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Interaction of triplet C_{60} with *p-tert*-butyl-calixarenes and their complexes with pyridine derivatives

Benedek Poór,[a] László Biczók*[a] and Miklós Kubinyi[ab]

[a] *Chemical Research Center, Hungarian Academy of Sciences, PO Box 17, 1525 Budapest, Hungary. E-mail: biczok@chemres.hu*
[b] *Department of Physical Chemistry, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

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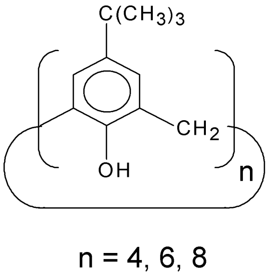
The interaction of triplet excited C_{60} with *p-tert*-butyl-calix[n]arenes (BCX*n*, $n = 4$, 6 or 8) and with their 2,4,6-trimethylpyridine (TMP) and pyridine complexes has been studied with laser flash photolysis experiments. It has been found that in polar solvents $^3C_{60}$ is quenched by BCX6 *via* electron transfer, producing $C_{60}^{-\bullet}$ radical anion with a yield of 0.45 ± 0.07 in benzonitrile. In contrast, no reaction occurs in nonpolar media or with BCX4 and BCX8. Upon the addition of TMP, the rate of quenching is enhanced considerably due to the formation of TMP-BCX*n* complexes. The significant deuterium isotope effect indicates that the electron movement from the calixarene to the triplet excited C_{60} is coupled to the proton displacement from the calixarene to the base. In the presence of pyridine, which has weaker hydrogen-bonding power, the enrichment of the solvate shell in the proton acceptor molecules may play an important role in promoting triplet C_{60} quenching.

Introduction

Calixarenes are macrocyclic phenolic compounds employed widely as building blocks in supramolecular chemistry.[1] Their host–guest complex formation can be exploited in the large-scale separation and purification of fullerenes.[2,3] Moreover, fullerenes can be solubilized in water by encapsulating them in the bowl-shaped cavity of water-soluble calixarenes, which is the prerequisite of many applications.[4] Ikeda *et al.* demonstrated that calixarenes with preorganized cone conformation and a proper inclination of the benzene rings can interact with C_{60}, even without a deep inclusion of the fullerene host in the calixarene cavity.[5] The thermodynamics of the complex formation between fullerene and various calixarene derivatives indicate that both solvophobic effect and π–π interactions are major driving forces for the association process.[6a–e]

Despite the fundamental scientific importance and potential applications of fullerene-calixarene supramolecular systems, very few information is available on the interaction between their constituents in the excited state. Islam *et al.* have studied the excited state properties of C_{60} incorporated into a cationic homooxacalix[3]arene in aqueous solution.[7] They observed a large blue shift in the triplet-triplet absorption maximum and a significantly accelerated triplet decay rate for the complex compared to those of bare C_{60}. Prat *et al.* found sharp difference in the properties of triplet C_{60}–calix[8]arene complexes.[8] The encapsulation of C_{60} in the cavity of *p-tert.*-butyl-calix[8]arene had only little effect on the triplet yield, the triplet lifetime and the efficiency of oxygen sensitisation. In contrast, in case of the other calixarene derivative, in which the phenolic OH-groups were substituted with propylsulfonate moieties, the absorption spectrum indicated a strong charge-transfer interaction between the components. In addition, light absorption gave rise to the formation of a long-lived unidentified transient, whose decay kinetics was insensitive to oxygen.



Scheme 1

The main goal of the present work has been to elucidate how calixarenes influence the kinetics of the photoinduced processes of C_{60}. The formula of the investigated substances is presented in Scheme 1. The calixarenes applied consist of 4, 6 or 8 phenolic units, with *tert*-butyl substituents attached in their para positions to reduce the flexibility of the macrocyclic systems.

Previous studies on the reaction of triplet excited C_{60} with hydrogen-bonded phenol-base pairs have given evidences for the occurrence of concerted electron and proton movement.[9–11] As an extension of these investigations, we now devote special attention to the role of calixarene-pyridine type complex formation in the reductive quenching of triplet C_{60}.

Experimental section

C_{60}(99.9%, SES Research Co.) and *p-tert*-butyl-calix[*n*]arenes (BCX*n*) (> 99%, FLUKA) were used without further purification. 2,4,6-Trimethylpyridine (TMP) and pyridine (Py) (Aldrich) were distilled before use. Solvents (HPLC grade, Aldrich) were dried over molecular sieve 4A (Aldrich). Samples containing *ca.* 10^{-4} M C_{60} were purged with nitrogen.

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The UV-visible absorption spectra were obtained with a GBC Cintra 10E apparatus. Flash photolysis experiments were carried out with a Nd-YAG laser (Continuum Surelight) giving 5 ns pulses at 532 nm. Absorption was detected perpendicular to the laser light using a 450 W xenon lamp, an Oriel 0.25 m monochromator and two detectors: a photomultiplier (Hamamatsu) for the 300–850 nm range and an InGaAs photodiode (Oriel 71898) for the near-IR. Transient absorption was digitised with a Hitachi VC-6041(Z) storage oscilloscope interfaced to a computer. The laser energy was reduced to $\leq$10 mJ to minimize the contribution of the triplet-triplet annihilation.

The time evolution of the triplet C_{60} absorbance at 750 nm was strictly single exponential if triplet lifetime was shorter than *ca.* 4 μs in the presence of quencher. The longer-lived traces (A(t)) were analysed taking into account the second-order disappearance of the triplet, fitting the following function to the experimental data:[12]

$$A(t) = \frac{A_0 \exp(-k_0 t)}{1 + A_0[1 - \exp(-k_0 t)]k_{\mathrm{TT}}/(k_0 \varepsilon_{\mathrm{T}} l)} \qquad (1)$$

where A_0 is the initial absorbance, l is the optical path, ε_{T} represents the molar absorption coefficient of triplet C_{60}, k_0 and k_{TT} denote the rate constants of the first- and second-order decay processes, respectively. When absorbance of long-lived radicals had significant contribution, the signals were fitted with the numerical solution of the set of the differential equations describing first-order followed by second-order kinetics.

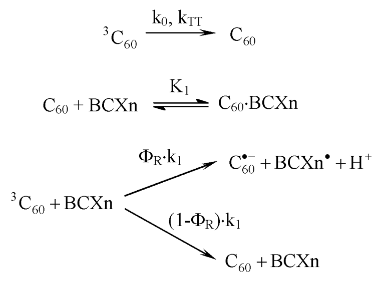
Results and discussion

1. Photoinduced electron transfer from calixarenes to C_{60}

An overview of the processes taken into account in the analysis of the experimental results is presented in Scheme 2. A fraction of the triplet C_{60} molecules returns to the ground state without interacting with the quencher in a simple first-order transition with rate constant k_0, or in a second order, annihilation type process with rate constants k_{TT}. The presence of calixarene (BCX*n*) in the system may cause a static quenching, *via* forming a supramolecular complex with ground state C_{60}. The equilibrium constant of this reaction is K_1. In addition, BCX*n* quenches triplet C_{60} dynamically, producing radicals with yield Φ_{R}, besides ground state C_{60}. Photoinduced processes following light absorption of the C_{60}-BCX*n* complex is not included in Scheme 2 because under the majority of our experimental conditions negligible or small fraction of C_{60} is bound to calixarenes in the ground state. The few cases, when the excitation of the C_{60}-BCX*n* complex has to be considered, will be discussed below.

Quenching of triplet C_{60}

Triplet C_{60} quenching by *p-tert*-butyl-calix[*n*]arenes (BCX*n*) has been studied in four solvents of various polarities: benzonitrile, CH_2Cl_2, chlorobenzene and toluene. Immediately after the laser flash the well-known characteristic absorption of triplet C_{60} appeared,[13] whose decay was followed at 750 nm, the maximum of the triplet-triplet absorption band. Addition of BCX4 or BCX8 did not alter the $^3C_{60}$ lifetime because no complex formation occurs for the former compound, and the binding of BCX8 does not affect the energy dissipation processes from the triplet state. In contrast, increasing amounts of BCX6 gradually accelerated the triplet deactivation in benzonitrile and CH_2Cl_2.



Scheme 2

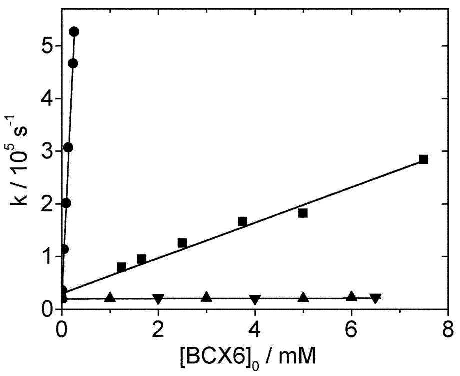


Fig. 1 Pseudo-first-order rate constants for triplet C_{60} quenching *vs.* BCX6 concentration in benzonitrile (●), CH_2Cl_2 (■), chlorobenzene (▲) and toluene (▼).

The variation of the pseudo-first-order decay rate constant (k) as a function of BCX6 concentration is shown in Fig. 1. As can be seen, there are linear dependencies in benzonitrile and dichloromethane, clearly demonstrating that triplet C_{60} readily reacts with BCX6 in a dynamic quenching process, whereas there is no observable quenching in chlorobenzene and toluene. The rate constants, taken from the slopes of the plots, are $k_1 = (1.7 \pm 0.3) \times 10^9$ M^{-1} s^{-1} and $(3.1 \pm 0.4) \times 10^7$ M^{-1} s^{-1} in benzonitrile and CH_2Cl_2, respectively. The pronounced diminishing trend of k_1 with decreasing solvent polarity suggests that electron transfer is the predominant quenching mechanism.

Effect of complexation in the ground state

The flash photolysis measurements on C_{60}-BCX6 system, applied to the study of dynamic quenching, have also shown that in dichloromethane the initial absorbance of triplet C_{60} gradually decreases with increasing calixarene concentration. *E.g.* a reduction of *ca.* 40% has been observed in case of the solution containing 7.5 mM BCX6. This effect is attributed to the change of the triplet yield upon complexation in the ground state. In the other solvents the triplet yield is invariant within the limits of experimental errors.

The interaction between the ground state components has been studied *via* recording the steady-state absorption spectra. The variation of the absorption spectrum of C_{60} upon the addition of BCX6 is shown in Fig. 2. The upper plot clearly demonstrates that the change of the absorbance at a particular wavelength (A) can be described well assuming the formation of a complex with 1:1 stoichiometry.

The data have been analysed using the following expression:

$$A = A_0(1 + K_1[\mathrm{BCX6}]\varepsilon_{\mathrm{C}}/\varepsilon_{\mathrm{F}})/(1 + K_1[\mathrm{BCX6}]) \qquad (2)$$

where A_0 is the absorbance in the absence of BCX6, K_1 the association constant for the C_{60}-BCX6 complex, $\varepsilon_{\mathrm{C}}/\varepsilon_{\mathrm{F}}$ denotes the ratio of the molar absorption coefficients for the complexed and free forms of C_{60}. The non-linear least-squares fit of this function to the experimental data has yielded $K_1 = 110 \pm 10$ M^{-1} in CH_2Cl_2. A comparison of this value to the one

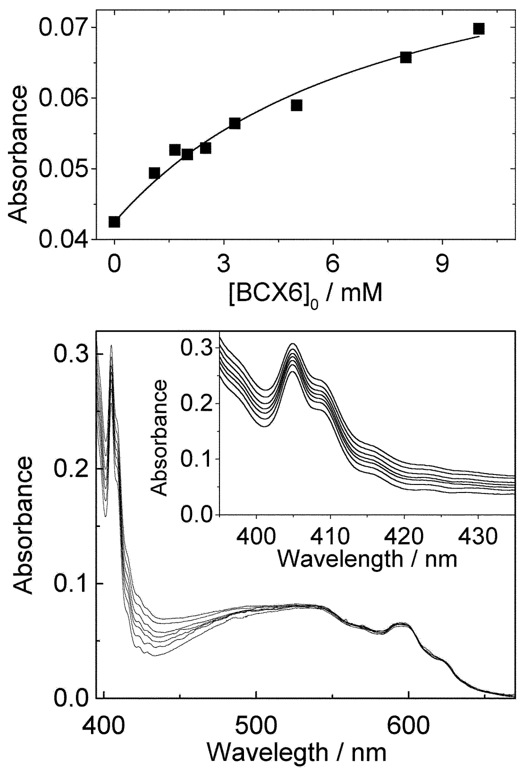


Fig. 2 (upper part) Variation of the absorbance at 445 nm *vs.* BCX6 concentration; line represents the best fit of eqn. 2. (lower part) Alteration of the absorption spectrum of C_{60} on addition of BCX6 in CH_2Cl_2. Insert: details of the spectral evolution in the 395–435 nm range.

reported in toluene[14] ($K_1 = 230\ M^{-1}$) indicates that the ground state complex is more stable in apolar solvent. It should be noted that no significant change in the absorption spectrum of C_{60} is detected on the addition of BCX6 in benzonitrile. This confirms the decrease of K_1 with increasing solvent polarity. It can be calculated from the equilibrium constant that in the dichloromethane solution with $\sim 10^{-4}$ M C_{60} and 7.5 mM BCX6 concentrations about 45% of C_{60} is complexed by the calixarene. This value agrees with the extent of the triplet yield diminution suggesting that the excitation of C_{60}-BCX6 complex does not lead to triplet formation. The electron transfer within the singlet-excited complex is so rapid in CH_2Cl_2 that the transition to the triplet state is not able to compete with it. The larger energy of the excited singlet relative to the triplet state enhances the driving force and expedites electron transfer. The electron back-transfer in the incipient singlet radical ion pair leads predominantly to rapid deactivation re-forming the ground state reactants.

In benzonitrile no change in the initial triplet absorbance was observed because the rapid triplet quenching required the use of low BCX6 concentrations, where ground state complexation is precluded. C_{60} readily binds to BCX6 in toluene, but the triplet yield for the complex remains the same as that of the free C_{60}. The nonpolar character of the solvent slows down the electron transfer significantly in the singlet excited complex and the intersystem crossing becomes the dominant deactivation process.

Transient absorption spectra

To provide a direct proof of electron transfer from BCX6 to triplet C_{60}, time-resolved transient absorption spectra have been recorded in benzonitrile (Fig. 3). The spectrum appearing concomitant to laser pulse corresponds to the triplet-triplet absorption of C_{60}. In the spectrum obtained following the decay of the triplet state, a strong IR band emerges with a maximum at 1080 nm together with some weaker bands in the 460–970 nm range. These features are unambiguously assigned to $C_{60}^{-\bullet}$ anion radical on the basis of general agreement with previous spectroscopic results.[15]

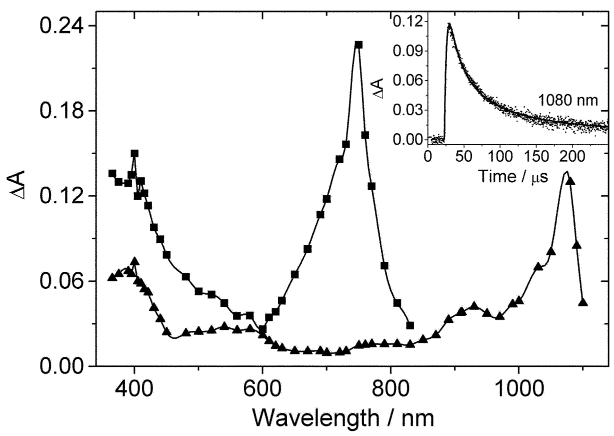


Fig. 3 Time-resolved absorption spectra in benzonitrile solution of 10^{-4} M C_{60} + 0.14 mM BCX6 immediately (■) and 9 µs after the laser flash (▲). Insert: decay of $C_{60}^{-\bullet}$ anion radical absorption at 1080 nm.

It is well-established that the radical cations of phenols are strongly acidic, *e.g.* the pK_a value of the 4-*tert*-butyl derivative is −7 in DMSO.[16] The incipient cation radicals, formed in the electron transfer from phenols to triplet excited molecule, lose a proton, rapidly leading to phenoxyl radicals.[17] Results of laser flash photolysis and time-resolved EPR experiments have confirmed the formation of phenoxyl radical and $C_{60}^{-\bullet}$ anion radical also in the photoreduction of C_{60} by hydroquinone.[13,18] Similar behaviour is expected when a macrocyclic phenol, BCX6 is used as electron donor. Based on the absorption spectra of phenoxyl,[19] 4-methylphenoxyl[20] and 4-*tert*-butylphenoxyl[21] radicals, the absorption of the phenoxyl type radical formed from the calixarene (BCX6$^\bullet$) is expected to be fairly weak and located below 450 nm. Hence, the band in the 360–450 nm region is ascribed to the superposition of the absorption of $C_{60}^{-\bullet}$ and BCX6$^\bullet$.

Yield of radical formation

The insert in Fig. 3 presents a typical transient absorption of $C_{60}^{-\bullet}$ anion radical recorded at 1080 nm and the result of the nonlinear least-squares fit assuming second-order decay kinetics. Using[15a] $\varepsilon(C_{60}^{-\bullet}) = 18\,300\ M^{-1}cm^{-1}$ for the molar absorption coefficient of $C_{60}^{-\bullet}$ at 1080 nm, $k_2 = 5.9 \times 10^9\ M^{-1}s^{-1}$ is obtained for the second-order rate constant of $C_{60}^{-\bullet}$ consumption, very close to the diffusion-controlled limit.

The absorbance at 1080 nm grows at the same rate as triplet decay (Fig. 4A) indicating that the triplet state is the precursor of $C_{60}^{-\bullet}$. The time evolution of the signals has been fitted with the numerical solution of the set of the differential equations describing first-order followed by second-order processes. Thus, we obtained the total absorbance ($\Delta A(C_{60}^{-\bullet})$) of $C_{60}^{-\bullet}$ corrected for reaction during the formation period, the pseudo-first-order (k_1[BCX6]) and the second order (k_2) rate constants.

The radical ion yield in the photoinduced electron transfer reaction from BCX6 to triplet C_{60} can be expressed as

$$\Phi_R = \frac{\Delta A_0(C_{60}^{-\bullet})}{\Delta A_0(^3C_{60})}\frac{\varepsilon(^3C_{60})}{\varepsilon(C_{60}^{-\bullet})}\frac{k_1[\mathrm{BCX6}]}{(k_0 + k_1[\mathrm{BCX6}])} \qquad (3)$$

where k_0 denotes the rate constant of triplet deactivation in the absence of additive. $\Delta A_0(^3C_{60})$ and $\Delta A_0(C_{60}^{-\bullet})$ represent

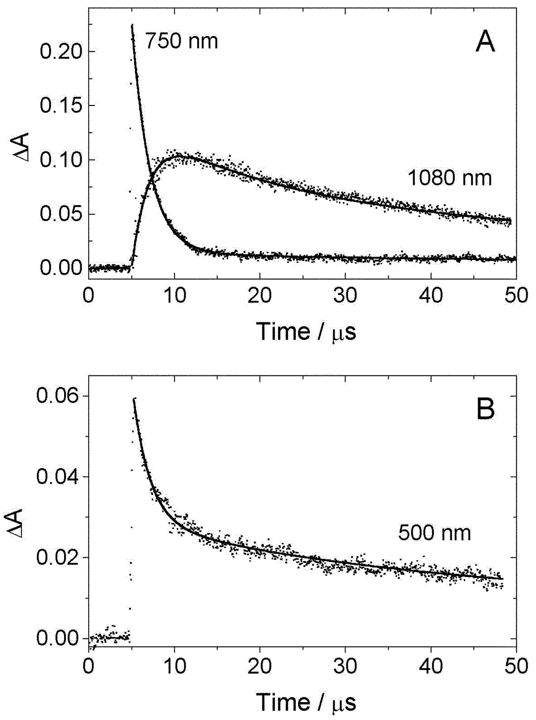


Fig. 4 Absorption–time profiles in the presence of 0.5 mM BCX6 in benzonitrile A, at 750 and 1080 nm; B, at 500 nm.

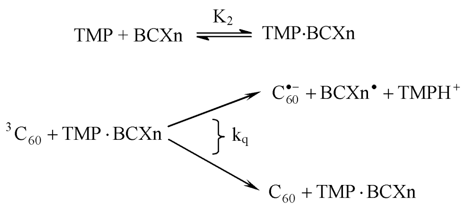
the initial absorbances of the respective species, $\varepsilon(^3C_{60})$ and $\varepsilon(C_{60}^{-\bullet})$ are their molar absorption coefficients. The absorbance changes have been measured on the same solutions applying the same laser energies.

The value of the radical yield has been determined from two sets of data:

(i) from the initial transient absorbances at 750 and 1080 nm, where the triplet and the radical anion forms of C_{60} can be detected selectively (see Fig. 3). Taking 16 100 $M^{-1}cm^{-1}$ and 18 300 $M^{-1}cm^{-1}$ for the molar absorption coefficient of $^3C_{60}$ and $C_{60}^{-\bullet}$, respectively at the above wavelengths,[13,15a] the results of several experiments have provided $\Phi_R = 0.48 \pm 0.04$ for the radical yield.

(ii) The transient absorbance at 500 nm, where the contributions of the two species are commensurable, allowed the determination of Φ_R from a single decay curve. The molar absorption coefficients at this wavelength[13] are $\varepsilon(^3C_{60}) = 3200\ M^{-1}cm^{-1}$ and $\varepsilon(C_{60}^{-\bullet}) = 2600\ M^{-1}cm^{-1}$. As an average of the values calculated from several decay curves, $\Phi_R = 0.42 \pm 0.04$ has been obtained, in a fair agreement with the result given above. Based on the two types of independent measurements, we suggest $\Phi_R = 0.45 \pm 0.07$ for the radical yield from triplet reaction in benzonitrile.

Calixarenes have many conformational isomers due to the rotational modes of the individual arene units. The flexibility of the macrocycle is highly dependent on the temperature, substituent, solvent and ring size. Temperature-dependent NMR measurements demonstrated[22] that BCX6 is more flexible than BCX8 and BCX4. The easier interconversion among the conformers in BCX6 helps to reach the molecular structure, which transfers most effectively electron to triplet C_{60}. The intramolecular hydrogen bonds among the phenolic HO-groups appended on the lower rim plays a decisive role not only in the stabilization of the conformers but it also may decrease the oxidation potential. Previous studies have established that hydrogen bonded phenols are much better electron donors.[9–11] The lack of effects on the yield and lifetime of triplet C_{60} upon addition of BCX4 and BCX8 arise probably primarily from the higher oxidation potential of these compounds compared with that of BCX6.



Scheme 3

2. Effect of the addition of pyridine derivatives

The addition of a pyridine base, like TMP, to C_{60}–calixarene mixtures opens a new channel for the quenching of triplet C_{60}, which is shown in Scheme 3. The base and the calixarene form a hydrogen-bonded adduct, the stability of which is characterized with the equilibrium constant k_2. Triplet C_{60} is quenched with this adduct with rate constant k_q. Based on the negligible change of the absorption spectrum, we conclude that no complexation occurs between C_{60} and the pyridine derivatives used in this study. In the absence of calixarenes pyridine derivatives do not quench triplet C_{60}.

Interaction of calixarenes with 2,4,6-trimethylpyridine (TMP) has been found to promote electron transfer to triplet C_{60}. Representative data are provided in Fig. 5, where the pseudo-first-order triplet decay rate enhancement, $k' - k'_0$, normalized with respect to total calixarene concentration, $[BCXn]_0$, is plotted against TMP concentration. It is worth noting that the observed reaction rate enhancements are independent of BCX*n* concentration in the presence of a large excess of TMP. As can be seen, the reaction rate acceleration depends markedly on the size of the calixarene ring. The extent of reaction rate increase is similar for BCX6 and BCX8, the compounds that readily form ground state inclusion complex[2,3,14] with C_{60}. However, the small size of BCX4 macrocycle prevents the close contact of the BCX-TMP complex with triplet C_{60}. The larger distance of the reactants in the collision complex decelerates the electron transfer. These results are in agreement with the ground state complex formation ability of BCX*n*. Molecular dynamic simulations and UV absorption spectroscopic experiments carried out by Schlachter *et al.*[14] led to the conclusion that the equilibrium constant of C_{60}–BCX8 and C_{60}–BCX6 complex formation has similar values, but C_{60} is not bound to BCX4.

It is well established that although calixarene–pyridine type complexes can have various structures, hydrogen bonding between the phenolic OH-group and the heterocyclic nitrogen is always the predominant interaction.[23] The hydrogen bonding expedites electron transfer because of two main reasons:

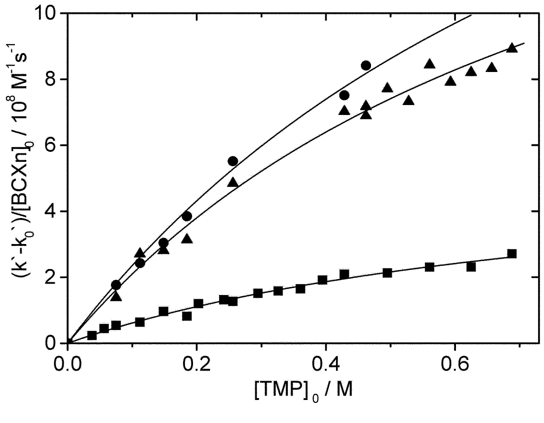


Fig. 5 Effect of calixarene structure on the TMP induced $^3C_{60}$ quenching in CH_2Cl_2 (▲) 2.5×10^{-4}M BCX8, (●) 6×10^{-4}M BCX6, (■) 2×10^{-3}M BCX4.

Table 1 Equilibrium constants of complex formation and rate constants of triplet C_{60} quenching by BCX*n*–pyridine type complexes

		BCX8			BCX6			BCX4		
Solvent	Base	$10^{-8}k_q$/ $M^{-1}\ s^{-1}$	K_2^{kin}/M^{-1}	K_2^{abs}/M^{-1}	$10^{-8}k_q$/ $M^{-1}\ s^{-1}$	K_2^{kin}/M^{-1}	K_2^{abs}/M^{-1}	$10^{-8}k_q$/ $M^{-1}\ s^{-1}$	K_2^{kin}/M^{-1}	K_2^{abs}/M^{-1}
PhCN	TMP	25 ± 3	11 ± 3	6 ± 3	Quenched without additive			Low solubility		
	Py	19 ± 3	0.3 ± 0.2	0.2 ± 0.1						
CH_2Cl_2	TMP	21 ± 3	1.1 ± 0.4	0.5 ± 0.2	22 ± 3	1.5 ± 0.3	1.0 ± 0.3	6.1 ± 0.6	1.1 ± 0.3	[a]
	Py	Concave			[a]			[a]		
PhCl	TMP	1.5 ± 0.9	0.5 ± 0.2	0.8 ± 0.3	16 ± 2	1.3 ± 0.2	1.3 ± 0.2	Low solubility		
	Py	Concave			Concave					
$PhCH_3$	TMP	Low solubility			9.1 ± 0.8	3.8 ± 0.5	3.7 ± 0.9	Low solubility		
	Py				Concave					

[a] Effect is too small to determine.

(i) it stabilizes the cone conformation of calixarenes and (ii) decreases their oxidation potential. Earlier studies proved that hydrogen-bonding with pyridine derivatives lowers the oxidation potential and consequently, increases the reducing power of phenols.[11]

The saturation character of the curves in Fig. 5 is attributable to the much higher reactivity of the calixarene-TMP complexes relative to the free calixarenes. After the steep initial rise the rate of each reaction tends to level off at high TMP concentrations, where most of BCX*n* is complexed. For the relative enhancement of the decay rate constant of triplet C_{60}, in the presence of calixarene BCX*n* and TMP, the latter in large excess, the formula

$$\frac{k' - k_0'}{[\mathrm{BCX}n]_0} = k_q \frac{K_2[\mathrm{TMP}]_0}{1 + K_2[\mathrm{TMP}]_0} \qquad (4)$$

can be derived. In eqn. (4) k' and k_0' denote the pseudo-first-order decay rate constants measured in the presence and in the absence of TMP, respectively, k_q is the rate constant of the triplet C_{60} quenching by the TMP-BCX*n* complex, k_2 is the equilibrium constant for the formation of the TMP-BCX*n* complex. A non-linear least squares fit of this function to the kinetic results provides the values for k_q and k_2. The calculated parameters are compiled in Table 1. As expected for electron transfer, k_q diminishes considerably with decreasing solvent polarity.

The bathochromic shift of the absorption spectra of calixarenes upon the addition of TMP offers further evidence for complexation. The equilibrium constants determined from UV-spectra (K_2^{abs}), also given in Table 1, agree closely with the corresponding values obtained from kinetic measurements (K_2^{kin}).

When we use a less basic additive, pyridine (Py), which possesses weaker hydrogen-bonding power,[24] both the binding equilibrium constant and the reaction rate enhancement is much smaller compared with the effect of TMP. It is apparent from Fig. 6 that even the form of the pyridine concentration dependence is entirely different in CH_2Cl_2 and chlorobenzene. Instead of approaching to a plateau, the reaction rate steadily rises with increasing slope. This behaviour cannot be attributed merely to the local polarity augmentation because BCX8 does not quench triplet C_{60} even in a strongly polar solvent, like benzonitrile. Hence, also the enrichment of the solvate shell in the proton acceptor pyridine and the conformation change of the macrocycle caused thereby may facilitate the oxidation of calixarenes.

In order to gain deeper insight into the quenching mechanism, we have studied the effect of the deuteration of the hydroxy moieties in the lower rim of calixarenes, comparing the reaction rate enhancement in 10^{-3} M BCX8 solutions equilibrated with 0.5 M CH_3OH or CH_3OD. NMR and mass spectra proved that fast isotope exchange takes place between the alcoholic and phenolic hydroxy-groups and the lower rim of BCX8 is fully deuterated in the presence of the *ca.* 100-fold excess of CH_3OD. The non-linear curve fitting of the data shown in Fig. 7 gives $k_q = (1.3 \pm 0.1) \times 10^9\ M^{-1}s^{-1}$ and $K_2 = 0.5 \pm 0.2\ M^{-1}$ for the undeuterated BCX8-TMP complex, whereas these quantities are $k_q = (0.9 \pm 0.1) \times 10^9\ M^{-1}s^{-1}$ and $K_2 = 0.4 \pm 0.2\ M^{-1}$ for the deuterated complex. Thus, we can conclude that the deuteration of the hydroxy groups in BCX8 influences predominantly the rate of electron-transfer from the complex to triplet C_{60}. Based on the marked isotope effect on this process, we suggest that the reaction is undergone *via* a trimolecular exciplex, in which the electron movement from the calixarene to the triplet excited C_{60} is coupled to the proton displacement from the calixarene to the base. A similar reaction mechanism was found when hydrogen-bonded

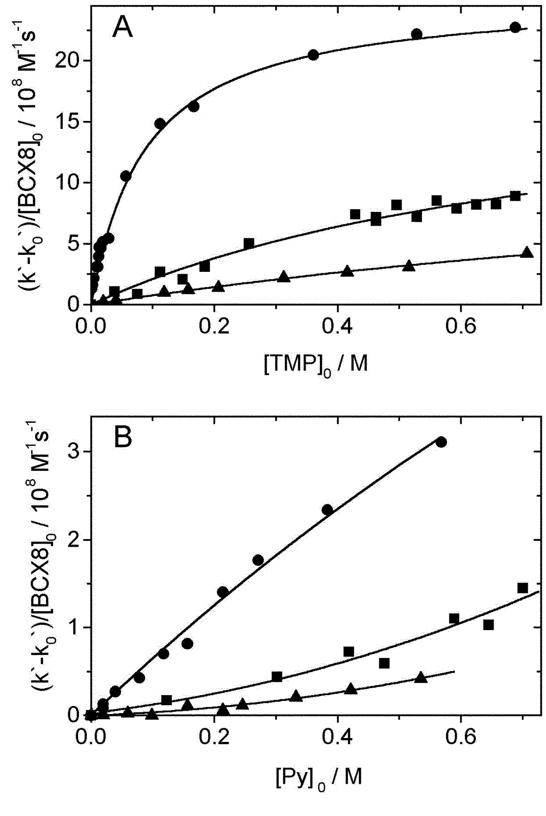


Fig. 6 Reaction rate enhancement on addition of TMP (A) and pyridine (B) in benzonitrile (●), CH_2Cl_2 (■) and chlorobenzene (▲).

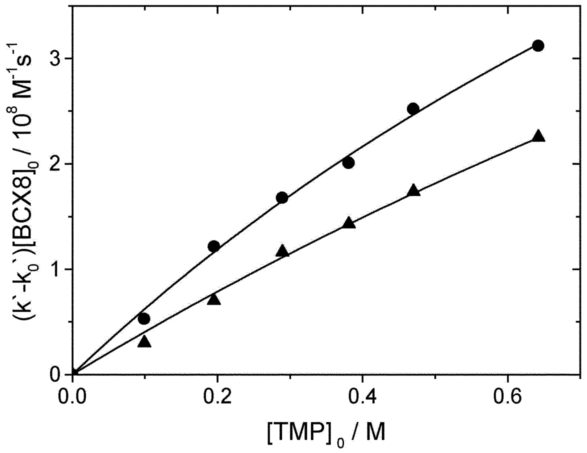


Fig. 7 Deuterium isotope effect on the reaction rate increase 10^{-4} M $C_{60} + 10^{-3}$ M BCX8 in benzonitrile containing 0.5 M CH_3OH (●) or 0.5 M CH_3OD (▲).

complexes of simple phenols with pyridine derivatives served as electron donors.[9–11]

Conclusion

Our steady-state spectroscopic and laser flash photolysis experiments revealed how the size of the calixarene macrocycle, solvent polarity and addition of pyridine derivatives affect the photoinduced reactions with C_{60}. We established that in benzonitrile triplet C_{60} is readily quenched by BCX6 in electron transfer forming $C_{60}{}^{-\bullet}$ radical anion with a yield of 0.45 ± 0.07. The rate constant of this process was found to be strongly dependent on the solvent polarity. In CH_2Cl_2, excitation of the C_{60}–BCX6 complex induced electron transfer in the singlet excited state, which was followed by fast recombination of the incipient radical ion pair leading to energy dissipation. In apolar solvents, intersystem crossing proved to be the dominant transition of the singlet excited C_{60}–BCX6 complex. Calixarenes consisting of 4 or 8 phenolic units (BCX4, BCX8) were unreactive with both the singlet and triplet excited C_{60}.

The addition of bases (trimethylpyridine or pyridine) forming hydrogen bonded adducts with calixarenes accelerated significantly the electron transfer to triplet C_{60}. The sensitivity of the rate of this process to deuteration indicates that the triplet quenching occurs *via* a trimolecular exciplex, in which coupled electron proton movement plays an important role. The concave dependence of the reaction rate enhancement on pyridine concentration was attributed to the enrichment of the solvate shell in the proton acceptor molecules.

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