

Research Letter

Surface Photochemistry: Benzophenone as a Probe for the Study of Modified Cellulose Fibres

L. F. Vieira Ferreira,¹ A. I. Costa,^{1,2} I. Ferreira Machado,^{1,3} T. J. F. Branco,¹ S. Boufi,⁴
M. Rei-Vilar,⁵ and A. M. Botelho do Rego¹

¹ Centro de Química-Física Molecular - Complexo Interdisciplinar, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

² Laboratório de Química Orgânica, Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, R. Conselheiro Emídio Navarro 1, 1950-062 Lisboa, Portugal

³ Escola Superior de Tecnologia e Gestão, Instituto Politécnico de Portalegre, Lugar da Abadessa, APT 148, 7301-901 Portalegre, Portugal

⁴ Laboratoire Sciences des Matériaux et Environnement (LMSE), Faculté des Sciences de Sfax, BP 802-3018 Sfax, Tunisia

⁵ Laboratoire ITODYS, Université Paris Diderot, CNRS, 75005 Paris, France

Correspondence should be addressed to L. F. Vieira Ferreira, luisfilipevf@ist.utl.pt

Received 18 July 2007; Accepted 27 October 2007

Recommended by Bern Kohler

This work reports the use of benzophenone, a very well characterized probe, to study new hosts (i.e., modified celluloses grafted with alkyl chains bearing 12 carbon atoms) by surface esterification. Laser-induced room temperature luminescence of air-equilibrated or argon-purged solid powdered samples of benzophenone adsorbed onto the two modified celluloses, which will be named C12-1500 and C12-1700, revealed the existence of a vibrationally structured phosphorescence emission of benzophenone in the case where ethanol was used for sample preparation, while a nonstructured emission of benzophenone exists when water was used instead of ethanol. The decay times of the benzophenone emission vary greatly with the solvent used for sample preparation and do not change with the alkylation degree in the range of 1500–1700 micromoles of alkyl chains per gram of cellulose. When water was used as a solvent for sample preparation, the shortest lifetime for the benzophenone emission was observed; this result is similar to the case of benzophenone adsorbed onto the “normal” microcrystalline cellulose surface, with this latter case previously reported by Vieira Ferreira et al. in 1995. This is due to the more efficient hydrogen abstraction reaction from the glycosidic rings of cellulose when compared with hydrogen abstraction from the alkyl chains of the modified celluloses. Triplet-triplet transient absorption of benzophenone was obtained in both cases and is the predominant absorption immediately after laser pulse, while benzophenone ketyl radical formation occurs in a microsecond time scale both for normal and modified celluloses.

Copyright © 2007 L. F. Vieira Ferreira et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. INTRODUCTION

Diffuse reflectance laser flash photolysis and laser-induced luminescence, both in time-resolved mode or ground-state absorption spectroscopy in the diffuse reflectance mode, are important techniques that have been used by several research groups to study opaque and crystalline systems [1–8]. These solid-state photochemical methods have been applied by us to study several organic compounds adsorbed onto different hosts such as microcrystalline cellulose [7, 8], *p*-tert-butylcalix[*n*]arenes (*n* = 4, 6, and 8) and their derivatives [10–12], silicalite, cyclodextrins [7, 12, 13], and silica [14].

Benzophenone (BZP) is an extremely useful molecule for probing new hosts. The $n \rightarrow \pi^*$ absorption transition was found to be very sensitive to the environment characteristics and also exhibits a photochemistry which depends on the host properties [10, 12, 14]. In a recent paper [14], we reported a comparative study of the luminescent properties of BZP adsorbed onto reversed phase silicas, “normal” silica, and silicalite (a de-aluminated zeolite). Apart from the triplet-state luminescence observed in all cases, in the case of “normal” silica the emission of an excited form of hydrogen-bonded benzophenone was also detected [14].

With this work we intend to contribute to the study of the mechanism by which modified cellulose fibres are able to trap dissolved organic pollutants from water. Indeed, as we have shown previously [15, 16], grafting of linear alkyl chains on the fibre's surface boosts its capacity to uptake organic solutes from aqueous solution. By ensuring grafted alkyl chains, one gives rise to hydrophobic domains on which organic solutes can be accumulated. The adsorption process occurs by transfer of the sparingly soluble organic molecules from water to organic zones of the modified cellulose where the most significant adsorbent-adsorbate interactions occur.

This work reports the use of BZP, a very well characterized probe, to study new hosts (i.e., modified celluloses). The modification consists in grafting with alkyl chains, bearing 12 carbon atoms, by surface esterification with a high density of alkyl chains [15], therefore, transforming the polar surface of the normal cellulose into surfaces with a certain degree of nonpolar character. A comparison of the photochemical behaviour of BZP in modified and nonmodified celluloses was made.

2. EXPERIMENTAL

2.1. Materials

Microcrystalline cellulose (Fluka D50) was used as powdered solid support, as received. Benzophenone (Koch-Light, Scintillation grade) and ethanol (Merck, LiChrosolv grade) were also used as received. The preparation of the modified cellulose fibres started with the use of microcrystalline cellulose and involved an acylation reaction based on a solvent exchange procedure, as described in detail in [15]. The aliphatic anhydrides have 12 carbon atoms (C12) per alkyl chain and the final modified cellulose has 1500 (C12-1500) or 1700 (C12-1700) micromoles of alkyl chains per gram of cellulose [15].

2.2. Sample preparation

Benzophenone adsorption on samples was performed using two methods: the solvent evaporation method for the case of ethanol [14], and, also, adsorption from water [15]. The former method consists in the addition of an ethanolic solution containing the probe to the previously dried powdered solid substrate, followed by solvent evaporation from the stirred slurry in a fume cupboard. In the case of water, the fibers were first swollen for at least two hours, and the addition of BZP was done by adding 500 micromoles of this probe dissolved in ethanol (saturated solution so that the added amount of ethanol was minimized). The water suspensions were kept under agitation for 24 hours and the modified cellulose (with the adsorbed BZP) was removed by filtration. From the initial $500 \mu\text{mole g}^{-1}$ of BZP, about $300 \mu\text{mole g}^{-1}$ remained into the powdered substrate (i.e., an increase in the retention capacity of the powdered substrate of about twelve times when compared to previous reported results) was obtained with nonmodified cellulose [15].

In both cases, the final solvent removal was performed for about two hours in an acrylic chamber with an electri-

cally heated shelf (Heto, Model FD 1.0–110) with temperature control ($30 \pm 1^\circ\text{C}$) and under moderate vacuum at a pressure of ca. 10^{-3} Torr.

2.3. Methods

2.3.1. Ground-state diffuse reflectance absorption spectra (GSDR)

Ground-state absorption spectra for the solid samples were recorded using an OLIS 14 spectrophotometer with a diffuse reflectance attachment. Further details are given in [1, 7].

2.3.2. Laser-induced luminescence (LIL) and diffuse reflectance laser flash photolysis (DRLFP) systems

Schematic diagrams of the LIL and of the DRLFP systems are presented in [1]. Laser flash photolysis experiments were carried out with the third or the fourth harmonic of an Nd:YAG laser (355 and 266 nm, ca. 6 ns FWHM, ~ 10 – 30 mJ/pulse) from B. M. Industries (Thomson-CSF, model Saga 12-10) in the diffuse reflectance mode. The light arising from the irradiation of solid samples by the laser pulse is collected by a collimating beam probe coupled to an optical fiber (fused silica), and is detected by a gated intensified charge-coupled device Oriel model Instaspec V (Andor ICCD, based on the Hamamatsu S57 69-0907). The ICCD is coupled to a compact fixed imaging spectrograph (Oriel, model FICS 77441). The system can be used either by capturing all light emitted by the sample or in a time-resolved mode by using a delay box (Stanford Research Systems, model D6535). The ICCD has high speed gating electronics (2.2 nanoseconds) and intensifier, and covers the 200–900 nm wavelength range. Time-resolved absorption and emission spectra are available in a time scale ranging from nanosecond to second. Transient absorption data are reported as percentage of absorption (%Abs.), defined as $100 \Delta J_t / J_0 = (1 - J_t / J_0) 100$, where J_0 and J_t are diffuse reflected light from sample before exposure to the exciting laser pulse and at time t after excitation, respectively. Laser-induced luminescence experiments were performed with an N_2 laser (PTI model 2000, ca. 600 ps FWHM, ~ 1.1 mJ per pulse). In this case, the excitation wavelength is 337 nm. With these setups, both fluorescence and phosphorescence spectra are easily available (by the use of the variable time gate width and start delay facilities of the ICCD).

3. RESULTS AND DISCUSSION

In both cases (benzophenone adsorption from water or from ethanol), similar results were obtained for the two modified celluloses C12-1500 or C12-1700 (within experimental error) (i.e., with degree of modification ranging in 1500–1700 μmol of alkyl chains per gram of cellulose). This is valid for all the experimental techniques used in this work. This paper reports data obtained for this specific degree of alkylation and compares samples obtained with two different solvents.

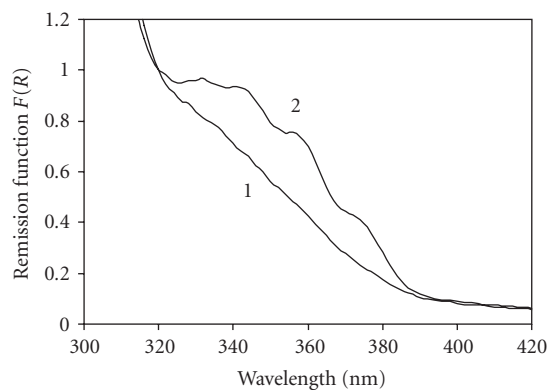


FIGURE 1: Ground-state diffuse reflectance absorption spectra for samples of benzophenone adsorbed onto C12-1500 (curve 1) and C12-1700 (curve 2) modified celluloses. Curve 1 refers to benzophenone adsorbed from water and curve 2 refers to benzophenone adsorbed from ethanol.

Ground-state diffuse reflectance absorption spectra

Ground-state diffuse reflectance absorption spectra for BZP adsorbed onto C12-1500, C12-1700, and microcrystalline cellulose [7] were obtained with the use of an integrating sphere [1, 7].

For BZP/C12-1700 samples prepared by solvent evaporation method with ethanol, the ketone's ground-state absorption $S_0 \rightarrow S_1$ transition ($n \rightarrow \pi^*$) has a maximum at about 347 nm and exhibits a clear vibronic structure characteristic of the excited carbonyl group of BZP in a hydrophobic environment [17].

For BZP adsorbed from water onto C12-1500 modified cellulose, the ground-state absorption curves appear now as broad bands, shifted hypsochromically when compared with BZP/C12-1700 ethanol case, where the vibronic absorption bands of the carbonyl group can be seen (Figure 1). These hypsochromic shifts are quite characteristic of the $n \rightarrow \pi^*$ transition with increasing polarity of the surface [7, 11, 14, 17]. The broadening of the spectra is probably also related both with heterogeneity of the adsorbent and a much smaller rigidity of the adsorbed probe. Solution absorption spectra of BZP, for instance in cyclohexane and ethanol, also exhibit this type of influence of polarity, characteristic of the $n \rightarrow \pi^*$ transition [17].

Clearly, going from C12-1700/EtOH to C12-1500/H₂O an increase in the surface polarity is observed, quite consistent with the surface characteristics and different adsorption sites to BZP: long alkyl chains with 12 carbons in the C12-1700/EtOH sample, and contact with the hydroxyl groups of the cellulose polymer chains in the C12-1500/H₂O case.

Room temperature laser-induced phosphorescence

Figure 2 presents the room temperature phosphorescence spectra of BZP onto the surfaces of the C12-1500/H₂O modified cellulose while Figure 3 refers to BZP within C12-1700/EtOH.

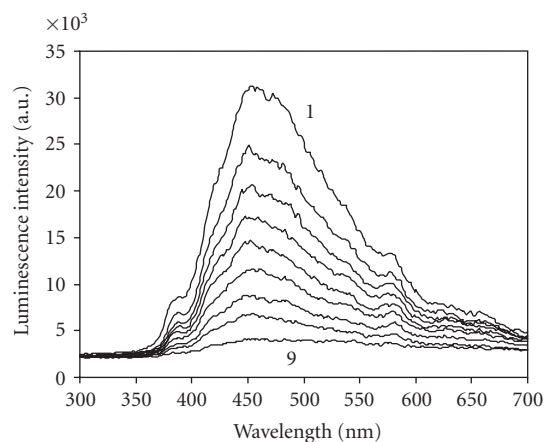


FIGURE 2: Laser-induced phosphorescence spectra for argon-purged samples of benzophenone adsorbed onto C12-1500 modified cellulose from water. Curves were recorded 0.5 microsecond, 2.0 microseconds, 4.5 microseconds, 8 microseconds, 16 microseconds, 30 microseconds, 70 microseconds, 120 microseconds, and 380 microseconds after the laser pulse. The excitation wavelength was 337 nm.

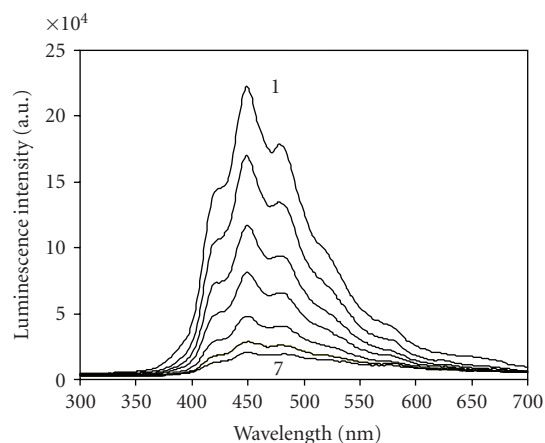


FIGURE 3: Laser induced phosphorescence spectra for argon-purged samples of benzophenone adsorbed onto C12-1700 modified cellulose from ethanol. Curves were recorded 1 microsecond, 5 microseconds, 20 microseconds, 45 microseconds, 75 microseconds, 150 microseconds, and 225 microseconds after the laser pulse. The excitation wavelength was 337 nm.

Those time-resolved spectra were obtained with air-equilibrated conditions and were identical to the ones obtained with argon-purged samples within experimental error. Half-lives of about 20 μ s can be obtained from time-resolved spectra shown in Figures 2 and 3.

For comparison purposes, lifetimes of about 80 microseconds were determined for the calixarene inclusion [10, 11] and 3.1 milliseconds for inclusion into the narrower channels of silicalite [12, 18], as compared to about 40 microseconds for benzophenone microcrystals, all determined at the maximum emission wavelength (about 448 nm) [14].

A new tool for a lifetime distributions analysis of emissions of probes adsorbed onto heterogeneous surfaces was recently developed by our research group [18]. This new

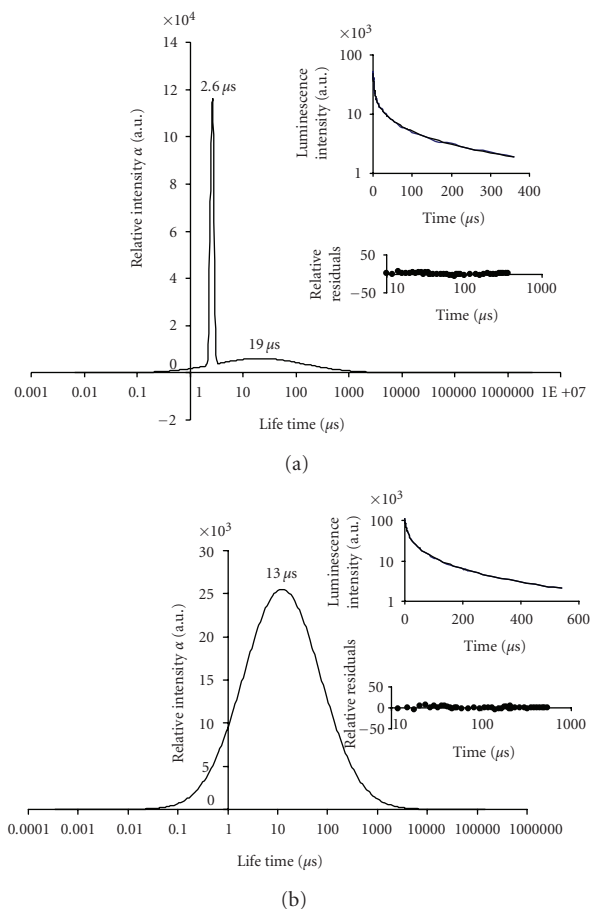


FIGURE 4: Lifetime distributions for benzophenone within C12-1500/H₂O (a) and for benzophenone within C12-1700/EtOH (b) recovered from luminescence decays observed at 450 nm. The insets show the fitting of the recovered decay to the experimental data and residuals.

methodology allows for asymmetric distributions and uses pseudo-Voigt profiles (Gaussian-Lorentzian product) instead of pure Gaussian or Lorentzian distributions. A very simple and widely available tool for fitting has been used, the Microsoft Excel Solver. This is a convenient way to treat the emission decay data because it reflects the multiplicity of adsorption sites available for the probe onto each specific surface. The use of a sum of a few exponentials to analyse the decay of probes onto heterogeneous surfaces is a description without physical meaning [18].

A detailed study of the luminescence decay curves of pyrene included within *p-tert*-butylcalix[4]arene cavities and benzophenone into silicalite channels has been reported recently [18, 19].

When applied to the C12-1700/EtOH and C12-1500/H₂O cases (see Figures 4(a) and 4(b)), and after recording the decay traces in various instrumental time scales (experimental information was obtained starting in the 0.02 microsecond or longer timescales), the lifetimes distribution analysis evidences a single broad band centred at ca. 13 microseconds, which we assigned to BZP adsorbed onto the long alkyl chains with 12 carbons in the C12-1700/EtOH case; but for the case of C12-1500/H₂O, another band (in this case

a sharp band) centred at 2.6 microseconds predominates, which we assigned to BZP in close contact with the hydroxyl groups of the cellulose polymer chains. The emission from BZP in contact with the alkyl chain still exists (peaking now at 19 microseconds) but it is of much less importance than the other component.

This kinetic information is consistent with previous data from ground-state absorption spectra as well as the spectroscopic information from laser-induced luminescence experiments.

The laser-induced emission experiments for BZP/C12-1500/H₂O also showed a special emission of BZP in the nanosecond time scale, very similar to the one reported in [20, Figure 3(b)] for BZP on MCM-41. This emission peaks at ca. 430 nm, and therefore it originates from hydrogen-bonded BZP (data not shown). In the case of the BZP/C12-1700/EtOH sample, no hydrogen-bonded BZP emission in the nanosecond time scale could be detected.

Previous work indicates that calixarene [10–12], cellulose [7, 8], or reversed phase silicas [14] are good hydrogen atom donors towards BZP (in solid powdered samples), so it sounds reasonable to assume that ketyl radical formation of benzophenone may also occur here. The emission maxima at 575 nm presented both in spectra of Figures 2 and 3 are a reasonable indication that this is also the case.

In order to perform the lifetime distribution analysis, several decay curves in different instrumental time scales were recorded. A superposition of those decay traces was made by normalization of each decay curve at a time range where they overlap, in order to produce a composite decay with closely spaced data at short times and larger spaced values at long times. This procedure was adopted before [14, 19], and is necessary because the abscissa is $\ln t$, therefore a very large time range had to be used.

Diffuse reflectance laser flash photolysis

Time-resolved absorption spectra of samples of BZP/C12-1700/EtOH and C12-1500/H₂O samples were obtained by the use of diffuse reflectance laser flash photolysis technique, developed by Wilkinson et al. [2–4]. In this study, the use of an intensified charge-coupled device as a detector allowed us to obtain time-resolved absorption spectra with nanometer spectral spacing (i.e., where the 200–900 scale is defined by the 512 pixels used for recording spectra in the array of the ICCD) [1, 8–14].

Both transient absorption spectra of the BZP/C12-1700/EtOH and C12-1500/H₂O samples have shown the simultaneous formation of triplet benzophenone and also of hydroxylbenzophenone radical (BZP[•]OH) (data not shown). The triplet-triplet absorption spectra of benzophenone (max. at 530 nm) was easily identified from comparison with the one published by Wilkinson et al. [4]. The transient absorption which peaks at 390 nm can be assigned to BZP[•]OH radical by comparison with previously reported spectra in solution or on the MCM-41 surface [20]. Ketyl radical formation peaking at about 550 nm was observed for both BZP/C12-1700/EtOH and C12-1500/H₂O samples a few microsecond after laser pulse, showing that hydrogen atom abstraction can occur either when adsorbed onto the

long alkyl chains or when BZP is close to the main polymer chain of cellulose where the hydrogen atoms, bound to the secondary carbons, are the most easily abstractable ones [7].

4. CONCLUSIONS

The photochemistry of BZP onto the modified celluloses is determined by the nature of the adsorption site (long alkyl chains or the hydroxyl groups of the polymer chains). The adsorption site of the probe depends on the solvent used for sample preparation: ethanol privileges the first case while water leads to the second situation. As a consequence of the detected BZP phosphorescence, BZP ketyl radical fluorescence and hydrogen-bonded BZP luminescence reflect the different sites for adsorption.

A lifetime distributions analysis provided important information and revealed an important quenching effect in the case of adsorption from water, comparable to the case of adsorption onto microcrystalline cellulose [7], due to the more efficient hydrogen abstraction reaction from the glycoside rings of cellulose when compared with hydrogen abstraction from the alkyl chains of the modified celluloses.

Diffuse reflectance transient absorption spectra revealed the presence of the triplet state of BZP in all supports under study, and also of the diphenylketyl radical and BZP[•]OH radicals.

ACKNOWLEDGMENTS

The authors thank Fundação para a Ciência e Tecnologia (FCT) for financial support (Project POCI/QUI/57491/2004), and A. I. Costa thanks Instituto Superior de Engenharia de Lisboa, (ISEL) for a Doctoral fellowship.

REFERENCES

- [1] A. M. Botelho do Rego and L. F. Vieira Ferreira, "Photonic and electronic spectroscopies for the characterization of organic surfaces and organic molecules adsorbed on surfaces," in *Handbook of Surfaces and Interfaces of Materials*, H. S. Nalwa, Ed., vol. 2, chapter 7, pp. 275–313, Academic Press, Boston, Mass, USA, 2001.
- [2] F. Wilkinson and G. P. Kelly, "Laser Flash Photolysis on Solid Surfaces" in *Photochemistry on Solid Surfaces*, M. Anpo and T. Matsuura, Eds., pp. 31–47, Elsevier, Amsterdam, The Netherlands, 1989.
- [3] F. Wilkinson and G. P. Kelly, "Diffuse reflectance flash photolysis," in *Handbook of Organic Photochemistry*, J. C. Scaiano, Ed., vol. 1, chapter 12, pp. 293–314, CRC Press, Boca Raton, Fla, USA, 1989.
- [4] F. Wilkinson and C. J. Willsher, "Detection of triplet-triplet absorption of microcrystalline benzophenone by diffuse-reflectance laser flash photolysis," *Chemical Physics Letters*, vol. 104, no. 2–3, pp. 272–276, 1984.
- [5] G. Cosa and J. C. Scaiano, "Laser techniques in the study of drug photochemistry," *Photochemistry and Photobiology*, vol. 80, no. 2, pp. 159–174, 2004.
- [6] J. K. Thomas, "Effect of SiO₂ and zeolite surfaces on the excited triplet state of benzophenone, B^T; a spectroscopic and kinetic study," *Photochemical & Photobiological Sciences*, vol. 3, no. 5, pp. 483–488, 2004.
- [7] L. F. Vieira Ferreira, J. C. Netto-Ferreira, I. V. Khmelinskii, A. R. Garcia, and S. M. B. Costa, "Photochemistry on surfaces: matrix isolation mechanisms study of interactions of benzophenone adsorbed on microcrystalline cellulose investigated by diffuse reflectance and luminescence techniques," *Langmuir*, vol. 11, no. 1, pp. 231–236, 1995.
- [8] L. F. Vieira Ferreira, I. Ferreira Machado, J. P. Da Silva, and A. S. Oliveira, "A diffuse reflectance comparative study of benzil inclusion within microcrystalline cellulose and β -cyclodextrin," *Photochemical & Photobiological Sciences*, vol. 3, no. 2, pp. 174–181, 2004.
- [9] L. Ilharco, A. R. Garcia, J. Lopes da Silva, M. J. Lemos, and L. F. Vieira Ferreira, "Ultraviolet-visible and Fourier transform infrared diffuse reflectance studies of benzophenone and fluorenone adsorbed onto microcrystalline cellulose," *Langmuir*, vol. 13, no. 14, pp. 3787–3793, 1997.
- [10] L. F. Vieira Ferreira, M. R. Vieira Ferreira, J. P. Da Silva, I. Ferreira Machado, A. S. Oliveira, and J. V. Prata, "Novel laser-induced luminescence resulting from benzophenone/*O*-propylated *p*-*tert*-butylcalix[4]arene complexes. A diffuse reflectance study," *Photochemical & Photobiological Sciences*, vol. 2, no. 10, pp. 1002–1010, 2003.
- [11] L. F. Vieira Ferreira, M. R. Vieira Ferreira, A. S. Oliveira, T. J. F. Branco, J. V. Prata, and J. C. Moreira, "Diffuse reflectance studies of β -phenylpropiophenone and benzophenone inclusion complexes with calix[4], [6] and [8]arenes," *Physical Chemistry Chemical Physics*, vol. 4, no. 2, pp. 204–210, 2002.
- [12] L. F. Vieira Ferreira, M. R. Vieira Ferreira, A. S. Oliveira, and J. C. Moreira, "Potentialities of diffuse reflectance laser-induced techniques in solid phase: a comparative study of benzophenone inclusion within *p*-*tert*-butylcalixarenes, silicalite and microcrystalline cellulose," *Journal of Photochemistry and Photobiology A*, vol. 153, no. 1–3, pp. 11–18, 2002.
- [13] J. P. Da Silva, L. F. Vieira Ferreira, A. M. Da Silva, and A. S. Oliveira, "A comparative study of the photophysics and photochemistry of 4-chlorophenol adsorbed on silicalite and β -cyclodextrin," *Journal of Photochemistry and Photobiology A*, vol. 151, no. 1–3, pp. 157–164, 2002.
- [14] L. F. Vieira Ferreira, I. Ferreira Machado, J. P. Da Silva, and T. J. F. Branco, "Surface photochemistry: benzophenone as a probe for the study of silica and reversed-phase silica surfaces," *Photochemical & Photobiological Sciences*, vol. 5, pp. 665–673, 2006.
- [15] S. Boufi and M. N. Belgacem, "Modified cellulose fibers for adsorption of dissolved organic solutes," *Cellulose*, vol. 13, no. 1, pp. 81–94, 2006.
- [16] F. Aloulou, S. Boufi, and J. Labidi, "Modified cellulose fibres for adsorption of organic compound in aqueous solution," *Separation and Purification Technology*, vol. 52, no. 2, pp. 332–342, 2006.
- [17] N. J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings, Menlo Park, Calif, USA, 1978.
- [18] T. J. F. Branco, A. M. Botelho do Rego, I. Ferreira Machado, and L. F. Vieira Ferreira, "Luminescence lifetime distributions analysis in heterogeneous systems by the use of Excel's Solver," *Journal of Physical Chemistry B*, vol. 109, no. 33, pp. 15958–15967, 2005.
- [19] T. J. F. Branco, L. F. Vieira Ferreira, A. M. Botelho do Rego, A. S. Oliveira, and J. P. Da Silva, "Pyrene-*p*-*tert*-butylcalixarenes inclusion complexes formation: a surface photochemistry study," *Photochemical & Photobiological Sciences*, vol. 5, no. 11, pp. 1068–1077, 2006.
- [20] J. P. Da Silva, I. Ferreira Machado, J. P. Lourenço, and L. F. Vieira Ferreira, "Photochemistry of benzophenone adsorbed on MCM-41 surface," *Microporous and Mesoporous Materials*, vol. 84, no. 1–3, pp. 1–10, 2005.