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Electronic Spectroscopy and Photophysics of Calix[4]azulene

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ABSTRACT

Calix[4]azulene is a non-alternant aromatic calixarene composed of four azulene chromophores linked by methylene groups. Its photochemical stability, photophysical properties and an analysis of its electronic spectra are reported using monomeric azulene as a known reference standard. The molecule is stable when excited in its visible and near uv absorptions and, unlike azulene, produces no measurable "anti-Kasha" fluorescence when excited to its second excited singlet state, S_2. This lack of fluorescence places the lifetime of the initially excited, photochemically stable S_2 species at less than 1 picosecond. A significant, bathochromic shift of the S_2 absorption band system in the calixarene, and the appearance of an additional weak, broad absorption immediately to the red signals significant intramolecular chromophore interaction. Femtosecond transient absorption spectroscopy using excitation in this red-shifted tail of the S_2 band system reveals a very weak transient signal most of which decays within one ps, but with suggestions of a slightly longer-lived underlying component. No longer-lived T_1 triplet transient is observed. A complete analysis of the data using monomeric azulene as a reference suggests, following elimination of several alternate mechanisms, that the initially excited S_2 species may be relaxing via a novel singlet-singlet fission process.

Keywords: Calix[4]azulene, azulene, photochemistry, transient absorption spectroscopy, second excited singlet state, singlet fission

1. INTRODUCTION

The chemical and physical properties of the calixarenes and their supramolecular complexes are well-established and are documented in detail in recent reviews.[1-4] A small, interesting subset of the calixarenes are those derived from azulene, the model non-alternant aromatic hydrocarbon. Although the photophysical properties of many molecules containing multiples of the azulene carbon framework have been reported,[5] to our knowledge there has been no such report for any non-alternant calixarene. Calix[4]azulene can be easily synthesized in a simple one-pot procedure[6] and has two very interesting properties that distinguish it from the vast majority of calix[4]arenes in which alternant aromatics are the basic units. First, the azulene chromophores are intrinsically polar in the ground electronic state with modest electric dipole moments (0.79 D and 1.1 D have been reported[7,8]) leading to the possibility of either a non-polar or a net dipolar calix framework depending on the relative orientations of the four chromophores. Second, due to azulene's non-alternant structure, the nature and spacings of the electronic energy levels of the calix[4]azulene will differ substantially from those of the alternant calix[4]arenes. This leads to the likely possibility, as yet unexplored, that its excited state photophysical processes will be completely different from those of most calixarenes.

Although the properties and possible uses of calix[4]azulene and its derivatives as complexation agents have been thoroughly investigated,[9,10] neither an analysis of its interesting electronic spectrum nor an experimental investigation of its photophysical properties have yet been attempted. Of particular interest, the wide spacing of the electronic states revealed in its uv-visible absorption spectrum suggests that the calix[4]azulene might undergo singlet fission from its second excited singlet electronic state, S_2. Such a possibility was suggested almost four decades ago by Nickel and coworkers[11] for dimeric aggregates of azulene itself, but such a process has never been documented experimentally. Recent reports by Ni, *et al.*[13] have shown that efficient singlet fission can occur from the second excited singlet state of a cofacial perylene dimer despite the existence of competing decay channels, as previously identified by Michl, *et al.*[14,15]

Here we analyze the electronic spectrum of the calix[4]azulene and report for the first time its fundamental photochemical and photophysical properties.

2. MATERIALS AND METHODS

The calix[4]azulene was synthesized from azulene and paraformaldehyde as previously described[6] and was purified by repeated recrystallization from toluene. Details are provided in the Supporting Material. A small residual amount of azulene, identified by its unusual "anti-Kasha" fluorescence in the violet region of the spectrum, was retained in even the most highly purified product, but did not affect the outcome of the photophysical measurements. For improved solubility reasons, unstabilized tetrahydofuran (THF, Sigma, used as received) was used as the preferred solvent for these experiments, although other solvents (methylcyclohexane, methanol, acetonitrile) were used for comparison purposes.

Absorption and emission spectra were taken as previously described[16] using either a Cary Eclipse spectrophotometer, a Cary 6000i instrument, a PTI fluorormeter or a custom-modified SPEX Fluorolog fluorometer fitted with a variety of single line cw laser sources and complementary notch filters to eliminate scattered excitation light. Femtosecond transient absorption measurements were performed using a pump-probe configuration based on a high repetition rate (96kHz, 60fs) Coherent RegA 9050 amplifier. Pulses of 800 nm were split and frequency doubled on one arm to generate the pump (400 nm) beam while the other arm generated the probe (near-IR/white light) beam using a 3 mm-thick sapphire window (CASTECH). An off-axis parabolic reflector focused the pump and probe pulses to overlap in the solution-phase sample with a pump spot size of approximately 200 µm, giving an excitation fluence of 0.80 µJ cm^{-2}. Pump-induced absorption changes (ΔOD) of the solutions in a 2 mm pathlength optical cell were measured by comparing adjacent transmitted probe pulses with and without pump pulses using a synchronized mechanical chopper in the path of the pump beam. The time-resolved transient absorption spectra were recorded using a high-speed fibre-optic spectrometer (Ultrafast Systems). The instrument response function was estimated to be *ca*. 150 fs FWHM.

The photostability of the calix[4]azulene was examined by irradiating 3 mL of a vigorously stirred 49 µM solution in THF with *ca.* 5 mW of 355 nm light (absorbance of 1.1) from a cw laser and following the rate of loss of the absorber by absorption spectroscopy. The quantum yield of overall photochemical consumption of the calixarene was much less than 10^{-4}.

3. RESULTS AND DISCUSSION

3.1 Azulene

A brief summary of the electronic spectroscopy and photophysics of azulene[17-19] is needed to interpret the results obtained with its calixarene. Azulene’s time-averaged structure belongs to the C_{2v} molecular point group with a ground state dipole moment directed along the C_2 axis from the electron-poor seven-membered ring to the electron-rich five-membered ring. The axis system used to assign azulene's electronic state symmetries, chosen to be consistent with the Mulliken convention (x axis perpendicular to the plane), is shown in Figure 1A. The radiative transition to the lowest excited singlet state, S_1 (1^1B_2), in the mid-visible region of the spectrum is short-axis polarized, consistent with the contraction of the transannular bond in the excited state, and with a very small oscillator strength, *f*, consistent with its weak HOMO-LUMO overlap. The S_1 excited state is very short-lived (*ca.* 1-2 ps) due to rapid internal conversion to S_0 facilitated primarily by a S_1 - S_0 conical intersection. Thus the emission intensity from S_1 to S_0 is extremely weak, yielding a fluorescence quantum yield, ϕ_f, of less than 10^{-5}.

The radiative transition to azulene's second excited singlet state, S_2 (2^1A_1), with its intensity maximum near 340 nm, is z axis polarized and also exhibits a relatively small oscillator strength. The transition gains much of its intensity by Herzberg-Teller vibronic coupling, via a_1 modes, with the overlapping $^1A_1$ states that produce the strong electronic transition near 275 nm. The $S_2 – S_0$ origin band is thus quite weak. The $S_2 – S_0$ absorption transition reverses the direction of the dipole moment so that the seven-membered ring in S_2 becomes electron rich with a dipole moment of magnitude 0.3 D[20,21] directed along the C_2 axis. As a result of azulene's large $S_2 – S_1$ electronic energy gap and the nesting of its S_2 and S_1 potential energy surfaces, internal conversion to S_1 is slow. Thus the S_2 state of azulene in dilute solution has a lifetime at room temperature of about 1 ns, and exhibits "anti-Kasha" fluorescence (S_2 to S_0) with a

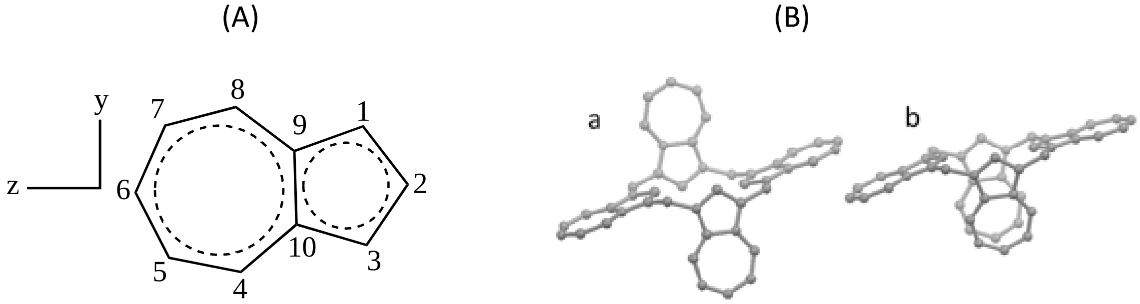

Figure 1: Structures. (A) azulene coordinate framework, and (B) calix[4]azulene in its two most stable conformations: (a) of C_i symmetry and (b) of C_s symmetry (from RSC Adv. **5**, 54848 (2015) – Published by the Royal Society of Chemistry. Ref. 9.)

quantum yield of *ca.* 0.03. Very weak $S_2 – S_1$ fluorescence has also been observed[22] with a quantum yield of *ca.* 7x10^{-5}.

Three other distinct absorptions of azulene are observable in the uv spectral region between 230 nm and the $S_2 – S_0$ transition. These have been identified by TD-DFT calculations[17] as S_3 2($^1B_2$) – S_0 near 297 nm with f = 0.03, a very strong broad band with a maximum near 275 nm consisting of several overlapping transitions to four $^1A_1$ states, followed by a strong S_8 3($^1B_2$) – S_0 transition near 238 nm. Of these the S_5 4($^1A_1$) – S_0 transition is the strongest, with an oscillator strength near unity, signifying a transition to a highly dipolar excited state. The energies of azulene's low-lying singlet and triplet electronic states in the gas phase have been obtained with high precision by anion photoelectron[17]and cavity ring-down[18] spectroscopy experiments in cold supersonic expansions. These data for azulene are summarized in Table 1.

Table 1: Electronic energies and transition oscillator strengths of the electronic states of azulene and calix[4]azulene in the near uv-visible. New measurements are in italics. See Table S1 for further detail.

Azulene			*calix[4]azulene*		
state	energy(a) (1000 cm^{-1})	*f* from S_0(c)	*state*	*energy(b) (1000 cm^{-1})*	*f from S_0(d)*
S_0 (1^1A_1)	0	-	S_0	*0*	-
S_1 (1^1B_2)	14.28; *14.4*	0.009	S_1	*13.2*	*0.03*
S_2 (2^1A_1)	28.76; *28.4*	0.06	S_2	*(~26.0)*	*0.4*
S_3 (2^1B_2)	33.7; *33.9*	0.03	S_3	*not observed*	-
S_n ((n-1)$^1A_1$) n=4-7	36.4; *36.3(e)*	1.0	S_n	*33.7(e)*	*2.5(e)*
T_1 (1^3B_2)	13.89	0	T_1	-	0
T_2 (1^3A_1)	19.20	0	T_2	-	0
T_3 (2^3A_1)	23.00	0	T_3	-	0
T_4 (2^3B_2)	31.16	0	T_4	-	0
Q_1(f)	34.3(f)	0	Q_1	-	0

(a) Gas phase at the origins (refs. 17, 18), and, following, in THF solution at the estimated singlet state origin band maxima (in italics, this work). (b) In THF solution with an estimate for the S_2 origin from observed vibrational spacings (this work). See text. (c) Ref. 19. (d) From integrated band intensities using azulene in THF as a standard. (e) At the maximum of the overlapped transitions. (f) Quintet, ref. 9.

3.2 Electronic spectroscopy of calix[4]azulene

Figure 2 shows the electronic absorption spectra of the calix[4]azulene in tetrahydrofuran compared with azulene in THF. The spectra in other solvents are shown in Figure S4 (Supporting Material). The origin transition energies and oscillator strengths are gathered in Table 1 for comparison with azulene itself. The wavenumbers of the observable transitions, and their vibrational features when resolved, are given in Table S1 (Supporting Material), together with comparative transition intensities from the band system areas. The following important points should be noted. (i) The spectra of the calix[4]azulene and azulene in the mildly polar solvents are similar, varying primarily by small bathochromic spectral shifts of the calixarene absorptions. The calixarene absorption band systems are also broader and exhibit less well-resolved vibrational structure. (ii) For the lowest energy transition ($S_1 - S_0$) the integrated molar

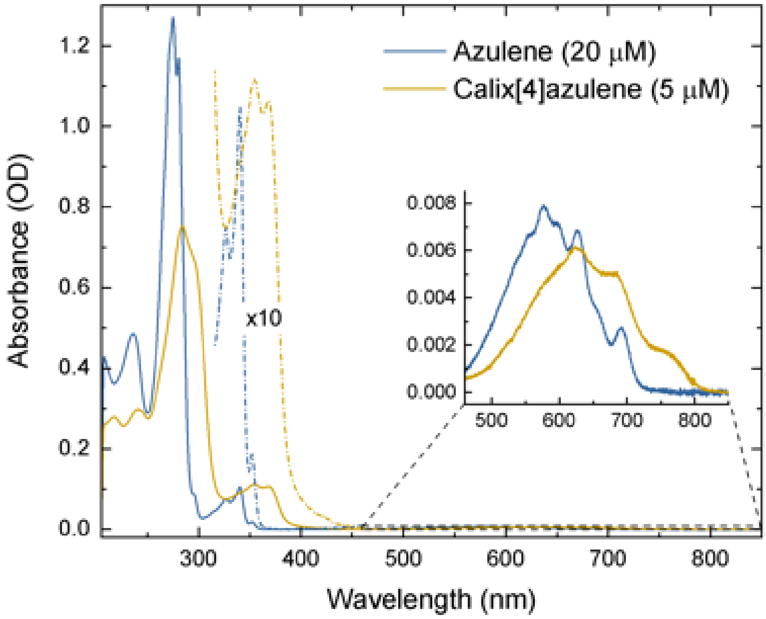

Figure 2: Absorption spectra of calix[4]azulene (5 μM) in THF compared with azulene in THF (20 μM) at room temperature. The backgrounds due to the absorption of the solvents in the UV have been subtracted. The short wavelength cutoff (10% transmission in a 1 cm cell) is 233 nm for pure THF. Spectra in other solvents are in the Supplementary Materials, Figure S4.

absorptivity of the calix approaches four times that of azulene. (iii) For the $S_2 – S_0$ transition, the molar absorptivity of the calix is at least six times that of azulene in the same solvent. The $S_1 – S_0$ transition of the calixarene is red-shifted by about 1250 cm^{-1} relative to azulene in similar moderately polar solvents. This is approximately what is expected from 1,3-dialkyl substitution of an azulene chromophore,[23] so there is little evidence in both the molar absorptivity and the spectral shift for this band of significant interchromophore exciton interaction associated with this transition in the calixarene. Consistent with the weak oscillator strength of this transition in azulene, its analogue in the calixarene is behaving as if it contains four independently absorbing azulene chromophores.

The origin band of the $S_2 – S_0$ transition of the calixarene in solution at room temperature is not distinguishable within the broadened low energy wing of its lowest energy resolved vibronic feature centered at *ca.* 27000 cm^{-1}. Nevertheless the position of the origin band can be estimated to be near 26000 cm^{-1} by comparisons with the vibrational spacings observed in the $S_1 – S_0$ and $S_2 – S_0$ transitions of azulene and the $S_1 – S_0$ transition of the calixarene. The whole of the $S_2 – S_0$ transition is shifted to the red by about 2600 cm^{-1} relative to azulene. Although this is only slightly more than that seen for $S_1 – S_0$, the effect of 1,3-dialkyl substitution of the azulene chromophore is expected to be smaller for the $S_2 – S_0$ transition than that for $S_1 – S_0$,[23] so the larger magnitude of the shift is indicative of a significant incremental interchromophore excitonic interaction in the calixarene. In addition, there is a weak, but significant, broad additional absorption feature on the low energy side of this band system. This feature is very similar to the weak absorption observed in the non-covalently aggregated azulene dimer in concentrated solutions of azulene in low temperature glasses.[24] However, neither the shape nor the relative intensity of this feature of the calixarene's $S_2 – S_0$ spectrum is a function of its concentration; it is an intramolecular effect indicative of chromophore interaction.

The weak transition corresponding to the $S_3 – S_0$ transition to the second $^1B_2$ excited state in azulene is not seen in the calixarene due to the substantial broadening of the strong absorption immediately to the blue. Nevertheless the position of its origin (near 32000 cm^{-1}) can be estimated from the red shifts its other electronic transitions, using the observed properties of monomeric azulene as a guide. (Note, for example, that the red shift of the very strong overlapping transitions of the calixarene near 300 nm relative to same group of features in azulene is similar to that of the $S_2 – S_0$ transition; about 2600 cm^{-1}.) The uncertainty in estimating the properties of the $S_3 – S_0$ transition in the calixarene renders the determination of the overall oscillator strength of its overlapped $S_2 – S_0$ transition somewhat uncertain. Nevertheless, the integrated intensity of the $S_2 – S_0$ transition of the calixarene must be at least six times larger than that of the corresponding band in monomeric azulene. Unlike $S_1 – S_0$, the azulene chromophores are not acting independently in the $S_2 – S_0$ transition in the calixarene; stronger excitonic interaction is expected.

Recent measurements and extended DFT calculations by Georghiou and coworkers[9,10,25] concerning the structure of calix[4]azulene (*cf.* Figure 1B) provide support for these observations. We concur with the crystallographic measurements of reference 9 showing that the calixarene crystallizes in the *C2/c* space group so that, in the solid, opposing pairs of azulene chromophores are oriented parallel to one another but with opposing ground state dipole moments. In the solid, the calix molecule thus exhibits near C_i molecular symmetry as shown in Figure 1B(a). However, the DFT calculations of reference 9 show that this is not the most stable structure in the gas phase or in mildly polar (chloroform) solution. Instead, when dispersion and solvation interactions are accounted for, the C_s conformation shown in Figure 1B(b) is predicted to be more stable than the C_i one by 9 kJ mol^{-1}. Although conformational equilibria will be present, this calculation suggests that a large fraction of the calixarene conformers will adopt the C_s conformation at room temperature in solutions of moderate polarity. This prediction is consistent with the similarities and differences between the azulene and calix[4]azulene absorption spectra shown in Figure 2.

Basic exciton theory[26] predicts that the degree of chromophore interaction in an aggregate depends on the magnitude, separation and orientation of the transition moments of the individual absorbing moieties. For any fixed geometry of a molecule containing two or more chromophores, the homo-chromophoric exciton interaction energy, ξ, is proportional to the square of the appropriate electronic transition moment, M^2, which in turn is proportional to the transition oscillator strength, f. The oscillator strength for the $S_1 - S_0$ transition in azulene is small ($f = 0.009$), so a very weak interaction energy, likely $\xi \leq k_BT$, is expected for the S_1 exciton in the calixarene. This is consistent with the observation of normal spectral shifts of the $S_1 - S_0$ band system of the calixarene and an oscillator strength that approaches four times that of monomeric azulene.

For transitions to two different electronic states, *i* and *j*, in a given chromophore,

$$\frac{\xi_i}{\xi_j} = \frac{M_i^2}{M_j^2} = \frac{f_i}{f_j} \qquad (1)$$

from which the *relative* values of ξ for excitons in a given aggregate may be calculated. From the data in Tables 1 and S1, $\xi_{S2}/\xi_{S1} = 7.2$. The excitonic interaction energy of the calixarene in its S_2

state (*i.e.*, the terminus of the dichromophoric transition analogous to $S_2 - S_0$ in the monomer) will therefore be much larger than that in S_1. The S_2 exciton interaction in the calixarene may well be augmented by the fact that the electric dipole moment of the chromophore reverses direction on excitation, going from vectorially parallel and repulsive in two partially cofacial chromophores in the ground state to opposed and attractive after excitation. A more substantial chromophoric interaction is thus seen when comparing the spectra and integrated absorptions of the $S_2 - S_0$ transitions in the calixarene with those in the monomer.

3.3 Photophysics of calix[4]azulene

Prompt $S_2 - S_0$ "anti-Kasha" fluorescence spectra of azulene were measured for reference in THF and other solvents at room temperature and are unremarkable. However, exciting the calixarene under the same sets of conditions as employed with the azulene monomer produced no measurable fluorescence from either S_2 or S_1, as shown in Figure S1 (Supplementary Material). This observation is consistent with the report that no measurable fluorescence could be found when exciting dimeric azulene aggregates formed in low temperature glasses in their weak absorption bands immediately to the red of the azulene monomer $S_2 - S_0$ origin band.[24] The $S_2 - S_1$ electronic energy spacing of the calixarene is no smaller than 12,000 cm^{-1}, so if this molecule exhibits the same weak interstate $S_2 - S_1$ coupling characteristic of the "nested" potential surfaces in azulene, its S_2 state should have a lifetime no shorter than 200 ps. Figure 3 shows the basis for this prediction, based on the existing structure-property relationship revealed by the energy gap law of radiationless transition theory and applicable in azulene, its fluorinated derivatives, benz[a]azulene and the d^0 and d^{10} *meso*-substituted metalloporphyrins.[5] The complete absence of detectable prompt S_2 fluorescence thus indicates that excitation

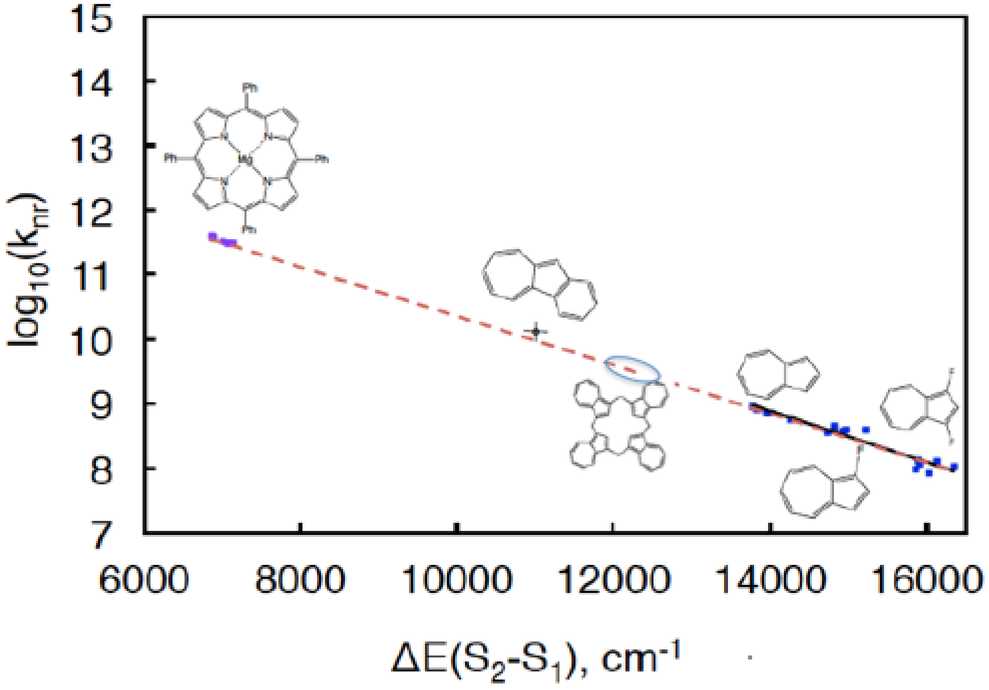

Figure 3: Energy gap law plot of the $\log_{10}$ of the $S_2 - S_1$ radiationless decay constant, k_{nr}, vs. the electronic energy spacing between S_2 and S_1 for known systems in which the S_2 and S_1 states are “nested” and hence weakly coupled (Ref. 5). The expected range of data for the calixarene, if S_2 and S_1 are weakly coupled, is indicated by the oval.

produces an S_2 state of the calixarene whose lifetime is several orders of magnitude shorter that that predicted for weak $S_2 - S_1$ coupling. With an S_2 radiative rate constant at least six times that of monomeric azulene, and an estimated upper limit of 10^{-5} for its S_2 fluorescence quantum yield, the calixarene’s initially-produced S_2 state thus must have a lifetime of less than 1 ps.

Photochemical decomposition of the calixarene can be ruled out as a source of the shortened lifetime of its S_2 state on the basis of the molecule’s observed photostability when subjected to prolonged cw laser excitation at 355 nm (Figure S2, Supporting Material). A photodecomposition quantum yield of less than 10^{-4} was observed, so S_2 excitation of the calixarene results, by some path, in a rapid repopulation of its ground electronic state.

Femtosecond transient absorption spectroscopy was then employed to identify any observable intermediates involved in the calixarene's S_2 decay route. The transient absorption spectrum of the calixarene in acetonitrile excited in the broad $S_2 – S_0$ absorption tail near 400 nm is shown in Figure 4A. Excitation at 400 nm probes a region of very weak absorption of the $S_0 – S_2$ spectrum (see Figure 2) and hence transient signals can be expected to be weak. Nevertheless, this wavelength is useful because it will excite the calixarene into a near thermally equilibrated S_2 state and the small azulene impurity present in the sample does not absorb at this wavelength. A very weak, broad transient absorption with a maximum near 583 nm is the only feature that can be distinguished. The temporal profile of the decay of this absorption and its fit to a single exponential decay function are given in Figure 4B. We assign this transient to the vibrationally cold S_2 state of the calixarene on the basis of (i) its short lifetime of 0.6 ± 0.3 ps, and (ii) comparisons with the previously reported transient absorption spectrum of

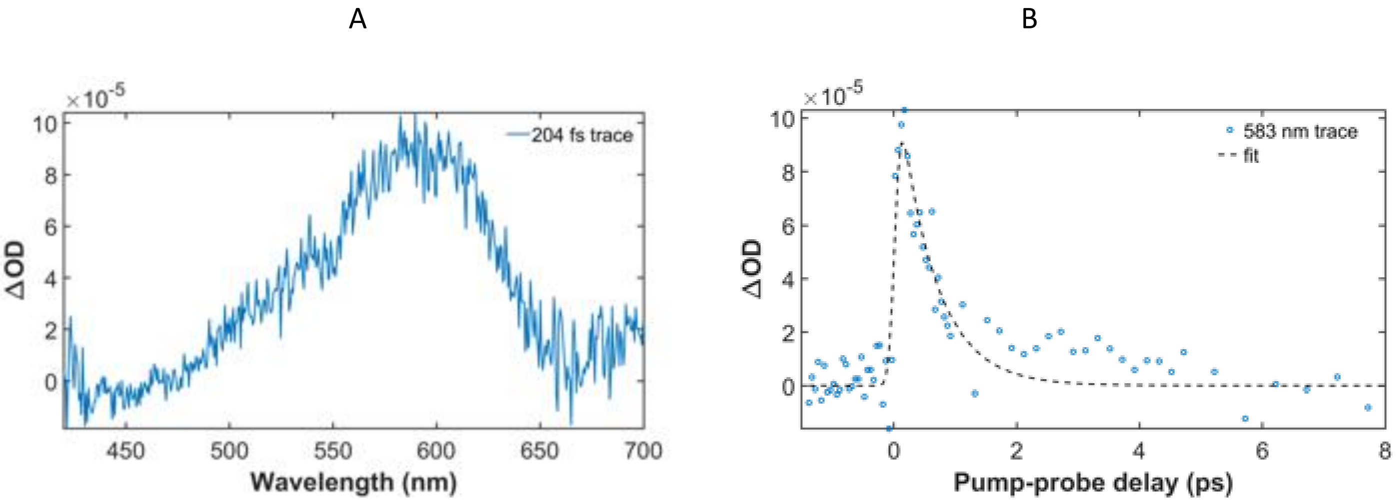

Figure 4: (A) Spectrum of the transient 204 fs following excitation of calix[4]azulene in acetonitrile (absorbance of 0.18) by 60 fs pulses at 400 nm. (B) Fit of the transient decay at 583 nm to a single exponential function; $\tau = 0.6 \pm 0.3$ ps (see text).

azulene.[27-29] When exciting azulene at 340 nm Foggi *et al.*[27,28] observe two broad bands assignable to S_2 in its transient absorption spectrum. Both are of approximately equal intensity with maxima, after correction for stimulated emission, near 565 nm and 397 nm and with lifetimes much longer than tens of ps. Allowing for a small red-shift of these azulene absorptions, we assign the broad band of the calixarene with a maximum near 583 nm to its initially formed S_2 state. A band corresponding to the 397 nm absorption of azulene, would not be observed in our system.

We then searched for evidence of the S_1 and T_1 states of the calixarene. When exciting azulene directly into S_1, Foggi *et al.*[27,28] observed a series of broad transients with distinct maxima initially near 450 nm (perhaps due to S_1 to S_3) and 380 nm. These features decay with a lifetime of *ca*. 1.4 ps and were assigned to S_1. After a few ps only a single weak absorption feature centered at 365 nm remained. It decayed with a time constant of *ca*. 8 ps and was assigned to the vibrational relaxation of an S_0 hot band absorption to S_2 , *i.e.,* S_0(vib) – S_2. We thus observe no distinct features in the transient absorption spectrum of Figure 4 that can be assigned unequivocally to an S_1 transient. However, a weak and noisy but reproducible tail on the main transient decay, Figure 4B, is of an approximately 1 to 2 ps duration and thus exhibits a decay rate that would be expected of the S_1 state of the calixarene. This tail becomes somewhat more prominent when following the transient absorption decay at 540 nm, as shown in Figure S3 (Supplementary Material). Further work to clarify the assignment of this feature is planned.

The only triplet transient absorption spectrum of azulene was reported by Goerner[29] in 1981 using a triplet photosensitization technique. Azulene's T_1 absorption spectrum consists of a broad band with a maximum at 360 nm and a lifetime of 3 to 5 microseconds in degassed fluid solution at room temperature. We would not see this band in our transient absorption system. However, calculations based on the known energies and symmetry species of azulene's excited triplet states (Table 1) predict that another strong, symmetry allowed triplet band, T_4 (2^3B_2) – T_1 (1^3B_2) with an origin near 550 nm, should appear in azulene's transient absorption spectrum. In Goerner's experiment, observation in this region was obscured by the overlapping strong triplet transient absorption spectrum of benzophenone, which was used as the sensitizer.[29] However, no absorption with a lifetime in the ns to μs duration range has been observed in this spectral region, either by Goerner or by us. There is no evidence of a triplet transient in our experiments with the near uv-visible excited calixarene.

We now consider the possible mechanisms of the calixarene's ultrafast S_2 relaxation process. We must rely on negative evidence; there is no significant photochemical decay; no triplet state transient absorption is observed, despite the possibility (based on azulene) of a symmetry-allowed transition in the sensitive spectral range of the spectrometer; there is a hint of a possible S_1 transient absorption, but no definitive evidence. There are relatively few alternative mechanisms for the calixarene's S_2 relaxation that are consistent with these observations and meet the required photophysical constraints. First we can eliminate the possibility that the calixarene undergoes direct singlet fission to T_1, i.e. $S_2 + S_0 \rightarrow 2\ T_1 \rightarrow 2\ S_0$. Although this process is both electron spin allowed and likely mildly exoergic, there is no reason to expect that the lowest triplet state of the calixarene would decay 10^6 times faster than that of azulene. The calixarene T_1 state is expected to have the same HOMO-LUMO electron occupancy as S_1, and, like azulene, to exhibit a very small $S_1 - T_1$ spacing due to the weak HOMO-LUMO overlap. Thus both the S_1 and T_1 states of the calixarene should behave like azulene itself, as shown by its $S_1 – S_0$ electronic absorption that behaves as if its four azulene chromophores were acting independently. Second, the likelihood of direct S_2 to $S_0(v')$ vibronic relaxation can almost certainly be ruled out because the Franck-Condon factor for such a process would be prohibitively small. Third, we consider a Förster $S_2 + S_0 \rightarrow S_1 + S_0(v'')$ decay mechanism, which in this case would have a somewhat larger Franck-Condon factor but would have a spectral overlap integral approaching zero.[22] Fourth we consider intersystem crossing from S_2 of the calixarene to T_n ($n > 1$). This process is expected to be slower than internal conversion, and it would almost certainly produce T_1 on the T_n decay path, but no T_1 was found.

Fifth, we consider the interesting possibility that excitation of the calixarene in its broad absorption band on the low energy side of its $S_2 – S_0$ absorption produces an S_2 exciton largely confined to a single azulene chromophore and that this excited species then transfers half of its electronic energy to a second nearby ground state azulene chromophore which is then excited to S_1. This essentially amounts to a near thermoneutral Förster resonant energy transfer process in which S_2 ($^1A_1$) falls to S_1 ($^1B_2$) in the initially excited chromophore and the transfer of energy promotes another from S_0 ($^1A_1$) to S_1 ($^1B_2$). The efficiency of such a process depends on the magnitude of the overlap between the (inferred) $S_2 – S_1$ emission spectrum and the $S_0 – S_1$ absorption spectrum of the constituent chromophores in the calixarene. Although the energies of these two transitions are almost equal, the weak $S_0 – S_1$ absorption of the calixarene runs to the blue of the origin whereas the $S_2 – S_1$ emission (also expected to be weak) must run to the red. The 0 - 0 bands of the required two electronic transitions in the calixarene will overlap, but the net overlap will be small enough and the two transition moments weak enough that Förstertype resonant electronic energy transfer on a sub-picosecond time scale can essentially be eliminated.

Finally, by elimination of all other possibilities, we consider the ultrafast decay of the calixarene to its ground state by singlet fission.[15,30,31] Here we propose a unique S_2 singlet excitonic fission process; $S_2 + S_0 \rightarrow 2\ S_1 \rightarrow 2\ S_0$. Azulene produces no observable T_1 by intersystem crossing from S_1 due to competing picosecond $S_1 - S_0$ decay brought about by its S_1/S_0 potential surface conical intersection. The failure to find T_1 in the calixarene decay therefore does eliminate conventional molecular singlet fission to $2T_1$,[15] but does not eliminate S_1 as an intermediate in its S_2 relaxation process. The fact that S_1 is not observed definitively in the transient absorption spectra is concerning, but the absorbance of the calixarene at its 400 nm excitation wavelength is small and the comparable azulene transients are observed in a wavelength range not probed with our instrumentation. A weak reproducible but noisy signal of 1 to 2 ps duration on the tail of the S_2 decay is observed and apparently is somewhat more prominent in the transient spectrum at 540 nm than at 583 nm. If the spectrum of azulene can be used as a guide, where the symmetry allowed S_1 ($^1B_2$) to S_3 ($^1B_2$) transition is predicted to have an origin near 514 nm (Table 1), we estimate that the comparable S_1 to S_3 transition in the calixarene would have an origin in the 530 to 550 nm range. In fact the proposed unique molecular singlet to singlet fission process is not only electron spin allowed and close to thermoneutral, but is also symmetry allowed; for azulene itself, S_2 ($^1A_1$) + S_0 ($^1A_1$) couples directly with 2 S_1 ($^1B_2$). The above noted spectroscopic, structural and photophysical observations also suggest that such an efficient excitonic coupling process does occur when the calixarene is excited to its S_2 state.

4. CONCLUSIONS

The non-alternant aromatic calixarene, calix[4]azulene, and its derivatives have been previously investigated for their properties as large molecular binding agents. Our measurements of this molecule's photostability support the choice of these species as robust complexation agents. They do not photodegrade significantly on illumination in the near uv-visible region of the spectrum. This molecule also exhibits remarkably interesting excited state decay properties. Excitation to the lowest energy excited singlet state results in the molecule behaving as if it consisted of four independently operating azulene chromophores; no significant intramolecular excitonic interaction is observed. Excitation of this calixarene to its second excited singlet state results in ultrafast relaxation to the ground state. No "anti-Kasha" fluorescence is observed, thus mimicking the known behaviour of non-covalently bound azulene dimers. The possible photophysical S_2 relaxation routes have been examined. No evidence of triplet intermediates is found, eliminating several potential S_2 decay routes, including conventional singlet fission. By further elimination, a unique S_2 decay route of this calixarene is proposed; singlet to product singlet excitonic fission.

Molecular singlet-singlet excitonic annihilation is well-established in the literature.[32] The principle of microscopic reversibility thus allows that excited singlet to product excited singlet fission can occur in polyatomic molecules that meet its energy and quantum mechanical requirements. Further exploration of this process will therefore require an examination of the relaxation dynamics of states that lie higher than S_1 in the excited singlet manifold, and that necessarily will be very short-lived. New developments in femtosecond laser technology will no doubt prove useful in this quest.

SUPPLEMENTARY MATERIAL

See supplementary material for the synthesis details of azulene and calix[4]azulene; table of absorption spectral data in THF; S_2-S_0 fluorescence spectra in THF; photolysis results for calix[4]azulene in THF; temporal decay at 540 nm for calix[4]azulene transient in THF; absorption spectra of calix[4]azulene in THF and azulene in MCH, MeOH and THF.

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DATA AVAILABILITY

Data that supports the findings of this study are available within the article and supplementary material.

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author Statement

Amy L Stevens: Investigation, Writing – Review and Editing, Funding acquisition. **Colleen Yeow**: Investigation, Writing – Review &. Editing. **Jonathan White**: Supervision, Writing – Review & Editing. **Siobhan J Bradley***:* Investigation, Writing – Review & Editing. **Kenneth P Ghiggino**: Supervision, Funding acquisition, Writing – Review & Editing: **Ronald P Steer:** Conceptualization, Supervision, Funding acquisition, Writing - Original Draft.