J Mater Sci (2007) 42:7866–7871
DOI 10.1007/s10853-007-1657-z

Optical switching of a photochromic bis-phenylazo compound in PMMA films

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Received: 9 November 2006 / Accepted: 5 March 2007 / Published online: 30 May 2007

Abstract We present our results on a newly synthesized bis-phenylazo derivative, namely bisperfluoroalkylsulfonylamino- arylazomethylene-triphenyl-phosphorane (BAM-TPP). Thin films of BAM-TPP in polymethylmethacrylate (PMMA) matrix were prepared. The films (thickness, $d < 60$ µm) were exposed to UV-vis light with variable intensity in order to stimulate the photochromic reaction of BAM-TPP. The resulting absorption changes of the BAM-TPP/PMMA films were investigated by spectrophotometry. The absorption spectra reveal that BAM-TPP molecules in PMMA undergo photoisomerization with resulting decrease of absorbance in the range 500–700 nm. Finally, the time response of film transmittance at 514 nm under increasing CW light intensity was recorded, showing that the reverse photochromic process brings the absorbance back to its pristine value. The obtained films thus proved to be suitable for optical switching applications.

Introduction

Azobenzenes constitute a class of conjugated organic materials that have received considerable attention for their reversible photochromism [1, 2] and remarkable second order nonlinear optical (NLO) properties [3]. These photochemical/physical properties combined with the ability of varying their chemical structure render azobenzenes particularly attractive candidates for optical data storage [4], optical switching [5] and in liquid crystals technology [6]. Azobenzenes undergo photoinduced isomerization between *cis* (*Z*) and *trans* (*E*) configurations with respect to the double bond N=N [7]. The absorption of UV(visible) light [8] transforms the *trans*(*cis*) isomer into the *cis*(*trans*) isomer. In particular, upon formation of the *cis* isomer of an azobenzene derivative the main spectral variation is the decrease of absorbance in the range 320–350 nm, which is associated with the π–π^* electronic transition of the starting *trans* form of an azobenzene [9]. This feature suggests that the back-photoisomerization reaction *cis* → *trans* induces an increase of absorption in the wavelength interval 320–350 nm that can be exploited in a mechanism of optical photoswitching [5]. The main absorption peak of azobenzenes in the *cis* configuration is usually located at about 430 nm, and it is originated by a $^1(\text{n} \rightarrow \pi^*)$ transition [9]. Since the exact wavelength at which azobenzene isomerization occurs depends on the particular electronic structure of the azobenzene derivative itself, tailoring its optical properties is possible upon modification of the molecular structure.

We investigated the photochromic properties of a particular phenylazo compound, namely bis-perfluoroalkylsulfonylamino-arylazomethylene-triphenyl-phosphorane (BAM-TPP, **1**) (Fig. 1), when included into poly(methylmethacrylate) (PMMA) films [10].

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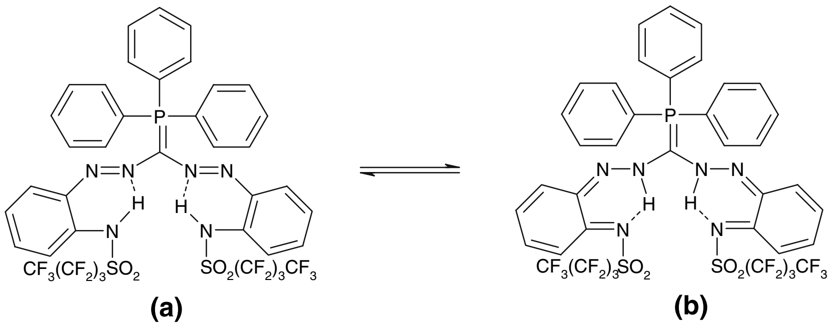

Fig. 1 Azo-(**A**) and hydrazone (**B**) tautomers of BAM-TPP (**1**). For the azo-form **A** only the *Z* configuration is reported

Experimental

BAM-TPP preparation

The synthesis of BAM-TPP (**1**) requires the double addition of nonafluorobutanesulfonyl-1*H*-benzotriazole to methyltriphenylphosphonium chloride in two consecutive steps. During the first step, one equivalent of methyltriphenylphosphonium chloride, and 1.5 equivalents of butyllithium are reacting in *n*-hexane. The solvent is tetrahydrofurane while reaction conditions are room temperature (25 °C) and a duration of 4 h. To the obtained solution of monoazo-compound, 2.2 equivalents of nonafluorobutanesulfonyl-1*H*-benzotriazole are added at the same temperature for half an hour. Total yield of synthesis for **1** is 45%. Melting point of BAM-TPP (**1**) was 190–193 °C. IR spectrum of **1** in KBr pellets shows absorption bands at 3,442, 1,350, 1,191, 1,440, 1,134 and 1,035 cm^{-1}. UV-vis spectra in acetonitrile solvent were taken: BAM-TPP exhibited a strong absorption peak at 534 nm. ^{1}H and ^{13}C spectra were recorded on a NMR spectrometer at 250 and 62.9 MHz, respectively, using deuterated chloroform as a solvent. ^{1}H-NMR:δ = 6.89–6.95 (m, 2H), 7.02–7.06 (m, 2H), 7.09–7.16 (m, 2H), 7.45–7.48 (m, 2H), 7.59–7.67(m, 12H), 7.71–7.81 (m, 3H), 16.5 (s, 2H). ^{13}C-NMR: δ = 115.8, 119.1(d, J = 92.3 Hz), 125.1, 126.6, 128.0 (d, J = 174 Hz), 130.0 (d, J = 12.9 Hz), 130.5, 134.2 (d, J = 10.2 Hz), 134.9, 135.1 (d, J = 3.2 Hz), 140.8.Fast Atom Bombardment-Mass Spectrometry (FAB-MS) was used to measure the mass-to-charge ratio of ions: 1078.9. The latter value corresponds to a single positive charged molecule plus one hydrogen atom.

Thin films preparation

The powder of BAM-TPP (**1**) was dispersed into a polymeric matrix of PMMA and some films were prepared. Previously, two different solutions were prepared using chloroform ($CHCl_3$) as solvent. Concentration values were $4.6 \cdot 10^{-5}$ M and $1.6 \cdot 10^{-4}$ M, respectively. The obtained solutions were then stirred for 24 h. PMMA (99.9%, from Aldrich) was used as a photochemically inert host polymer. It was added to the initial solutions of **1** and $CHCl_3$. Two different set of films were prepared with a weight percentage of 0.35% for the solution in the polymer being the only difference the molarity of the initial solution. The mixtures of PMMA and BAM-TPP (**1**) were stirred for 48 h at room temperature. The deposition of the polymeric films was realized by casting the obtained PMMA and BAM-TPP (**1**) mixture into Petry dishes. The complete removal of the solvent was achieved after an annealing process at 90 °C for 1 h. Film thicknesses were measured with a surface prophilometer and their values were found to be between 30 and 60 μm. The transmittance spectra of both solutions and films were recorded in the visible-NIR range by a standard spectrophotometric technique.

Results and discussion

The optical spectrum of bis-phenylazo BAM-TPP **1** in solution is characterized by the presence of two absorption maxima at 536 and 348 nm, and a shoulder at about 488 nm (Fig. 2). The strongest absorption at the longer wavelength, namely 536 nm, indicates the predominant presence of the hydrazone form of **1** (tautomer **B** in Fig. 1) in neutral solution [11]. The formation of the hydrazone

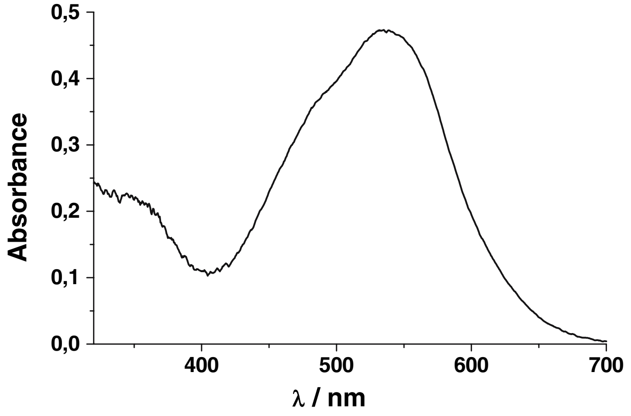

Fig. 2 Absorption spectrum of BAM-TPP (**1**) in acetonitrile. Concentration of **1**: 7.4×10^{-5} M. Quartz cuvette thickness: 10 mm

tautomer **B** is particularly favoured in the neutral solutions of BAM-TPP **1** for the reduced basic strength of the *o*-amino as a consequence of the presence of the electron-withdrawing perfluoroalkylsulfonyl group [11]. The weaker absorptions at 488 and 348 nm are due to the co-existence of the azo form of **1** (tautomer **A** in Fig. 1) [12] in lower percentage with respect to the hydrazone form **B**. In particular, the peak at 348 nm is ascribed to the $^1(\pi \rightarrow \pi^*)$ transition of the azo tautomer of **1** in the *trans*-(*E*,*E*)-configuration (Fig. 3) [9]. The presence of the azo tautomer **A** becomes predominant if BAM-TPP(**1**) is dissolved in basic conditions (Fig. 4) [13]. If the spectrum of the bis-phenylazo derivative **1** in neutral solution is compared with the one of an analogous mono *o*-amino benzene [14] a general red shift of the main absorption bands is observed for BAM-TPP(**1**). This is caused by the presence of a more extended network of conjugated electrons in **1** with respect to an analogous mono *o*-amino benzene [15]. The embedding of BAM-TPP(**1**) in PMMA does not produce any relevant change in the transmission spectrum of **1** when compared to its neutral solution (Fig. 5), and indicates that the chosen pattern of substitution prevents **1** from intermolecular aggregation in this polymeric matrix. This is an important result since the funcionalization of the bis-phenylazo compound here considered allows the excitation of **1** also in a polymeric film at the specific wavelengths of available visible lasers.

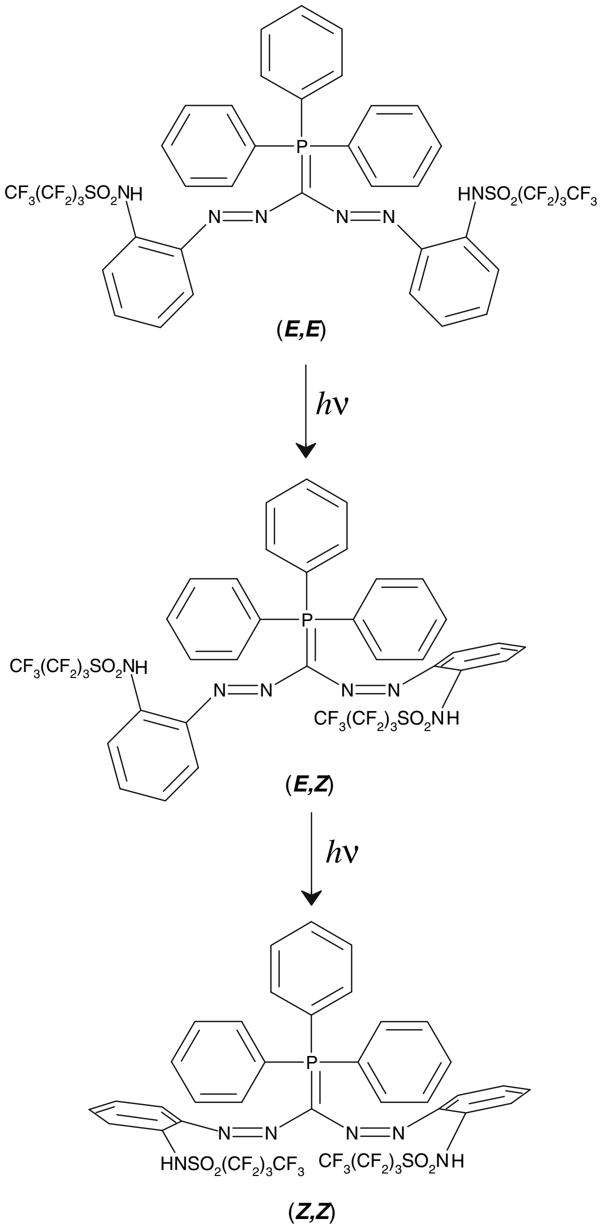

Fig. 3 *Trans* → *cis* isomerization steps for BAM-TPP (**1**) in the azo form **A**

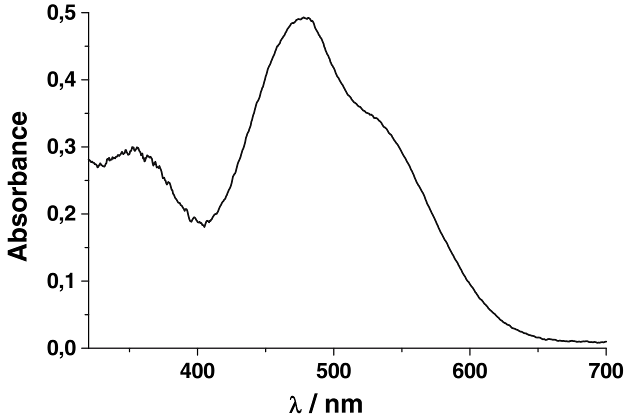

Fig. 4 Absorption spectrum of BAM-TPP (**1**) in basic acetonitrile upon addition of NaOH. Concentration of **1**: 7.4 × 10^{-5} M. Quartz cuvette thickness: 10 mm

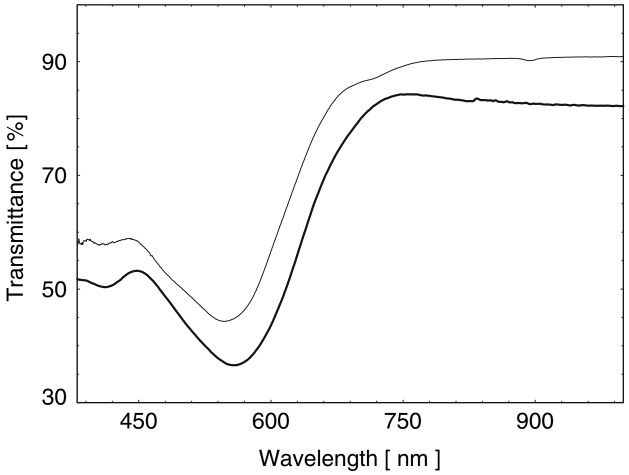

Fig. 5 Comparison between the optical transmittance of a 53.7 μm thick film of PMMA embedded with BAM-TPP (**1**) (thick line), and the corresponding starting solution of BAM-TPP in $CHCl_3$ (quartz cuvette thickness: 0.5 mm)

In order to induce a photochromic reaction the films of BAM-TPP(**1**) in PMMA were irradiated with a UV lamp with incident power 275 W. The UV dose was increased with consecutive exposures, each having a duration of 10 s. A spectrophotometer was employed to analyze the film transmittance after each UV exposure. The absorption spectra of films at normal incidence with increasing UV light dose are reported in Fig. 6. The optical changes provoked by UV irradiation on BAM-TPP(**1**) are the simultaneous decrease of the absorption peak at 560 nm and the increase of absorption at about 430 nm. The resulting spectrum resembles the one of a generic azobenzene in the *cis* (*Z*) configuration [9, 11–13]. By analogy, we associated such an effect to the formation of the *Z* isomers of BAM-TPP(**1**) in the azo form (Fig. 3) when in PMMA. The spectral changes induced by UV irradiation of **1** are analogous to the ones provoked by the addition of HCl in a solution of BAM-TPP(**1**) (Fig. 7). In fact, a new absorption peak appears at 430 nm with the concomitant disappearance of the peak at 560 nm, which characterized the spectrum of **1** in neutral solution (Fig. 2). In this context we suppose that UV irradiation of BAM-TPP(**1**) in PMMA brings about a transformation of the hydrazone tautomer **B** into the *cis* configuration of the corresponding azo tautomer **A** (Fig. 3). The lack of an isosbestic point in the spectral variations of photochromic BAM-TPP(**1**) in PMMA upon UV irradiation (Fig. 6) is ascribed to the existence of several conformations with varying extent of electronic conjugation for the *cis* configuration of **1** in the azo tautomeric form **A** (Fig. 3). Therefore, the photochromic effect produced by BAM-TPP(**1**) in PMMA is a consequence of a reaction of intramolecular proton transfer. The rate constant for such a process could not be evaluated because at the wavelength of analysis the changes of reflectance associated with the photochromic reaction of BAM-TPP(**1**) in PMMA are too low for being detected.[1]

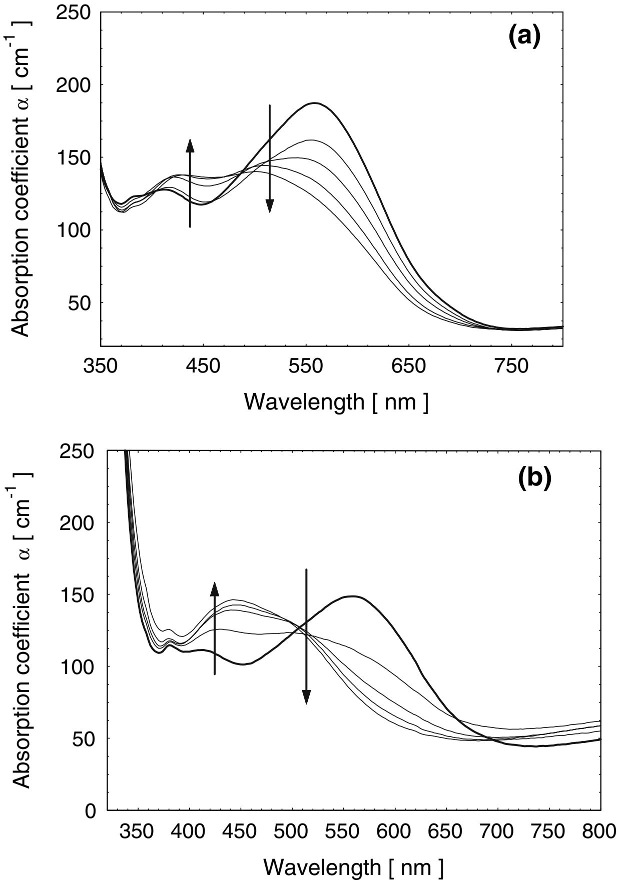

Fig. 6 Variations of the absorption coefficient, α, for two different films of BAM-TPP (**1**) in PMMA [film thickness values: (**a**) 53.7 and (**b**) 29.5 μm]. The thick solid line represents the film spectrum before UV exposure, while other lines stand for spectra taken every 10-s of UV exposure. The arrow head indicates the verse of spectral variations following the increase of UV dose

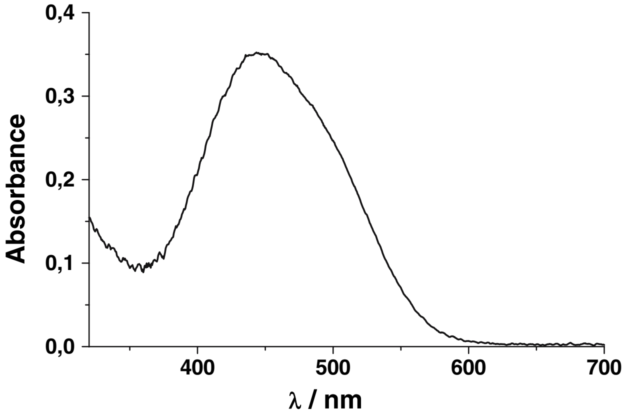

Fig. 7 Absorption spectrum of BAM-TPP (**1**) in acidic acetonitrile upon addition of HCl. Concentration of **1**: 7.4×10^{-5} M. Quartz cuvette thickness: 10 mm

The position of the initially strong absorption peak of BAM-TPP(**1**) (Fig. 6) at 560 nm is particularly attractive for optical switching and limiting applications [16]. In order to restore such a strong absorption of **1** after UV irradiation we determined the spectral changes induced by illumination with a green laser beam. The transmittance of

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[1] The evaluation of the rate of intramolecular proton transfer of a photochromic molecule embdedded in a polymer requires the determination of the change of reflectance at a critical wavelength that is sensitive to the photochromic effect. The reflectance should be detected only in correspondence of the surface on which the radiation first impinges. This is because the reflectance variations at the sole external surface are not affected by radiation diffusion phenomena through the sample with a finite thickness and by self-absorption of the inner layers of the sample.The kinetics of film reflectance variation is thus directly correlated with the kinetics of photo-isomerization of the photochromic molecule on the first layers of the reflecting sample.

both samples at 514 nm was recorded under increasing laser power. The experimental setup consisted of a CW Ar$^+$ laser (λ = 514.5 nm), lenses that focussed the light onto the samples with variable area of illumination, a photodiode to measure the transmitted signal at the chosen wavelength, and a 500 MHz digital oscilloscope to monitor the time evolution of the transmitted signal.

The time evolution of the transmitted signal for different power values of the incident light is reported in Fig. 8 for the thicker sample of **1** in PMMA (thickness = 53.7 μm). For incident power up to 30 mW the sample transmittance at 514 nm, T_{514}, is not altered (T_{514} = 47.5%). When the incident laser power is increased to 40 mW, some effects of transmission reduction at 514 nm take place (Fig. 8). At 50 mW the transmittance is further reduced to 37% after 1.4 s of irradiation with Ar$^+$ laser, while an additional power increase, 60 mW, results in irreversible sample damaging. The observed decrease of transmittance at 514 nm in the range of incident power 40–50 mW is ascribed to the back-tautomerization of **1** into the hydrazone form **B** (Fig. 1) in PMMA. The polymer film with smaller thickness (thickness = 29.5 μm) displayed a lower reduction of absorbance at 560 nm upon UV exposure with respect to the thicker sample (Fig. 6b). The variation of T_{514} for the thinner sample upon irradiation with Ar$^+$ laser was practically negligible and no optical damage at 514 nm occurred up to 100 mW of incident power. For this sample the optical stability of the film was not affected by the power of the Ar$^+$ laser beam in the adopted range. The reason for that has to be found in the lower absorption value at this wavelength due to the smaller amount of **1** in the film with respect to the thickest film, which prevented the laser damaging of the thinner film. Since the value of linear absorption at the investigated wavelength depends on the concentration of the photoactive molecules in the film, the obtained results indicate that by choosing the appropriate amount of photochromic BAM-TPP(**1**) in the film a suitable process of self-switching at a given wavelength of the visible range can be achieved.

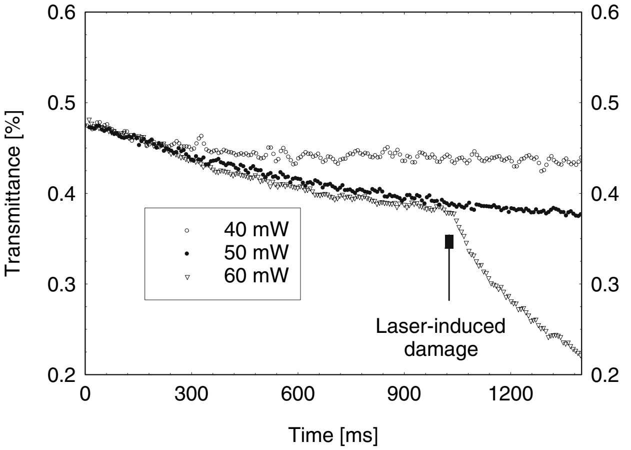

Fig. 8 Time profile of the reduction of transmittance at λ = 514 nm for film (**a**). Transmittance changes are induced by irradiation with Ar+ laser at different values of incident power: 40 mW (○), 50 mW (●) and 60 mW (∇)

Conclusions

Bis-perfluoroalkylsulfonylamino-arylazomethylene-triphenyl-phosphorane BAM-TPP(**1**) has been synthesized and its photochromic properties in thin films of PMMA have been investigated. In ambient conditions BAM-TPP(**1**) is formed by a mixture of both hydrazone and azo tautomers with predominant presence of the first tautomer. Upon UV exposure of the polymeric film containing BAM-TPP(**1**), the system undergoes spectral changes which are consistent with the formation of the azo isomer of BAM-TPP(**1**) possessing *cis* configuration with accompanying increase of transmittance in the visible spectrum. The back tautomerization process in the polymeric matrix could be induced with a CW Ar$^+$ laser. In particular, we found that transmittance at 514 nm is reduced to approximatively 75% of its initial value for an incident power of 40–50 mW of the Ar$^+$ laser. We also observed that a further increase of the incident power to 60 mW, results in laser-induced damaging of the sample. The dependence of the optical switching properties on BAM-TPP(**1**) concentration and film thickness was also determined. In this study it has been demonstrated that the investigated mechanism of photoisomerization of BAM-TPP(**1**) can be suitable for self-switching applications at wavelengths of the visible range.

Acknowledgements S. Macri at the Instituto Superiore di Sanità (Rome, Italy) is gratefully acknowledged for helpful discussion. This work was supported by EU NoE Phoremost.

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