Synthesis, characterization and photoisomerization behavior of some organic modified silica – azo dye hybrid films

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The paper presents organic-inorganic hybrid materials prepared from a derivative of 2-(4-aminobenzenesulphonyl)-ethanol having triethoxysilane groups, tetraethoxysilane and organic trialkoxysilane derivatives frequently used in sol-gel processes. Structure-properties relationships on obtained hybrid materials are discussed on basis of XRF spectrometry, FT-IR spectrometry, UV-VIS reflectance spectra and thermal analysis. Photoisomerization of the chromogen was studied in relationship with environments of the organic dye obtained by modifying silica network with different organic groups during sol-gel processes.

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1. Introduction

Preparation of solid-state optical switching devices from organic dyes and organic polymeric matrices, by dispersing or covalently linking to the polymer backbone (side-chain or main-chain type) is a difficult task, because of several restrictions that the host material must satisfy [1-6].

Hybrid organic-inorganic materials with chromogens grafted on the inorganic network have used in the last few years, in order to develop materials with optical switching properties [7]. This kind of materials are an attractive alternative to organic polymers, chemistry of sol-gel processing and the relatively low temperature of synthesis being compatible with organic dyes as guest molecules [8]. These materials have the advantage of an irreversible greater network rigidity, that can be achieved after chromogen orientation that leading to longer-term stability [9]. Furthermore, hybrid sol-gel materials are easily processed as films with excellent optical properties, and the aggregation of the chromogens does not occur even at high levels of functionalization [10].

One of the main tasks of this work was to study photochromic behavior of an azo dye derived from 2-(4-aminobenzenesulphonyl)-ethanol. The dye, which was previously prepared by us [11], was functionalized with 3-isocyanatopropyltriethoxysilane through a nucleophilic addition reaction and after that, obtained product was grafted on some silica organic networks modified with different organosilane reagents by simultaneous sol-gel processes. The materials prepared by us can be tailored through modifying the environments of the organic dye [12]. Thus, optical and thermal properties of the new materials were studied in relationship with the structure of the organic modifying agents and interactions with dyestuff molecules [13].

2. Experimental

2.1 Materials

Tetraethylorthosilicate (TEOS), methyltriethoxysilane (MeTES), phenyltriethoxysilane (PhTES), octyltriethoxysilane (OTES), titanium (IV) isopropoxide (TIP), dimethylsulphoxide (DMSO) and acetylacetone (AA) were purchased from Aldrich and used as received. Tetrahydrofuran (THF) was purchased from Carlo Erba and was purified by distillation followed by anhydrization on molecular sieves 3Å (Merck). Silicon anhydride (SiO_2 content: 83.71%) from Merck was used as standard for quantitative XRF measurements.

2.2 Procedures

Hybrid materials were obtained following a reaction pathway that consists of generating the inorganic matrix by hydrolysis-condensation of TEOS and different organosilane derivatives in the presence of (3-triethoxysilyl-propyl) carbamic acid 2-{4-[4-(benzyl-ethyl-amino)-phenylazo]-benzenesulfonyl} ethyl ester (AZPTES), in the usual manner of sol-gel processes.

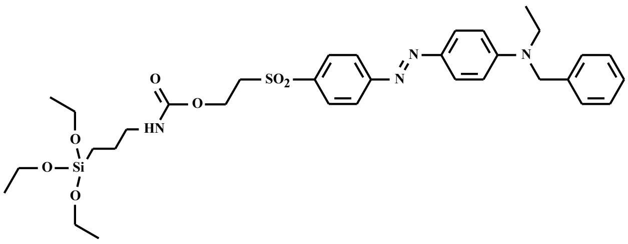


Fig. 1. Chemical structure of the chromogen (AZPTES).

Obtaining the hybrid composites

A solution made from 1.35 ml TEOS, 1.1 ml organosilane precursor (MeTES, OTES, PhTES), 3.25 ml AZPTES solution (1.68 g / 100 ml THF), 1.7 ml ethanol and a few drops of hydrochloric acid was stirred one hour at room temperature, and then it was added a mixture formed of 0.1 ml AA, 0.2 ml TIP and catalytic quantities of hydrochloric acid. The mixture was maintained under vigorous stirring at room temperature and used immediately for obtaining films by dip coating on microscope glass slides, previously cleaned in piranha mixture. All organic modified hybrid materials were prepared and used similarly.

Photoisomerization experiments

Hybrid films were deposited on glass slides by dip-coating and then the slides were dried at room temperature for 24 hours and cured thermally at 130^0C for 60 min. The films were irradiated with 470 nm linearly polarized light from a commercially available blue LED having a power of 60 mW and a light yield of 2.5 lm/W.

2.3 Measurements

UV-VIS absorption spectra of the filmogen materials were acquired in the range 380-780 nm using a spectrometer UV-VIS-NIR Jasco V-570.

FTIR spectra of the hybrid materials were recorded on a Jasco FTIR 6300 spectrometer equipped with an ATR Specac Golden Gate (KRS5 lens), in the range 400-4000 cm^{-1} (30 scans at 4 cm^{-1} resolution).

XRF analyses were performed on a PW4025-MiniPal-Panalytical EDXRF spectrometer. Measurements were carried out in helium atmosphere, for 300 sec., without any filter, at 20 kV and automatically adjustment of the current intensity.

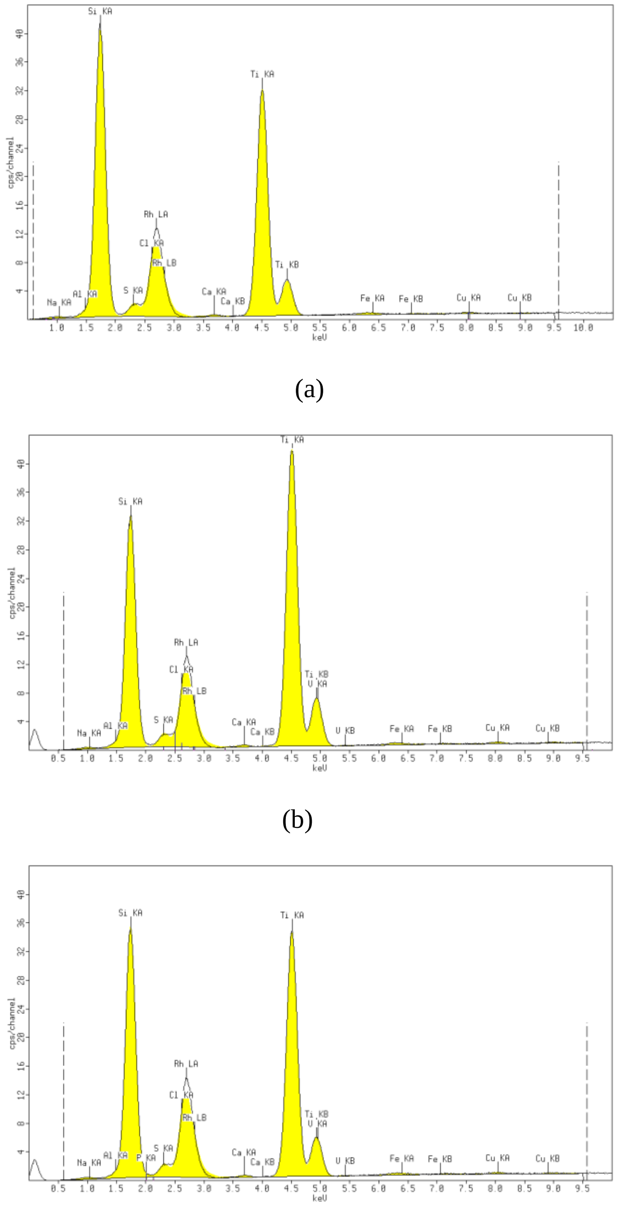
Thermal analysis was conducted on a TA Q 5000 IR instrument, in nitrogen atmosphere, at a heating speed of 10^0C/min. in the temperature range 25-900^0C (samples of 5-10 mg in platinum crucibles).

3. Results and disscusion

The aim of this work is to study hybrid organic-inorganic materials with chromogens obtained through sol-gel processes and to investigate photochromism due to azo dye linked to inorganic matrices and influences of different vicinities in the network on the trans-cis-trans isomerism.

Hybrid materials obtained by sol-gel methods from mixtures of silane precursors at specific ratio, exhibited major differences in optical, chemical and thermal properties. The main component of the sol was TEOS, while all the others components were used only as modifiers at a sufficient level, to establish major differences mainly in optical properties.

Hybrid composites obtained as a result of sol-gel reactions, which generate the inorganic matrices by hydrolysis-condensation of different organic modified trialkoxysilanes in the presence of AZPTES, were analyzed by means of XRF spectrometry and silicon content was determined related to a SiO_2 standard (Merck). The analysis performed for hybrid materials confirmed (Fig. 2) the presence of silicon in organic-inorganic hybrid samples. Quantitative analysis shows a silicon content of 12.6%, 11.18%, respectively 11.67% for the hybrid materials studied (MeTES, OTES, PhTES) which is consistent with proportion of organic residues in the matrices.



(a)

(b)

(c)

Fig. 2. X-ray fluorescence spectra of hybrid materials: (a) TEOS+MeTES; (b) TEOS+OTES; (c) TEOS+PhTES.

The hybrid materials were characterized also through UV-VIS absorption spectra and it was observed that environments created in the inorganic matrices, through variations in the organic residues from organic substituted trialkoxysilanes used for sol-gel reactions, establish different ways of interaction between the organic dye and the network and as a consequence, optical properties of the new obtained materials are modified in a large domain.

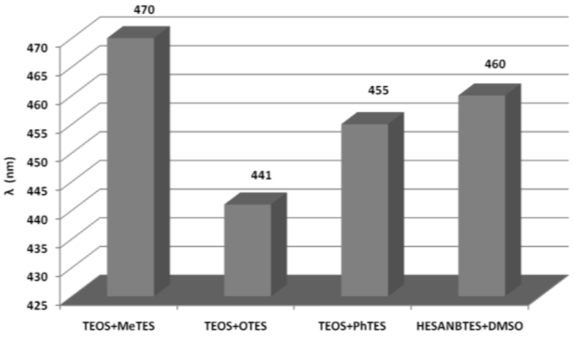


Fig. 3. Absorption maxima of the transparent hybrid films.

The nature and amount of organic groups determine the polarity of the inner surfaces of the pores, where the dyestuff molecules were located and therefore their spectral properties. If the surfaces of the pores are unmodified, the resulting matrix consists mainly of uncondensed OH groups, which confer a very polar environment. Grafting organic groups on the inorganic matrix lead in a decreased polarity of the network. The large organic chains may hinder the influence of the OH groups at the pores surfaces reducing further the polarity of the network.

For samples prepared from MeTES this effect is not observed due to the smaller size of the organic groups which prevents screening of the OH groups from the network. The shape and the larger size of the octyl groups are probably responsible for the more effective screening observed even in pores with relative high amounts of OH groups. Probably, micelle like structures is formed at high loadings that are able to accommodate the organic dye. Thus dye molecules are in an environment with a much lower polarity and the absorption maxima of the transparent film was shifted to lower wavelengths.

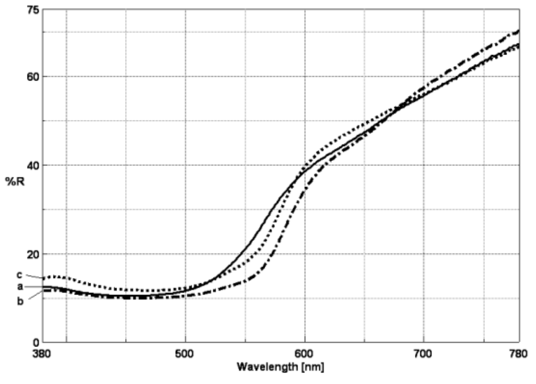


Fig. 4. Diffuse reflective spectra of hybrid materials: (a) TEOS+MeTES; (b) TEOS+OTES; (c) TEOS+PhTES.

For silica network modified with methyl residues the wavelength of the absorption maximum was bathochromically shifted to 470 nm. This behavior could be explained by easy interactions between OH groups from the silica network and carbonyl group from urethane residue of the chromogen, caused by the small volume of the methyl residue of the organic modified silica network. A similar behavior was recorded for the same dyestuff in DMSO solution, in which case the wavelength of the absorption maximum was situated at 460 nm, probably due to hydrogen bond interactions established between amino group from urethane residue of the chromogen and sulphoxide groups of the solvent.

For silica materials modified with phenyl residues having grafted on the backbone the same chromogen a hypsochromic shift of the wavelength of the absorption maximum to 455 nm was recorded. An explanation for this behavior could be linked to possible π-π interactions between phenyl rings of the organic modified silica networks and phenyl rings from the organic dyestuff. Moreover in this case the relatively high volume of the phenyl rings of the network probably hinder a possible interaction between OH groups of the silica network and urethane residue of the chromogen.

When octyl residues where employed for obtaining hybrid silica networks it was recorded the largest hypsochromic shift of the absorption maximum to 441 nm, on the one hand probably because of the apolar environment surrounding the chromogen and on the other hand because the voluminous octyl groups hinder sufficiently possible hydrogen bonds that can be established between OH groups of the silica network and urethane residue of the chromogen. Sustaining our theory are observations assuming that the voluminous non-polar groups of OTES tend to adhere to one another in polar environments of the silica matrix [14].

Analyzing UV-VIS diffuse reflective spectra for the obtained hybrids it was found that the largest value for the dominant wavelength was recorded for the hybrid material having PhTES as a modifying agent, while the lowest value was recorded for the material having MeTES as organic modifier.

The position of the dominant wavelength was found to depend on the matrix used for film preparation, a progressive shift to the ultraviolet was observed as the organic/silica ratio in the matrix was decreased. The position of the band was also found to depend on the nature of the organic substituent used in the matrix. In this sense samples prepared with phenyl groups showed a more significant batochromic shift of the dominant wavelength comparatively to samples prepared with aliphatic residues (OTES, MeTES). An explanation was the bulky phenyl ring that leads to a material with large pores and establishment of π-π interactions between dyestuff molecules and phenyl rings ultimately leading to associations.

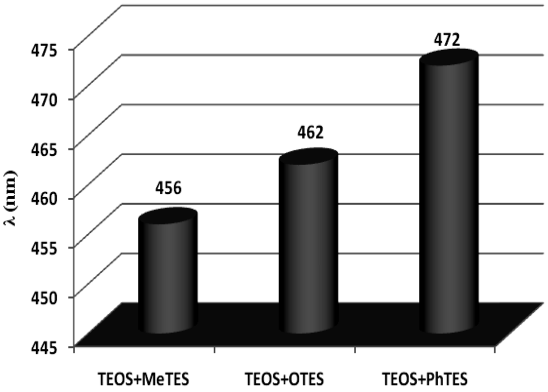


Fig. 5. Dominant wavelengths from diffuse reflective spectra of powder hybrid materials.

Infrared absorption spectra showed for all organic-inorganic hybrids investigated a broad absorption band centered at 3360 cm^{-1}, corresponding to O-H stretching vibrations of hydrogen bonded molecular water. Bands intensities were small, because the water content is low, as it was seen from thermal analysis. Characteristic for material obtained from PhTES was the presence of an absorption band situated at 3063 cm^{-1}, corresponding to ν (CH) aromatic stretching vibrations.

For the materials obtained from MeTES, infrared spectra exhibited the asymmetric stretching vibrations of the methyl group situated at 2976 cm^{-1}, respectively at 2958 cm^{-1} for silica films modified with OTES. For the last were observed two strong absorption bands belonging to the ν (CH) asymmetric stretching vibration situated at 2925 cm^{-1}, respectively at 2855 cm^{-1} for the symmetric stretching vibration.

Common for all the materials studied by us, are bands situated in the range 1584-1594 cm^{-1} and at 1525 cm^{-1}due to molecular water present into the network pores and characteristic vibrations δ(OH), δ (NH) and δ_{asym} (H_3C-Si). The weaker band at 1431-1465 cm^{-1} is due to asymmetric bending δ(CH) superposed with scissoring vibrations of hydrogen atoms of methylene groups. At 1271-1282 cm^{-1} it was detected a characteristic strong and sharp signal δ_{sym} (H_3C-Si) together with ν(C-O-H) stretching vibrations from alcohols.

For PhTES hybrid material at 1129 cm^{-1} was recorded a band corresponding to ν (Ph-Si) stretching vibration, while for all the materials the intense band at 1018-1045 cm^{-1} was attributed to asymmetric ν (Si-O-C) stretching vibrations

The bands situated at 931-933 cm^{-1} correspond to Si-O-Si stretching vibrations and the intense peak situated at 770-789 cm^{-1} was attributed to γ (H_3C-Si) deformation and ν (Si-C) symmetric stretching vibrations.

Other characteristic bands for PhTES hybrid material were situated at 736 cm^{-1} corresponding to δ (CH) and at 697 cm^{-1} to phenyl rings. Also the band situated at 444-449 cm^{-1} was assigned to Si-O-Si bending.

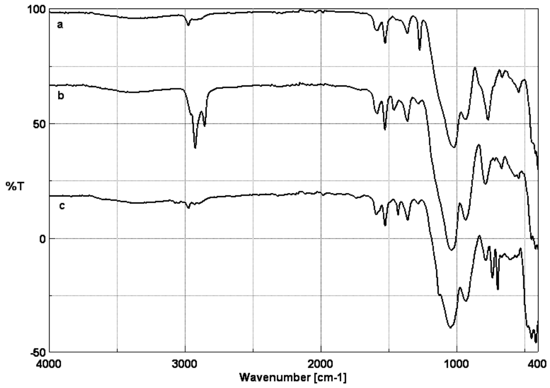


Fig. 6. FT-IR spectra of organic-inorganic hybrids: (a) TEOS+MeTES; (b) TEOS+OTES; (c) TEOS+PhTES.

The thermal stability of the hybrid films was determined by TGA analysis. As the temperature rises up to 100^{0}C materials loose in a first step volatile compounds (residual solvents and unbounded water) from sol-gel processes. The step was recorded having maximum of the mass looses, situated at 40^{0}C and weight lost was in accordance with hydrophobicity of the network. Thus OTES modified silica network presents the minimum weight loss of 0.9%, while MeTES modified films lose 1.82% and PhTES 1.37%, respectively.

Another step of decomposition was recorded till about 200^{0}C when the weight loss was 2.24% for octyl and 1.89% for phenyl modified network, amount that may be due to bounded water. The next step recorded is more important because was determined by the beginning of thermal decomposition of organic residues and weight loss is situated between 7.25-13.03%. Temperatures for maximum decomposition rate are 322^{0}C for MeTES, 311^{0}C for OTES and 329^{0}C for PhTES. Based on this property, we can estimate that thermal stability of the hybrids increase in order PhTES, MeTES, OTES.

The largest thermal effect due to decomposition was recorded in the next step, weight loss being situated in the range 11.08-35.5%, that probably correspond to condensation to siloxyl groups and temperatures for maximum decomposition rate varied in the same order, from 508^{0}C for OTES modified network, to 540^{0}C for MeTES and 556^{0}C for PhTES, respectively.

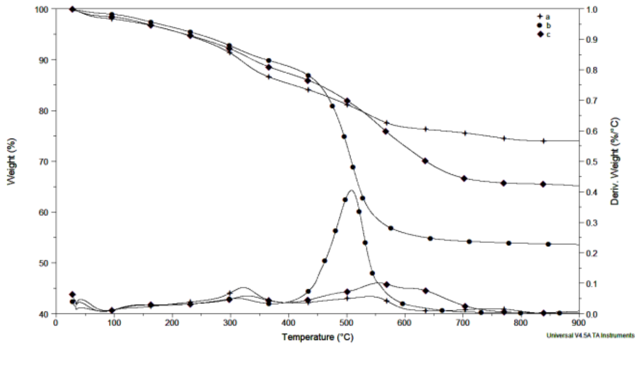


Fig. 7. TGA of the hybrid materials: (a) TEOS+MeTES; (b) TEOS+OTES; (c) TEOS+PhTES.

Residues at 900^{0}C are in accordance to organic rest grafted on the network and consisting of charcoal and silicon dioxide. The amount varies from 53.61% for OTES (the largest molecular weight of the organic group), to 65.15% for PhTES and 74.04% for MeTES.

From thermal analysis it was very clear that the chemical structure of the organic group bounded to the silicon atom is extremely important for the thermal stability of the hybrid network. It was seen that the most thermally stable material from the series was PhTES modified silica network.

Sol-gel silica hybrid materials studied by us contain an azo dye covalently bounded to silica matrix through a flexible spacer. This approach allows to obtain increased concentration of the dye without aggregation phenomena and crystallization and to tailor molecular and optical properties of the material. The spacer improves the flexibility of the dyestuff and had an effect on response rate of the materials on illumination.

Because n-π^* transition peak characteristic for cis isomer correspond to a forbidden band, the absorption coefficient is lower than that corresponding to π-π^* allowed band for trans isomer. Thus, under irradiation the enhancement of cis isomer n-π^* transition peak is practically unobservable, while weakening of trans isomer π-π^* transition peak is very well observable. Isosbestic points in the spectra sustain isomerization and eliminate the probability to interpret weakening of trans isomer π-π^* transition peak as a result of photodegradation.

A LED light operating at 470 nm in resonance with AZPTES intense electronic transition in the visible domain, has been used in the irradiation experiments, because a good matching of the absorption wavelength with the wavelength of the excitation light, has a positive effect on efficiency of the process.

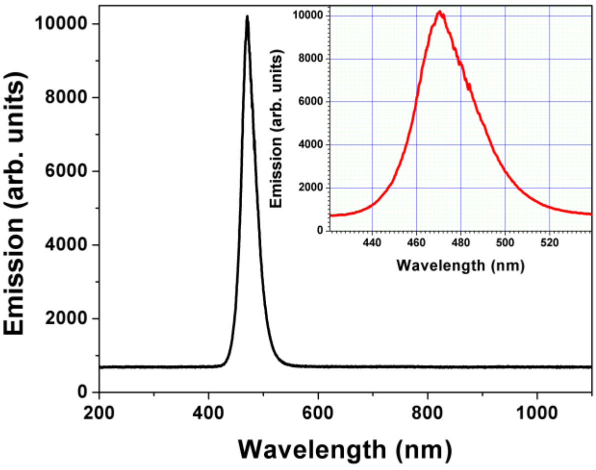


Fig. 8. Emission spectra of the blue LED used for photoisomerization experiments.

UV-VIS absorption spectra of the sol-gel hybrid films made by dip coating technique, were recorded to investigate trans-cis isomerization of the azo moiety and by comparison the chromogen AZPTES as solution in DMSO. The materials investigated underwent isomerization even during short time illumination with a light of relatively low power. Thus trans-cis photoisomerization was observed under the exposure to blue light from a blue led.

The maximum absorption band of the stable trans form of the AZPTES dye in DMSO solution, was situated at λ=460 nm. For transparent films coated on glass slides the maximum of the absorption spectra recorded, were situated at 470 nm for MeTES, 441 nm for OTES, and 455 nm for PhTES silica modified networks, respectively. The bathochromic shift of the maximum absorption band of the chromogen grafted on the hybrid material, made of TEOS/PhTES comparatively to TEOS/OTES might be ascribed to interactions between aromatic groups from organic residues of the inorganic network and azo dye molecules and between azo dye molecules itself.

The highest degree of isomerization was recorded for (TEOS/PhTES) hybrid material, while for (TEOS/OTES) material it couldn't be observed a linear transformation of the azo chromogen at successive irradiation cycles. The reason was the thermal cis-trans transformation which occurs very fast, probably because of the "solvent like" behavior of the octyl residues grafted on the inorganic network, as environment for the azo dye. Similarly, in organic solutions like DMSO, experimentally we couldn't record any visible tran-cis transformation for AZPTES. Probably, after generation of the metastable cis isomer, the azo groups relaxed thermally to the thermodynamically stable trans form and recover initial state relatively fast, due collision with more mobile solvent molecules. Thus in solutions mobility is higher enough to determine the kinetic behavior and thus processes are faster than in solid matrices.

Only for materials having rigid and voluminous residues grafted on the network, the stability of the cis form was high enough to be recorded. The absorbance specific to the trans form decreased and the other band attributable to the cis form appear probably at short wavelengths, ca. 375 nm. The presence of an isosbestic point around λ=393 nm for TEOS/MeTES hybrid material and at λ=389 nm for TEOS/PhTES material, demonstrates that no noticeable photodegradation occurred.

The absorption changes very fast at first and the rate becomes very slow after 3 minutes indicating that the equilibrium was reached, while after switching off the irradiation light the reverse process took place relatively fast, due to the thermal relaxation of the photoisomerizable units, to the thermodynamically stable trans ones and the time for full recovery of its original color intensity was within 1 minute.

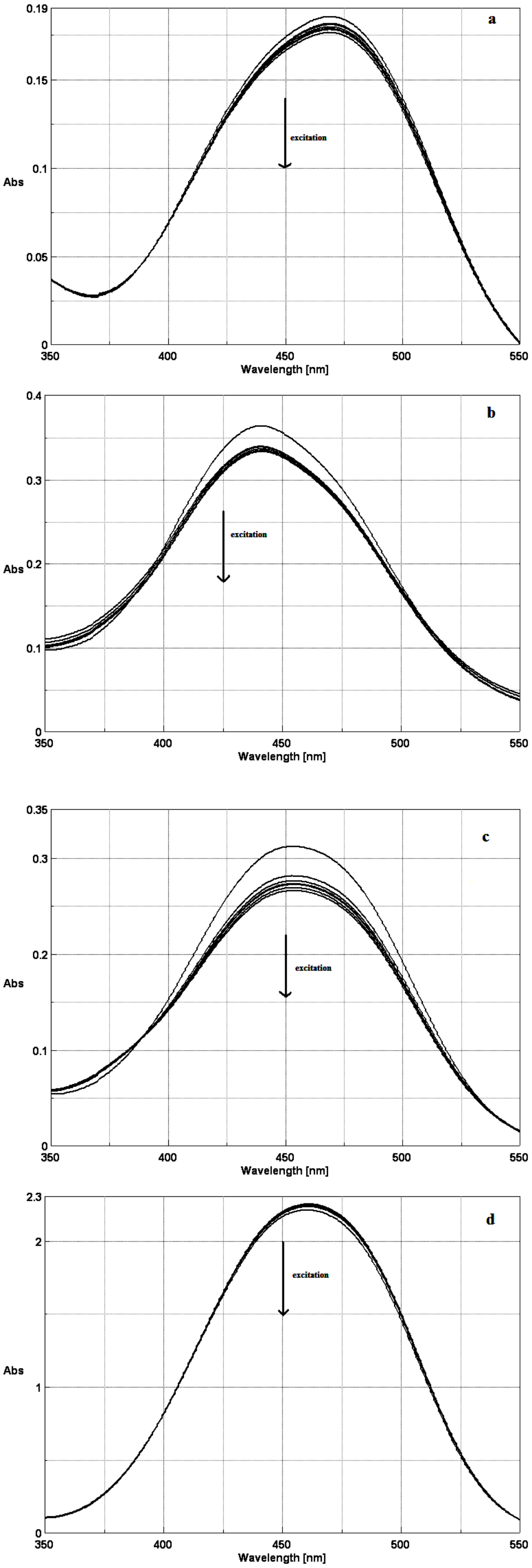


Fig. 9. Photochromic behavior: (a)TEOS+MeTES; (b)TEOS+OTES; (c)TEOS+PhTES;(d)AZPTES in DMSO.

As a conclusion of the photoisomerization experiments, the main factors that influenced the photochromic behavior of the dye, were its structure rigidity and environment in the matrix. When the rigidity of the host is high, organic dye within, will be completely immobilized and molecules separated from each other. In a less polar environment, less polar form of azo dye (trans) would be favored, while a more polar environment would stabilize the more polar form cis. This was the main reason for marked differences in kinetics of the isomerization process for all three types of materials investigated. For hybrid materials investigated by us, degree of isomerization at increasing irradiation time varied in order PhTES>TEOS>OTES>DMSO.

4. Conclusions

New organic-inorganic hybrid materials containing an azo dye covalently linked with different organomodified silica matrices, were prepared through sol-gel processes, from different alkoxysilanes and AZPTES, as an azo chromogen bearing triethoxysilane residues, and their properties are discussed with respect to the structure and nature of the organic modifying agents.

The spectral and dynamic properties of the azo dyes in organic modified silica matrices could be controlled by the composition of the matrix. Organic groups covalently attached to the silica network, have provided a way of controlling the pore surface and as a result the polarity of the dyestuff environments, while the spacer improve flexibility and mobility of the dye, prevent aggregation and have an effect on response rate of material on illumination.

The films deposited on glass plates, even at low power of excitation blue light, show reversibility of the trans-cis photoisomerization of the chromogen without recording any photodegradation phenomena. Matrices having a decreased polarity or a higher volume of the organic modifying groups, leads to an accelerated isomerization process of the dyestuff molecules upon irradiation.

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