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Novel laser-induced luminescence resulting from benzophenone/*O*-propylated *p-tert*-butylcalix[4]arene complexes. A diffuse reflectance study

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Laser-induced room temperature luminescence of air-equilibrated benzophenone/*O*-propylated *p-tert*-butylcalix[4]arene solid powdered samples revealed the existence of a novel emission, in contrast with benzophenone/*p-tert*-butylcalix[4]arene complexes, where only benzophenone emits. This novel emission was identified as phosphorescence of 1-phenyl-1,2-propanedione, which is formed as the result of an hydrogen atom abstraction reaction of the triplet excited benzophenone from the propoxy substituents of the calixarene. Room temperature phosphorescence was obtained in air-equilibrated samples in all propylated hosts. The decay times of the benzophenone emission vary greatly with the degree of propylation, the shortest lifetimes being obtained in the tri- and tetrapropylated calixarenes. Triplet–triplet absorption of benzophenone was detected in all cases, and is the predominant absorption in the *p-tert*-butylcalix[4]arene case, where an *endo*-calix complex is formed. Benzophenone ketyl radical formation occurs with the *O*-propylated *p-tert*-butylcalix[4]arenes hosts, suggesting a different type of host/guest molecular arrangement. Diffuse reflectance laser flash photolysis and gas chromatography–mass spectrometry techniques provided complementary information, the former about transient species and the latter regarding the final products formed after light absorption. Product analysis and identification clearly show that the two main degradation photoproducts following laser excitation in the propylated substrates are 1-phenyl-1,2-propanedione and 2-hydroxybenzophenone, although several other minor photodegradation products were identified. A detailed mechanistic analysis is proposed. While the solution photochemistry of benzophenone is dominated by the hydrogen abstraction reaction from suitable hydrogen donors, in these solid powdered samples, the α-cleavage reaction also plays an important role. This finding occurs even with one single laser pulse which lasts only a few nanoseconds, and is apparently related to the fact that scattered radiation exists, due to multiple internal reflections possibly trapping light within non-absorbing microcrystals in the sample, and is detected until at least 20 µs after the laser pulse. This could explain how photoproducts thus formed could also be excited with only one laser pulse.

1 Introduction

Time-resolved laser-induced luminescence, diffuse reflectance laser flash photolysis and ground-state diffuse reflectance absorption spectroscopy are relatively new techniques that can be applied to study opaque and crystalline systems.[1–3] These solid-state photochemical methods have been recently applied by our group to study several organic compounds adsorbed onto different hosts, including *p-tert*-butylcalix[4]-, -[6]- and -[8]arenes,[4] microcrystalline cellulose,[5] silicalite, cyclodextrins[6] and silica,[7] amongst others.

Benzophenone (BZP) is an extremely useful molecule for probing new hosts. The n ⟶ π* absorption transition is known to be very sensitive to the nature of the environment and also exhibits a photochemistry which depends on the properties of the host.[4b,c,5a,8]

Calixarenes are important macrocyclic phenol–formaldehyde polycondensates with hydrophobic bowl-shaped cavities.[9,10] The ability of calixarenes and calixarene derivatives to form inclusion complexes, accommodating guest molecules in their intramolecular cavities, greatly depends on the size and geometry of guest molecule, but also on the host cavity.[4,9,10]

Very few photochemical studies of neutral organic compounds within calixarenes have been presented until now (ref. 4 and references therein). As an example, we have recently used β-phenylpropiophenone and benzophenone to study the formation of inclusion complexes of these neutral organic compounds with *p-tert*-butylcalix[4]arene.[4c] Time-resolved diffuse reflectance absorption and emission techniques were applied to powdered solid samples of these compounds, establishing beyond doubt that the ketones are included within the cavity of the calixarene through the observation of room temperature phosphorescence in air-equilibrated samples for both guests, following laser excitation.

Calixarenes can be extremely useful hosts for use in environmental chemistry studies due to their ability to selectively bind, separate and sense neutral organic (and ionic) contaminants, depending not only on the size of the calixarene nanocavity, but also on the substituents attached to the upper and lower rims.[9,10] Calixarene derivatives can also be used for stabilisation of reaction intermediates, for catalysis through encapsulation and also for molecular transport and delivery studies.[10]

In this paper, a new family of calixarene hosts is studied using a well-known probe as a guest molecule: we present a

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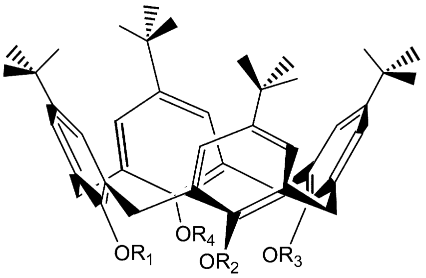
diffuse reflectance and laser-induced luminescence study of solid powdered samples of benzophenone included into *p-tert*-butylcalix[4]arene (H_4CLX[4]) and partially or totally *O*-propylated *p-tert*-butylcalix[4]arenes ($H_n$$Pr_m$CLX[4], $n = 2$, 1 and 0; $m = 2$, 3 and 4, respectively) (Scheme 1).



H_4CLX[4]: R_1=R_2=R_3=R_4=H
H_2Pr_2CLX[4]: R_1=R_3=Propyl; R_2=R_4=H
HPr_3CLX[4]: R_1=R_2=R_3=Propyl; R_4=H
Pr_4CLX[4]: R_1=R_2=R_3=R_4=Propyl

Scheme 1

Experimental evidence showing the occurrence of a photochemical reaction between benzophenone and H_nPr_mCLX[4], resulting in the formation of a new ketone, which is also excited within a single laser pulse and emits its own phosphorescence, will be presented for the first time.

2 Experimental

Materials

All reagents and solvents used for synthetic work were reagent grade and were purified and dried by standard methods. Organic extracts were dried over anhydrous magnesium sulfate. Analytical thin layer chromatography was performed on 0.2 mm thick plates of E. Merck Kieselgel 60, F-254 silica gel.

Chloroform (Merck, Uvasol grade) was used as received for sample preparation. 1-Phenyl-1,2-propanedione, benzil, benzaldehyde, benzoin, methyl benzoate, 2-hydroxybenzophenone, benzhydrol and acetophenone used as authentic samples were from Aldrich, biphenyl was from Eastman-Kodak (highest purity available) and benzophenone from Koch-Light (scintillation grade).

H_4CLX[4] were prepared in accordance with Gutsche method.[11a] H_nPr_mCLX[4] ($n = 2$, 1 and 0; $m = 2$, 3 and 4, respectively) were obtained by the following procedures.

25,27-Dipropoxy-26,28-dihydroxy-*p-tert*-butylcalix[4]arene (H_2Pr_2CLX[4])[11b]. Obtained from H_4CLX[4] as colourless crystals after recrystallisation ($CHCl_3$–MeOH) in 77% yield. IR (KBr): ν_{OH} 3397 cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C): δ 1.01 and 1.28 (*t*-Bu, both s, 18H each), 1.24 (CH_3, t, 6H), 2.01–2.06 ($CH_2$$CH_3$, m, 4H), 3.31 and 4.31 (ArCH_2Ar, both d, 4H each; $J = 13$), 3.95 (OCH_2, t, 4H), 6.85 and 7.04 (ArH, both s, 4H each), 7.86 (OH, s, 2H).

25,26,27-Tripropoxy-28-hydroxy-*p-tert*-butylcalix[4]arene (HPr_3CLX[4])[11b]. Obtained from H_4CLX[4] as a slightly yellowish solid after recrystallisation ($CHCl_3$–MeOH) in 67% yield. IR (Nujol): ν_{OH} 3543 cm^{-1}; ^1H NMR ($CDCl_3$, 25 °C): δ 0.82 (*t*-Bu, s, 18H), 1.32 and 1.34 (*t*-Bu, both s, 9H each), 0.95 and 1.09 (CH_3, both t, 3H and 6H), 1.85–1.98 ($CH_2$$CH_3$, m, 4H), 2.30–2.36 ($CH_2$$CH_3$, m, 2H), 3.16, 3.23, 4.33, 4.37 (ArCH_2Ar, all d, 2H each; $J = 13$), 3.75 and 3.84 (OCH_2, both t, 4H and 2H), 5.58 (OH, s, 1H), 6.51 (ArH, s, 4H), 7.05 and 7.14 (ArH, both s, 2H each).

25,26,27,28-Tetrapropoxy-*p-tert*-butylcalix[4]arene (Pr_4CLX[4]). Alkylation (*n*-PrBr, NaH, THF–DMF; reflux, 19h) of cone-HPr_3CLX[4] above yielded colourless crystals after recrystallisation ($CHCl_3$–MeOH) in 82% yield. IR (KBr): no ν_{OH}; ^1H NMR ($CDCl_3$, 25 °C): δ 1.00 ($CH_2$$CH_3$, t, 12H), 1.08 (*t*-Bu, s, 36H), 2.06 ($CH_2$$CH_3$, m, 8H), 3.11 and 4.42 (ArCH_2Ar, both d, 4H each; $J = 12.4$), 3.82 (OCH_2, t, 8H), 6.78 (ArH, s, 8H) [lit.[11b]]. The ^1H NMR spectrum of H_2Pr_2CLX[4] shows a pair of doublets for the ArCH_2Ar protons at 3.31 and 4.31 ppm ($J = 13$), pointing to a cone conformation. Also, the pattern arising from the methylene protons of HPr_3CLX[4], two pairs of doublets at 3.16, 3.23 and 4.33, 4.37 ppm ($J = 13$), indicates the adoption of a cone conformation. For Pr_4CLX[4], a cone conformation was again confirmed, as shown by the split pattern of the ArCH_2Ar protons at 3.11 and 4.42 ppm ($J = 12.4$). In the case of H_4CLX[4], a pair of slightly broad doublets at 3.49 and 4.25 ($J = 12$), owing to rapid inversion at r.t., indicates a preference for the cone conformation.

Sample preparation

The solid powdered ketone/calixarene (molar ratios 1 : 1, 1 : 2.5) samples used in this work were prepared using the solvent evaporation method. This method involves the addition of a solution containing the probe to a saturated solution of the calixarene (~10^{-2} M), both in chloroform. The resulting mixture was magnetically stirred for at least 24 h and the solvent then allowed to evaporate in a fume cupboard. The final solvent removal was performed overnight in an acrylic chamber with an electrically heated shelf (Heto FD 1.0-110) with temperature control (30 ± 1 °C), and under a moderate vacuum of *ca.* 10^{-3} Torr. The existence of final traces of solvent was checked for using FTIR spectroscopy.

General techniques

Infrared spectra were measured on a Nicolet Impact 400D FTIR spectrometer in transmittance mode using KBr pellets (or Nujol dispersions). Spectra were recorded at 1.0 cm^{-1} resolution, in the range 4000–500 cm^{-1} as a ratio of 36 single-beam scans of the sample to the same number of background scans from air. Baseline corrections were introduced whenever needed. The original samples were diluted in KBr (*ca.* 2% w/w) and ground to a finely divided powder using an agate mortar and pestle.

^1H NMR spectra were recorded on a Brüker ARX 400 (400 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilane as internal standard; *J* values are given in Hz.

Diffuse reflectance ground-state absorption spectra for the solid samples were recorded using an OLIS 14 spectrophotometer with a diffuse reflectance attachment. Further details are given elsewhere.[1,4,5]

Diffuse-reflectance laser flash photolysis and laser-induced luminescence systems

Schematic diagrams of the diffuse-reflectance laser flash photolysis system and of the laser-induced luminescence systems are presented elsewhere.[1,6b] Laser flash photolysis experiments were carried out with the third or the fourth harmonic of a YAG laser (355 and 266 nm, *ca.* 6 ns FWHM, ~10–30 mJ $pulse^{-1}$) from B. M. Industries (Thomson-CSF Saga 12-10), in the diffuse reflectance mode.[1,4] The light arising from irradiation of solid samples by the laser pulse is collected by a collimating beam probe coupled to an optical fibre (fused silica) and is detected by a gated intensified charge-coupled device (Andor ICCD detector, based on the Hamamatsu S5769-0907). The ICCD is coupled to a fixed imaging compact spectrograph (Oriel FICS 77440). The system can be used either to capture all light emitted by the sample or in a time-resolved mode by using a delay box (Stanford Research Systems D6535). The

ICCD has high speed (2.2 ns) gating electronics and intensifier and covers the 200–900 nm wavelength range. Time-resolved absorption and emission spectra are available in the nanosecond to second time range.[1,4] 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 the sample before exposure to the exciting laser pulse and at time *t* after excitation, respectively.[1,2,4,5a]

For the laser-induced luminescence experiments, a N_2 laser (PTI 2000, *ca.* 600 ps FWHM, ~1.0 mJ pulse^{-1}) was also used.

Irradiation and product analysis

Photodegradation studies were conducted in a reactor previously used to study the photochemistry of pesticides.[6a] The samples were irradiated at 254 nm using a 16 W low pressure mercury lamp (Applied Photophysics) without filters and without refrigeration. Laser irradiation at 355 nm was also used. The degradation products were analysed after extraction with methanol (a known weight of sample in a known volume of solvent), followed by centrifugation. Photolysis was followed by HPLC using a Merck-Hitachi 655A-11 chromatograph equipped with 655A-22 UV and Shimadzu SPD-M6A photodiode array detectors. A Merck LiChroCART 125 (RP-18, 5 μm) column was used and the runs were performed using 40%–60% or 60%–40% water–acetonitrile mixtures as the eluent. The extracts were also analysed by GC-MS using a Hewlett Packard 5890 Series II gas chromatograph with a 5971 Series mass-selective detector (E.I. 70 eV). A DB-1 capillary column 30 m long and of 0.25 mm I.D. (J & W Scientific) was used. An initial temperature of 70 °C was maintained for 5 min and then raised to 250 °C at a rate of 5 °C min^{-1}.

3 Results and discussion

Ground-state diffuse reflectance and FTIR absorption spectra

Ground-state diffuse reflectance absorption spectra for benzophenone included within $H_4CLX[4]$ and $H_nPr_mCLX[4]$ were obtained using an integrating sphere (further details in ref. 5), and are presented in Fig. 1 after subtraction of the remission function of the substrate.

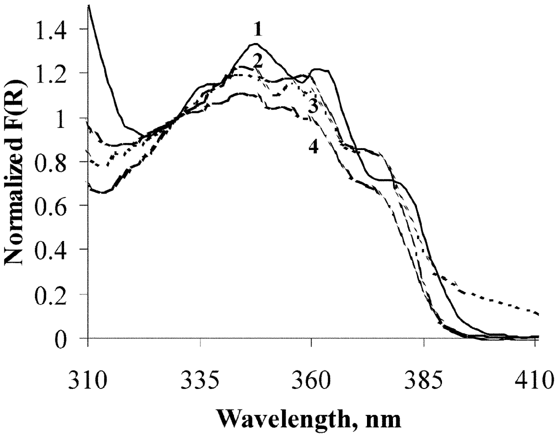


Fig. 1 Remission function for $BZP/H_4CLX[4]$ (curve 1) and $BZP/H_nPr_mCLX[4]$ (n = 2, 1 and 0; m = 2, 3 and 4, respectively) inclusion complexes, normalised to unity at 330 nm (curves 4, 3 and 2 respectively). The guest–host molar ratio is 1 : 2.5 in all samples.

Table 1 Carbonyl stretching and skeletal breathing mode bands from FTIR absorption spectra of microcrystalline samples of BZP, and $BZP/H_4CLX[4]$ and $BZP/H_nPr_mCLX[4]$ (n = 2, 1 and 0; m = 2, 3 and 4, respectively) inclusion complexes (1 : 2.5 guest–host molar ratio in all cases, except for $H_4CLX[4]$, where a 1 : 1 molar ratio was used)

	$\nu_{C=O}$[a]/cm^{-1}	$\nu_{C=C}$[a]/cm^{-1}
Microcrystals of BZP	1651	1593
$BZP/H_4CLX[4]$	1655	1599
$BZP/Pr_4CLX[4]$	1655	1598
$BZP/HPr_3CLX[4]$	1656	1599
$BZP/H_2Pr_2CLX[4]$	1660	1598

[a] Error ±0.5 cm^{-1}.

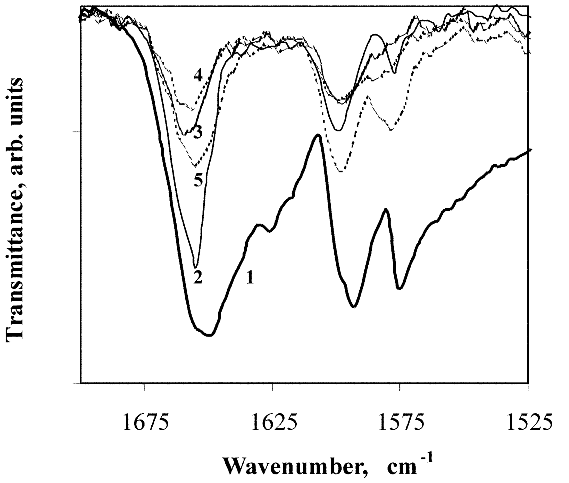


Fig. 2 FTIR absorption spectra of microcrystalline samples of BZP (1), and $BZP/H_4CLX[4]$ (2) and $BZP/H_nPr_mCLX[4]$ (n = 2, 1 and 0; m = 2, 3 and 4, respectively) inclusion complexes (3–5, respectively). All spectra are normalised in order to have a common baseline with a 1 : 2.5 guest–host molar ratio (except for $BZP/H_4CLX[4]$, where a 1 : 1 molar ratio was used) in a KBr matrix.

The benzophenone n ⟶ π* transition has an absorption maximum at 348 nm for $H_4CLX[4]$ inclusion and presents a clear vibronic structure, characteristic of this ketone absorption.[5a] In all propylated calixarenes, the absorption spectra of the included benzophenone is hypsochromic shifted, with an absorption maximum at 344 nm in all $H_nPr_mCLX[4]$ hosts. These data are consistent with a non-polar environment in the $H_4CLX[4]$ case and a more polar environment in the $H_nPr_mCLX[4]$ cases, suggesting *endo*- and *exo*-calix inclusion, respectively.[9a]

The n ⟶ π* absorption region of benzophenone within $H_nPr_mCLX[4]$ does not present the very clear vibronic structure seen for $BZP/H_4CLX[4]$, but rather, a less structured and broad band in these hosts. This broadening effect increases in the order $Pr_4CLX[4] < HPr_3CLX[4] < H_2Pr_2CLX[4]$, suggesting conformational behaviour as a result of increased flexibility in the above-mentioned order, possibly due to the greater mobility of the less propylated calixarenes.

The other important information regarding the geometry of the benzophenone molecule within the calixarenes comes from the FTIR spectra. Table 1 presents the carbonyl stretching frequencies obtained from FTIR absorption spectra for microcrystalline samples of benzophenone, benzophenone/$H_4CLX[4]$ and benzophenone/$H_nPr_mCLX[4]$.

The C=O stretching band of microcrystalline benzophenone is located at 1651 cm^{-1} and the C=C skeletal breathing mode at 1593 cm^{-1}.[4c] For the planar conformations of benzophenone (microcrystals), an important resonance interaction exists. Inclusion into calix[4]arene and $H_nPr_mCLX[4]$ results in a clear increase in the energy of the C=O stretching mode due to enhancement of C=O double bond character (inclusion of the calixarenes into cavities promotes deviations from planarity in the phenyl–carbonyl conjugated system, thereby decreasing resonance). A similar argument applies to the C=C skeletal breathing mode. Data from Table 1 clearly show that benzophenone is included into the calixarenes cavities in all cases, although it does not distinguish between $H_4CLX[4]$ and $H_nPr_mCLX[4]$ inclusion.

As indicated in the Experimental, the FTIR spectra have a resolution of 1.0 cm^{-1}, so the fact that the peaks are not sharp in Fig. 2 reflects the heterogeneity of the environment felt by the probe, benzophenone.

Room temperature laser-induced phosphorescence

Room temperature phosphorescence spectra of the benzophenone/H_4CLX[4] inclusion complex were reported previously.[4c] These time-resolved spectra were obtained under air-equilibrated conditions and were identical those obtained using argon-purged samples. Lifetimes of about 80 µs were found, as compared to about 50 µs for benzophenone microcrystals,[4b] determined at the maximum emission wavelength (448 nm).

Fig. 3, 4 and 5 present similar data for benzophenone as the guest in H_2Pr_2CLX[4], HPr_3CLX[4] and Pr_4CLX[4] hosts (air-equilibrated samples). As before,[4] short pulses were used as excitation sources, either from a N_2 laser pulse at 337 nm (600 ps halfwidth, ~1.0 mJ pulse^{-1}), or from a Nd:Yag laser at 355 nm (6 ns halfwidth, 1–5 mJ pulse^{-1}), both being quite suitable for benzophenone time-resolved luminescence studies, due to their short durations when compared with the lifetime of benzophenone in all samples.

The data presented in Fig. 3, 4 and 5 were obtained using two different time gates: a small time gate (500 or 1000 ns width) to evidence the short time behaviour following the laser excitation pulse, and a very large time gate (20 ms width) to record all room temperature phosphorescence.

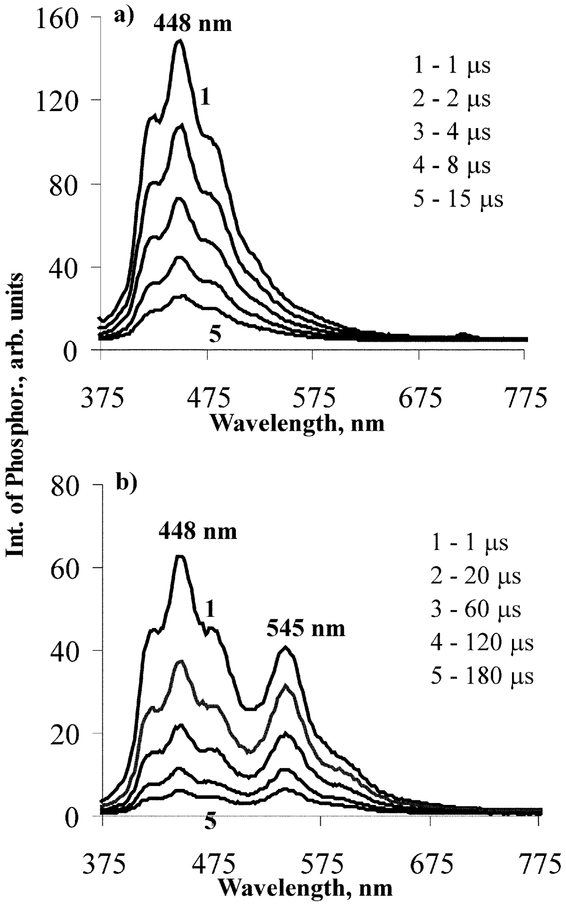


Fig. 3 Laser-induced room temperature phosphorescence emission spectra from air-equilibrated samples of BZP/H_2Pr_2CLX[4] inclusion complex (guest–host molar ratio 1 : 2.5): (a) 500 ns gate width; (b) 20 ms gate width. The excitation wavelength was 337 nm in both cases.

The small time gate width enabled us to observe the appearance of a new emission, which peaks at 545 nm (a few microseconds after the laser pulse), superimposed on the normal benzophenone phosphorescence emission. The rise time of the new emission is quite clear in Fig. 5(a) (tetrapropylated calixarene host), when compared with Fig. 3(a) (dipropylated calixarene), which shows no new emission superimposed on the benzophenone phosphorescence. This new emission in Fig. 5(a) does not appear in trace 1, but can be clearly seen in traces 2–5 (about 3–10 ms timescale). The new emission could not be observed either on shorter timescales with the short time gate width (500 ns). Only with the use of larger gate widths could the emission of the photoproduct (PhPD) be recorded, which is the predominant emission for the tri- and tetrapropylated hosts It is also important to note that the relative importance of the new emission at 545 nm increases with the degree of propylation, as Fig. 3(b), 4(b) and 5(b) clearly show. This means that this propoxy group plays a decisive role in the formation of the new emissive species, because no new emission was detected in the case of the benzophenone/H_4CLX[4] inclusion complex.

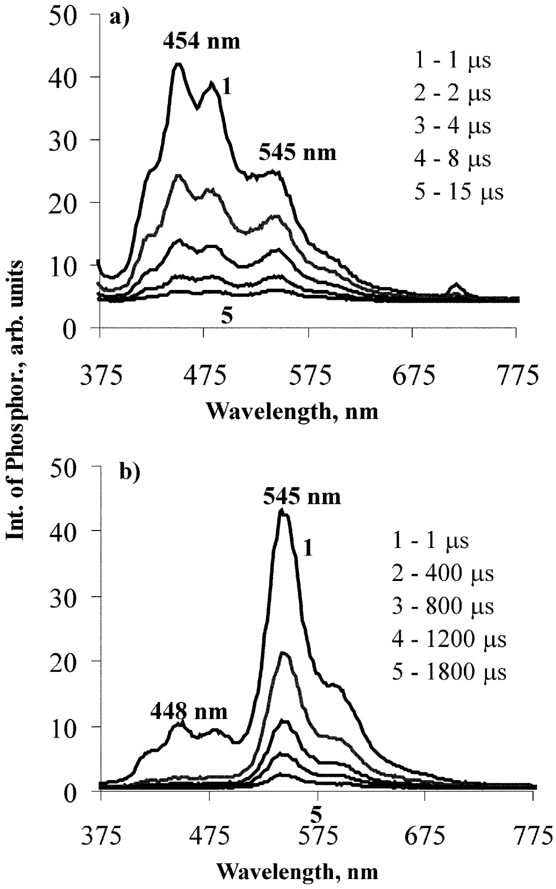


Fig. 4 Laser-induced room temperature phosphorescence emission spectra from air-equilibrated samples of BZP/HPr_3CLX[4] inclusion complex (guest–host molar ratio 1 : 2.5): (a) 500 ns gate width; (b) 20 ms gate width. The excitation wavelength was 337 nm in both cases.

These samples were also argon purged and their spectra recorded. In all cases, the air-equilibrated and argon-purged spectra are identical, within experimental error, as are the lifetimes, showing that inclusion into propylated calixarenes prevents oxygen reaching the excited benzophenone molecule during the lifetime of its triplet excited state. Table 2 summarises the lifetimes obtained for all samples, for benzophenone and for the new emission. Clearly, there is a quenching of benzophenone triplet state as the degree of propylation increases, with a consequent decrease in the benzophenone lifetime.

The assignment of this new emission was difficult. Two main hypotheses were assumed as starting points: emission from transient species derived from benzophenone alone or from new molecules resulting from photochemical reaction of benzophenone with the host. The second hypothesis seems to be the

Table 2 Phosphorescence emission lifetimes (longer components, air-equilibrated samples) for samples of BZP/H_4CLX[4] and BZP/H_nPr_mCLX[4] (n = 2, 1 and 0; m = 2, 3 and 4, respectively) inclusion complexes, compared with equivalent data for microcrystals of benzophenone

	$\tau_P{}^a$/μs	
	At 448 nm	At 545 nm
BZP microcrystals	50	50
BZP/H_4CLX[4]	70	70
BZP/H_2Pr_2CLX[4]	6	80
BZP/HPr_3CLX[4]	3	580
BZP/Pr_4CLX[4]	2	580

[a] Estimated error ±5%.

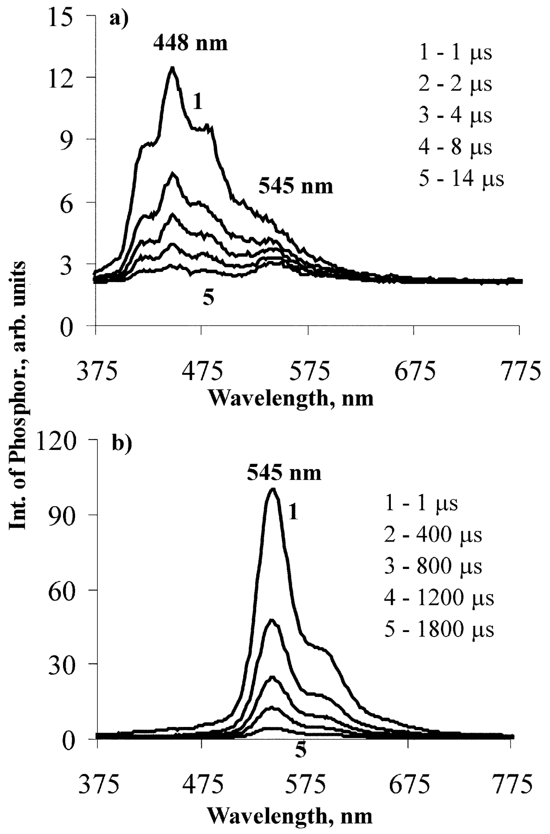


Fig. 5 Laser-induced room temperature phosphorescence emission spectra from air-equilibrated samples of BZP/Pr_4CLX[4] inclusion complex (guest–host molar ratio 1 : 2.5): (a) 500 ns gate width; (b) 20 ms gate width. The excitation wavelength was 337 nm in both cases.

most logical. The simple fact that the new emission peaks at 545 nm, and also its lifetime, excludes emission from the ketyl radical of benzophenone, which peaks at about 570 nm as the result of a two-photon excitation process (fluorescence emission).[12] It also excludes emissions from aryl alkyl ketones which phosphoresce around 420 nm.[6b] Good candidates for the new emission could be α-diketones, like benzil, resulting from an α-cleavage of benzophenone, leading to benzoyl radicals (which requires a two-photon absorption process[13]), which could combine to form benzil. However, the phosphorescence of this ketone within calix[6]- and -[8]arenes peaks at about 565 nm.[4a] A second good candidate is 1-phenyl-1,2-propanedione (PhPD). A parallel experiment was done with PhPD included within Pr_4CLX[4]: the phosphorescence emission maximum was observed at 545 nm, with a similar phosphorescence decay, suggesting that the new emitting species was PhPD because the spectra were identical within experimental error. We also tried to prepare a sample of benzil/Pr_4CLX[4] complex; we concluded that there is no inclusion at all in this case because benzil emits as if it were in the form of microcrystals, with a maximum at 522 nm from an *s-cis* conformation, and not as a guest, as in ref. 4*a*, for a benzil/H_4CLX[4] sample.

Previous work[4] indicates that calixarenes are good hydrogen atom donors, so it seems reasonable to assume that efficient formation of the ketyl radical of benzophenone may also occur here.

Diffuse reflectance laser flash photolysis

Time-resolved absorption spectra of samples of benzophenone/H_nPr_mCLX[4] inclusion complexes were obtained using the diffuse reflectance laser flash photolysis technique, developed by Wilkinson and co-workers.[2] In this study, the use of an intensified charge-coupled device as the detector allowed us to obtain time-resolved absorption spectra with nanometer spectral resolution.[1,4] Fig. 6 shows the time-resolved absorption spectra of these inclusion complexes with a guest–host molar ratio of 1 : 2.5. All spectra were obtained with air-equilibrated samples, exciting at 355 nm.

Diffuse reflectance laser flash photolysis provided us with further relevant experimental information to help solve the

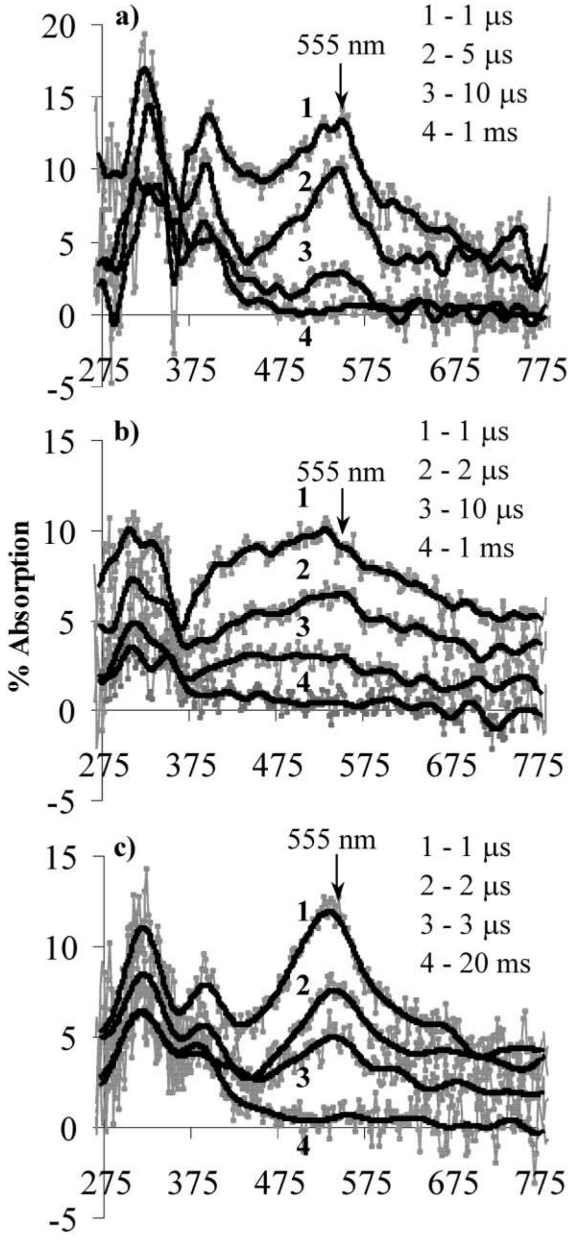


Fig. 6 Time-resolved absorption spectra of BZP/H_2Pr_2CLX[4] (a), BZP/HPr_3CLX[4] (b) and BZP/Pr_4CLX[4] (c). The guest–host molar ratio is 1 : 2.5 and the excitation wavelength 355 nm in all cases.

problem of the identification of the species responsible for the new emission peaking at 545 nm.

Transient absorption spectra of benzophenone/H$_4$CLX[4] samples have revealed the simultaneous formation of triplet benzophenone and also of the hydroxybenzophenone radical ($\mathrm{BZPOH}^{\bullet}$),[4c] as Fig. 7 shows. This time-resolved absorption spectra relate to a 1 : 10 guest–host molar ratio sample, *i.e.* a rather dilute sample.

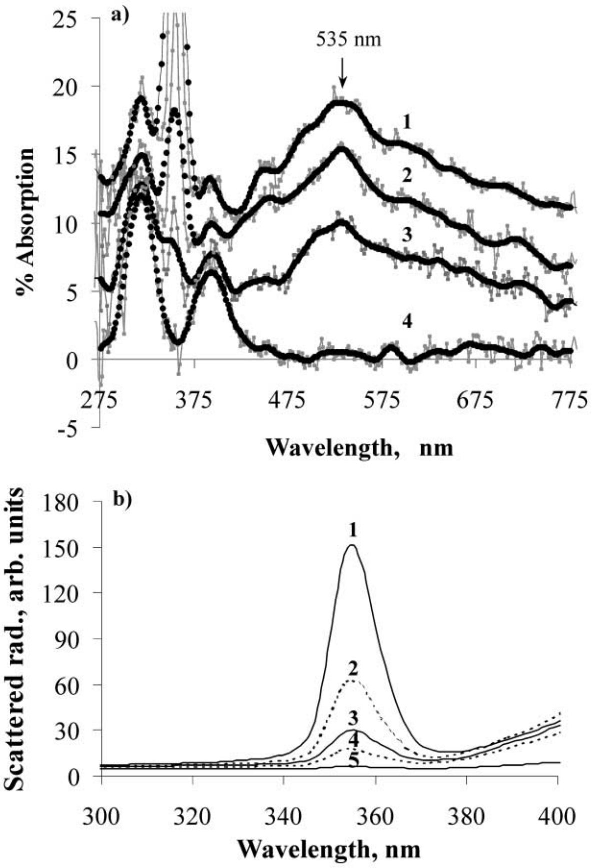


Fig. 7 (a) Time-resolved absorption spectra of a BZP/H$_4$CLX[4] sample (guest–host molar ratio 1 : 10). Traces 1–4 were recorded 5, 10, 20 and 100 µs after the laser pulse, respectively. (b) Scattered radiation obtained with the ICCD using a 500 ns time gate and delay times after laser pulse of 2 (1), 5 (2), 10 (3), 20 (4) and 100 µs (5). The sample is the same as in (a) and the excitation wavelength was 355 nm.

The triplet–triplet absorption spectra of benzophenone were easily identified by comparison with that published by Wilkinson and Willsher.[14] Two absorption maxima at 322 and 535 nm can be seen in the 1 µs spectrum, corresponding to the $T1 \longrightarrow T3$ and $T1 \longrightarrow T2$ absorption transitions of benzophenone. The fact that these maxima are retained at longer timescales (10 and 20 µs after the laser pulse) shows that no ketyl radical of benzophenone is formed by inclusion of benzophenone into H$_4$CLX[4], as reported in ref. 4*c* for more concentrated samples (1 : 2.5 guest–host molar ratio). The transient absorption which peaks at 395 nm can be assigned to the $\mathrm{BZPOH}^{\bullet}$ radical by comparison with previously reported spectra in solution.[15]

Another very important feature regarding the transient absorption spectra relates to the scattered radiation at the excitation wavelength, 355 nm. This scattered radiation originates from the Nd:YAG laser (third harmonic) used in the diffuse reflectance laser flash photolysis set-up.[1b] The original pulse width is only 6–7 ns and, in spite of this, scattered radiation is detected in the ICCD, using its time-gated detector, at least 20 µs after the laser pulse. This shows that many photons may remain available and could possibly excite the solid powdered sample a long time after the initial laser pulse, possibly due to multiple internal reflections trapping light within the non-absorbing microcrystals in the powdered substrate. This could explain how the photoproduct formed in the microsecond timescale could be excited following a single nanosecond laser pulse, and is in accordance with our product formation hypothesis.

Scattered radiation (at 355 nm) was detected with our ICCD for low [see Fig. 7(b)] and high loadings of benzophenone included into the H$_n$Pr$_m$CLX[4] samples, although its importance decreases with increasing *F*(R) of benzophenone at the excitation wavelength (*i.e.* with increasing probe concentration), because the more excitation radiation is absorbed, the less scattered radiation is detected. Diffuse reflectance transient absorption spectra are corrected for emission (and scattered) radiation. Scattered radiation affects only a small and localised spectral region, while the phosphorescence emission is broader in spectral terms. It is therefore reasonable to correct for emission in the first place. Whenever the intensity of the scattered radiation is three or four times more intense than the emission itself, to completely correct the emission, the scatter is overcorrected, as is the case of Fig. 7(a). This is probably due to the occurrence of some degradation of the probe, which occurs because each spectrum is an average of several laser shots (depending on the sample).

Transient absorption spectra of benzophenone included into H$_n$Pr$_m$CLX[4] are presented in Fig. 6 (peaking at 535 nm, about 1 µs after the laser pulse). In these spectra, a new species appears and becomes more evident at longer times (~2–10 µs after the laser pulse), which appears as a shoulder at about 555 nm, characteristic of the benzophenone ketyl radical absorption.[5a,4c,16] So the H$_n$Pr$_m$CLX[4] compounds behave as hydrogen atom donors towards the excited aromatic ketone. The same behaviour was detected for the benzophenone/CLX[6] and CLX[8] inclusion complexes.[4c] The fact that no benzophenone ketyl radicals were formed in the H$_4$CLX[4] samples, but evidence for ketyl radical formation was obtained in the H$_n$Pr$_m$CLX[4] cases (and in the CLX[6] and CLX[8] cases),[4c] reflects the fact that only in the latter are spatial arrangements suitable for the hydrogen atom abstraction reaction to occur possible, whereas, due to the reduced internal space of the H$_4$CLX[4] cavity, no reaction occurs with this host.[4c] This again suggests *exo*-calix inclusion of benzophenone within the propylated calixarenes.

It is important to point out that at very long times (≥1 ms), a residual transient absorption is still detected [see trace 4 of Fig. 6(a) and (c)]. This transient peaks at about 395 nm ($\mathrm{BZPOH}^{\bullet}$ radical) and also shows a kind of long absorption 'tail' which ends at about 500 nm. This tail may be due to the formation of an α-diketone, namely 1-phenyl-1,2-propanedione. Benzophenone/HPr$_3$CLX[4] does not show such strong evidence for $\mathrm{BZPOH}^{\bullet}$ radical formation, and only the superimposed triplet–triplet and ketyl radical absorptions of benzophenone could be detected.

The fact that the photoproduct is formed with a single pulse could also be explained by assuming that PhPD was formed in an excited state. However, to form a PhPD molecule, a benzoyl radical and an acetyl radical have to come into contact. From the combination of the two radicals, a ground-state PhPD molecule is most probably formed. However, if an excited state was formed—and this is not a common hypothesis in literature—it could also explain the PhPD phosphorescence.

Photodegradation products studies

Initially, lamp irradiation conditions (15 W mercury lamp) were used. The analytical results showed that 2-hydroxybenzophenone is one of the major degradation products of all the samples under study. A typical GC-MS chromatogram of the irradiated extracts is shown in Fig. 8(a). However, this is a well-known and very stable and non-luminescent compound due to the very rapid intramolecular non-radiative mechanism of de-excitation, involving hydrogen bond formation between the

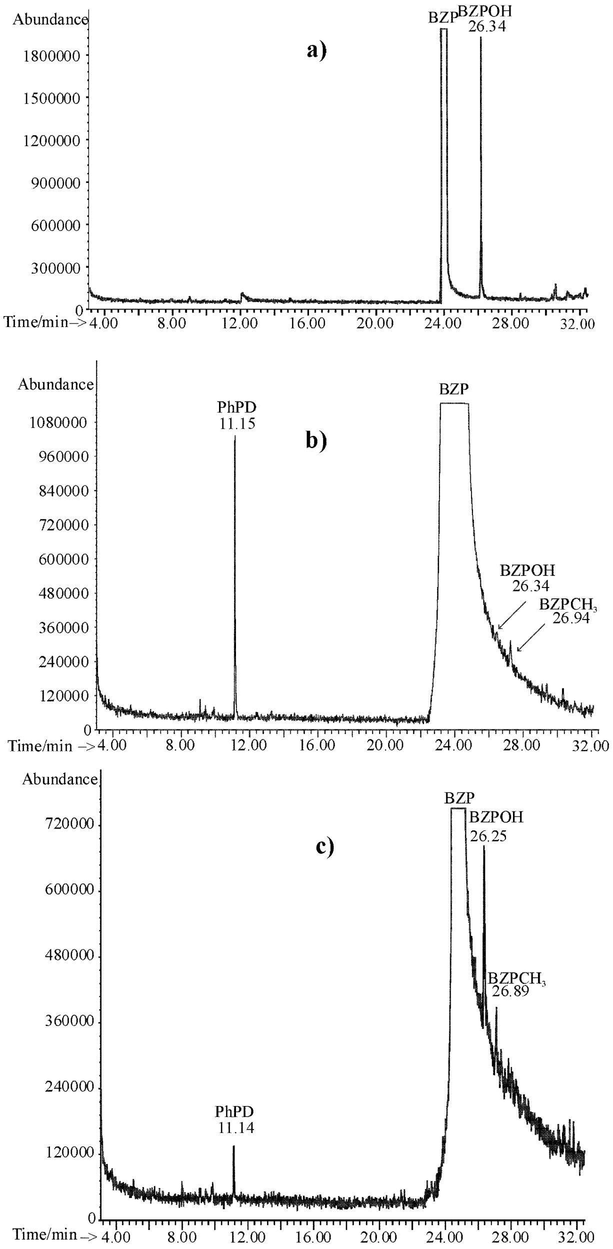


Fig. 8 Typical chromatograms (GC-MS) of: (a) an extract of a sample of BZP/$Pr_4CLX[4]$ irradiated with a mercury lamp at 254 nm; (b) a laser-irradiated (at 337 nm) sample of benzophenone within $Pr_4CLX[4]$; (c) a laser-irradiated (at 337 nm) sample of benzophenone within $H_2Pr_2CLX[4]$.

carbonyl and the nearby hydroxy groups.[17a] Analysis of the extracts of the benzophenone/$Pr_4CLX[4]$ sample after prolonged irradiation (4 h), at a distance of 5 cm from the lamp housing, showed only traces of benzil and PhPD. However, the analyses of the BZP/$H_2Pr_2CLX[4]$ and BZP/$HPr_3CLX[4]$ samples, irradiated under the same conditions, showed no traces of these compounds. Since all the samples showed the same emission results, it is clear that another process must be present.

Assuming that the formation of an α-diketone is the process that leads to the observed new emission, the failure to detect this compound in significant amounts could be due to differences in the experimental conditions used to obtain the phosphorescence emission spectra and the photodegradation products. The same luminescence results were obtained with 337, 355 and 266 nm laser excitation; therefore, the observed result cannot be attributed to differences in the excitation wavelength used (the mercury lamp employed here irradiates mainly at 254 nm) but could due to the high fluency of the laser excitation and the possibility of a two-photon process occurring.[12b,13] Therefore, the same analyses were conducted on samples irradiated with a laser at 355 nm [see Fig. 8(b) and (c)]. The samples were irradiated for 1 h and shaken every 5 min.

1-Phenyl-1,2-propanedione was the main degradation product of benzophenone in $H_nPr_mCLX[4]$ hosts, as detected by GC-MS, in all cases. This result agrees with the assignment made in the time-resolved luminescence as an α-diketone phosphorescence emission, and clearly indicates significant differences depending on whether laser or lamp irradiation is employed. Extracts of samples containing $H_2Pr_2CLX[4]$ showed lower levels of PhPD, whereas increased amounts were formed with $HPr_3CLX[4]$ and the $Pr_4CLX[4]$. This result is in agreement with the luminescence results, since the emission increases with the degree of propylation of the host. As expected, no PhPD was detected when the non-propylated calixarene was used. 2-Hydroxybenzophenone was detected in all cases. Other products found include biphenyl, benzoic acid, methyl benzophenone and benzhydrol, the latter detected by HPLC. Also, traces of acetophenone and benzene were found. All identifications were based on comparison with authentic samples and/or GC-MS spectra.

The solution photochemical reactions of carbonyl compounds have been extensively studied and include photoreduction (eqn. 3), α-cleavage (eqn. 4), intramolecular hydrogen abstraction and dimerisation.[13,8a,16] The solution photochemistry of benzophenone was studied by flash photolysis a long time ago,[8a,17a] and may be briefly described by the following processes:

$$\text{Ph–C}(\text{=O})\text{–Ph} \xrightarrow{h\nu} {}^{1}\left[\text{Ph–C}(\text{=O})\text{–Ph}\right]^{*} \quad (1)$$

$$ {}^{1}\left[\text{Ph–C}(\text{=O})\text{–Ph}\right]^{*} \longrightarrow {}^{3}\left[\text{Ph–C}(\text{=O})\text{–Ph}\right]^{*} \quad (2)$$

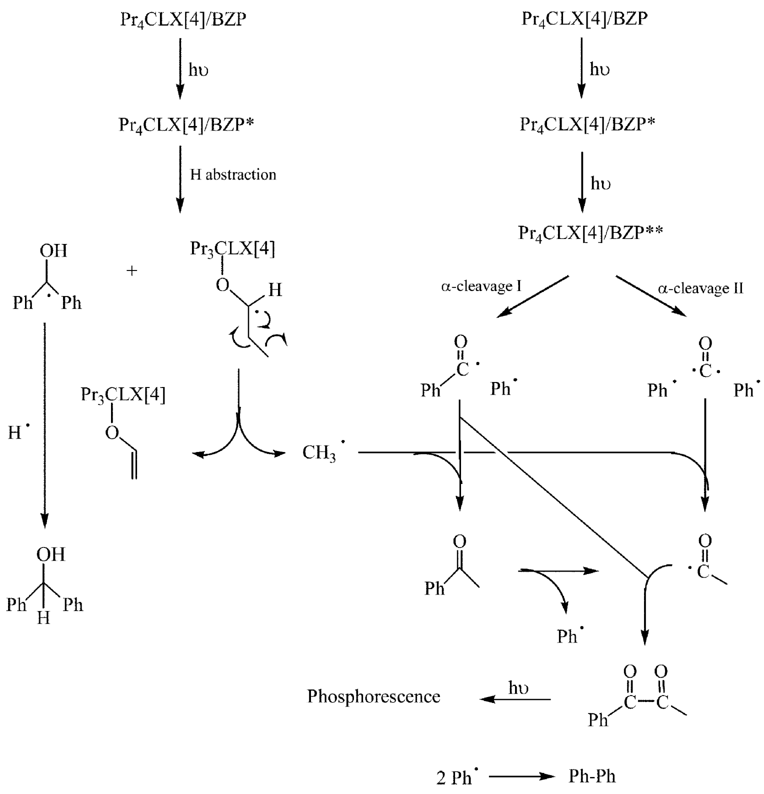
$$ {}^{3}\left[\text{Ph–C}(\text{=O})\text{–Ph}\right]^{*} \xrightarrow{+\text{H}^{\bullet}} \text{Ph–C}^{\bullet}(\text{OH})\text{–Ph} \quad (3)$$

$$ {}^{3}\left[\text{Ph–C}(\text{=O})\text{–Ph}\right]^{*} \xrightarrow{h\nu} \text{Ph–C}^{\bullet}\text{=O} + \text{Ph}^{\bullet} \quad (4)$$

Solution photochemical studies of benzophenone have shown that the hydrogen abstraction reaction with formation of the benzophenone ketyl radical (intermolecular hydrogen atom abstraction from suitable H-donating solvents) clearly predominates over the formation of the benzoyl radical (Norrish type I cleavage).[13,17] A two-step photon absorption process is necessary for benzophenone to produce a highly excited triplet state from which the benzoyl and phenyl radicals, and decarbonylation may occur.[12b,13] As we said, this process occurs within a single laser pulse, probably because of the diffuse reflected excitation radiation (355, 337 or 266 nm) detected long after the laser initial pulse (depending on the concentration of benzophenone in the sample).

The new emission shown in Fig. 3, 4 and 5 for benzophenone encapsulated in $H_2Pr_2CLX[4]$, $HPr_3CLX[4]$ and $Pr_4CLX[4]$, respectively, was obtained by irradiating either with a Nd:YAG laser (at 355 nm, 1–30 mJ pulse^{-1}, irradiating an area of about 1 cm^2) or with a N_2 laser (at 337 nm, 0.3–1.0 mJ pulse^{-1}, irradiating approximately the same sample area). Due to the rather large difference in fluence and to the fact that the new emission appears under both types of excitation, it is logical to assume that the two-photon absorption is sequential and not simultaneous, and therefore depends on the pulse length, as described in the literature for the formation of highly excited states of benzophenone.[13]

As we described, product analysis and identification was attempted following laser excitation (355 nm). HPLC and GC-MS analysis clearly show that the main degradation product of the benzophenone/$H_4CLX[4]$ samples was 2-hydroxybenzo-



Scheme 2

phenone and, for the BZP/$H_2Pr_2CLX[4]$ and BZP/$Pr_4CLX[4]$ pairs, the main photoproducts were 1-phenyl-1,2-propanedione and 2-hydroxybenzophenone. In contrast with the solution behaviour, the α-cleavage of benzophenone occurs and becames a very important degradation pathway in solid powdered samples.

All the experimental observations described herein, which lead to the PhPD phosphorescence emission and to the appearance of the trace compounds, are summarised in Scheme 2. In this scheme, the crucial reaction is the benzophenone hydrogen abstraction from the methylene group bound to the oxygen of the ether linkage. Further α-cleavage of this intermediate generates a methyl radical and an aryl enolether. The methyl radical thus formed could further react with several of the intermediate radicals resulting from the α-cleavage of BZP**, and thus accounting for the products formed: mainly PhPD, from which the new phosphorescence emission originates.

4 Conclusions

We can therefore conclude that inclusion of benzophenone into $H_4CLX[4]$ and $H_nPr_mCLX[4]$ (n = 2, 1 and 0; m = 2, 3 and 4, respectively) results in significant changes in both the ground-state absorption spectra and the time-resolved emission and transient absorption spectra. Product analysis and identification showed that the two main degradation products detected in the latter case were 1-phenyl-1,2-propanedione and 2-hydroxybenzophenone. The α-diketone is efficiently excited by scattered laser radiation long after the initial nanosecond laser pulse and a new phosphorescence emission occurs, which becomes the predominant luminescence on the millisecond timescale.

The fact that benzil is not formed as a result of the recombination of two benzoyl radicals suggests that stereochemical constrainments play a decisive role inside the calixarene cavity, *i.e.* the acetyl radical and the benzoyl radical are able to recombine, while two benzoyl radicals are not.

Comparing the results presented in this paper with those reported by Barra and Scaiano[18] for benzophenone within *p*-*tert*-butylhexaethoxycalix[6]arene, very important differences are apparent. In the case of ref. 18, no photochemistry was reported. The simple difference in the phenolic substituent group (a propyl group in our case) prompts some remarkable photochemical behaviour of benzophenone, with the formation and emission of a new α-diketone, 1-phenyl-1,2-propanedione.

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