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Calibration of the triplet–triplet absorption of xanthone as a microenvironment sensor

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Abstract

The wavelength of maximum absorption of triplet xanthone (λ_{max}) is strongly dependent on the nature of the solvent, shifting to the red as the solvent polarity decreases. Thus triplet xanthone can be employed as a probe for polarity of microenvironments such as micelles, cyclodextrins and zeolites. Using nanosecond laser flash photolysis we have measured λ_{max} in a variety of solvents using a Gaussian fitting routine to obtain an objective value for the triplet maximum. These data were compared with two different measures of solvent polarity: the solvent dielectric constant and the pyrene fluorescence band ratio (I_1/I_3). There is a modest correlation ($R = 0.89$) with dielectric constant. The value of λ_{max} shows two different correlations with I_1/I_3, one with hydrogen bonding solvents and one with non-hydrogen bonding solvents. The triplet lifetime and absorption band width (FWHM) also exhibit some solvent dependence. We propose the triplet xanthone scale as a convenient tool for probing supramolecular systems using laser flash photolysis; this tool complements nicely the fluorescence of pyrene, which requires a different experimental technique and probes a shorter time scale.

Keywords: Xanthone; Microenvironment sensor; Laser flash photolysis

1. Introduction

Photochemical studies in supramolecular systems have helped to understand the nature of numerous guest–host systems, and provided interesting routes to chemical pathways that either do not occur, or occur inefficiently in homogenous systems [1–5]. At the same time, the interest in supramolecular systems has generated the need for adequate sensor systems, capable of reporting on the local properties of the microenvironment, such as polarity, restriction to mobility, acid–base, and electron donor/acceptor characteristics.

The vibrational structure of the fluorescence from pyrene and its excimer emission provided a valuable tool to estimate the polarity and mobility in various guest–host systems [3,4,6–12]. One important limitation to these fluorescent probe techniques is that the fluorescence lifetime is relatively short. Excited triplet states are much longer lived and, thus, in principle can offer an extended time scale to probe properties such as mobility-induced polarity changes in organized media. In addition, it is useful to count on an arsenal of techniques which can allow probing of a wide range of systems; further, it is sometimes useful to be able to use the same technique that may be employed in other aspects of a given study (e.g., laser flash photolysis or fluorescence spectroscopy).

The location of the band maximum of the triplet–triplet absorption of xanthone (λ_{max}) depends strongly on solvent polarity [13,14]. This is due to the fact that the lowest energy triplet of xanthone changes from π,π^* in character in polar solvents to n,π^* in non-polar solvents [13,14]. The variation in xanthone triplet λ_{max} has already been used as a sensor of environmental polarity [15,16], as well as of mobility [15–18]. While a number of studies have reported on the triplet λ_{max} for xanthone in various solvents, no systematic study of the spectral dependence has been reported. In this article we use laser flash photolysis to examine in some detail the triplet–triplet spectroscopy of xanthone, and compare the values of λ_{max} with other measures of environmental polarity. We note that homogeneous systems simply provide a basis for calibration, while the practical use of this sensor is in heterogeneous systems, where xanthone can report on local properties.

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2. Experimental

Xanthone (Aldrich) was recrystallized from methanol. All solvents were Omnisolv grade (BDH) and were used as received, except for dioxane which was distilled once. Cyclohexane-d_{12} (Cambridge Isotopes, 99 atom %) was used as received. Water was purified through a Millipore Milli-Q system.

Laser photolysis studies were performed in static cells. The cells (constructed of 7×7 mm^2 Suprasil quartz tubing) were typically filled to a volume of 4.5 ml. Three lasers were used. A Lumonics EX-530 excimer laser operated with Xe/HCl/He mixtures provided 308 nm pulses. The dose per pulse was ca. 60 mJ. A Molectron UV-24 nitrogen laser provided 337 nm pulses of ca. 3 mJ energy. The third harmonic from a Surelite Nd:YAG (355 nm, ~20 mJ per 8 ns pulse) was also used in some experiments. All measurements were carried out at room temperature (ca. 298 K). Typically the sample had a concentration such that the absorbance at the laser wavelength in the laser photolysis cell was in the 0.2–0.3 range.

Determinations of $\lambda_{\max}$ were straightforward for most solvents which were either not good hydrogen donors or of polarity exceeding that of dioxane. Triplet xanthone has n,π^* character only in non-polar solvents [14]. The high reactivity of xanthone triplets in hydrogen abstraction reactions [13,14] makes a measurement of the xanthone triplet spectrum difficult in solvents such as hexane or cyclohexane. Attempts to observe the triplet in these two solvents yielded only the spectrum of the xanthone ketyl radical ($\lambda_{\max}$ near 480 nm and a second band with peaks at 560, 615 and 660 nm). To try and assess the triplet maximum in a very non-polar, alkane-like solvent we made use of cyclohexane-d_{12}. We hoped that the kinetic isotope effect would facilitate the measurement. The sample was examined between 590 and 670 nm. Each point on the spectrum consisted of only three laser shots and the sample was shaken after every laser shot. While it was clear that $\lambda_{\max}$ was in the 640–660 nm region, even with these precautions the signal was extensively contaminated by the xanthone ketyl-O-*d* radical. A flow experiment would have been desirable, but solvent costs would have been prohibitive. Similarly, the triplet lifetime in dimethylformamide was too short to permit a reliable evaluation of $\lambda_{\max}$.

Data analysis in order to determine $\lambda_{\max}$ was carried out both by visual inspection and by fitting the top of the absorption maximum to a Gaussian function (Eq. (1)); the latter approach is, in the context of the present work, simply a convenient non-subjective approach to determine the best position for $\lambda_{\max}$ [18]. It should be regarded simply as a convenient approach and is not meant to indicate that a Gaussian shape is required by theory.

$$\Delta\mathrm{OD} = \beta \frac{1}{\Delta\lambda\sqrt{\pi/2}} \mathrm{e}^{-(2(\lambda-\lambda_{\max})/\Delta\lambda^2)} \qquad (1)$$

where ΔOD is the transient absorbance at wavelength λ, β is a scaling parameter, $\lambda_{\max}$ is the value at the maximum (the mean value) and $\Delta\lambda$ is the spectral width (two standard deviations, 2σ). Typical fits included the same amount of data (~50% of the $\lambda_{\max}$ signal) on each side of the maximum. We have also noted some dependence of the width of the absorption band on the solvent polarity. Appropriate widths ($\Delta\lambda$) are expressed in nanometers at half-signal intensity.

The pyrene I_1/I_3 fluorescence band ratio was recorded for several solvents in which the data were not readily available. These measurements were made with a Perkin-Elmer Lambda 50 instrument following the recommendations of Street and Acree [9] and were used as comparative values.

3. Results and discussion

Typical decay traces were recorded in time scales such that about 80% of the triplet decay would be covered. The spectra shown in Fig. 1 correspond to about the first 10% of the decay, so that even in hydrogen donating solvents there would be minimal contamination from the ketyl radical which shows an absorption maximum near 500 nm. Fig. 1 shows representative, normalized triplet spectra determined in ethyl acetate, ethylene glycol and trifluorotoluene. The insert shows the peak region in ethyl acetate, fitted with a Gaussian function yielding $\lambda_{\max} = 628$ nm. The data for all the solvents examined are summarized in Table 1. Inspection of Table 1 clearly shows a qualitative trend of $\lambda_{\max}$ with the polarity of the solvent, illustrated in Fig. 2 as a plot of $\lambda_{\max}$ against the solvent dielectric constant, showing a modest correlation with $R = 0.89$ ($R = 0.86$ if acetonitrile is included in the best line fit). It is apparent from this plot that aprotic solvents tend to lie above the line, while protic solvents are on or below the line. This suggests that the hydrogen bonding ability of a solvent also influences $\lambda_{\max}$. Compare, for example, acetonitrile and methanol, two polar solvents of similar dielectric constant and molecular dimensions. Using the data from the solid line in Fig. 2, the expected value of $\lambda_{\max}$ can be estimated according to

$$(\lambda_{\max})_{\mathrm{calc}} = 638 - 0.82 \times \varepsilon \ (\mathrm{in\,nm}) \qquad (2)$$

Another spectroscopic parameter frequently employed as a sensor for local polarity is the 'I_1/I_3' ratio of pyrene fluorescence, based on the 'Ham Effect' [19]. Essentially the relative intensities of the first and third vibronic bands of pyrene fluorescence (372 and 383 nm, respectively) vary with solvent polarity [6–9] and this has been used as a polarity probe (the Py scale [7,8]) in a variety of media [3,4,6,10].

Fig. 3 shows the values of xanthone triplet $\lambda_{\max}$ plotted as a function of the pyrene I_1/I_3 ratio. The data fall into two distinct groups, one involving non-protic ($R = 0.90$) and the other involving protic solvents ($R = 0.83$) [7,8]. Ethyl

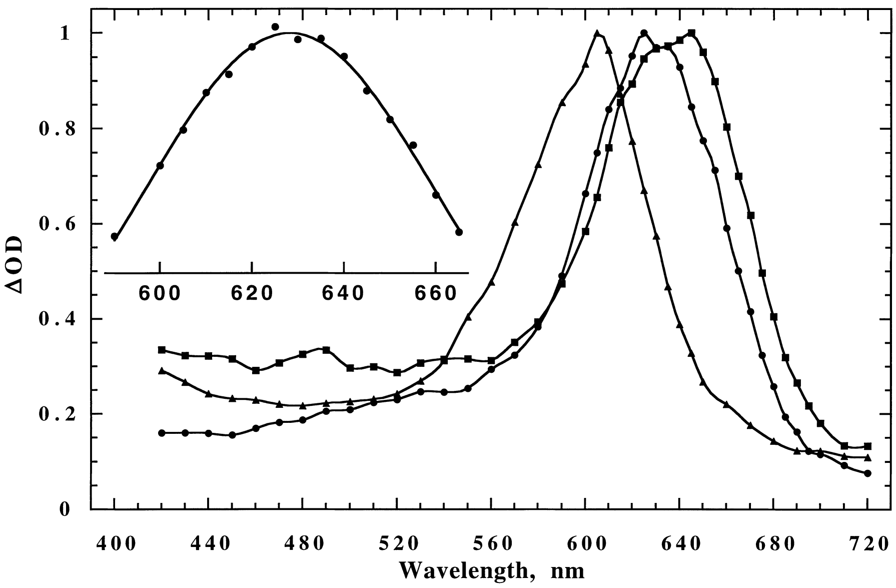

Fig. 1. Triplet absorption spectra of xanthone in ethylene glycol (triangles), ethyl acetate (circles) and trifluorotoluene (squares). The spectra were recorded 600, 100 and 100 ns after 308 nm laser excitation of the samples, respectively. The insert shows the peak region in ethyl acetate, fitted with a Gaussian function yielding $\lambda_{max} = 628$ nm.

acetate does not correlate well with either data set, while it shows no unusual behavior in Fig. 2.

Whereas the data of Fig. 2 only hint at a difference in behavior between protic and non-protic solvents the difference in Fig. 3 is unambiguous. Earlier studies [8] in which the Py scale was related to other solvent polarity scales (the E_T scale [20], Kosower's Z scale [21–24] and Kamlet, Abboud and Taft's π^* scale [25–27]) show a similar difference in correlation between protic and aprotic solvents. These differences were attributed [8] to the existence of specific interactions, usually hydrogen bonding, between the solvent and the molecule being used to calibrate the Py scale, frequently anionic indicator such as a betaine or carbomethoxypyridinium salt.

The differences observed in the present study can also be traced to the different interactions that triplet xanthone will experience in different solvents. In aprotic solvents one expects the polarity and polarizability of the solvent to dominate the interaction with the xanthone excited state, provided that hydrogen abstraction from the solvent is

Table 1
Xanthone triplet absorption maximum (λ_{max}), band width ($\Delta\lambda$), lifetime (τ) and pyrene I_1/I_3 values for a variety of solvents

Solvent	ε^a	$\lambda_{max}{}^b$ (nm)	τ (ns)	$\Delta\lambda^c$ (nm)	$I_1/I_3{}^d$	$I_1/I_3{}^e$	$I_1/I_3{}^f$
1. Water	80.37	580	11300	67	1.97	1.87	1.59
2. CF_3CH_2OH		577	6300	50	1.61[g]		
3. Glycol	37.50	601	5400	74		1.64	1.64
4. CH_3CN	37.50	627	946	67	1.93	1.79	1.75
5. Methanol	33.62	605	1770	70	1.44	1.35	1.33
6. 2-Propanol	18.30	616	330	64		1.09	0.91
7. 1-Pentanol	13.9	610	490	70	1.04[g]		
8. $CF_3C_6H_5$	9.03	636	492	70	1.09[g]		
9. Ethyl acetate	6.02	628	372	74			1.45
10. $CHCl_3$	4.81	635	305	60	1.38	1.25	1.28
11. Freon 113	2.41	627	170	75			
12. Benzene	2.284	649	74	107		1.05	1.14
13. CCl_4	2.238	648	540	94			
14. Dioxane	2.209	642	33	78		1.50	

[a] From R.C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton, 1985.
[b] ±2 nm.
[c] Bandwidth at half-height.
[d] From Street and Acree [9].
[e] From Dong and Winnik [8].
[f] From Kalyanasundaram and Thomas [6].
[g] From this work.

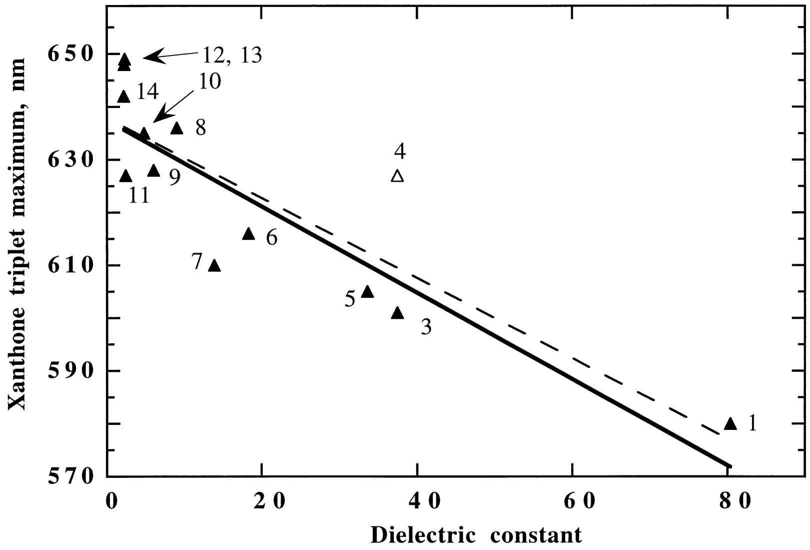

Fig. 2. Plot of the xanthone triplet absorption maximum (λ_{max}) as a function of dielectric constant. The solid best line ($R = 0.89$) is calculated excluding the open triangle acetonitrile point, while the dashed line includes all the data.

minimal. The dielectric constant, ε, measures the ability of a solvent to polarize and stabilize charge. While ε reflects the polarity of a solvent, it does not reflect the solvent's ability to participate in hydrogen bonding. Thus, the dependence of xanthone's triplet λ_{max} will reflect the dielectric constant as well as the hydrogen bonding ability of the solvent. If we compare the data (Table 1) for 2-propanol ($\lambda_{max} = 612$ nm, $\varepsilon = 18.3$) and acetonitrile ($\lambda_{max} = 627$ nm, $\varepsilon = 37.5$) we see that the trend in λ_{max} is opposed to that in dielectric constant. Thus, in protic solvents the hydrogen bonding to the xanthone triplet seems to determine the energy of the triplet–triplet transition. In polar protic solvents (i.e., essentially all protic solvents), the lowest energy triplet is expected to have π,π^* character. In this type of transition the electron density at the oxygen atom of the carbonyl group will be enhanced compared to the ground state [28]. This additional electron density will be stabilized by solvents of higher dielectric constant but additional stabilization will occur if hydrogen bonding is also possible. These factors would increase the energy gap between the π- and π^*-molecular orbitals; the fact that this results in a blue shift (Fig. 3) suggests that upper orbital levels are not stabilized as much as the π,π^* triplet. Thus we attribute the fact that we see two different correlations with the Py scale to the fact that hydrogen bonding plays an important role in the interaction of xanthone triplet with protic solvents.

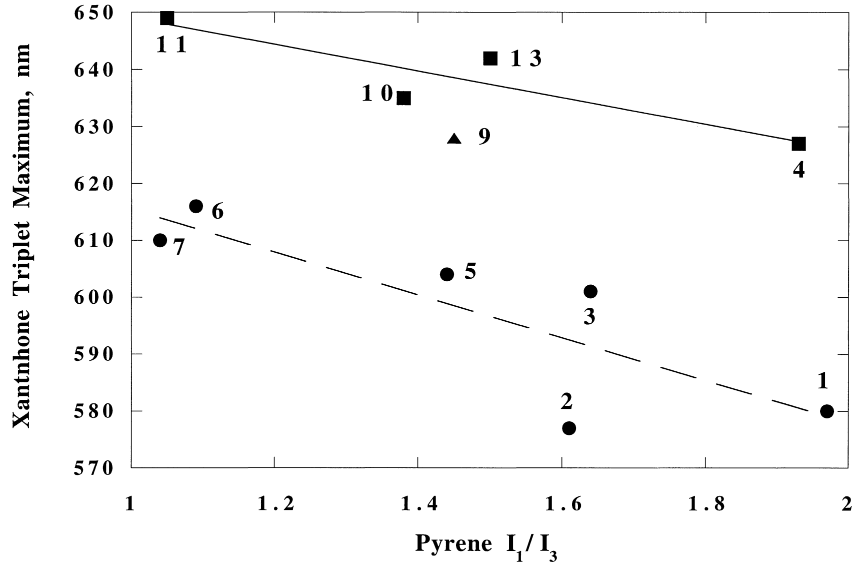

Fig. 3. Plot of the xanthone triplet absorption maximum (λ_{max}) as a function of the pyrene I_1/I_3 ratio for aprotic (squares, $R = 0.90$) and protic (circles, $R = 0.83$)) solvents. When more than one I_1/I_3 value is given in Table 1, the leftmost one was used. The triangle (#9) is the data point for ethyl acetate.

The xanthone triplet lifetime is dramatically lengthened in polar solvents. This can be attributed in part to the inherent lower reactivity of π,π^* triplets towards hydrogen abstraction [29–31]. Thus more polar solvents result in a less reactive triplet and longer triplet lifetimes. In benzene, a very poor hydrogen donor, the lifetime is in fact very short; this can be attributed to charge transfer quenching of triplet xanthone by benzene. We examined the quenching of triplet xanthone by benzene in acetonitrile. By monitoring the change in the rate of triplet decay at 630 nm as a function of added benzene concentration we determined that the rate constant for this process to be $7.6 \times 10^5\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$.

Table 1 also shows that there is a trend towards a broader absorption band for triplet xanthone in non-polar solvents. In such solvents the lowest lying triplet has n,π^* character, but the energy difference between the n,π^* state and the π,π^* state is rather small. This energy difference becomes much larger in polar solvents and the lowest energy triplet becomes π,π^* in nature. For example, the energy gap between these two triplets, ($E_{n,\pi*}$–$E_{\pi,\pi*}$), is nearly 4.0 kcal/mol in neat 2-propanol but is close to zero for a solution of xanthone in CCl_4 containing 0.3 M 2-propanol [14]. When the two states are so close in energy it is possible that transitions can occur from both of them at room temperature, or that significant state mixing is involved. This would result in band broadening in non-polar solvents. In a polar solvent such as water the triplet–triplet absorption will originate exclusively from the state and the band will be anticipated to be narrower, as observed.

One of the goals of this work is to calibrate xanthone triplet against known measures of solvent polarity (ε and the Py scale) with a view to enhancing the usefulness of xanthone as a microenvironment probe in aggregated media by quantifying the solvent-induced spectral changes. Clearly, there is a reasonable correspondence between solvent polarity as measured by either of these established scales and that reported by the xanthone triplet. In principle xanthone can be used as a polarity probe for aggregated systems of interest in supramolecular chemistry. Further, xanthone absorption is also sensitive to the hydrogen bonding strength of a particular environment.

From a technical standpoint, the xanthone scale is well suited for use with laser flash photolysis, while pyrene is used with steady-state or time resolved fluorescence instruments. As laser flash instruments have become more common in recent years it makes sense to calibrate a microenvironment probe specifically tailored for this technique.

Another positive feature of xanthone as a probe is that it generally decays over a much longer time than does pyrene fluorescence. One can imagine applications where this is a valuable feature. For example, the rate of exit of an organic species from an aggregated environment may be rather slow and, indeed, xanthone has already proved useful in this respect [15–17,32]. A probe like excited pyrene may decay completely before there is a significant amount of pyrene exit from a given environment, and under some conditions be a less versatile probe. A longer lived excited state, such as triplet xanthone in environments of low reactivity, would be preferred. Even in cases where kinetic processes are rapid xanthone triplet can be useful; e.g., a recent study from our group [18] made use of the xanthone triplet to identify several stages in the overall exit of this transient from micelles [18].

In summary, the xanthone and Py scales can complement each other in terms of the types of information they provide and in terms of the time scales for which they are most well suited, as well as in the use of different experimental techniques. We do not suggest that xanthone should be viewed as a replacement for the Py scale or other probes of microenvironment. However, it is an advantage to have available a range of tools to report on the properties of supramolecular systems, and we believe that xanthone should be a valuable addition to this tool box.

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References

[1] N.J. Turro, M. Grätzel, A.M. Braun, Angew. Chem. Int. Ed. Engl. 19 (1980) 675.
[2] N.J. Turro, Pure Appl. Chem. 58 (1986) 1219.
[3] P. Bortolus, S. Monti, in: D.C. Neckers, D.H. Volman, G. von Bünau (Eds.), Advances in Photochemistry, Wiley, New York, Vol. 27, p. 1, 1996.
[4] K. Kalyanasundaram, Photochemistry in Microheterogeneous Systems, Academic Press, 1987.
[5] J.K. Thomas, S. Hashimoto, New J. Chem. 11 (1987) 145.
[6] K. Kalyanasundaram, J.K. Thomas, J. Am. Chem. Soc. 99 (1977) 2039.
[7] D.C. Dong, M.A. Winnik, Photochem. Photobiol. 35 (1982) 17.
[8] D.C. Dong, M.A. Winnik, Can. J. Chem. 62 (1984) 2560.
[9] K.W. Street Jr., W.E. Acree Jr., , Analyst 111 (1986) 1197.
[10] V. Ramamurthy, Photochemistry in Organized and Constrained Media, VCH, Weinheim, 1991.
[11] F.L. Cozens, M. Régimbald, H. García, J.C. Scaiano, J. Phys. Chem. 100 (1996) 18165.
[12] F.M. Winnik, Chem. Rev. 93 (1993) 587.
[13] A. Garner, F. Wilkinson, J. Chem. Soc., Faraday Trans. II 72 (1976) 1010.
[14] J.C. Scaiano, J. Am. Chem. Soc. 102 (1980) 7747.
[15] J.C. Scaiano, J.C. Selwyn, Can. J. Chem. 59 (1981) 2368.
[16] M. Barra, C. Bohne, J.C. Scaiano, J. Am. Chem. Soc. 112 (1990) 8075.
[17] Y. Liao, C. Bohne, J. Phys. Chem. 100 (1996) 734.
[18] N. Mohtat, F. Cozens, J.C. Scaiano, J. Phys. Chem. B 102 (1998) 7557.

[19] J.S. Ham, J. Chem. Phys. 21 (1953) 756.
[20] K. Dimroth, C. Reichardt, T. Siepmann, F. Bohlmann, Liebigs Ann. Chem. 661 (1963) 1.
[21] E.M. Kosower, J. Am. Chem. Soc. 80 (1958) 3253.
[22] E.M. Kosower, J. Am. Chem. Soc. 80 (1958) 3261.
[23] E.M. Kosower, J.A. Skorez, J. Am. Chem. Soc. 82 (1960) 2188.
[24] T.R. Griffiths, D.C. Pugh, J. Sol. Chem. 8 (1979) 247.
[25] M.J. Kamlet, J.L. Abboud, R.W. Taft, J. Am. Chem. Soc. 99 (1977) 6027.
[26] M.J. Kamlet, J.L. Abboud, R.W. Taft, J. Am. Chem. Soc. 99 (1977) 8325.
[27] M.J. Kamlet, T.N. Hall, J. Boykin, R.W. Taft, J. Chem. Soc. Perkin Trans. 2 (1979) 2559.
[28] R.W. Fessenden, P.M. Carton, H. Shimamori, J.C. Scaiano, J. Phys. Chem. 86 (1982) 3803.
[29] P.J. Wagner, T. Nakahira, J. Am. Chem. Soc. 95 (1973) 8474.
[30] M.V. Encina, E.A. Lissi, E. Lemp, A. Zanocco, J.C. Scaiano, J. Am. Chem. Soc. 105 (1983) 1856.
[31] A. Gilbert, J. Baggot, Essentials of Molecular Photochemistry, Blackwell Scientific Publications, London, 1991.
[32] Y. Liao, J. Frank, J.F. Holzwarth, C. Bohne, J. Chem. Soc., Chem. Commun. (1995) 199.