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Luminescence properties of pHEMA-TiO₂ gels based hybrids materials

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Abstract

Photoluminescence (PL) of photochromic pHEMA-TiO₂ gels-based hybrids was studied by means of time- and energy-resolved spectroscopy at temperatures between 300K and 10K. The PL band at 485 nm is assigned to S₀←T₁ transition of methoxyphenol (organic molecule added to the commercial monomer hydroxyethyl methacrylate, HEMA and used as an inhibitor of spontaneous polymerization) in the polymer environment, while the PL band at 600 nm is assigned to the self-trapped exciton onto octahedral TiO₆ site of the inorganic component. The mechanisms of the excited states population are discussed. In particular it is shown that both singlet-triplet energy transfer in methoxyphenol and methoxyphenol-TiO₂ charge transfer are strongly affected by the material composition and temperature. The hypothesis about the photoexcited holes annihilation with the trapped electrons is confirmed to be one of main mechanisms limiting the Ti³⁺ centres concentration.

I Introduction

Hybrid organic-inorganic compounds have deserved much interest last decade [1-4]. Their important advantage consists in combining useful properties of both constituting components, e.g. the flexibility and shaping versatility of organic polymer and high refraction index of the inorganic component. Consequently, they have been considered for many potential applications in photonics, biomedicine, etc [5]. Besides many efforts, electronic structure of the fabricated hybrid materials has not been yet adequately addressed. In fact, a large interface between the two constituting components of these open-structure materials can strongly affect their bulk electronic structure and electron transport properties [6]. Among these hybrid materials, titania-based hybrids deserved a particular interest because of the reversible photochromism. Previously, we have reported on elaboration of the TiO₂ gel-based hybrids including macroscopic interpenetrating inorganic oxo-titanate, and organic poly(hydroxethyl methacrylate) PHEMA, networks [7]. These nanocomposites obtained without shrinkage show high transparency and mechanical stability, allowing optical-grade surface polishing, as well as high photonic sensitivity, which permits 3D laser writing [7, 8]. Well-defined nanoparticulate pHEMA-TiO₂ hybrids with record charge separation efficiency have been recently demonstrated [9]. The photochromism of the pHEMA-TiO₂ hybrids is related to the efficient charge separation at the organic-inorganic interface: the conduction-band (CB) electron remains in the inorganic component whereas the valence-band (VB) hole leaves to the polymer component. The electron localisation as polaron-like Ti³⁺ centre explains the material absorption in the visible spectral range according to: $Ti^{3+} + h\nu(VIS) \rightarrow Ti^{4+} + e^{-}(CB)$. The relevant physical mechanisms have been discussed in Refs [10, 11]. While the charge separation efficiency appeared to be dependent on the inorganic unit size and morphology, the maximum number density of the photoinduced Ti³⁺ centres that the material can acquire is determined by several limiting mechanisms, which becomes important at high electron loadings. In particular, (i) recombination of rapid VB

holes with Ti^{3+} centres and (ii) annihilation of the trapped charges due to the Ti^{3+} reoxydation by oxygen were proposed to be two major sources of the darkening efficiency decrease.

Electronic applications of the organic-inorganic hybrids require reversibility of the charge storage process and its photonic control. Therefore, detailed understanding of photo-generated charges recombination processes and analysis of the interface energy and charge transfer become to be of paramount importance. It is not clear to what extent the electronic structure and charge and energy transfer processes are controlled by the constituting components and by the interface between them.

In this paper we report on first study of the organic-inorganic hybrids by means of time- and energy- resolved photoluminescence (PL) spectroscopy with synchrotron radiation (SR), in a broad range of temperatures from 300K to 10K. The pHEMA-TiO₂ materials are considered with traces of methoxyphenol, which is a standard component in HEMA monomer used for its stabilisation against spontaneous polymerisation, and in the same time strongly emitting chromophore. We assign the observed PL emission bands and discuss energy and charge transfer mechanisms in the hybrid materials.

The article is organized as follow. The PL experimental setup and sample preparation procedure are described in section II. The PL properties of organic and inorganic components of hybrids are discussed in section III. Finally, in the section IV we discuss peculiarities of energy relaxation channels in our hybrid material.

II Experiment.

The luminescence properties of samples were studied using VUV synchrotron-radiation (SR) source of DORIS storage ring at HASYLAB (DESY, Hamburg). The facility of the SUPERLUMI station used in the experiments is described in details elsewhere [12]. Briefly, samples mounted on cryostat were cooled down to 8K and excited with monochromatized SR ($\Delta\lambda=3.3\text{\AA}$) under high vacuum ($\sim 10^{-9}$ mbar). The measurements of luminescence

spectra were carried out using a visible 0.275-m triple-grating ARC monochromator equipped with a CCD detector or a photomultiplier operating in the photon-counting mode. The pulse structure of SR (130 ps, 5 MHz repetition rate) enables time-resolved luminescence analysis at time-scale of 200 ns with sub-nanosecond temporal resolution. Spectra were recorded within a time gate $\Delta\tau$ delayed after the SR excitation pulse. Typically two time gates have been used simultaneously: a fast one of $\Delta\tau_1=2-8$ ns and a slow one of $\Delta\tau_3=50-200$ ns. The recorded spectra were corrected for the primary monochromator reflectivity and SR current.

The samples were prepared according to a method proposed by Kameneva et al [7, 8]. In short, the chemical modification of titanium tetraisopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$ or TTIP) by 2-hydroxyethyl methacrylate (HEMA) was firstly carried out at room temperature; the released 2-propanol was gently pumped out on mixing overnight. The new modified precursor $\text{Ti}(\text{OEMA})_4$ is obtained at the end of the exchange stage. The residual traces of 2-propanol in the precursor solution in HEMA were less than 5% according to a control of the HEMA (1640 cm^{-1} and 905 cm^{-1}) and 2-propanol (818 cm^{-1}) Raman bands intensity [7, 9]. The precursor dissolved in HEMA was then hydrolyzed in acidic conditions to generate the macroscopic titanium-oxo network via polycondensation (gelation). The typical composition of the samples was $\text{Ti}/\text{HEMA}/\text{H}_2\text{O}/\text{H}^+=1/6/3/0.18$ (molar ratio) and titanium concentration of 2.0 mol/l, which shows the gelation time about 10 min. After completing the gelation stage, free-radical polymerization of Ti-bound and free HEMA monomers was carried out thermally in the presence of azobisisobutyronitril (AIBN) as thermal radical initiator. The polymerization was proceeded at $65\text{ }^\circ\text{C}$ for 20 hours and then at $120\text{ }^\circ\text{C}$ for 3 hours.

III Results.

The PL of the pHEMA- TiO_2 gels-based hybrids at cryogenic temperatures is shown in figure 1a. Depending on excitation wavelengths two broad luminescence bands, red (H1) and blue (H2), are observed respectively at 600 nm (2.06 eV) and 485 nm (2.55 eV). Both

emissions are characterized by a microsecond lifetime: on a timescale of 200 ns, which corresponds to the interval between two SR pulses, their intensities do not change. Both PL bands exhibit strong sensitivity to temperature: their intensity attains maximum below 100K and becomes negligible at room temperature (see in figure 2).

Different origins of the two observed PL bands are evidenced from PL excitation (PLE) spectra shown in figure 1b. The H1 band appears at excitation wavelengths longer than 250 nm (below 250 nm the spectrum is featureless). Its intensity increases monotonically from 250 nm to 330 nm (the cut off at 330 nm is due to the primary monochromator). Conversely, the H2 band is only detected at excitation shorter than 250 nm. Its PLE spectrum shows three broad maxima: at 225 nm, 180 nm and 160 nm.

We assign the PL bands H1 and H2 respectively to radiative transitions involving inorganic and organic components of the hybrid material. The assignment discussed below is based on the comparison with the PL of basic constituents of hybrid samples: titanium-oxo-alkoxy nanoparticles and pHEMA.

III.1 Organic component luminescence

Prior to discuss the origin of the luminescence band H2 observed in the hybrids samples at 485 nm, we will first analyse luminescence observed in polymer pHEMA samples. The time integrated PL spectrum of pHEMA is shown in figure 3b. It is composed of two bands: O1 band with a rather symmetric shape with maximum at 330 nm (3.81 eV) and broad asymmetric-shape O2 band with maximum at 420 nm (2.95 eV).

The time-resolved photoluminescence method allows separating of contributions from different superposed PL bands if their respective lifetimes are noticeably different. Time-resolved luminescence spectra of pHEMA, integrated respectively in short $\Delta\tau_1$ and long $\Delta\tau_2$ time-windows are shown on the figures 3c and 3d. These measurements evidence a short lifetime of the O1 band characterised by the monoexponential decay law with lifetime of 2.6 ns. In contrast, the O2 band has much longer lifetime.

The organic component (HEMA) of the fabricated hybrids does not have any active chromophore groups and is not expected to be a luminescent material. The observed luminescence can originate from small quantities of methoxyphenol, used as the inhibitor of spontaneous polymerization and added to the commercial HEMA product. Spectroscopic data about electronic states of methoxyphenol are rather rare and fragmentary in literature [13]. However, it is possible to argue on available data for other similar molecules: hydroquinone, dimethoxybenzene, phenol, etc. Indeed, a broad fluorescence around 330 nm from hydroquinone in water solution at room temperature is reported in references [14, 15]. Moreover a phosphorescence around 420 nm, assigned to the $S_0 \leftarrow T_1$ transition, has been previously observed at low temperature in dimethoxybenzene [16]. Taking into account the measured lifetimes and general picture of phenolic compounds [17], we have assigned the O1 (330 nm) and O2 (420 nm) bands observed in pHEMA sample, respectively to the singlet $S_0 \leftarrow S_1$ and triplet $S_0 \leftarrow T_1$ radiative transitions of methoxyphenol molecule. This attribution of bands has been confirmed by PL luminescence of methoxyphenol crystals at cryogenic temperature (8 K). Except for the intensity ratios, the obtained spectra in figure 4 are very similar, in terms of the energetic positions and lifetimes of the PL bands, to those observed in pHEMA sample.

The PLE spectra of solid methoxyphenol are shown in figure 5a. The short-lived PL band at 330 nm (figure 5a) is in a good agreement with the absorption spectra of hydroquinone and dimethoxybenzene in different environments [18, 19] that confirms its assignment to the lowest singlet state of methoxyphenol. The PLE bands at 280 nm and 225 nm can then be attributed to the $S_0 \rightarrow S_1(\pi, \pi^*)$ and $S_0 \rightarrow S_2$ transitions. Moreover, we assign the intense peak at 190 nm to the $S_0 \rightarrow S_3$ transition. The PLE spectrum intensity vanishes below 175 nm apparently due to the ionisation limit, which is 7.71 eV for free methoxyphenol molecule [13].

The PLE spectrum of the triplet state phosphorescence at 420 nm (figure 5b) looks very similar to that of the singlet state fluorescence, evidencing a common origin of both PL bands. This is explained by an efficient intersystem energy conversion at low temperatures.

Indeed, PLE spectra can be discussed in terms of the material absorption only in first approximation. More precisely, they include two contributions: absorption (A) and energy transfer (ET) to an excited state, which luminescence is observed: $PLE = A \otimes ET$. Therefore, a comparison of PLE bands intensities resulted in $S_0 \leftarrow S_1$ (figure 5a) and $S_0 \leftarrow T_1$ (figure 5b) emissions shows that a part of the S2 and S3 states excitation directly relaxes to the T1 state and avoids the S1 state. This is in a strong contrast with solute methoxyphenol, which manifests the dominant emission of the lowest singlet S1 state (see dotted curve in figure 4a).

The PLE spectra observed in pHEMA polymer samples are presented in figure 5 as well. They are quite different from those of pure methoxyphenol. The PLE spectrum of short-lived S1 emission at 330 nm (figure 5a) exhibits only one band at 280 nm corresponding to the $S_0 \rightarrow S_1$ transition whereas the higher-lying singlet states do not show up. In contrast, the PLE spectrum of long-lived T1 state (figure 5b) is observed at excitation of S1, S2 and S3 singlet states. This indicates a strong interaction between methoxyphenol molecule and polymer chains, which prevents the internal energy conversion to the S1 state and favours direct intersystem energy conversion to the triplet states. Furthermore as this can be seen in figure 5b, the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions are relatively less intense than the $S_0 \rightarrow S_1$ one and red shifted with respect to the bands observed in solid methoxyphenol. This shift could be explained by dielectric relaxation of polymer matrix around excited dipole. Interestingly, the contribution of states above the ionization limit to the triplet emission becomes significant, which confirms the above conclusion about the polymer matrix contribution to the relaxation pathways. Actually, due to its supposed negative electron affinity, the pHEMA matrix can not accommodate an extra electron and favours the recombination inside the methoxyphenol molecule. A similar effect of ionisation suppression induced by the environment has been previously reported in He clusters [20].

Based on the above observations, the schemas of energy relaxation channels at low temperature in solid methoxyphenol and methoxyphenol molecules in pHEMA matrix are

shown in figure 6. On this figure the rate constants k_S , k_{ST}^* , k_{ST} and k_T stand for respectively: internal conversion $S_2, S_3 \rightarrow S_1$, intersystem crossing $S_2, S_3 \rightarrow T_2, T_3$, intersystem crossing $S_1 \rightarrow T_1$ and internal conversion $T_2, T_3 \rightarrow T_1$ processes.

The solute methoxyphenol molecules show only singlet state transition: the energy relaxation goes down to the lowest S_1 state (dotted curve in figure 4). Conversely in solid environment at low temperature, an exchange between states with different multiplicity is no more strictly forbidden. In solid methoxyphenol, both singlet S_1 and triplet T_1 states are populated after excitation of S_2 , S_3 and higher-lying singlet states up to the ionisation limit (figure 6a). In contrast, the energy relaxation channels of methoxyphenol molecules in pHEMA polymer matrix are modified (figure 6b). While $S_1 \rightarrow T_1$ energy conversion takes place, no energy relaxation $S_1 \leftarrow S_i$ ($i \geq 2$) appears. This means that the polymer alters the coupling between singlet and triplet states leading to an isolation of the lowest S_1 state, which can receive energy only by a direct excitation.

Keeping in mind the above attribution of the PL bands, we discuss below the origin of the H2 band in PL of the pHEMA-TiO₂ hybrids (figure 1a). Methoxyphenol (MQ) is known to form Ti-MQ complexes [11], which are responsible for yellowish coloration of samples. Based on its long lifetime, similar shapes and spectral position, we assign the H2 PL-band observed at 485 nm to the triplet state luminescence $S_0 \leftarrow T_1$ of this Ti-MQ complex.

The PLE spectrum of pHEMA-TiO₂ hybrids supports this assignment. Two excitation transitions at 225 nm ($S_0 \rightarrow S_2$) and 190 nm ($S_0 \rightarrow S_3$) observed in methoxyphenol molecule show up in figure 1b. As in case of pure polymer environment, the both excitations do not contribute to the lowest S_1 singlet state population. However in contrast to pure polymer environment, the $S_0 \rightarrow S_1$ band at 280 nm does not manifest itself neither in short-lived singlet $S_0 \leftarrow S_1$ nor in long-lived triplet $S_0 \leftarrow T_1$ luminescence spectra. This observation allows concluding about a strong quenching of the S_1 state by the inorganic component (TiO₂) of the hybrid. We will discuss this point in section IV.

This red shift of the H2 PL-band (485 nm) compared to the O2 band (420 nm) by 0.4 eV is characteristic of hybrid materials and conveys the interaction between their two constituting components. Considering a large polarisability of TiO₂ lattice [21], this shift is likely due to a polarization of TiO₂ nanodomains in the vicinity of the excited methoxyphenol molecule. Moreover this shift is not constant and depends on hybrid samples composition and morphology: we have observed spectral positions of S₀←T₁ luminescence ranging from 460 to 500 nm depending on the sample preparation. In particular, both higher Ti concentration and longer aging before polymerization result in a stronger red shift of the H2 PL-band. This finding could account for variability of the material nanoscale morphology, which depends on aging time of the inorganic gel, varying from isolated nanoparticles to macroscopic branched chains.

III.2 Inorganic component luminescence.

Titanium-oxo-alkoxy nanoparticles assembled in gel chains constitute the inorganic component of the hybrid sample. Therefore, it is instructive to compare both spectra of the inorganic component alone and mixed with the polymer.

The luminescence spectrum of pure titanium-oxo-alkoxy nanopowder sample obtained after the colloid precipitation and drying is shown in figure 3a. This luminescence is also very weak and can be successfully observed only at low temperatures $T < 100\text{K}$. The spectrum looks similar to that of the pHEMA-TiO₂ hybrids (band H1 on figure 1a). Moreover, both excited states have long lifetimes. Additionally, the PLE spectrum of the nanopowder (not shown in the figure) is identical with that observed in the hybrid samples (figure 1b). It is therefore reasonable to conclude about the inorganic origin of the H1 luminescence band observed at 600 nm (2.06 eV) in the hybrids. Moreover because the H1 band shows no appreciable sensitivity to surrounding solvents, the emitting species are not related to an excited state at the organic-inorganic interface and/or do not interact with the polymer component.

In many titania compounds, a broad-band emission has been observed in the visible spectral region and assigned to radiative recombination of a self-trapped exciton (STE) [22]. For example, in anatase TiO_2 under interband photo-excitation this luminescence is found at ~ 2.3 eV with $\Delta_{\text{FWHM}}=0.6\text{--}0.7$ eV [23-29]. From the steepness parameter of the Urbach tail, Tang et al. [30] have concluded about the stability of STE in anatase TiO_2 and ascribed the observed PL to the radiative recombination of the STE localized into TiO_6 octahedron. Such centre can also be considered as charge-transfer exciton due to correlated electron-hole states, where the electron is located in a neighbor site to that one where the hole is located. Optical transition involving charge-transfer excitons have generally weak oscillator strength. In pHEMA- TiO_2 hybrids this exciton is formed due to a Coulomb interaction of a conduction band (CB) electron located as polaron-like Ti^{3+} within TiO_6 octahedron with a valence band (VB) hole built on a neighbour oxygen atom. Formation and relaxation processes of Ti^{3+} polarons are discussed in details in ref [11]. In agreement with the experimental observations, a lower dielectric constant of the organic-inorganic hybrids (compared to the anatase and rutile titania polymorphs) results in a strongly bounded CTE and, consequently, stronger shift of the STE PL band to red spectral region: 2.06 eV in the hybrids versus 2.3 eV in solid TiO_2 . The H1 luminescence lifetime is long, $\tau > 200$ ns, which is in agreement with previous observations of the relevant titania emission [31].

Different contributions to this emission were proposed based on the Gaussian-type band decomposition: STE (2.40 eV) and STE bound to reduced Ti^{3+} centres (2.15 eV) and oxygen vacancies (1.95 eV) [23-29]. Oxygen vacancies are known defects in TiO_2 nanoparticles. If excitons are trapped near oxygen vacancies, their energy level can be lowered by the extrinsic or impurity assisted self trapping process [32]. As a result, the luminescence band corresponding to exciton shifts to low energies. Such influence of oxygen vacancies on the STE luminescence has been recently reported in anatase TiO_2 thin films [33]. Since the observed H1 band (2.06 eV) fits the low-energy component observed in anatase at 1.95 eV, it might be explained by the presence oxygen vacancies. However, our hybrid materials are obtained at relatively low temperatures (below 100°C), which makes appearance of oxygen

vacancies less probable. More probably, the STE band earlier reported at 2.15 eV in anatase TiO_2 [34] can be the origin of H1 band observed in pHEMA- TiO_2 hybrids. The slightly lower energy in the hybrids may be related to a non-crystalline nature of the TiO_2 nanoparticles. Consequently, the exciton localization is favoured by a lower compactness of the TiO_6 octahedral units in the hybrids. It seems then reasonable to keep the STE assignment for the inorganic component luminescence observed in our pHEMA- TiO_2 hybrid sample.

In titanates compounds the electrons, promoted to CB by UV-photon absorption, form small polarons. At low excitation densities, these polarons interact with VB holes trapped near crystal defects or impurities resulting in STE [35]. A similar process may occur in the titanium oxide hybrids. At UV photons absorption, a majority of the VB holes escape to the pHEMA component while a very small part is trapped on the inorganic TiO_2 gel nanoparticles, probably at their surface. This bulk polaron – surface hole complex may result in the observed weak H1 luminescence. Between plausible explanations of the VB-hole stabilisation allowing charge-transfer exciton formation, one can mention non-polymerised OEMA ligands, adsorbed methoxyphenol molecules and residual 2-propanol after the exchange stage of the material preparation.

IV Discussion.

Based on the above bands assignment we can draw conclusions concerning energy relaxation channels in nanostructured pHEMA- TiO_2 hybrids.

The observed tendency to the increase of the PL intensity in pHEMA- TiO_2 hybrids with temperature lowering (figure 2) is characteristic of the thermally activated energy transfer, which leads to the excited state quenching. The relevant excited states may not be necessary the emitting states (S1 and T1 in methoxyphenol and STE in TiO_2) but also higher-lying excited states, which relaxation produces the emitting states population; therefore, many excited states contribute to each of the observed PL.

We remark that our experimental data cannot be satisfactorily described by single activation energy. The solid lines in figure 2 are traced with a model explaining the variation

of the normalized PL intensity (I) by an energy transfer involving several electronic states (i) characterized by different activations energies E_i of thermal quenching:

$$I_1 = \left(1 + \sum_{i=1}^n r_i e^{-E_i/kT} \right)^{-1} \quad (1)$$

$$I_2 = \prod_{i=1}^n \left(1 + r_i e^{-E_i/kT} \right)^{-1} \quad (2)$$

where r_i is a constant reflecting the branching ratio of the energy-transfer and quenching relaxation channels from the i -th state and kT is the thermal energy. Two presentations can be used. Eq. (1) describes an emitting state quenching through different channels, while Eq. (2) describes a cascade energy transfer towards the emitting state. Accordingly to the previous discussions, we ascribe the models presented by Eq. (1) and Eq. (2) respectively to luminescence of inorganic and organic components of the hybrids. The obtained couples of parameters (E_i , r_i) are given below. We want to remark that the fit is more sensitive to the energy parameters E_i than to amplitude parameters r_i which are rather indicative. Two energies of 8.5 meV ($r=3.2$) and 43 meV (50) were sufficient to successfully describe the H1 band with Eq (1) while three energies of 11 meV ($r=2$), 30 meV (2) and 65 meV (120) were needed to describe the H2 band with Eq. (2).

The exciton emission in anatase [34] is known to intensify at low temperatures, which has been explained by release from a shallow localised state, with an activation energy about 4 meV. The higher activation energy observed for H1 band in pHEMA-TiO₂ hybrids may be related to a deeper relaxation of STE in non-crystalline solids. Moreover, the two activation energies of 8.5 meV and 43 meV may account for heterogeneous nature of the STE traps and, more probably, be related to two types of surface traps for VB holes. Two state activation of the red PL quenching in titania powders has been earlier reported [36]. Anyway, taking into account low yield of the H1 luminescence, the observed PL cannot be the major relaxation channel but only an indicator of the stored energy in the sample.

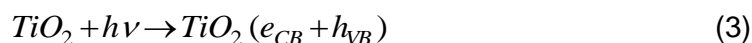
In contrast to the inorganic component, at least three activation energies in Eq. (2) were necessary in order to successfully fit the organic PL temperature dependence (H2 band). We remark that this number may be even larger, however, the fit with larger number of free E_i parameters cannot be considered as significant since it does not further improve the χ^2 criterion. The obtained activation energies apparently describe the branching of energy relaxation channels involving high-lying excited states S_i and T_i ($i \geq 2$) leading to PL and quenching: the last channel becomes stronger at heating.

The energy relaxation pathways of methoxyphenol molecules in solid methoxyphenol and in pHEMA matrix have been discussed above and schematized on figure 6c. A coupling between titania and polymer components considerably change the energy transfer in the hybrids. In particular, the S0-S1 transition is no more observed in both PL (330 nm) and PLE (280 nm) spectra (see figure 1). Furthermore in contrast to pure pHEMA polymer matrix, no energy transfer has been observed in methoxyphenol from S1 to the lowest triplet T1 state. The S1 state does not contribute to the STE emission of the titania component. All these observations strongly indicate the S1 state quenching. This quenching is apparently related to the electron transfer over the organic-inorganic interface to TiO₂ nanoparticles.

According to our knowledge, no calculations of the methoxyphenol-TiO₂ system exist in literature. Moreover, absolute values of HOMO and LUMO orbitals of methoxyphenol are not reliable. However, recent quantum-chemical calculations of rather similar system, phenol and larger molecule adsorbed on TiO₂ small anatase clusters [37], have shown that the total LUMO of the system is localized on the cluster surface. The LUMO of the adsorbed molecule were obtained to situate about 2 eV above the conduction band of TiO₂, while the molecular HOMO orbitals were ~1 eV above the valence band. Although, the absolute values of the electronic transition energies were overestimated in this work, some conclusions about the electronic states coupling of the considered system can be drawn. This particularly concerns a possibility of the charge transfer: according to these results an electron tends to be transferred to the CB of TiO₂ and a hole localised onto the molecular HOMO states.

This general picture provides a theoretical support to the present observations. Consequently, the schema of energy and charge transfer in pHEMA-TiO₂ hybrids is shown in figure 6c. According to this picture, the photoexcited electron is rapidly injected to titania whereas the hole in HOMO levels of methoxyphenol cannot (from energy considerations) be filled by a VB electron. The charges are then stored on different components constituting the hybrid material. The same final state is realised after interband TiO₂ excitation. Therefore, the S1 state of methoxyphenol provides no contribution to the hybrids PL. We remark that the fact that TiO₂(e⁻)-methoxyphenol(h⁺) pair do not emit probably indicates that methoxyphenol molecule is not involved in hole localisation of the titania charge-transfer exciton.

Our pHEMA-TiO₂ gel based hybrids materials demonstrate a high charge separation quantum efficiency (12%) and electron loading capacity (14%Ti atoms) in form of polaron-like Ti³⁺ centres (reactions 3 and 4) [23, 38] :



The excitation spectral range of the above mechanism (3)-(4) is situated between 280 and 380 nm [39], which corresponds to that of the H1 PL-band in figure 1b. This supports a common origin of both photochromism and self-trapped exciton emission. The above discussed (section III.2) charge-transfer exciton formation may be a reason.

In previous studies [23, 38] an important mechanism was suggested, limiting the trapped electrons concentration at high irradiation doses:



Along with the quenching of Ti³⁺ centres, this process serves to be an additional energy relaxation channel, which decreases the PL excitation efficiency of STE in TiO₂. We have verified the hypothesis of Eq.(5) by an intensity analysing of the STE luminescence (H1 band) in presence of Ti³⁺ centres. In these experiments, the pHEMA-TiO₂ sample was confined between glass plates and irradiates from both sides in UV(A) spectral range. A slab was then cut in the cross-section perpendicular to the plates and PL intensity of the H1 band

(600 nm) was measured as a function of distance from a plate. The grey colour distribution directly related to the Ti^{3+} centres absorption [23, 38] is qualitatively depicted along this distance at the top of figure 7, and the measured PL intensities are shown below. This result undoubtedly confirms the hypothesis of mechanism (5). The low activation energy of STE luminescence may be related to the VB hole localisation energy and confirms its fragile stability against non-radiative recombination.

Conclusion

We report on the first study of the photoluminescence (PL) properties of photochromic pHEMA-TiO₂ gel-based hybrids. The observed luminescence bands were attributed to their constituent organic and inorganic components. The broad band at 485 nm is assigned to S₀←T₁ transition of methoxyphenol-titania complex in pHEMA polymer, and the broad band at 600 nm is assigned to the self trapped exciton into octahedral TiO₆ site. The luminescence of both organic and inorganic components, being negligible at room temperature, strongly intensifies at low temperatures below 100K. It is shown that both singlet-triplet energy transfer in methoxyphenol and methoxyphenol-TiO₂ charge transfer are strongly affected by the material composition and temperature. In particular, two kinds of traps are suggested for the self-trapped excitons with activation energies about 8.5 meV and 40 meV; those of methoxyphenol indicate cascade character of the lowest triplet T₁ state population. The hypothesis about the photoexcited holes annihilation with the trapped electrons as one of main mechanisms limiting the storage of photoinduced charges in these hybrids is experimentally confirmed. The results of the present study provide important information about energy and charge transfer mechanisms and show perspectives of the time- and energy- resolved PL studies of the electronic organic-inorganic hybrids.

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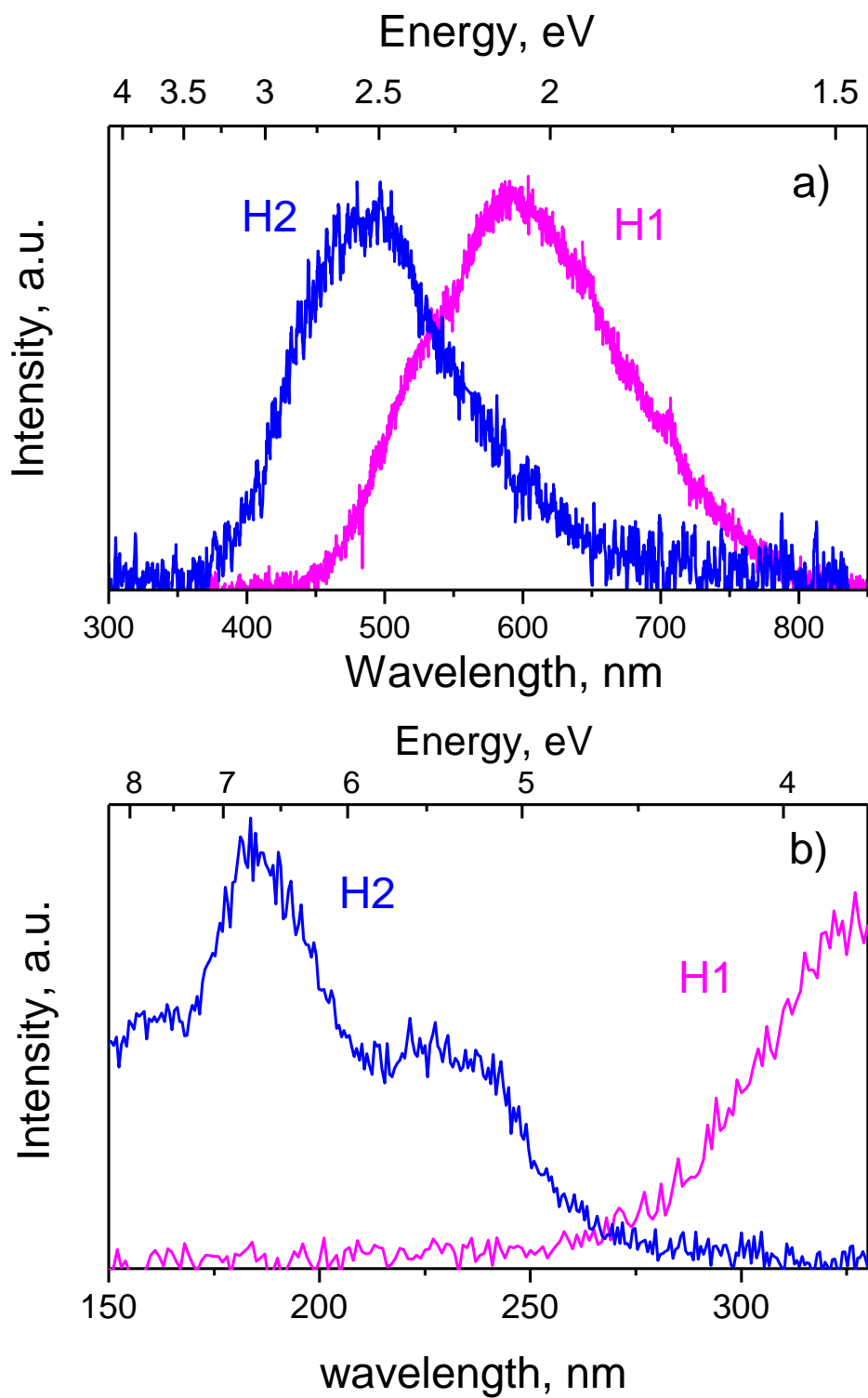


figure 1. Luminescence (a) and PLE (b) spectra of the hybrid sample. The H1 and H2 bands (a) are respectively excited at 210 nm and 320 nm.

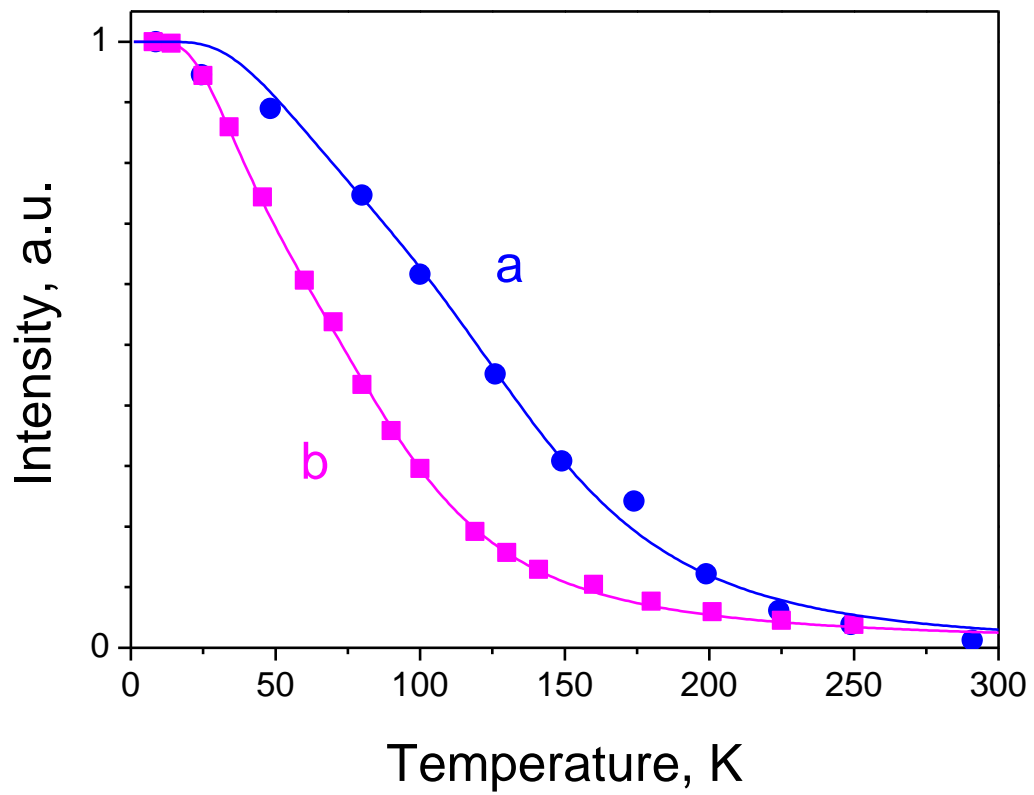


figure 2. Temperature dependence of normalised intensities of the H2 ($\lambda_{\text{exc}}=200$ nm) (a) and H1 ($\lambda_{\text{exc}}=320$ nm) (b) PL bands. The solid lines represent a thermal activation model with energies of 11/30/65 meV (a) and 8.5/40 meV (b).

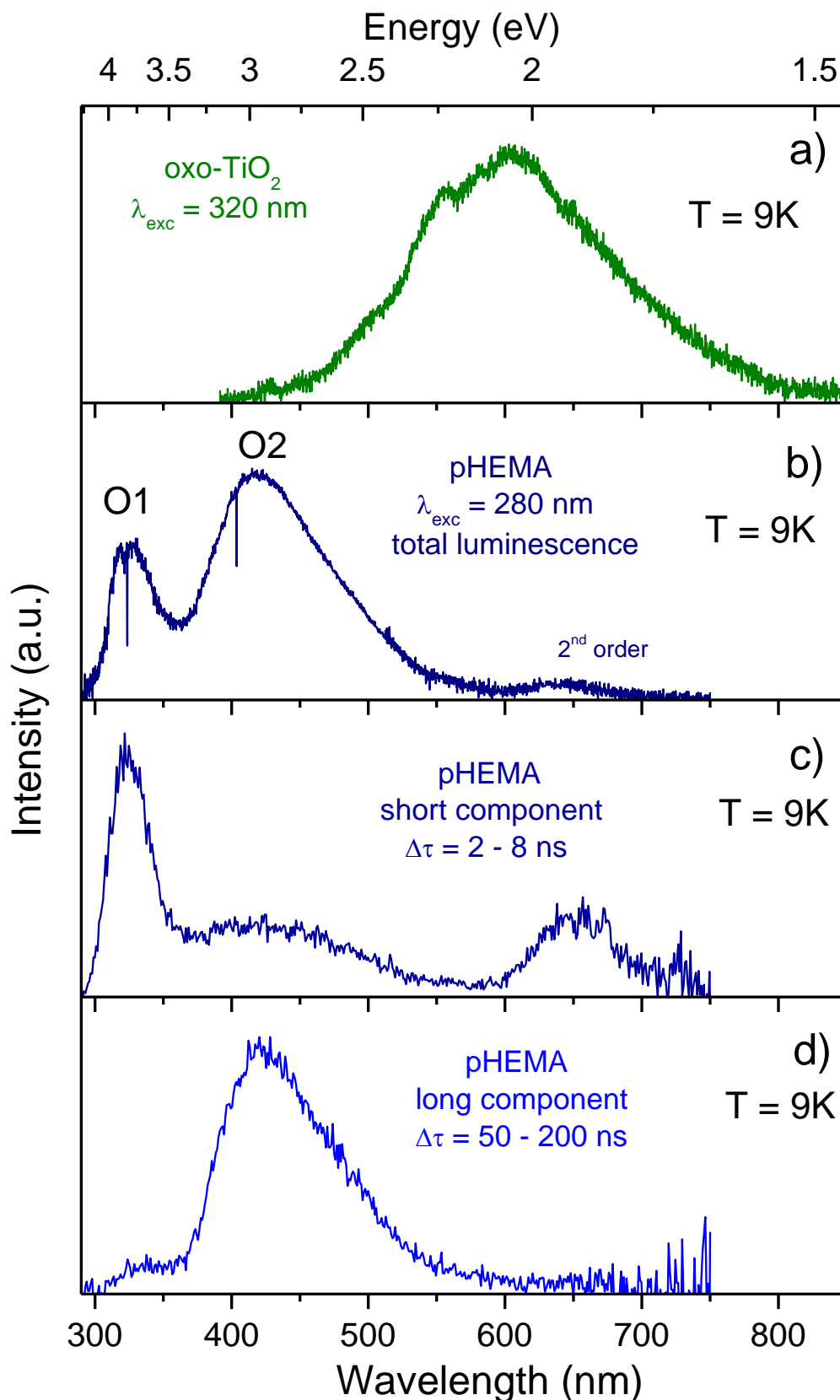


figure 3. a) Luminescence spectrum of amorphous oxo-TiO₂ film .b)Luminescence spectrum of pHEMA sample ($\lambda_{exc} = 280$ nm) c) Short component ($\Delta\tau_1 = 2-8$ ns) of the pHEMA luminescence. d) Long component ($\Delta\tau_2 = 50-200$ ns) of the pHEMA luminescence.

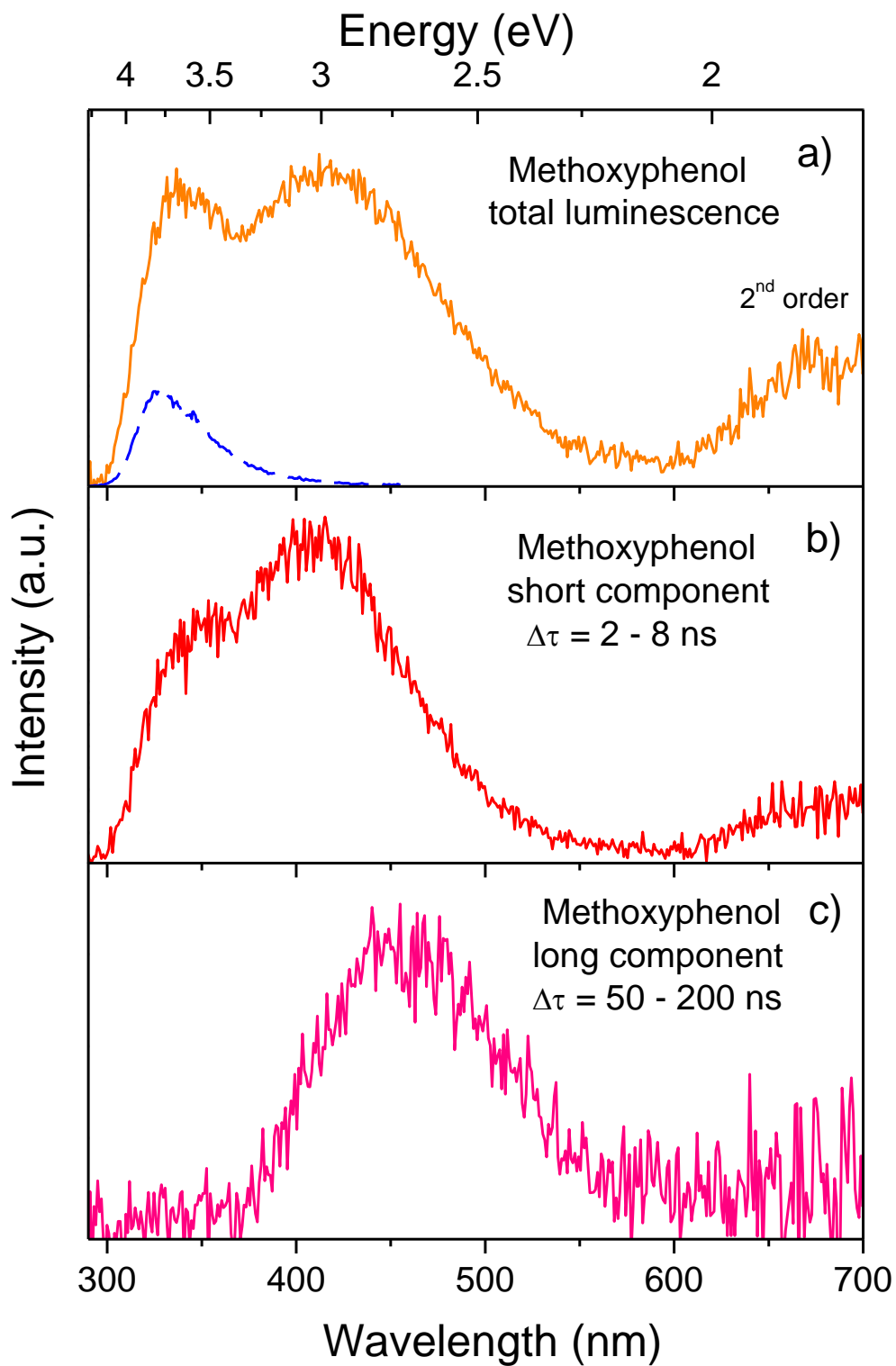


figure 4. PL spectra of methoxyphenol sample ($\lambda_{exc} = 190$ nm, T=8K): integral spectrum (a) and spectra in time-window $\Delta\tau_1 = 2 - 8$ ns (b) and $\Delta\tau_2 = 50 - 200$ ns (c). The dashed line in (a) shows the PL in diluted 2-propanol solution ($\lambda_{exc} = 240$ nm).

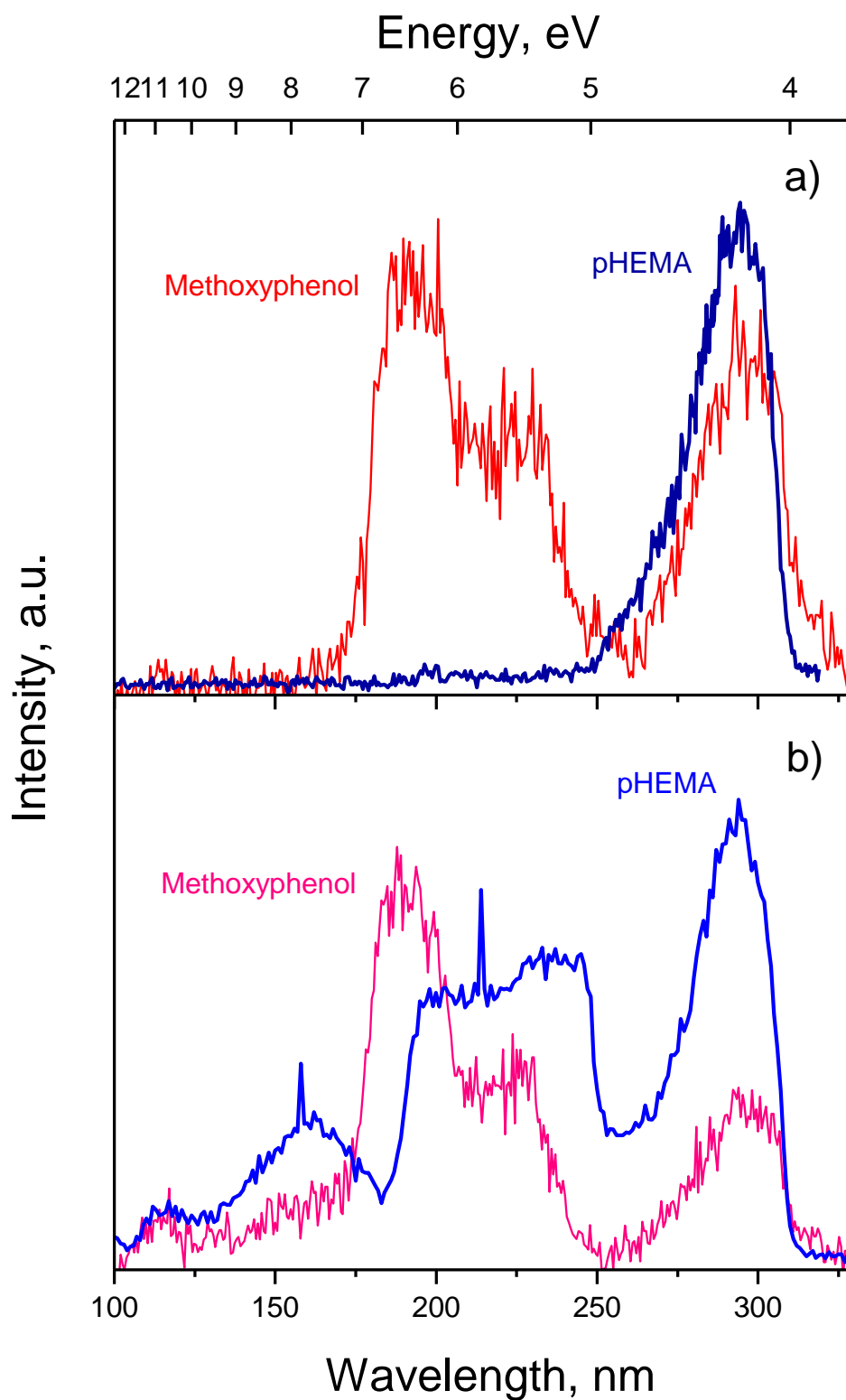


figure 5. Excitation spectra of PL ($T= 9\text{K}$) at 330 nm (a) and 440 nm (b) of methoxyphenol and pHEMA samples: $\Delta\tau_1=2\text{-}8\text{ ns}$ (a) and $\Delta\tau_2=50\text{-}200\text{ ns}$ (b).

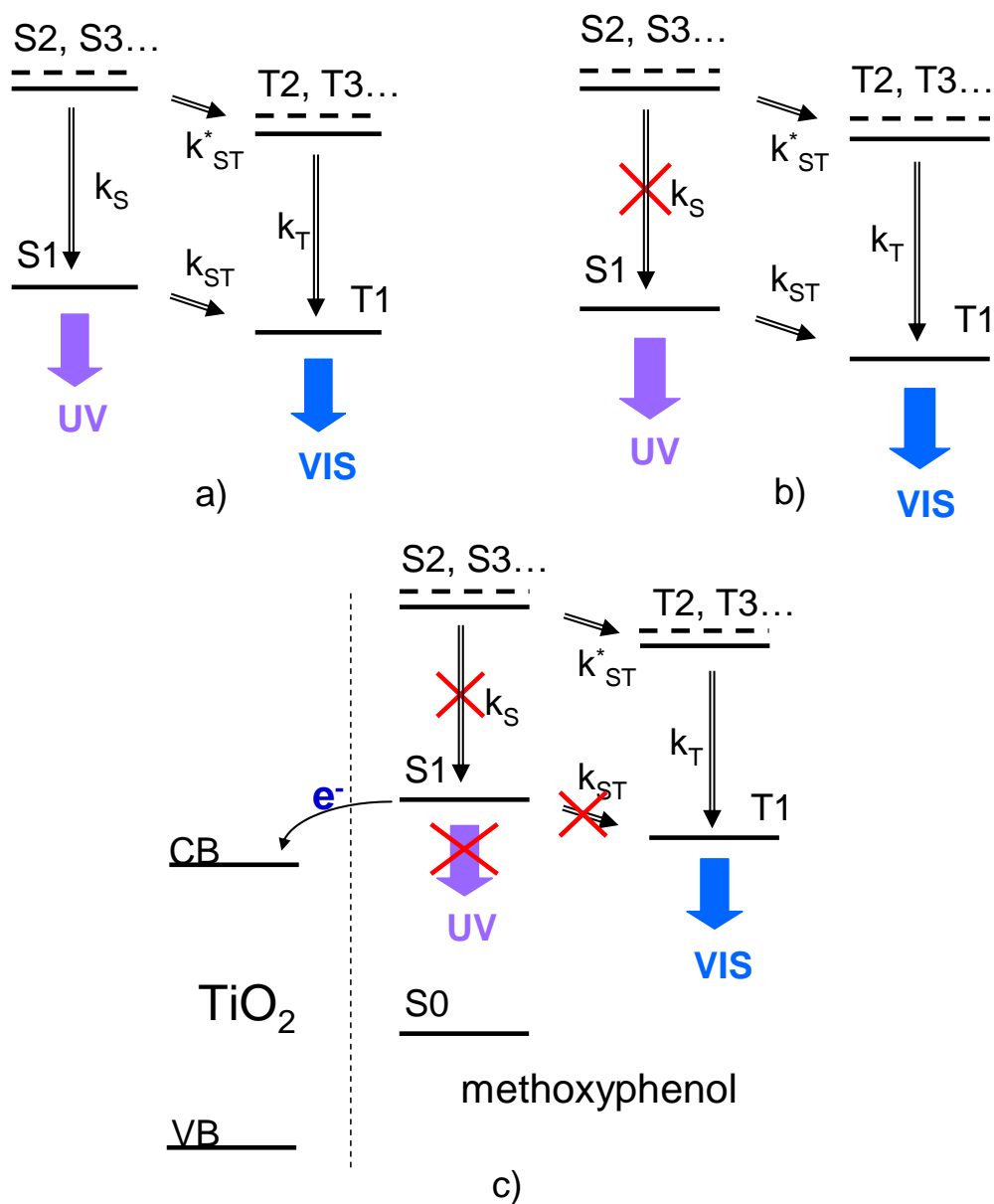


figure 6. Schemas of the energy relaxation pathways of methoxyphenol at low temperature in different environments (a) methoxyphenol molecules in solid methoxyphenol, (b) methoxyphenol molecules in pHEMA matrix and (c) methoxyphenol molecules in pHEMA-TiO₂ hybrids. The meaning of rate constants k is given in the text.

