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MICROPOROUS AND
MESOPOROUS MATERIALS

Diffuse reflectance UV–Visible spectroscopy for the qualitative and quantitative study of chromophores adsorbed or grafted on silica

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Abstract

Diffuse reflectance UV–Visible spectroscopy (DRUV) is used to study the adsorption and grafting of the pyrene derivative **1** on different types of silicas. For the adsorbed silicas, the formation of dimeric aggregates is evidenced both by DRUV and by fluorescence spectroscopy. The processing of the UV spectrophotometric data allows, as in solution, the determination of apparent equilibrium constants and of the spectra of the dimer. From these results, two sets of silicas are distinguished according to the amount of dimer formed and to its UV spectrum. Lower amounts of dimeric species are found on silica with either large pore size or low particle size. The spectrum in this case is only slightly red-shifted relative to that of the monomeric compound. When the pore size decreases, dimer formation is more significant and its spectrum is more characteristic. The results obtained for adsorbed silicas were quantitatively treated and the Kubelka–Munk function, $F(R)$, plotted against the concentration. Attempts to estimate the loading of silicas grafted with **1** were undertaken. It appears that small particle size silica gives rise to the highest loading and to the best quality DRUV spectra as a consequence of a minor amount of fluorescent dimer. On the other hand, it is shown that the loading of grafted silica is difficult to control by the used grafting process and that milder conditions are required. © 2001 Published by Elsevier Science B.V.

Keywords: Silica; Adsorption; Grafting; Diffuse reflectance UV–Visible spectroscopy

1. Introduction

Grafted silicas are commonly used in different areas such as specific chromatographic separa-

tions, heterogeneous catalysis [1] or heterogeneous photosensitization [2]. The characteristics of the grafted silicas are of utmost importance for these applications. In the particular case of photochemical reactions, a good knowledge of the supported photosensitizer concentration is required, besides the important parameters of the silica itself: specific surface area, size of the pores and of the particles. Microanalysis is most often used for

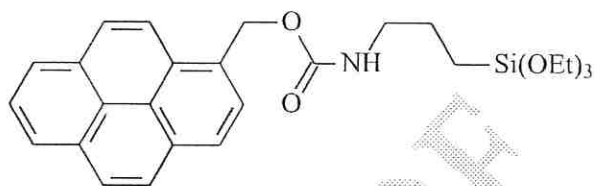
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38 this goal. However, when working with weakly
39 loaded silicas, discrepancies are observed between
40 the results obtained from the different analyzed
41 elements [3]. In some cases, specific chemical
42 analysis may be achieved like for instance acido
43 basic titrations [4]. More recently, solid state ^{13}C
44 and ^{29}Si -NMR [5,6] has allowed the determination
45 of the grafting yields of various functionalized
46 silicas. Quantitative determination of the grafting
47 ratios can also be made by diffuse reflectance infra-
48 red spectroscopy (DRIFT) [7–9].

49 Diffuse reflectance UV–Visible spectroscopy
50 (DRUV) has been most often considered as a tool
51 for the qualitative characterization of supported
52 catalysts [10–14] or modified zeolites [15–17]. Few
53 quantitative analyses have been performed with
54 this method [18,19], although they could be possible
55 using the Kubelka–Munk remission function
56 [20].

57 In this work, the use of DRUV spectroscopy
58 aimed to measure the loading of silica powders
59 grafted with organic chromophores has been
60 studied. Pyrene-grafted silicas were chosen due to
61 their easy synthesis and to their characteristic ab-
62 sorption and emission spectra. In a preliminary
63 step, the triethoxysilyl derivative **1** is simply ad-
64 sorbed on different silica-gels. The DRUV spectra
65 of these adsorbed solids are collected as the basis
66 data set for a calibration curve used for the esti-
67 mation of the loading of the grafted silicas. During
68 the adsorption study, the influence of the pore and
69 particle size on the spectroscopic behavior of ad-
70 sorbed chromophore has been assessed. The fluo-
71 rescence spectroscopy of the adsorbed samples has
72 been used to evaluate possible excimer formation
73 [21,22].



2. Experimental

The silica gels were purchased from Aldrich or
from Fluka (Table I) and were used for adsorption
after drying 12 h at 100°C in an oven. Toluene was
dried over sodium and stored on molecular sieves.
The triethoxysilyl precursor **1** and the different
grafted silicas were prepared according to reported
methods. Toluene was used instead of DMF for
the grafting of the silicas [22].

2.1. Preparation of the calibration samples

Adsorbed samples are usually prepared by
mixing the inorganic support with a solution of the
chromophore followed by a slow evaporation of
the solvent [19,23]. In order to avoid the formation
of crystallites on the surface and to mimic the
adsorption step occurring at the beginning of a
grafting process, an alternative method has been
used in this work. Solutions of **1** in toluene at
known concentrations are prepared. A known
amount of dry silica is then introduced, and the
mixture is placed on a stirring orbital table for 1 h
at room temperature. The silica is then filtered
under vacuum on a porous glass and dried in an
oven under vacuum at 100°C. The amount of ad-
sorbed compound is deduced by UV spectroscopy,
from the difference between the chromophore
concentrations in the solvent before and after ad-
sorption.

Table I
Characteristics of the silicagels used in the study

Notation	Particle size (μm)	Specific surface area (m^2/g)	Pore size (\AA)	Origin and commercial reference
Si1100	63–210	300	100	Aldrich 40,360-1
Si160-1	63–210	500	60	Aldrich 28,862-4
Si140	63–210	750	40	Aldrich 40,356-3
Si160-2	<63	500	60	Fluka 60739

103 2.2. DRUV and fluorescence spectroscopy

104 DRUV measurements were made on a Varian
105 Cary 5 Spectrometer equipped with a Praying
106 Mantis (Harrick Scientific Corporation). For each
107 silica, several measurements were made and a
108 mean value of the reflectance (%*R*) was used in
109 order to take into account the problems arising
110 from a possible inhomogeneity of the surface. The
111 UV range is limited to 250 nm on the high energy
112 side by the absorption of silica in this region. The
113 spectra are displayed in *F(R)* Kubelka–Munk
114 units, with:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{k}{S} \quad (1)$$

116 where *k* and *S* are the absorption and scattering
117 coefficients [24]. This equation only applies to
118 optically thick samples for which any further in-
119 crease of the thickness does not affect the experi-
120 mentally determined reflectance. For an ideal
121 diffuser, the reflected radiation has the same in-
122 tensity in all the directions.

123 In the absence of intermolecular interactions or
124 if these interactions are constant, i.e. at low con-
125 centrations

$$k = \varepsilon C \quad (2)$$

127 where ε and *C* denote, respectively, the molar ex-
128 tinction coefficient and the concentration of the
129 adsorbate. A linear relation for the remission
130 function *F(R)* as a function of the concentration of
131 the adsorbate is expected, provided that the scat-
132 tering coefficient *S* remains the same and therefore
133 that the same type of silica is used for the blank
134 spectrum as for the other samples (especially re-
135 garding the particle size).

136 If intermolecular interactions occur

$$k = \sum_i \varepsilon_i C_i \quad (3)$$

138 where the summation refers to the possible pres-
139 ence of different species (monomer, dimers, ag-
140 gregates, etc.).

141 Due to the definition of the Kubelka–Munk
142 function (Eq. (1)), values greater than 25 cannot be
143 used because reflected light *R* is less than 1% at this
144 level and a bad detector response is expected.

In order to obtain quantitative information on 145
the dimerization process (apparent dimerization 146
equilibrium constant and adsorption coefficients 147
for monomer and dimer species), the spectropho- 148
tometric data are processed with the Letagrop- 149
Spefo program which uses the Newton–Raphson 150
algorithm to solve mass balance equations and a 151
pit-mapping method to minimize the errors and to 152
determine the best parameter values [25–29]. Flu- 153
orescence spectra of the powdered samples were 154
measured on the dried powder and in front surface 155
on a SLM Aminco 4800S spectrofluorimeter 156
working in the ratio mode and with an excitation 157
wavelength at 340 nm. 158

3. Results 159

Different types of silica (Table 1) have been used 160
in order to evaluate the influence of the specific 161
surface area (related to the pore size) and of the 162
particle size, on the spectroscopic features of ad- 163
sorbed **1** and on the grafting yields. 164

3.1. DRUV and fluorescence study of adsorbed **1** 165

The DRUV spectra obtained for Sil60-1 are gi- 166
ven in Fig. 1a. In Fig. 1b, the same spectra have 167
been normalized on the most intense band at 337 168
nm. In Fig. 2 scaled spectra are given for the other 169
silicas. The normalization of the spectra allows one 170
to evidence the formation of aggregates related to 171
band shape deformation or broadening. 172

The scaled spectra displayed in Fig. 1b for Sil60- 173
1 and in Fig. 2 for the other silicas deserve the 174
following comments: 175

- The spectrum of adsorbed pyrene is close to its 177
spectrum in solution with a slight hypsochromic 178
shift (Fig. 3).
- A distortion of the scaled spectra may be ob- 180
served at high concentrations, i.e. in the range 181
4.5–8.9 $\mu\text{mol/g}$ for Sil60-1: the 337 nm band 182
broadens on the low energy side, while the rela- 183
tive intensities of the 322 and 308 nm bands on 184
the high energy side increase. At the same time, 185
the intensity variation of the band at 262 nm is 186
less straightforward. Although very characteris-

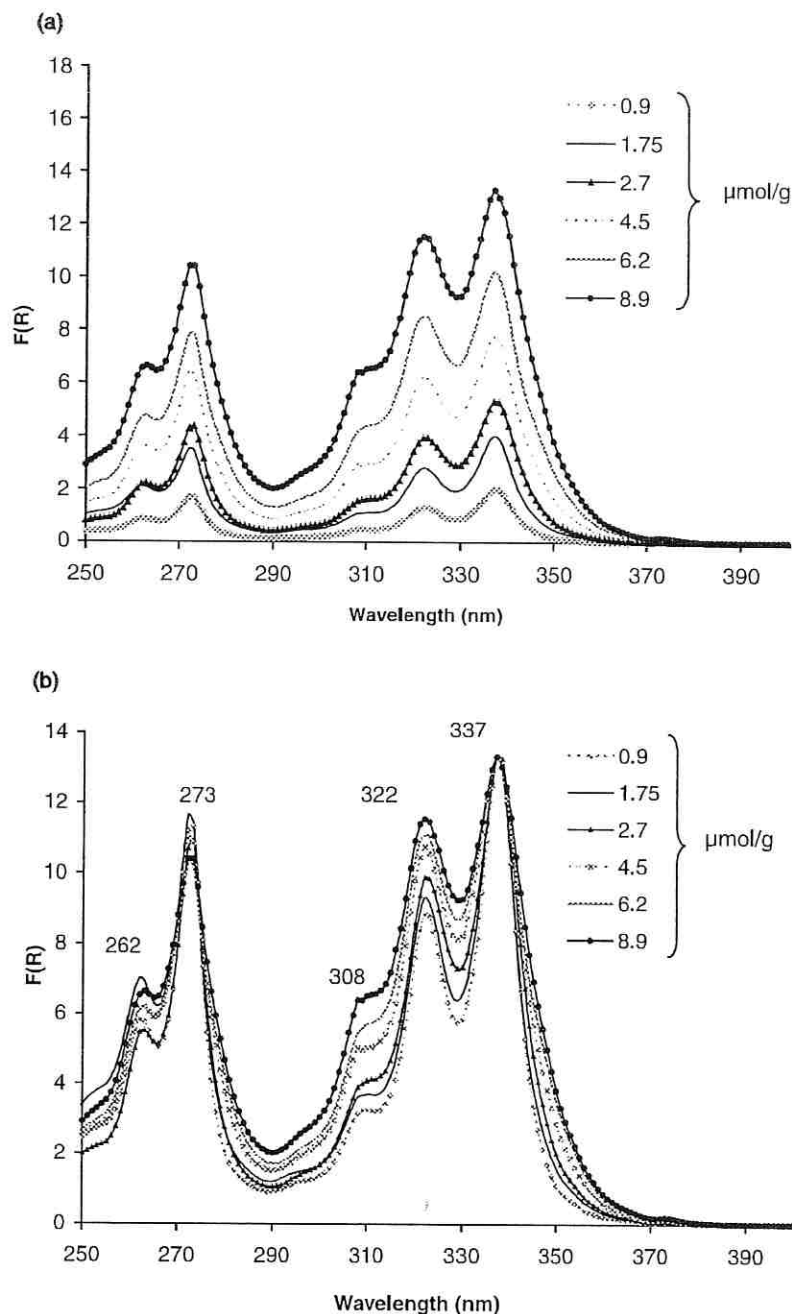


Fig. 1. DRUV spectra of the pyrene derivative **1** adsorbed on Sil60-1 at different concentrations. (a) Unnormalized spectra. (b) Spectra normalized on the intensity of the 337 nm band.

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tic for Sil60-1 (Fig. 1b), Sil100 (Fig. 2a) and Sil40 (Fig. 2b), these deformations are much less obvious for Sil60-2 (Fig. 2c) with smaller particle size.

• The $F(R)$ scale is very different from one silica to the other, due to different scattering coefficients. For the same pyrene concentrations, the smallest $F(R)$ values are observed for

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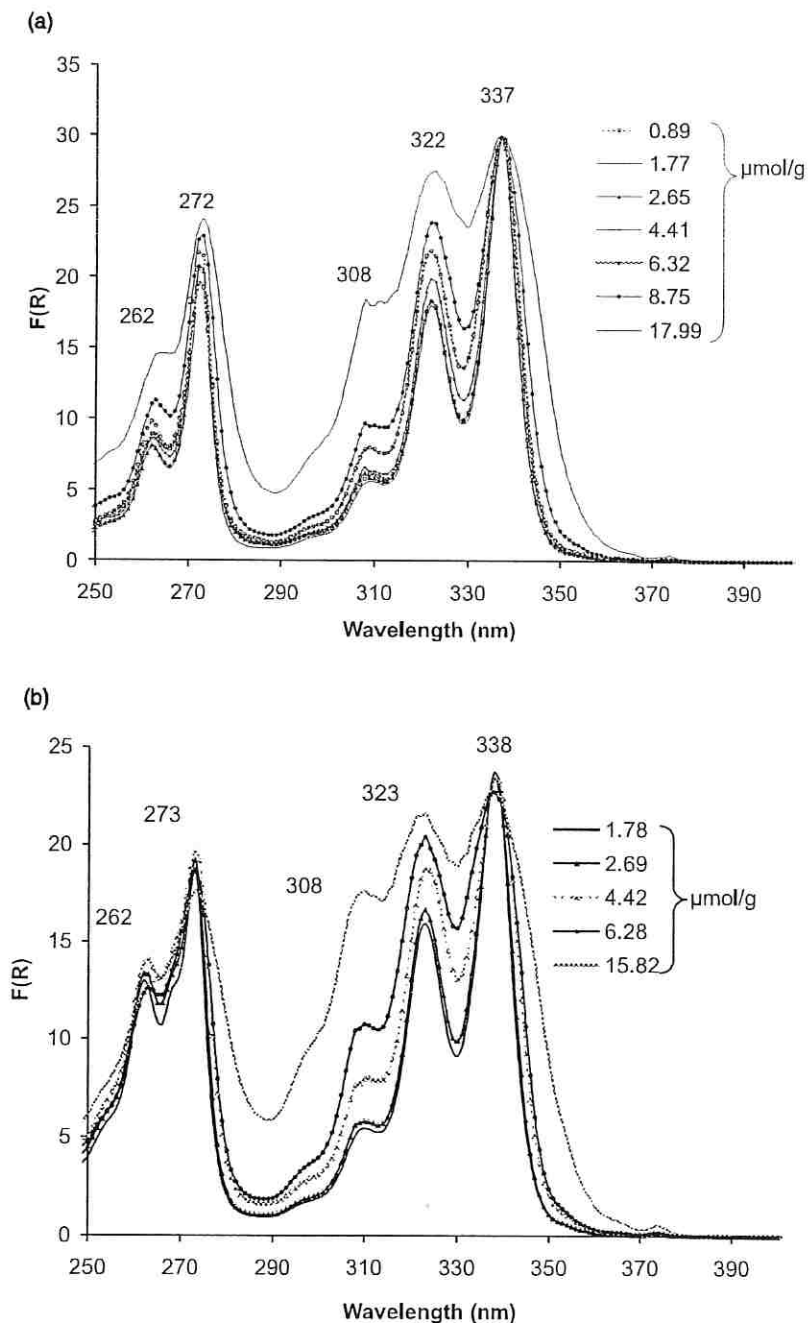


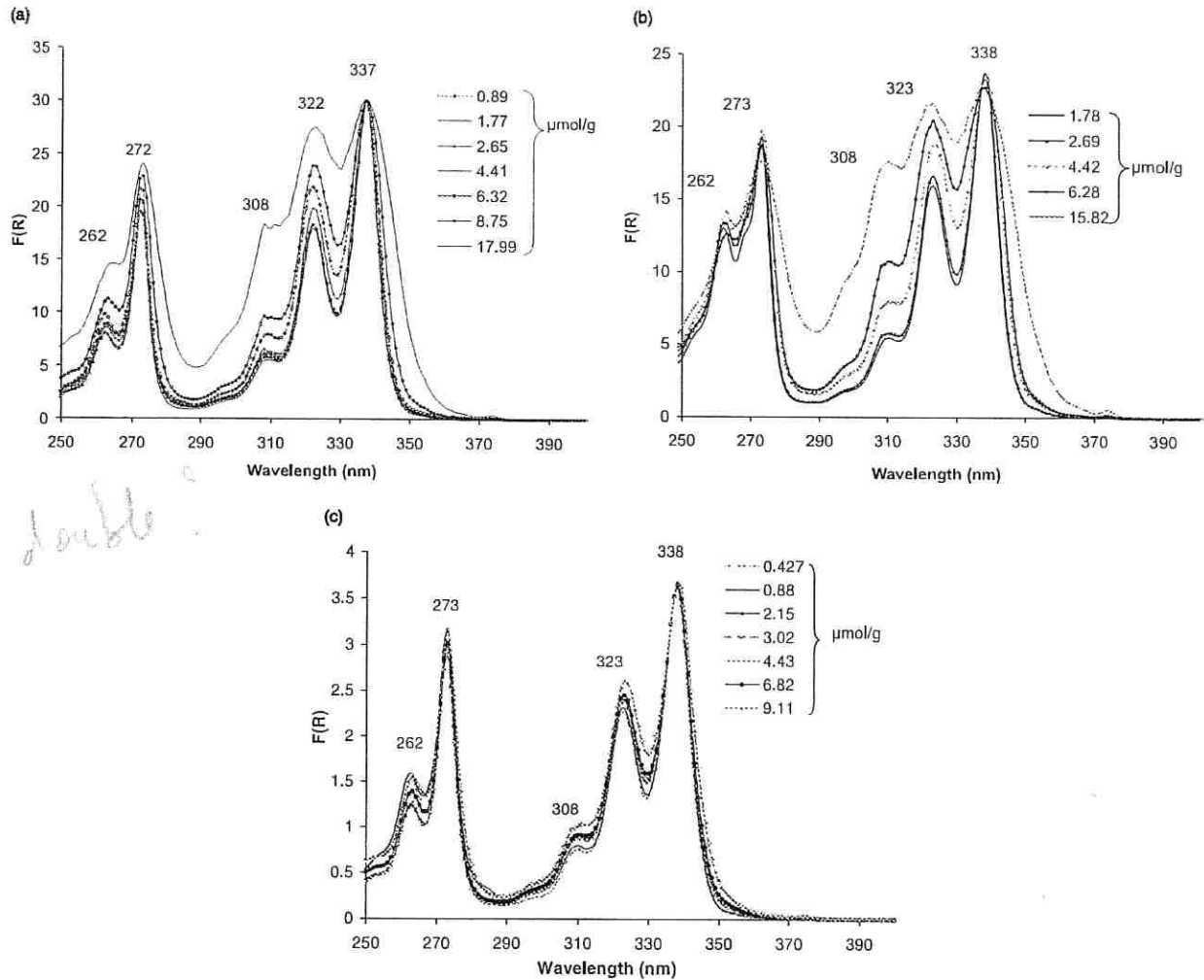
Fig. 2. DRUV spectra of the pyrene derivative **I** adsorbed on different types of silica at different concentrations and normalized on the intensity of the 337 nm band. (a) Sil100, (b) Sil40 and (c) Sil60-2.

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196

Sil60-2 which corresponds to the highest scattering coefficient.

The deformation of the spectra at high concentration may be related to the possible formation of aggregates. These observations are substantiated

197
198
199



an double

Fig. 2 (continued)

200 by the fluorescence spectra of the powdered ad-
 201 sorbed samples Sil60-1 and Sil60-2 (Fig. 4a and b).
 202 In all spectra, the expected structured emission
 203 of monomeric pyrene may be seen between 360
 204 and 425 nm. A structureless emission centered
 205 around 470 nm and normally related to excimers is
 206 also observed. The excimeric emission is probably
 207 the result of the close proximity of molecules ad-
 208 sorbed as aggregates on the surface: this emission
 209 will be therefore referred to as “excimer-like”
 210 emission [22]. For both silicas, two sets of curves
 211 are obtained. For Sil60-1 (Fig. 4a), in the range
 212 0.90–1.75 μmol/g, the amount of aggregates, indi-
 213 cated by the broad featureless “excimer-like” band

is small and increases slightly with concentration. 214
 In the range 2.7–8.9 μmol/g, excimer formation is 215
 more obvious, but its concentration reaches a 216
 maximum at 6.2 μmol/g. The same observation 217
 still holds true for Sil60-2 (Fig. 4b) but the ag- 218
 gregates emission is only significant after reaching 219
 higher concentrations ranges (6.82–9.11 μmol/g). 220
 In Fig. 5, the intensities of the excimer band at 472 221
 nm relative to that of the monomer at 375 nm are 222
 given for both silicas (black lines), and it appears 223
 that excimer formation occurs at a somewhat 224
 lower concentration for Sil60-1 than for Sil60-2. In 225
 the same figure, the ratio of the relative intensities 226
 of the bands at 375 and 394 nm (grey lines) is 227

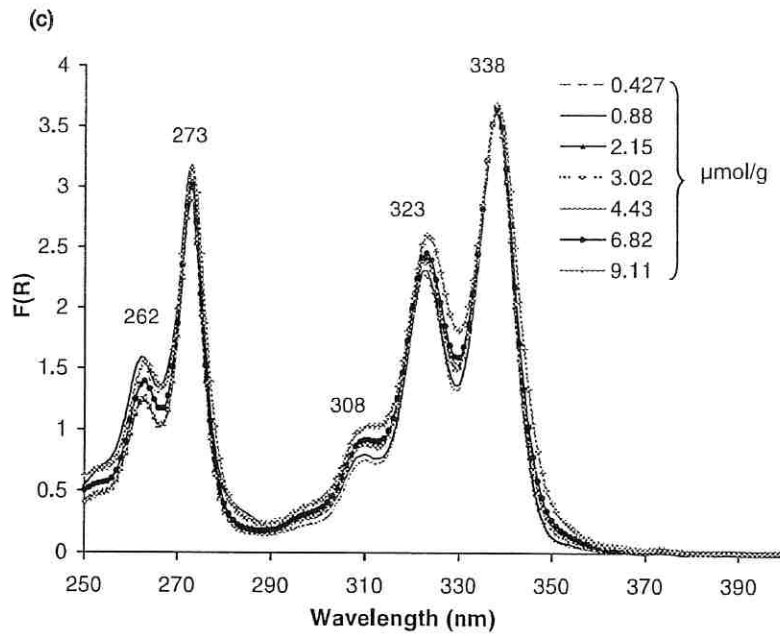


Fig. 2 (continued)

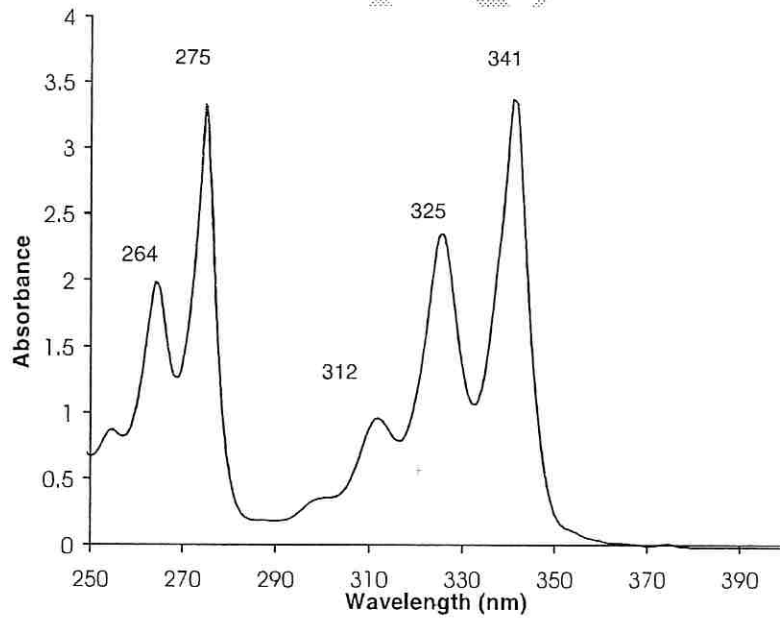


Fig. 3. UV spectrum of the pyrene derivative **1** in CH_3CN solution.

$[\text{pyrene}] = ?$ $l = ?$

228 shown to decrease slowly for Sil60-1, while no
 229 significant change is recorded for Sil60-2. This
 230 ratio is known to decrease when the medium po-
 231 larity decreases [21,22,30]. Our observations are

thus coherent and again indicative of a greater
 232 proximity of the pyrene molecules **1** for Sil60-1
 233 than for Sil60-2.
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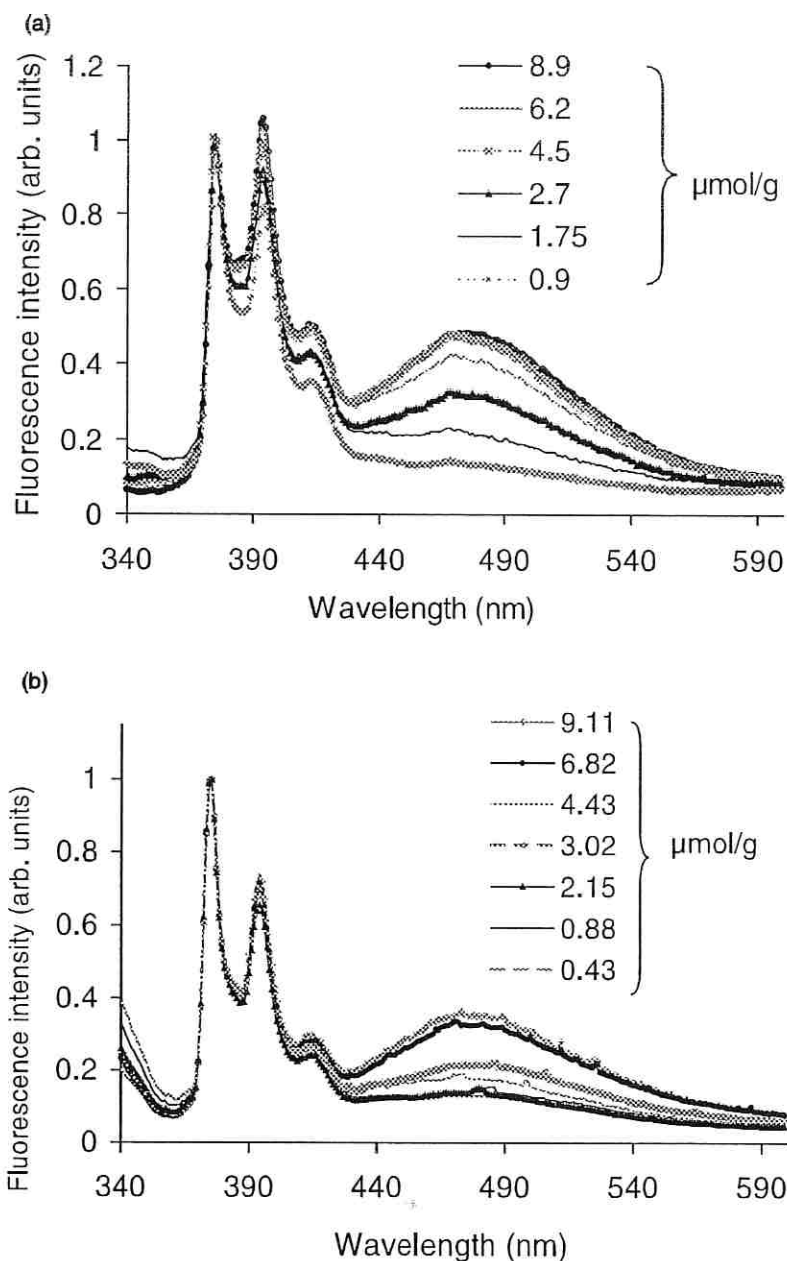


Fig. 4. Normalized fluorescence spectra of the powdered pyrene derivative **1** adsorbed on (a) Sil60-1 and (b) Sil60-2 at different concentrations (λ_{exc} : 340 nm).

235 To summarize, the UV spectra are indicative of
 236 the formation of aggregates in the ground state,
 237 while in the same concentration ranges excimer-
 238 like emission is rising up in the fluorescence spec-
 239 tra. It probably follows that fluorescent aggregates
 240 are formed on the silica surface for concentrations

around 2.7 $\mu\text{mol/g}$ for Sil60-1 and 6.82 $\mu\text{mol/g}$ for
 Sil60-2. In other words, the excimer-like emission
 is related to the intermolecular ground state asso-
 ciation as already observed from fluorescence ex-
 periments [31,32].

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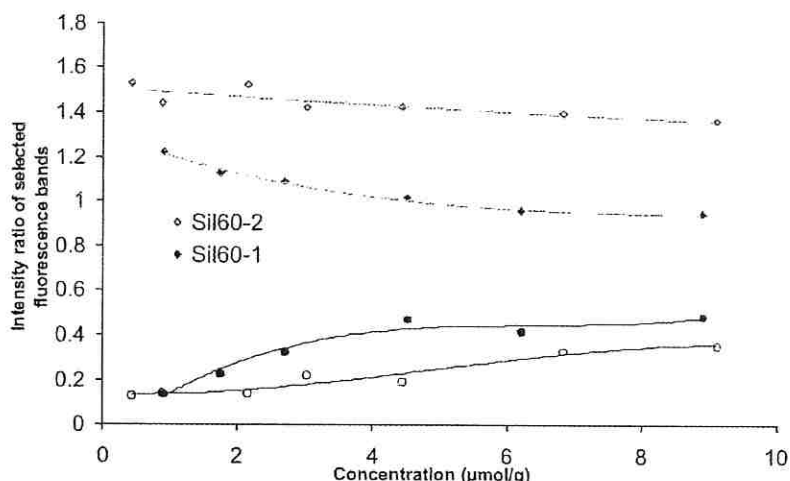


Fig. 5. Relative intensities of the fluorescence bands. (●) I_{472}/I_{375} , (◆) I_{375}/I_{394} .

246 3.2. Quantitative model of aggregation from DRUV
247 data

248 As already proposed in the literature [19], a di-
249 merization model may be assumed



251 where K_D is an apparent equilibrium constant re-
252 lating the monomer M_{ad} and the dimer $(M_2)_{ad}$
253 concentrations. At the solid interface, contrary to
254 solutions, there is no actual equilibrium between
255 adsorbed species. Accordingly K_D should be con-
256 sidered here only as a constant relating monomer
257 and dimer concentrations of adsorbates on the
258 surface.

259 If C_0 is the initial pyrene derivative concentra-
260 tion, and C_M and C_D the concentrations of the
261 monomer and dimer for a given spectrum, then

$$C_0 = C_M + 2C_D$$

$$F(R) = \epsilon'_M C_M + \epsilon'_D C_D$$

263 According to the dimerization model:

$$K_D = \frac{C_D}{C_M^2}$$

265 It follows:

$$F(R) = \frac{\epsilon'_D}{2} C_0 - \frac{2\epsilon'_M - \epsilon'_D}{8K_D} + \frac{2\epsilon'_M - \epsilon'_D}{8K_D} (1 + 8K_D C_0)^{1/2} \quad (5)$$

with $\epsilon'_M = \epsilon_M/S$ and $\epsilon'_D = \epsilon_D/S$, the absorptivities
(including the scattering coefficient of the given
silica) of the monomer and dimer, respectively.

If a first order limited expansion of the square
root is applied, i.e. if $8K_D C_0$ is small, then $F(R)$
becomes

$$F(R) = \epsilon'_M C_0 \quad (6)$$

As expected, it follows that at a given wavelength,
the curve giving $F(R)$ versus the concentration
should be a straight line passing through the origin
at low concentrations and inflecting its shape at
higher concentrations.

The whole set of $F(R)$ data at different concen-
trations for each silica was processed with the
Letagrop–Spefo program [25–29], which adjusts
the equilibrium constants and the absorptivities.
The K_D values was calculated at several wave-
lengths in the 265–278 and 330–340 nm ranges of
high absorptivity. The resulting constants are gi-
ven in Table 2, and the relative monomer and di-
mer concentrations deduced from K_D for each
silica are displayed in Fig. 6. For the silicas with
the same particles size, K_D follows the reverse pore
size order, increasing from 4.6×10^4 mol/g for
Sil100 to 13×10^4 mol/g for Sil40: the dimer con-
centration thus increases progressively when the
pore size decreases. When comparing the silicas
with the same pore size, Sil60-1 (8×10^4 mol/g)
and Sil60-2 (1.8×10^4 mol/g), the smallest constant

Table 2

Calculated apparent equilibrium constants K_D (mol/g) and maxima absorption wavelengths of the monomer and dimer of **1** adsorbed on different silicas

Silica	K_D	λ_{\max} (nm)	
		Monomer	Dimer
Sil100	4.6×10^4	262, 272, 308, 322, 337	265, 276, 317, 328, 343
Sil60-1	8×10^4	262, 273, 322, 338	268, 279, 316, 329, 344
Sil40	13×10^4	263, 273, 309, 323, 338	266, 277, 318, 331, 344
Sil60-2	1.8×10^4	262, 273, 310, 322, 338	265, 276, 314, 327, 344

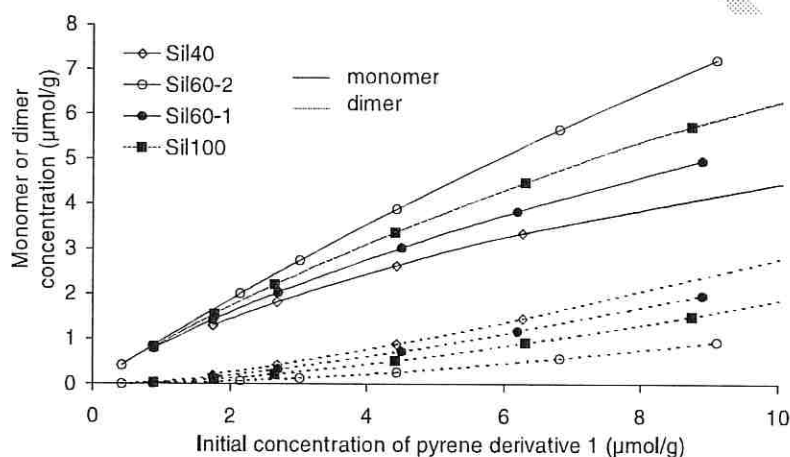


Fig. 6. Relative monomer and dimer concentrations for different silicas at several adsorbate ratios.

296 is obtained for the silica with the smallest particle
 297 size: Sil60-2 presents the lowest ratio of dimer
 298 formation among all the silicas studied. From
 299 these results, it may be deduced that the dimer
 300 concentration is lowest when either a large pore
 301 size or a small particle size silica is used.

302 The obtained absorptivities ϵ' at each wave-
 303 length allow to plot the UV-Visible spectra of
 304 both the monomer and the dimer (Fig. 7). It may
 305 be noticed that throughout the complete series, the
 306 monomer spectra are, as expected, always roughly
 307 identical with a very slight hypsochromic shift
 308 (Table 2) relative to solution spectra (Fig. 3). As
 309 far as the dimers are concerned (Table 2), the ab-
 310 sorption maxima wavelengths are all bathochro-
 311 mically shifted versus the monomer. On the other
 312 hand, the relative intensities of the dimer bands
 313 vary from case to case and, in particular, in the 310
 314 nm range, a broad band noticeably increases when
 315 the pore size decreases (Fig. 7a–c). The intensity of

this band remains weak for the small particle size
 silica Sil60-2 (Fig. 7d). It is to be noticed that the
 obtained dimer spectra are not modified if the
 highest concentration spectra are omitted in the
 data processing. This result implies that higher
 order aggregates are not necessary to explain the
 observed evolution of the relative intensities of the
 bands: the dimer model is thus validated.

324 According to these observations, it may be as-
 325 sumed that different kinds of dimers occur de-
 326 pending on the silica morphology, pore size or
 327 particle size. It is well known that two molecules
 328 forming an excimer are arranged in parallel or
 329 near-parallel pairs [33]. Fujii et al. [32] already
 330 reported that relative configurations of neighbor-
 331 ing pyrene molecules, depend on the pore size: as
 332 the pore size decreases, the dimers tend to have a
 333 face-to-face or sandwich configuration. Similarly,
 334 our results on Sil100, Sil60-1 and Sil40 with pore
 335 sizes of 100, 60 and 40 Å respectively may be ac-

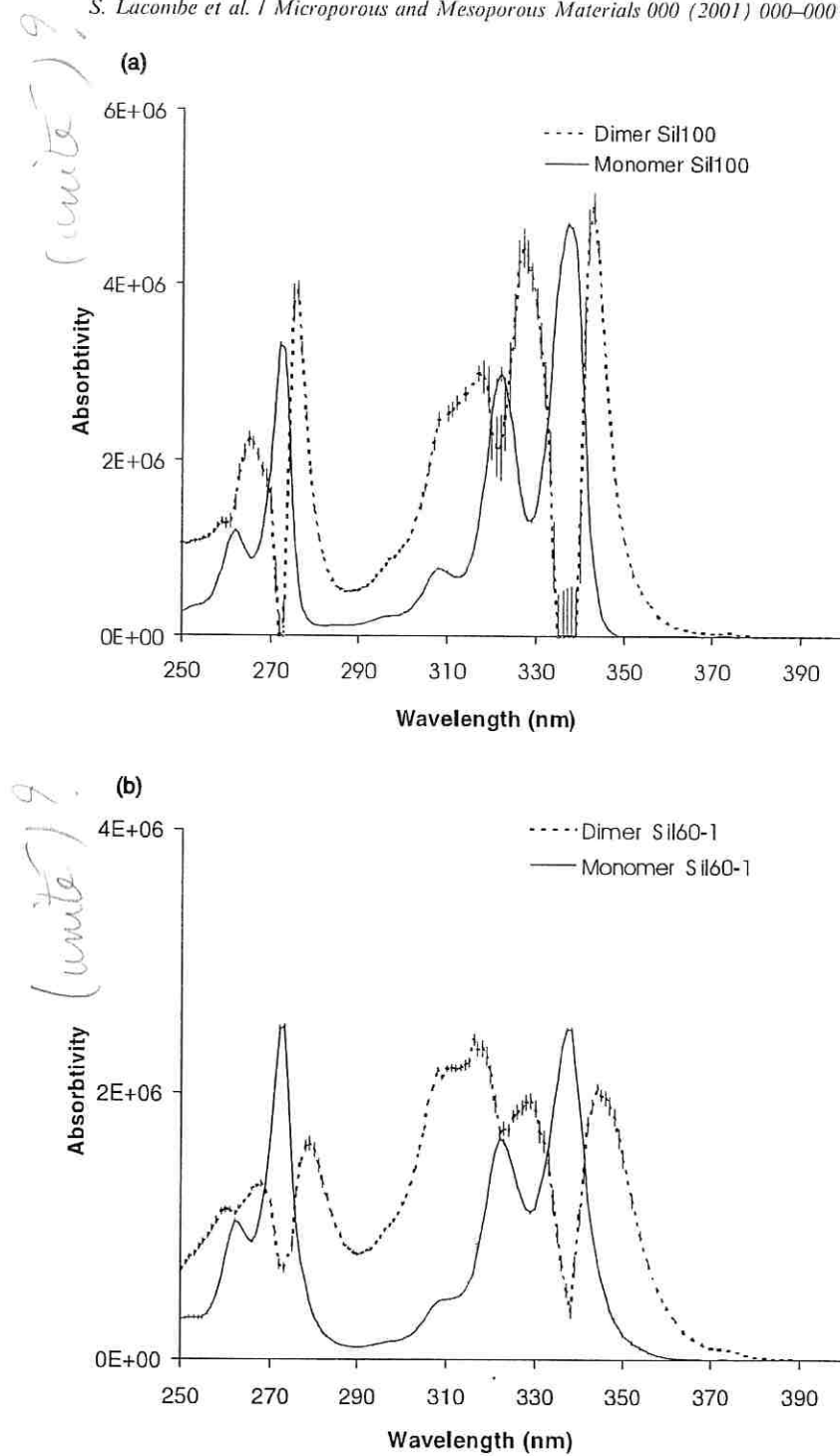


Fig. 7. Calculated UV spectra of the monomer and dimer of **1** on different silicas. Absorbivity $\epsilon' = \epsilon/S$ and includes the scattering coefficient S (Eq. (5)). (a) Sil100, (b) Sil60-1, (c) Sil40 and (d) Sil60-2.

336 counted for by different relative overlapping situ- 338
 337 ations of the pyrene-pairs. For the small particle size Sil60-2, where the aggregates were seen to be 339
 formed at higher concentrations, the spectrum

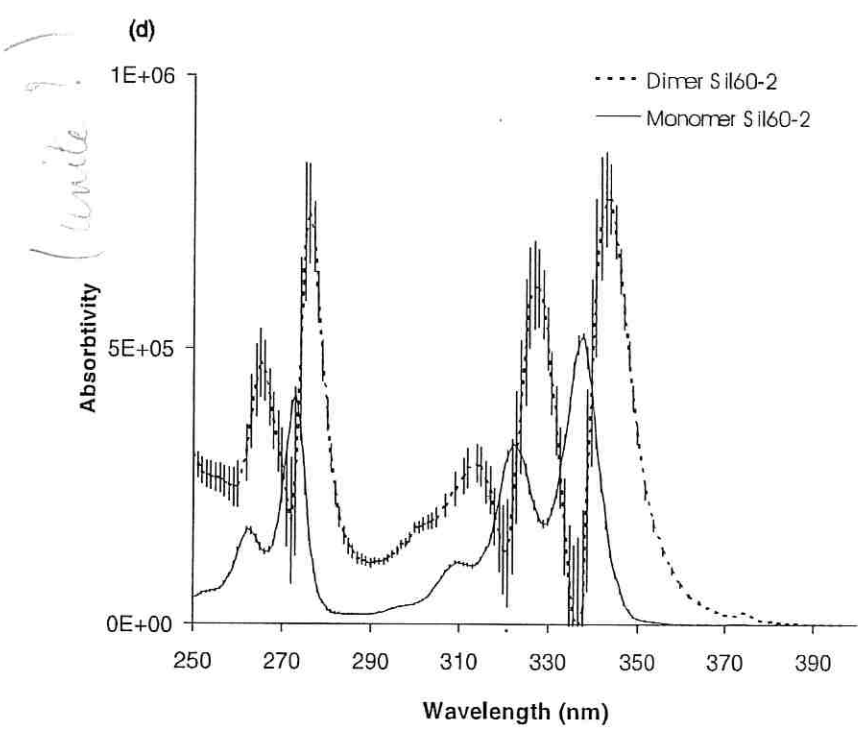
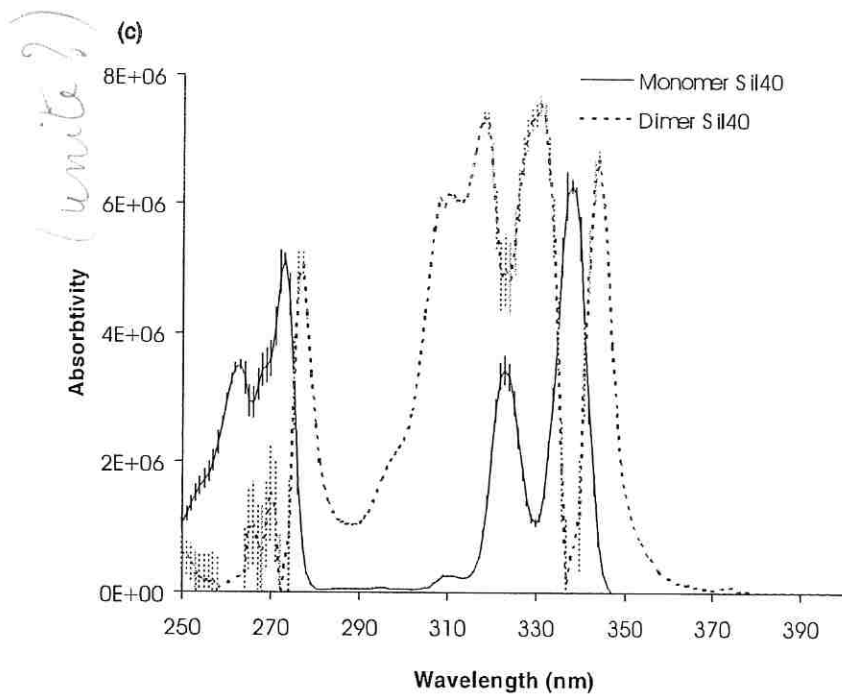


Fig. 7 (continued)

340 distortion is the weakest of the series and only a
341 slight red shift of the spectrum (4–6 nm) is ob-

served relative to that of the monomer (Fig. 7d). 342
This may might indicate that in this case, either the 343

344 dimer configuration is no longer face-to-face or
 345 that the shift is due to a change in the nature of
 346 local adsorption site environment, as for instance a
 347 different number of Si–OH per unit area [31] in the
 348 Sil60-2 (Fluka) relative to the other silicas (Ald-
 349 rich). On the other hand, for the small pore size
 350 silicas Sil60-1 and Sil40, the enhanced intensity of
 351 the 310–318 nm band may be related to the forma-
 352 tion of type H (face to face or sandwich) ag-
 353 gregates [19]. In any case, Sil60-2 should be
 354 obviously preferred in order to avoid aggregates
 355 formation.

356 3.3. Quantitative determination of 1 grafted on 357 different silicas

358 The experimental points giving $F(R)$ versus the
 359 concentrations for the different silicas used for the
 360 calibration have been fitted according to Eq. (5) at
 361 three maximum absorption wavelengths: 273, 323
 362 and 338 nm (Fig. 8 at 337 nm for example). It may
 363 be noticed that the fit can be used over a large
 364 concentration range for Sil60-1 and Sil60-2, as
 365 $F(R)$ only smoothly increases with the concentra-
 366 tion. However, for Sil100 and Sil40, $F(R)$ becomes
 367 too large at about 10 $\mu\text{mol/g}$ so that accurate
 368 measurements are no longer possible. All the ex-
 369 perimental points are correctly fitted, the largest
 370 deviation from the calculated curves being ob-
 371 served for Sil-100. As expected from the model, all

372 curves obtained show a limited linear part at low
 373 concentration (below 3 $\mu\text{mol/g}$ except Sil60-2 for
 374 which the curve is linear up to 7 $\mu\text{mol/g}$) and a
 375 deviation from linearity at higher concentration.

376 These fitted curves can be used on the whole
 377 concentration range to evaluate grafted silicas
 378 provided that the spectra of adsorbed or grafted
 379 compounds are similar. The spectra of the grafted
 380 silicas compared to those of selected adsorbed
 381 silicas are displayed in Fig. 9. The grafted silicas
 382 are noted with a letter G in the following to dis-
 383 tinguish them from adsorbed silicas. For the G1
 384 series, i.e. grafted silicas at low concentration, the
 385 $F(R)$ spectra are nearly identical to those of ad-
 386 sorbed silicas at similar concentrations. This im-
 387 plies similar host-guest interactions in both cases
 388 and accordingly, the determination of the loading
 389 of the grafted silicas can be deduced from the
 390 calibration curves (Fig. 8) obtained for the ad-
 391 sorbed samples. For the G2 series (high concen-
 392 tration grafted silicas), the comparison between
 393 $F(R)$ spectra of adsorbed and grafted samples in
 394 the same concentration range only holds true for
 395 Sil100 (Fig. 9b) and Sil60-2 (Fig. 9d). On the
 396 contrary, the spectra of Sil40 G2 (Fig. 9a) and
 397 Sil60-1 G2 (Fig. 9c) obviously deviate from those
 398 of the adsorbed samples. The fluorescence spectra
 399 of all these high concentration samples are roughly
 400 similar to those of the adsorbed samples, showing
 401 high ratio of excimer-like emission around 470 nm,

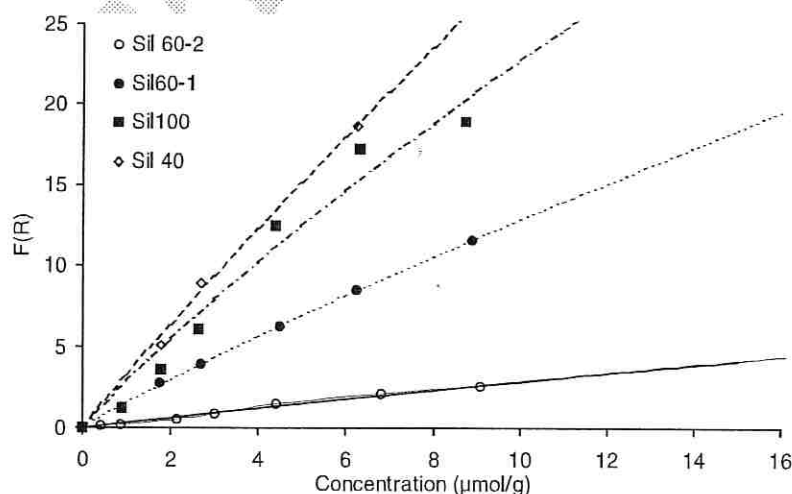


Fig. 8. Experimental points and fitted curves giving $F(R)$ versus the concentrations of adsorbed 1 for different silicas at 337 nm.

402 except Sil60-1 G2 for which the maximum of the
 403 excimer-like emission is shifted to 490 nm. In the
 404 case of Sil40 G2 and Sil60-1 G2, this may reflect
 405 different host-guest interactions and/or, for these
 406 high concentrations, different degrees of aggrega-
 407 tion. Alternatively, some hydrolysis and polymer-
 408 ization reaction of **1** during the grafting step,
 409 leading to the formation of polymeric species on

the surface could account for these deviations,
 especially for Sil60-1 G2. In these two latter cases,
 it is excluded to obtain a consistent determination
 of the loading from the DRUV calibration curves
 presented previously. Accordingly, the grafting
 yields for Sil40 G2 and Sil60-1 G2 have been
 thrown out in the following.

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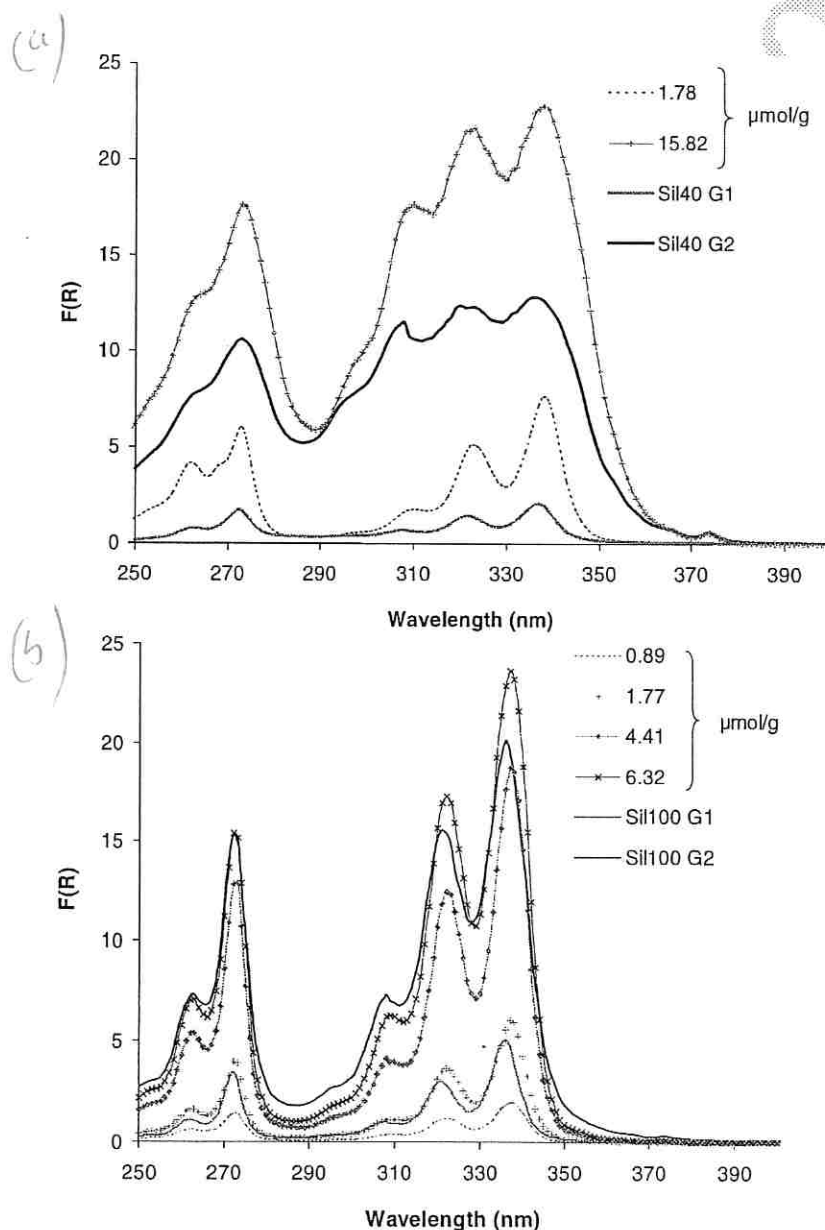


Fig. 9. DRUV spectra of the pyrene derivative **1** grafted on silica compared to spectra of **1** adsorbed on silica at selected concentrations: (a) Sil100, (b) Sil40, (c) Sil60-1 and (d) Sil60-2.

40 100

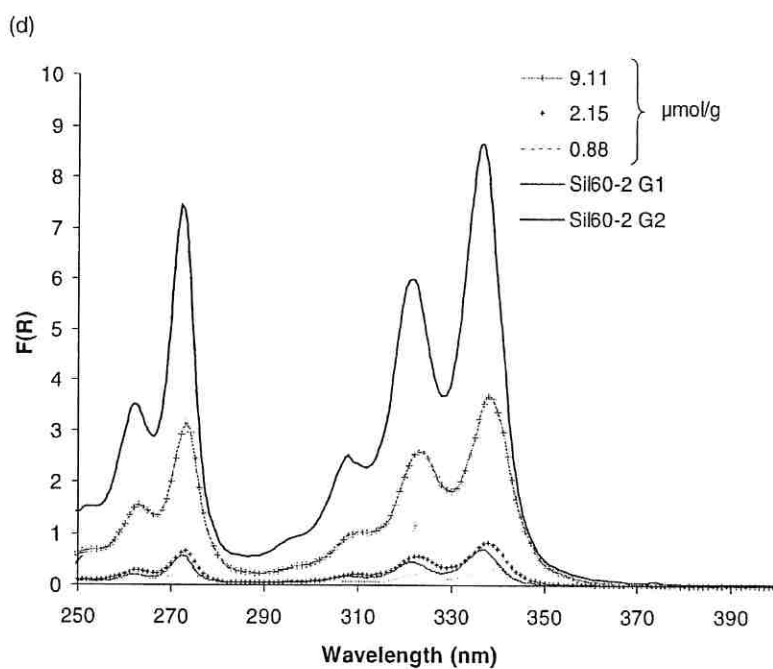
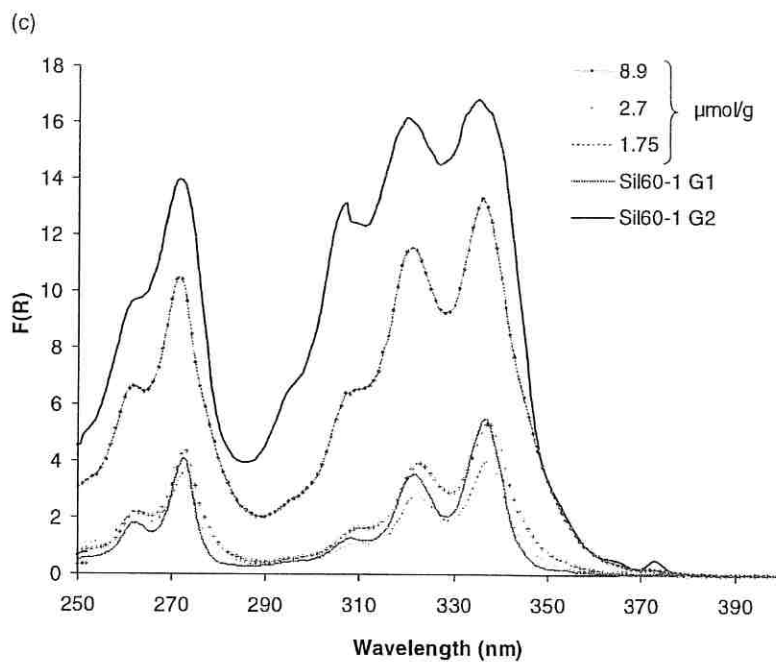


Fig. 9 (continued)

417 For all the other grafted samples, a quantitative
 418 determination has been made at each wavelength
 419 already used for the calibration procedure (273,
 420 323 and 338 nm). The results are displayed in

Table 3 together with the concentrations of **1** in- 421
 troduced in the solvent for the grafting step [22]. 422

Table 3

Calculation of the grafting yields of pyrene derivative **1** on different silicas, using Eq. (5)

Reference of the silica	Pyrene 1 ^a (μmol/g)	$F(R)_{323}$	Pyrene 1 ^b (μmol/g) (323)	$F(R)_{337}$	Pyrene 1 ^b (μmol/g) (337)	$F(R)_{273}$	Pyrene 1 ^b (μmol/g) (273)	Grafting yields
Sil100 G1	2.6	2.95	1.0	4.97	1.2	2.97	1.0	41 ± 4
Sil100 G2	25	15.20	6.3	19.67	5.8	15.34	6.7	25 ± 2
Sil60-1 G1	3.0	3.51	2.4	5.46	2.9	4.08	2.0	80 ± 15
Sil40 G1	2.7	1.35	0.4	1.98	0.3	1.71	0.4	14 ± 2
Sil60-2 G1	2.4	0.45	1.4	0.72	1.4	0.57	1.4	60
Sil60-2 G2	24.5	5.73	21.6	8.13	23.8	7.43	23.7	93 ± 4

^a Concentration of pyrene **1** used in the grafting process.^b Concentration of pyrene **1** calculated with measurements at the indicated wavelength (nm).

423 Except for the cases of Sil60-1 G1, the confi-
 424 dence limits for the calculated grafting yields are
 425 found to be below 8%.

426 In the case of Sil-100, the grafting yields de-
 427 crease from 41% to 25% (1.1 and 6.3 μmol/g of
 428 grafted **1** for Sil100 G1 and Sil100 G2 respectively)
 429 in spite of the fact that the concentration of **1** has
 430 been increased, owing to the saturation of the
 431 grafting sites on silica.

432 High grafting yields are obtained for Sil60. For
 433 Sil60-1 G1, the results vary significantly between
 434 the three considered wavelengths (2.0–2.9 μmol/g
 435 for Sil60-1 G1). This inaccuracy is related to the
 436 slight deviation of the spectrum of the grafted
 437 compound relative to those of adsorbed ones (Fig.
 438 9c). In the case of Sil60-2, the highest grafting yield
 439 is obtained for the highest concentration of **1**, in-
 440 dicated that the surface silanols are not saturated
 441 even at high concentration.

442 Finally, for grafted Sil-40 G1 the amount of
 443 grafted **1** is 0.4 μmol/g corresponding to a very low
 444 grafting yield (14%).

445 No clear-cut explanation can be given to ac-
 446 count for the results on Sil60-1 G2 and Sil40 G2: is
 447 the deviation related to higher-order aggregates or
 448 to hydrolysis and polymerization reactions of **1**
 449 before grafting? Some preliminary results indicate
 450 that the adsorbed triethoxysilyl derivative **1** can be
 451 covalently grafted spontaneously at room tem-
 452 perature. Under these mild conditions, hydrolysis
 453 and polymerization reactions of **1** before grafting
 454 are thus unlikely. If this can be confirmed, a better
 455 control of the loading might be possible since
 456 calibration and grafting should be run under

similar conditions. Further experiments are being
 carried out to verify this proposal.

In any case, the DRUV spectroscopy appears as
 a very useful tool to assess qualitatively and
 quantitatively organic adsorbates on silica, espe-
 cially in low concentration domains where other
 more usual methods are rather inaccurate.

4. Conclusions

This study further confirms that DRUV is a
 powerful technique to evidence qualitatively the
 interactions between molecules adsorbed on an
 inert substrate like silica. This work moreover
 demonstrates that a quantitative treatment of the
 data is also possible even at high concentrations,
 provided that the sampling methods and recording
 conditions are carefully controlled. By extension of
 a well known processing of the spectrophotometric
 data in solution, the relative dimer and monomer
 concentrations as well as their respective spectrum
 in the adsorbed state may be derived.

This set of results yields a calibration curve
 giving $F(R)$ versus the concentration of adsorbed
 species, against which the signals of the same
 species grafted on silica can be evaluated. Grafting
 ratios, hardly obtained by other techniques, are
 thus available and the method appears especially
 sensitive at low or very low loading.

These results also give some indications for fu-
 ture uses of grafted photosensitizers in photo-
 chemical applications. A silica with small particle
 size or large pore size should be preferred to avoid
 excimer formation. Furthermore, in order to use

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489 the DRUV determination method, small particle
490 size silica offers an additional advantage such as a
491 reduced $F(R)$ scale owing to a large scattering
492 coefficient.

493 Finally, the general grafting method used in this
494 study leads to poorly controlled loading at high
495 concentration. In some cases, unexplained defor-
496 mation of the spectra relative to those of adsorbed
497 samples are observed. Some improvement in the
498 synthetic method is thus under investigation.

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