic and emitting units as dopants or side chains.[10-18] The main advantage of the doped systems is that the photochromic characteristics of photosensitive moieties and the emission properties of fluorophores depend reciprocally on the photoinduced electron transfer or energy transfer in the ground or excited states.[6] The most important condition for an efficient energy process is the existence of a significant degree of overlap between the emission band of fluorophore and the absorption band of the photochromic partner.[3,8,10] Under these conditions the photoinduced conversion of the isomeric forms of the photochromic switch can modulate the emission intensity of the fluorophore and thus the fluorescence emission can be altered by operating the photochromic switch between the two isomer states.

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* Corresponding author: airineia@icmpp.ro
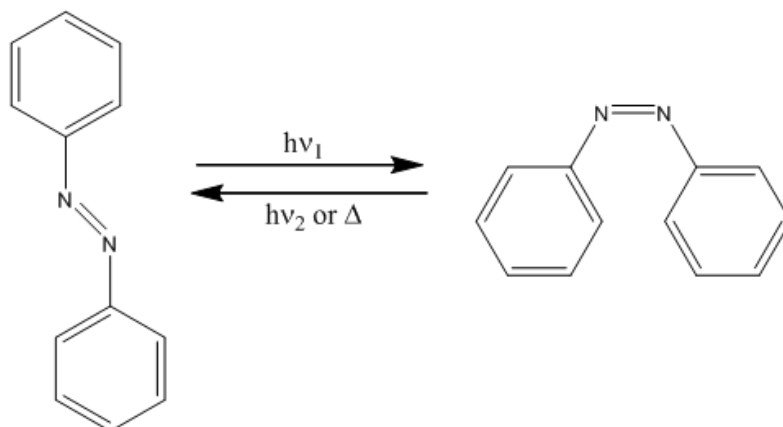
Scheme 1 – Trans-cis photoisomerization in azobenzene.

Azobenzenes are well-known photochromic compounds that exhibit photochromism by isomerization. Under UV light irradiation, the thermally stable trans-isomer is converted to an unstable cis-isomer and the cis form reverts to trans isomer thermally or upon irradiation with visible light (Scheme 1). The trans-cis isomerization involves substantial structural and electronic changes, which translate in different absorption spectra, different dipole moments and polarizabilities of the two isomers.[19,20]

Reversible trans-cis isomerization of azobenzene compounds generally does not determine a modification in fluorescence because azo derivatives do not fluoresce with appreciable quantum yield.[21,22] By choosing a suitable coupling of the fluorescent compound and the photochromic derivative, the trans-cis photoisomerization can induce desired changes in the fluorescence characteristics of the fluorophore. When the two components are blended into a polymer matrix, the fluorescent partner acts as an energy donor and the azobenzene photochromic component is an energy acceptor.

In this article, we report on the reversible photoswitchable fluorescence system based on photochromic azobismaleimide derivativate and an aryleneimine fluorescent monomer. The reversible isomerization processes of photochromic component were monitored by electronic absorption spectra and emission spectra.

RESULTS AND DISCUSSION

The photoinduced changes in emission intensity of N,N'-bis(2-naphthalenethylene)-1,4-diaminobenzene (MI) depends on the state of the photoswitch, trans and cis isomers of azobismaleimide (ABM) (Scheme 2).

Absorption and fluorescence spectra of azobismaleimide (ABM) and aryleneimine monomer (MI) in dilute dimethylformamide (DMF) solution are presented in Figs. 1 and 2. The azobenzene chromophores are predominantly in the trans form at room temperature and electronic absorption spectrum of azobismaleimide exhibits two absorption bands, an intense absorption at 345 nm corresponding to a $\pi \rightarrow \pi^*$ transition of trans azobenzene isomer and an additional band situated at 442 nm assigned to the weak $n \rightarrow \pi^*$ transition of the trans azobenzene.[20,23] It is noticed that the fluorescence excitation band was situated at 384 nm and the emission fluorescence band appeared at 452 nm with excitation wavelength of 370 nm for aryleneimine monomer (Fig. 1, curves 3 and 4). The imine monomer (MI) shows an intense absorption band at about 370 nm (Fig. 2).

Taking into account that there is a significant overlap between the emission band of fluorophore (MI) and the absorption band corresponding to $n \rightarrow \pi^*$ transition of the photochromic component (ABM), the latter can be used as quenching agent in the two isomer forms for the fluorescent partner. No significant absorption and fluorescence spectral modifications of MI were found during UV and visible light irradiation, proving that aryleneimine monomer is stable under UV light.

Fig. 3 reveals the effect of increasing concentration of trans ABM used as quenching agent on the emission intensity of aryleneimine monomer. With the increase concentration of ABM, the fluorescence intensity of MI decreases without any change in the position and shape of emission band (Fig. 3). The quenching experiment was performed using a 1.01×10^{-5} M solution in DMF of MI and the concentration of ABM (1.16×10^{-4} M) was changed gradually. The quenching process was continued until the intensity of emission reached 30% of that the initial

fluorophore. These results show that a strong interaction takes place between the fluorescent partner and photochromic compound.

The solution obtained by the quenching of fluorophore emission by trans azobismaleimide ABM was subjected to UV irradiation of 365 nm light in order to generate the trans-cis photoisomerization of ABM. While the irradiation time was increased, the emission intensity of MI increases progressively until ca 80% of its initial value, after 170 s of UV irradiation. In the same time upon irradiation with 365 nm light the intensity of $\pi \to \pi^*$ absorption band decreased while a concomitant increase in the cis $\pi \to \pi^*$ and $n \to \pi^*$ bands

occurred due to the trans-cis photoisomerization of azobenzene chromophores in ABM (Fig. 4). The trans-cis photoisomerization process reaches a stationary state after 210 s of UV irradiation and the cis isomer fraction becomes 0.85.[24] The increase in the fluorescence intensity of fluorophore concurrently with the increase of cis isomers in system through the consumption of trans isomers indicates that the fluorophore quenched selectively by the trans isomer of ABM. In order to explore the mechanism of fluorescence changes of fluorophore, the above solution already finding out in photostationary state was irradiated with 436 nm light resulting in the recovery of trans isomers.
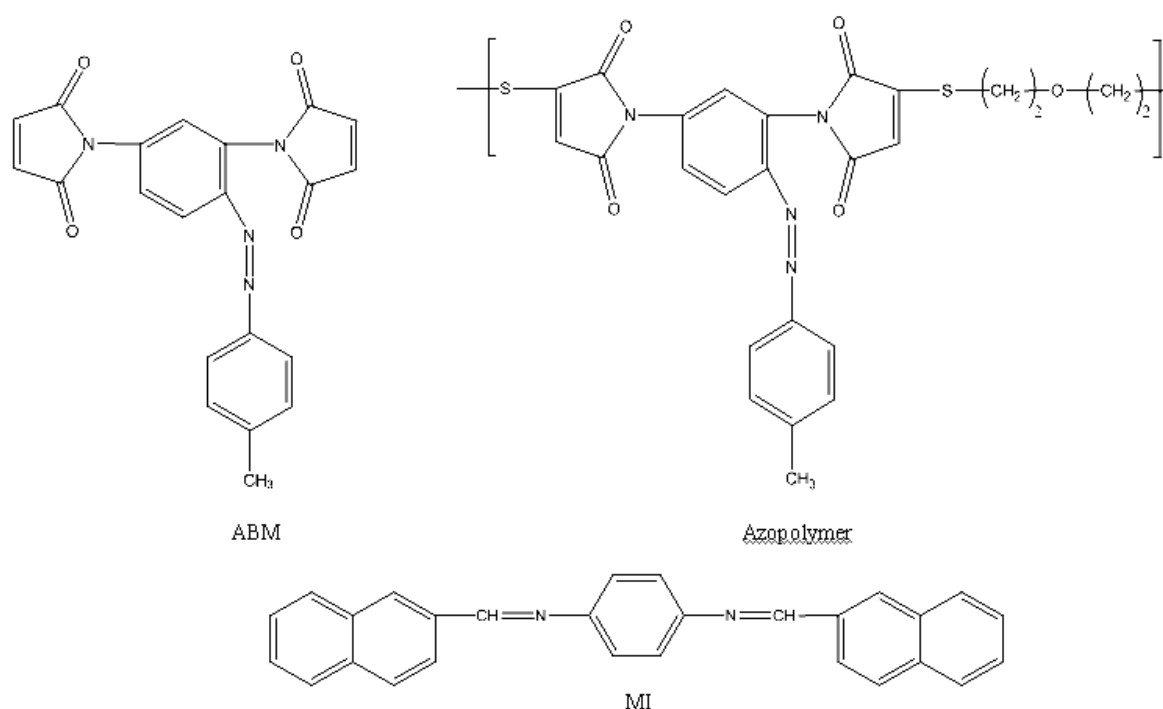
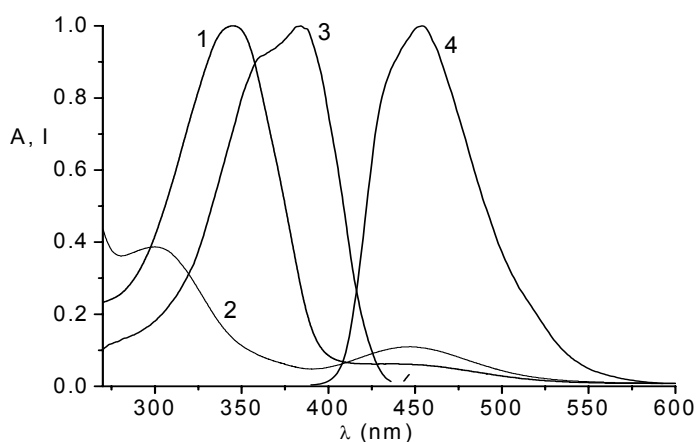Scheme 2 – Structure of azoaromatic derivatives and imine monomer.

Fig. 1 – Normalized electronic absorption spectra of ABM (1 – trans isomer; 2 – cis isomer) and excitation and emission spectra of MI in DMF (3 – excitation; 4 – emission).
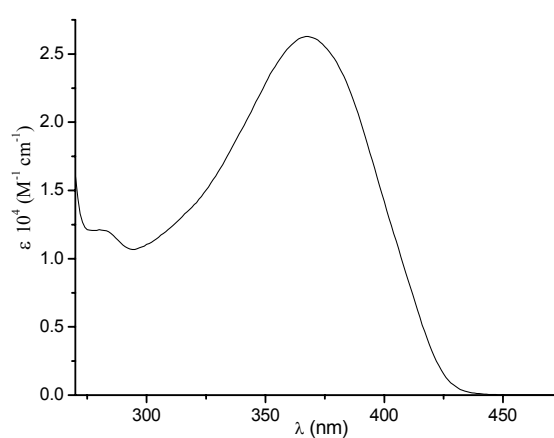
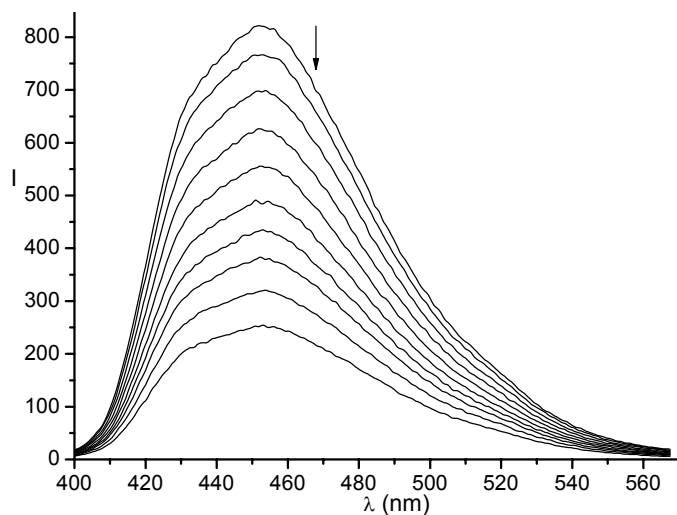Fig. 2 – UV-Vis absorption spectra of aryleneimine monomer MI in DMF.

Fig. 3 – Fluorescence changes of MI/ABM system in DMF solution during quenching with ABM (λ_{ex} = 370 nm).
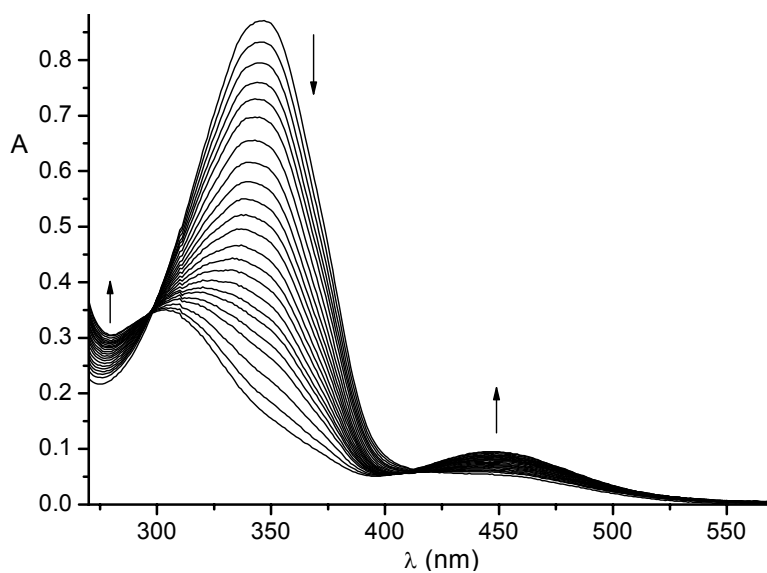

Fig. 4 – UV-Vis absorption spectra of ABM during irradiation with 365 nm light.
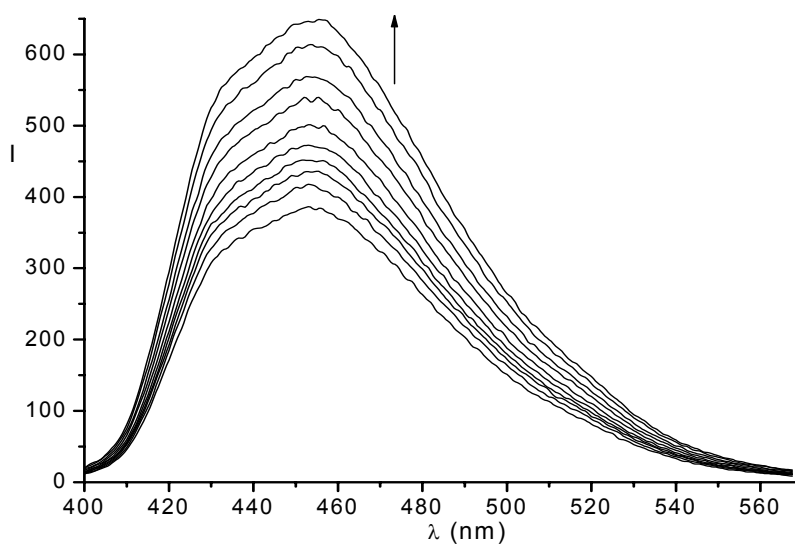

Fig. 5 – Fluorescence changes of MI/ABM in DMF solution under irradiation with blue light.
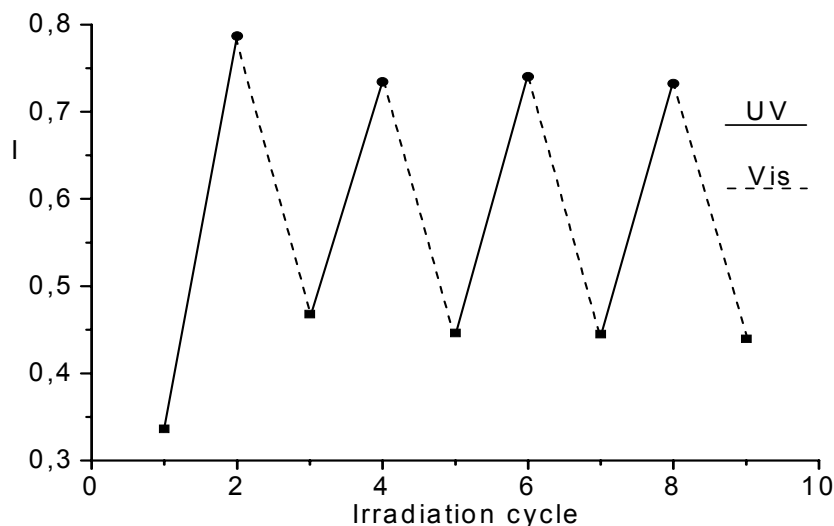
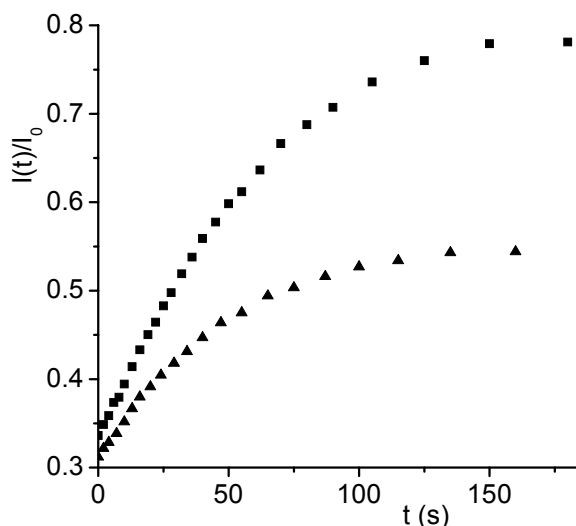Fig. 6 – Emission switching cycles of MI/ABM in DMF solution by alternating irradiation with UV/Vis light.

Fig. 7 – Profiles of the fluorescence recovery in DMF solution for ABM/MI (■), azopolymer/MI system (▲).

In this case the emission of fluorophore was gradually diminished down to 45 % of the starting value of the fluorophore emission (Fig. 5). This irradiation cycle was accompanied with the trans-cis photoisomerization of azobenzene chromophores evidenced by the increase in intensity of the trans isomer absorption due to the consumption of cis isomers. In order to demonstrate that the emission intensity of MI can be modulated based on photoisomerization of ABM, other measurements on solution fluorescence were carried out under new cycle of irradiation and the procedure can be repeated after many cycles of UV and Vis irradiation (Fig. 6).

The fluorescence quenching of aryleneimine derivative was carried out using polyazothioetherim-ide which include the free chromophore ABM (Scheme 2). Also, corresponding to the absorption spectral changes of photochromic polyazothioetherimide, the fluorescence emission in DMF solution is modified as shown in Fig. 7, similarly for ABM/MI/ system. In the case of fluorophore-photochromic component (polyazothio-etherimide), the recovery degree of fluorescence by irradiation with 365 nm is lower as compared ABM, due to the smaller conversion degree during photoisomerization (Fig. 7). In these conditions the azobismaleimide works as a switch controlling the

emission intensity of fluorophore using alternative irradiation with UV/Vis light.

EXPERIMENTAL

Measurements. Electronic absorption spectra were measured by UV-3600 Shimadzu spectrophotometer. Fluorescence spectra were taken on a Perkin Elmer LS55 luminescence spectrometer in solution using quartz cells with a 10 mm optical path length at room temperature. Emission spectra were determined at an excitation wavelength of 370 nm, UV irradiation was provided by a 500 W high pressure mercury arc lamp equipped with narrow glass filters of appropriate wavelengths.

Materials. Solvents used for the study were of spectroscopic grade and obtained from Sigma-Aldrich. Azobismaleimide was obtained by the condensation reaction of 2,4-diamino-4'-methylazobenzene with maleic anhydride in acetone by a two-step method.[24-26] Polyazothioetherimide was synthesized by the reaction of azobismaleimide and bis-2-mercaptoethylether.[24,26] The iminic monomer N,N'-bis(2-naphthylmethylene)-1,4-diaminobenzene was prepared according to methods published previously.[27,28]

CONCLUSIONS

A photoresponsive switchable system which is consisted of a photochromic azobismaleimide and a fluorescent compound of aryleneimine type was described. The merit of this system is that the appropriate properties of both azobismaleimide and fluorescent component can be retained. The changes of fluorescence emission intensity according to the isomerization states of azobenzene chromophore are more pronounced in azobismaleimide solution than in azopolymer solution.

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