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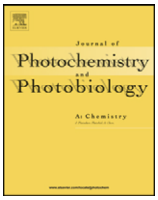

$E_T(33)$ dye as a tool for polarity determinations: Application to porous hybrid silica thin-films

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ABSTRACT

$E_T(33)$ (2,6-dichloro-4-(2,4,6-triphenyl-N-pyridino)-phenolate) was proven to be an effective tool to determine the polarity of the pore environment in sol–gel matrices prepared using acid catalysis. The probe molecules have been trapped during the formation of the organically modified silica matrices, occupying both, the inner porosity and the outer porosity of the matrix.

The effect of the chemical modification of the silica film on the polarity of the pore environment was studied as a function of the organic modifying groups and their relative amount in the silica matrix. The usage of the $E_T(33)$ polarity probe allowed the identification of different pore environments (sites) within a matrix, attending to the relative amount of functional groups in the pores. A progressive decrease of the polarity of the samples prepared was observed as the amount of the organic modifying groups was increased. Hybrid matrices could be prepared via sol–gel processing, having polarities between 40 and 60 kcal mol^{-1} in the Reichardt's $E_T(30)$ scale, which can be controlled by the amount and nature of the organic modifying groups. A particular case was observed in samples modified with pentafluorophenyl groups ($-C_6F_5$), which showed very high pore polarities, close to that of unmodified matrices, in which pore environments rich in OH groups and rich in $-C_6F_5$ groups could not be distinguished, due to their similar polarity.

The $E_T(33)$ polarity dye was found to provide a four times higher sensitivity than the known probe Nile Red for the determination of the polarity of the pore environment, as reflected by the much larger shift of the absorption peak of the dye due to changes in polarity. Due to its stability in acidic media, the $E_T(33)$ is suitable to be used in hybrid matrices prepared using acid catalysis, as are most of those prepared by the sol–gel method.

1. Introduction

The usage of polarity probes as a general tool for the determination of environmental polarities in different media has found widespread applications during the last years. Solvatochromic dye probes were used to determine the polarity of solvents [1,2] and solid matrices, such as polymers [1,3,4] or hybrid organic inorganic materials [5–9].

Among the different solvatochromic dyes, the most widely used is a betaine derivative $E_T(30)$, known as Reichardt's dye (2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridino)-phenolate) (Fig. 1). This dye exhibits a charge-transfer absorption band in the visible range of the spectrum, whose spectral position depends strongly on the polarity of the environment where the dye molecules are located [10]. In strongly acidic solvents the dye is protonated at the oxygen atom of the phenolate, preventing the charge-transfer transition and losing, therefore, its capability as a polarity probe [10]. The dichloro-substituted betaine $E_T(33)$, shown in Fig. 1, is less basic ($pK_a = 4.78$) than $E_T(30)$ ($pK_a = 8.64$) and therefore it can be used as a polarity probe in acidic environments [11]. The $E_T(33)$ dye exhibits negative solvatochromism, showing a spectral shift of the absorption maxima to the blue as the polarity of the environment increases [10,12].

Hybrid organic inorganic materials, most of them prepared by the sol–gel procedure, have been widely used to entrap active molecules in its porosity, conferring their specific properties to the hosting material (matrix). The chemical environment where these molecules are located is of a great importance, as it affects the properties of these molecules, and hence the performance of the active material. In previous works we have demonstrated the important effect of the pore environment of the host matrices on the properties and performance of optical devices based on dispersion of active organic molecules in modified silica matrices [13–15]. This effect was tentatively attributed to changes in the polarity of the environment, even though we had no way to determine this

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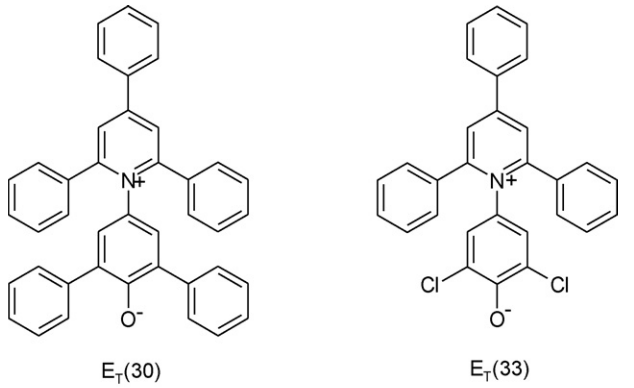

Fig. 1. Structures of the $E_T(30)$ and $E_T(33)$ polarity probes.

polarity, since the preparation of the samples involves the usage of acids.

In most cases, the preparation of materials via the sol–gel procedure includes the usage of acid as a catalyst for the hydrolysis and condensation reactions, typical of this method. Acid catalysis leads to materials with much better mechanical properties as compared with those prepared using base catalysis, as it forms closer structures, conferring the resulting materials higher durability and regular surfaces [16–18].

The usage of betaine derivatives as polarity probes in sol–gel prepared materials was first reported by Rottman et al. [19,20], who successfully embedded $E_T(30)$ dye in bulk matrices prepared from methyltrimethoxysilane and tetramethoxysilane. $E_T(33)$ dye was used by different researchers to examine the outer surface polarity of organically modified silica particles [21], synthesized by reacting thermally pre-treated silica particles with different alkyltrimethoxysilanes. The evolution of the polarity during the gelation process of sol–gel materials was also studied using fluorescent probes such as 7-Azaindole, Nile Red, PRODAN or pyranine [22–24].

The aim of this work is to determine the resulting polarity of the pore environment in sol–gel matrices prepared using acid catalysis, by the spectral behaviour of the polarity probe molecules ($E_T(33)$) incorporated into the network of different matrices. The probe molecules will be added to the precursor sol and will be trapped into the hybrid silica networks during the gelation process, occupying both, the inner porosity and the outer porosity of the matrix. The effect of the organic modification of the silica film on the polarity of the pore environment will be studied as a function of the modifying group and their relative amount in the silica matrix.

The possibility of determining the polarity of the pore environment in modified silica matrices is of a great importance for the design of new hybrid materials, as it will allow adapt the environment of the host matrix to the specific requirements of the trapped molecules.

2. Experimental

2.1. Materials

Tetracetoxysilane (TAS), phenyl triethoxysilane (PhTES), pentafluorophenyl triethoxysilane (pFPhTES), isobutyl triethoxysilane (iBuTES) and propyl triethoxysilane (PrTES) were from ABCR. Methyl triethoxysilane (MeTES), 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridino)-phenolate [$E_T(33)$] and tetrahydrofuran (THF) were purchased from Aldrich Chemicals. Ethyl triethoxysilane (EtTES) and 9-diethylamino-5-H-benzo [α]-phenoxazin-5-one (Nile Red) were from Fluka and Ethanol from Merck. Double-distilled water was used for all preparations.

Table 1
Chemical composition of the sols used for film deposition. R accounts for Me, Et, Pr, Bu, pFPh and Ph.

Molar composition			
R/Si = *x*	TAS	RTES	H_2O
0.975	0.05	1.95	6.05
0.95	0.10	1.90	6.10
0.90	0.20	1.80	6.20
0.70	0.60	1.40	6.60
0.50	1.00	1.00	7.00
0.30	1.40	0.60	7.40
0.10	1.80	0.20	7.80
0.00	2.00	0.00	8.00

2.2. Preparation of coatings

Samples were prepared from mixtures of tetracetoxysilane (TAS) and organically modified triethoxysilanes (RTES-RSi$(OEt)_3$), where R is the organic functional substituent in the ormosil precursor ($-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_6H_5$ and $-C_6F_5$), in the appropriate ratio (see Table 1). The amount of water to hydrolyzing group was kept 1:1 in all samples. The reaction was self-catalyzed by the slow release of acetic acid from the TAS during hydrolysis. The sols were allowed to hydrolyze for 24 h under stirring at 25 °C. The polarity-sensitive dye was added as a THF solution, after the hydrolysis of the sol, to reach a polarity dye:Si molar ratio of 3:200. THF was used as solvent due to its good miscibility with the coating sol. Fig. 2 shows a representative scheme of the preparation process of the coatings.

The deposition of the films about glass slides was carried out after the addition of the dye using the spin-coating technique (Fig. 2). A sol volume of 0.1 mL was used for the preparation of each film with the sample-holder spinning at 2000 rpm. The films were cured for 24 h at 100 °C.

2.3. Characterization

The absorption spectra of the resulting samples were measured between 300 and 800 nm in a Varian Cary 50 Bio UV–vis spectrophotometer.

$E_T(33)$ was used due to its lower pK_a value as compared to $E_T(30)$, 4.78 and 8.64 respectively [10,11], allowing its usage on more acidic solutions. The $E_T(33)$ scale is defined equally to that of $E_T(30)$ via

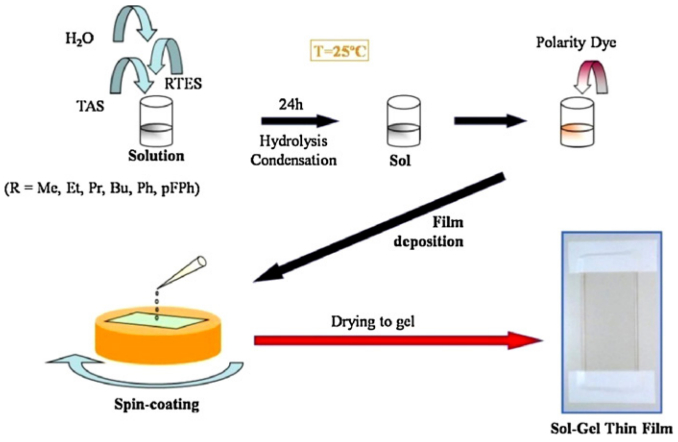

Fig. 2. Scheme of the preparation process of the coatings.

Table 2

Absorption maxima and E_T values of $E_T(33)$ and calculated $E_T(30)$ of the samples prepared with different R groups and different amount of $-C_6H_5$ groups.

Sample name	R groups (R/Si = 0.5)	λ_{max} (nm)	$E_T(33)$ (kcal mol^{-1})	$E_T(30)$ (kcal mol^{-1})	Ph/Si molar ratio	λ_{max} (nm)	$E_T(33)$ (kcal mol^{-1})	$E_T(30)$ (kcal mol^{-1})
No R group	–	414	69.06	60.15	0.0	414	69.06	60.15
pFPh	$-C_6F_5$	419	68.23	59.34	0.1	426	67.12	58.24
Me	$-CH_3$	501	57.07	48.41	0.3	477	59.94	51.22
Et	$-C_2H_5$	533 479	53.65 59.68	45.05 50.97	0.5	516 453	55.41 63.12	46.78 54.33
Pr	$-C_3H_7$	519 430	55.08 66.49	46.47 57.63	0.7	586516457	48.80 55.41 62.56	40.31 46.78 53.78
iBu	$-C_4H_9$	523 439	54.66 65.13	46.06 56.30	0.9	533	53.64	45.05
Ph	$-C_6H_5$	516 453	55.41 63.12	46.78 54.33	0.95	535	53.44	44.86
					0.975	539	53.04	44.47

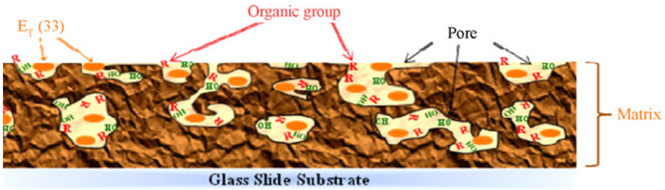

Fig. 3. Schematic representation of the pore structure in the modified silica matrix.

equation:

$$E_T(33)(\text{kcal mol}^{-1}) = hc\nu_{max} \quad N_A = 28591/\lambda_{max}(\text{nm}),$$

where h is Plank's constant, c is the speed of light in the vacuum, N_A is Avogadro's number, and ν_{max} and λ_{max} are the frequency and the wavelength of the maximum absorption of this dye in the different matrices, respectively. The $E_T(30)$ and $E_T(33)$ scales can be interconverted according to the following equation [25]:

$$E_T(30)(\text{kcal mol}^{-1}) = 0.979E_T(33) - 7.461.$$

The effect of the R groups on the degree of condensation of the organic–inorganic hybrid matrices was studied by ^{29}Si CP MAS NMR and FTIR. The ^{29}Si CP MAS NMR spectra of the resulting samples were measured in a Bruker Avance 400 MHz (solids) spectrometer, operating at 79.4 MHz for silicon; the Fourier transform infrared (FTIR) spectra were measured in a Bruker IFS 66v/S spectrometer.

3. Results and discussion

The $E_T(33)$ dye was successfully incorporated in the precursor sol used for the deposition of the modified silica films. The dye withstood the acidic conditions of the preparation of the samples and remained active in the films after the drying process. The dye is occupying both, the closed and the open porosity within the silica matrix as is shown in Fig. 3.

The spectral behaviour of the solvatochromic dye $E_T(33)$ was measured to determine the effect of the organic modification in the silica matrix on the polarity of its pore environment. Matrices were modified with different organic functional groups (R = $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-C_6H_5$ and $-C_6F_5$) and different R/Si ratios.

In unmodified silica matrices (R/Si = 0), the surface of the pores in the resulting matrix is formed mainly of uncondensed OH groups, which confer the pore a very polar environment [20]. The incorporation of the R groups into the structure results in a decrease in the polarity of the silica matrix, which is a function of the nature and amount of R groups in the matrix [20].

The absorption spectra of $E_T(33)$ trapped in matrices with the same relative amount of different modifying R groups was measured, as well as the spectra of the dye in matrices with different amounts of modifying groups in the matrix. The spectra are given in Fig. 4 and the calculated polarity values of the different matrices are summarized in Table 2. The environments with the highest polarity were observed in unmodified and pFPh modified matrices, where the peak maxima of the absorption band of the $E_T(33)$ is around 410 nm (Fig. 4a), corresponding to a polarity value of 59–60 in the Reichardt's scale. Matrices modified with CH_3, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$ and $-C_6H_5$ groups showed a clear existence of more than one absorption band, which is attributed to the coexistence of different pore environments in the same matrix. The existence of different pore environments in modified silica matrices (pores with different degree of functionalization) was previously observed by the kinetic performance of photochromic molecules trapped in those matrices [13]. The degree of functionalization of the pore surface will determine the polarity of the specific pore environment; therefore, a broadening of the absorption band evidences the existence

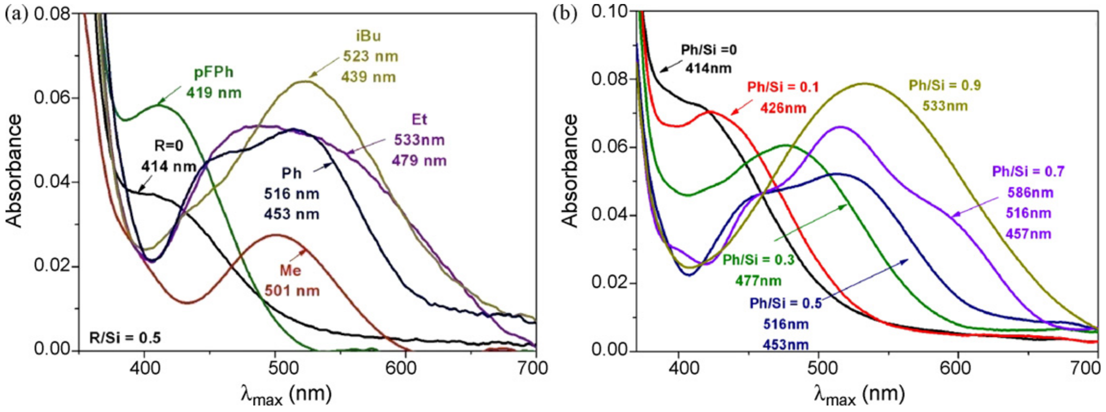

Fig. 4. UV–vis absorption spectra of the $E_T(33)$ dye in silica matrices modified with (a) different R groups (R/Si molar ratio = 0.5) and (b) different amounts of $-C_6H_5$ groups.

of a wide distribution of pores with different relative amount of R groups in their surface. However, the peak maxima of the different bands in samples modified with $-C_2H_5$, $-C_3H_7$, $-C_4H_9$ and $-C_6H_5$ groups point out to the presence of two different environments with specific polarity values (45–47 and 50–57), which are observed in all different samples.

In pFPh functionalized matrices, a narrower band is observed as compared to the analogous R functionalized samples (same R/Si molar ratio). This effect can be explained by the higher polarity of the $-C_6F_5$ substituents, which is much closer to that of the OH groups, showing small changes in polarity ($\Delta\lambda = 5$ nm) for different degree of functionalization of the pores. Another possible explanation for this effect is the formation of micellar-like structures by the hydrolysis of the pFPhSi(OEt)$_3$ species [26]. The hydrolyzed monomers tend to arrange themselves such that the polar $-Si(OH)_3$ groups form the shell of the micelle and the hydrophobic $-C_6F_5$ is buried within the core of that micelle [26]. Due to the highly hydrophobic character of the $-C_6F_5$ groups, the micelle core should be less accessible for dye molecules and therefore, these molecules will mainly probe environments rich in OH groups. Another plausible way to explain this behavior is based on the formation of hydrogen bonds between the F atoms of the pFPh groups and the OH groups of the growing silica surface at the very early stages of the condensation reaction. This situation can prevent the formation of distinctive pore environments in the matrix and hence the formation of a unique type of pores in the sample where the dye molecules can be allocated. However, this situation cannot occur in the case of the other R substituents in the matrix as they cannot form H-bonding with the OH groups, and the R substituents can move freely to arrange themselves distinctively in the different pores. Table 2 summarizes the $E_T(33)$ and the calculated $E_T(30)$ values of samples prepared with the same relative amount of different R groups. The $E_T(30)$ values for the different samples were calculated by the $E_T(33)$ values as is mentioned in Section 2.

In order to study the distribution of the R groups in the pores of the modified silica matrices, the polarity of the pore environment was measured as a function of the amount of $-C_6H_5$ groups in the matrix. The absorption spectra of the $E_T(33)$ in the different samples are given in Fig. 4b. The change in the spectral behaviour of the $E_T(33)$ in thin-films prepared with different amount of $-C_6H_5$ groups can be clearly observed by the coloration of the dye in the different matrices, as shown in Fig. 5.

A progressive shift of the absorption band of the dye to longer wavelengths was observed as the Ph/Si ratio in the matrix was increased. The introduction of $-C_6H_5$ groups, of lower polarity, into the sol–gel matrix, results in a reduction of the relative amount of silanol groups in the inner pore surface and therefore, in a reduction of the pore environment polarity [20].

In samples having low Ph/Si molar ratio (between 0 and 0.3), the pore surface is composed mainly of OH groups from uncondensed silanol and low amounts of $-C_6H_5$ groups. Therefore, small changes in the composition of the pore surface result in large differences in polarity. The spectra of $E_T(33)$ in samples prepared with Ph/Si > 0.3, show broad bands with maxima in the range 450–550 nm. The broadening of the absorption bands of the $E_T(33)$ dye is an indicative of the presence of different pore environments in the organically modified matrix [27]. Two and three absorption peaks are observed in samples with a Ph/Si ratio of 0.5 and 0.7 respectively, and very broad bands are observed in samples prepared with higher amount of $-C_6H_5$ groups (Ph/Si > 0.9). This is due to the coexistence of different pore environments in the matrix in which the polarity-sensitive dye is located. Some of the sites, showing higher polarity (absorption band at the lowest wavelength) are associated with pores rich in OH groups. This type of pores are present in all samples, including those with R/Si > 0.9. On the other hand, matrices with higher R/Si ratios showed an increasing amount of $E_T(33)$ dye molecules allocated in pores with lower polarity as interpreted by the position of the absorption bands.

The aggregation of the dye can lead to changes in the absorption band of the dye, and therefore to deviations in the polarity values obtained. The UV/vis absorption maxima of the dye embedded matrix was measured as a function of the concentration of the $E_T(33)$ in the film, in order to determine the concentration at which the dye start to aggregate. This preliminary study has been performed in an unmodified matrix and in films prepared with $-C_6H_5$ and $-C_6F_5$ groups, having the R/Si ratio of 0.9 and 0.5, respectively (Fig. 6a). A lineal increase of the absorbance was observed as the concentration of the dye was increased reaching a saturation value around Dye/Si = 6/200 in functionalized matrices and

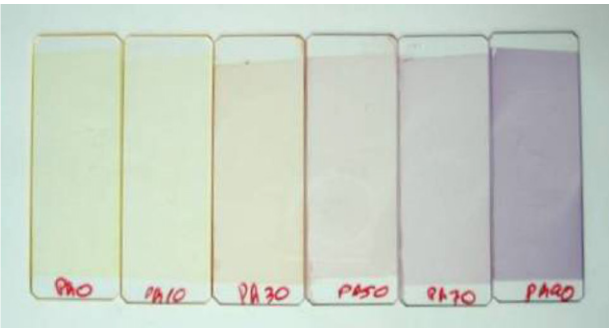

Fig. 5. Coloration of the $E_T(33)$ dye in the films prepared with different amounts of $-C_6H_5$ groups in the matrix. The amount of $-C_6H_5$ groups increases from left to right (R/Si = 0 to R/Si = 0.9).

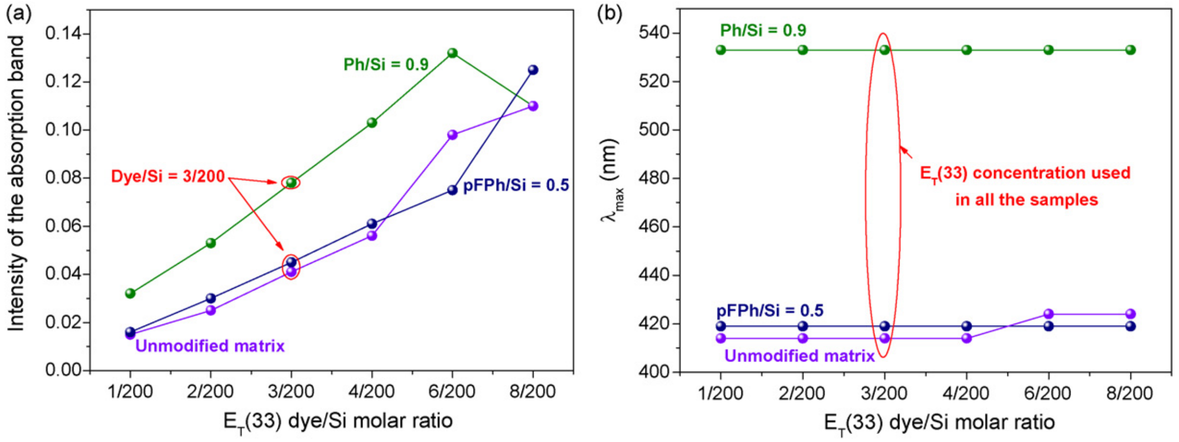

Fig. 6. Intensity (a) and λ_{max} (b) of the absorption band of the $E_T(33)$ dye in an unmodified matrix and in films prepared with $-C_6H_5$ groups (Ph/Si = 0.9) and $-C_6F_5$ groups (pFPh/Si = 0.5) as a function of the dye concentration.

Dye/Si = 4/200 in an unmodified matrix, showing that no aggregation occurs with dye concentrations below this value. The samples prepared in this work have a $E_T(33)$ dye concentration much below this limit to avoid any aggregation of the dye in the modified silica films. The spectral position, practically, does not change with the concentration of the dye in the different matrices (Fig. 6b).

As a general consideration and taking into account all the different pore environments in the matrix the polarity was observed to decrease as the amount of $-C_6H_5$ groups in the matrix is increased. This issue can be corroborated using ^{29}Si CP MAS NMR and FTIR, as they can provide information on the amount of the polar OH groups that remained un-reacted in the matrix. Fig. 7 shows the NMR spectra of the samples prepared with different amount of $-C_6H_5$ groups in the matrix. The mean number of bridging Si–O–Si bonds formed by both, unmodified (Q) and modified Si atoms (T) can be calculated according to $(1-x)\mathrm{AF}_Q + x\mathrm{AF}_T = \mathrm{AF}_{\mathrm{Tot}}$ [28], and provides an indication of the degree of condensation (network bonds formed) of the silica matrix. The calculated values for the different matrices, summarized in Table 3, show in all cases a decrease in the total number of network bonds in matrices with increasing amounts of $-C_6H_5$ groups.

The FTIR spectra of samples prepared with different amount of $-C_6H_5$ groups in the matrix is given in Fig. 8. The band at 930 cm^{-1}, which is attributed to Si–OH vibration [29], indicate the existence of Si atoms on the surface of the pores as hydroxylated species [30–32]. A decrease of the intensity of this band was observed as the amount of $-C_6H_5$ groups was increased in the modified silica matrix, due to the replacement of superficial hydroxyls by $-C_6H_5$ groups. These results, together with those of the NMR account for the lower amount of un-reacted OH groups in matrices with increasing amounts of $-C_6H_5$ groups, which can be correlated with the reduction of the polarity of the pore environment as measured by the $E_T(33)$ polarity probe.

The widely used polarity probe Nile Red was incorporated in the modified silica matrices, following the same procedure as with the $E_T(33)$, in order to compare its performance with that of the $E_T(33)$ dye. The Nile Red is also stable in acidic media and has been used to study the pore environment properties of ormosil films [8,33].

The absorption spectra of Nile Red molecules trapped in matrices prepared with different amounts of modifying groups was measured and is given in Fig. 9. The sensitivity of the Nile Red upon changes in polarity was found to be much lower than that of the $E_T(33)$ dye. The position of the absorption peak of Nile Red ranges from 574 nm in unmodified samples to 545 nm in samples modified with $-C_6H_5$ groups with a Ph/Si ratio of 0.9 (Fig. 9), giving a variation of 29 nm. The $E_T(33)$ dye, on the other hand, shows a much wider change in the position of the absorption peak (of about 119 nm),

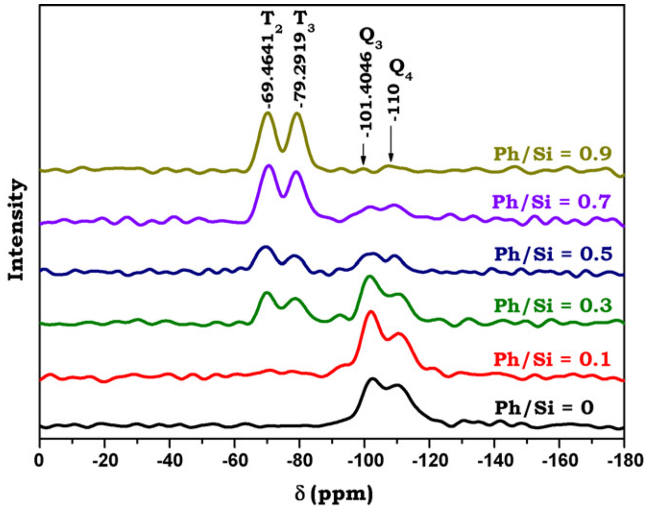

Fig. 7. ^{29}Si CP MAS NMR spectra of the samples prepared with different amount of $-C_6H_5$ groups in the matrix.

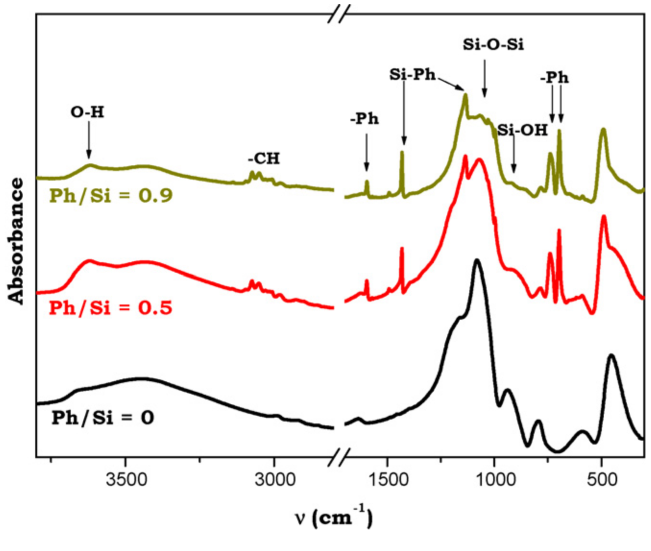

Fig. 8. FTIR spectra of the samples prepared with different amount of $-C_6H_5$ groups in the matrix.

Table 3
^{29}Si CP MAS NMR spectroscopy data of the samples prepared with different amount of –C_6H_5 groups in the matrix.

Samples (Ph/Si)	Q_4 (%)	Q_3 (%)	T_3 (%)	T_2 (%)	AF_T	AF_Q	AF_{Tot}
0.9	3.85	–	47.83	48.33	2.50	4	2.65
0.7	11.86	10.65	36.49	41.00	2.47	3.53	2.78
0.5	21.45	24.17	21.45	32.93	2.39	3.47	2.93
0.3	22.34	35.39	18.91	23.36	2.45	3.38	3.10
0.1	36.32	55.77	3.47	4.45	2.44	3.39	3.29
0	46.04	53.96	–	–	–	3.46	3.46

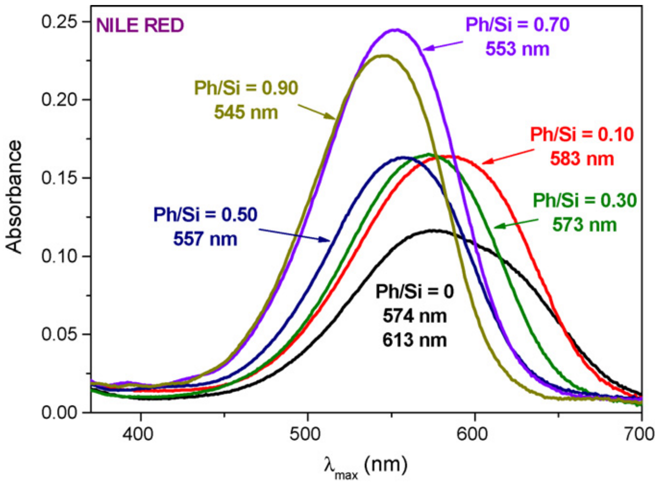

Fig. 9. UV–vis absorption spectra of the Nile Red in samples prepared with different amounts of –C_6H_5 groups in the silica matrix.

ranging from 414 nm in unmodified matrices to 533 nm in matrices with Ph/Si = 0.9. This allows a much higher sensitivity in the determination of the polarity of pore environment.

4. Conclusions

The usage of the $E_T(33)$ dye resulted in an important tool for the determination of the polarity of the pore environment in modified silica matrices prepared by acid catalysis, which is the most frequently used in sol–gel preparations. The usage of the $E_T(33)$ polarity probe allowed to identify different pore environments attending to the modifying group and its relative amount in the matrix. In some cases the $E_T(33)$ revealed the existence of different pore environments (sites) within a matrix, as a result of the inhomogeneous distribution of the R groups in the pores. The polarity of the pore environment in modified silica matrices was found to decrease as the amount of the organic substituent groups is increased, due to the replacement of the polar silanol groups (Si–OH) by the less polar R groups and the screening exerted by the larger R groups to the silanols in the surface of the pores.

The $E_T(33)$ polarity dye was found to be much more sensitive to changes in polarity than the known probe Nile Red, providing a four times higher sensitivity in the determination of the polarity of the different pore environments in modified silica matrices.

The ability of determining the polarity of the pore environment in acidic media is of a great importance from the point of view of the design of new hybrid materials that require acid catalysis for their preparation.

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