2005

Photocontrol of Upper and Lower Rim Complexation of Neutral and Cationic Species by p-tert-butylcalix[4]arene Tetraethyl Ester

Mary Deasy
Technological University Dublin, mary.deasy@tudublin.ie

Bernadette Creaven
Technological University Dublin, bernadette.creaven@tudublin.ie

Brian A. Murray
Technological University Dublin, brian.murray@tudublin.ie

See next page for additional authors

Recommended Citation

Deasy, M., Creavin, B. & Murray, B. (2005). Photocontrol of Upper and Lower Rim Complexation of Neutral and Cationic Species by p-tert-butylcalix[4]arene Tetraethyl Ester. *European Journal of Inorganic Chemistry*, pg. 1282-1292. DOI:10.1002/ejic.200400705

European Journal of Inorganic Chemistry

Article Title[‡] Photocontrol of Complexation of Neutral and Cationic Species by *p-tert*-Butylcalix[4]arene Tetraethyl Ester

Authors: Bernadette S. Creaven,[*] Mary Deasy, Catherine McKenna and Darren Tobin

Department of Applied Science, Institute of Technology, Tallaght, Dublin 24, Ireland.
National Centre for Sensor Research, Institute of Technology, Tallaght, Dublin 24, Ireland.
Fax: 353-1-4042700
e-mail: bernie.creaven@it-tallaght.ie

Rceived (will be filled in by the editorial staff)
Calixarene /photocontrol/ anion effect/ solvent effect/ sodium complexes

Abstract: A number of sodium salt complexes of *p-tert*-butylcalix[4]arene tetraethyl ester, **1**, were isolated both with and without upper-rim encapsulated solvent. Selective decomplexation of lower rim bound sodium cations and upper rim encapsulated solvent molecules could be successfully achieved using low pressure light sources. Oxidation of the counter anion at the lower rim of *p-tert*-butylcalix[4]arene tetraethyl ester triggered both the upper and lower rim decomplexation process. The extent of decomplexation at both rims is controlled both by the nature of the counter-anionic species at the lower rim and by the fate of the photoproducts generated. The calixarene host molecule, **1**, remains intact during the decomplexation process.

Introduction

Most photoresponsive systems that have been described in the literature employ photoisomerisable systems such as those based on the azobenzene[1] or stilbene[2] functionality as well as systems based on redox active units such as ferrocene,[3,4] tetrathiafulvalenes[5] and the

[*] Author to whom correspondence should be addresses

dithiol-disulphide couple.[6] As early as 1980, Shinkai and his colleagues synthesised an azobenzene-containing crown ether, the *cis* form of which bound K^+, Rb^+, and Cs^+ whereas the *trans* isomer preferentially bound Li^+ and Na^+.[7] Photocontrol of receptor binding is usually *via* the photochemical inter-conversion of two isomeric forms of a macrocycle.[8-10] Our previous work on photo-controllable systems has concentrated on molecules that have high inherent selectivity for targeted guests, specifically calixarene macrocycles (Figure 1), which selectively complex alkali cations.[11-13] ((Figure 1)) The cone conformation of calix[4]arenes, in which all four aromatic rings are upright, possesses a π-rich cavity defined by these rings, and as a result calix[4]arenes are capable of forming inclusion complexes with neutral molecules of appropriate size.[14,15] Their distinctive molecular architecture has therefore well-defined hydrophobic and hydrophilic regions, allowing easy structural and functional modification, thus enabling their widespread use as phase transfer catalysts, ion selective electrodes, and metal ion sequesters, all of which have been well documented in recent reviews.[14-16]

We have previously reported photodecomplexation studies on sodium iodide and tetraphenylborate complexes of calixarenes.[17,18] The % decomplexation of the complexes was found to be anion-dependent and did not appear to involve a structural change in the calixarene macrocycle. This work also showed that for complexes isolated from acetonitrile (MeCN), rather than chloroform, the overall % decomplexation of the complexes was reduced by up to 20%.[18] Solution thermodynamic studies of *p-tert*-butylcalix[4]arene tetraethyl ester **1** (Figure 1: R-$CH_2COOCH_2CH_3$) with a series of alkali metal salts in MeCN, MeOH and benzonitrile have been undertaken by a number of groups who had noted the increased stability of sodium complexes of **1** in MeCN.[19-24] MeCN was seen to produce an "allosteric effect" whereby the interaction of MeCN with the hydrophobic cavity of **1** preorganises the hydrophilic cavity to interact with cations. Another paper by Stibor *et al.* had investigated the complexation of neutral guests, including MeCN, by **1** in $CDCl_3$.[25] They reported that the presence of a sodium cation at the lower rim of the calixarene significantly enhanced the binding of neutral guests at the upper rim. In this paper we investigate the relationship between the presence of a molecule of MeCN and MeOH in the upper-rim of the calixarene and the extent of lower-rim decomplexation of sodium cation.

The control of the release of a bound guest by external means, to a pre-determined level, would allow the development of an analogue switching device, where controlled amounts of bound guests are required to be released, such as in drug therapies or in controlled syntheses.

Results and Discussion

To investigate the apparent stabilising effect of encapsulated solvent on the photodecomplexation behaviour of **1,** a number of Na^+ complexes of **1** were isolated from acetonitrile, methanol, dichloromethane and chloroform. While it has been reported that calix[4]arenes tightly bind chloroform, benzene, toluene, xylene, anisole and acetonitrile[26-30], the limited stability of the sodium complexes in some of these solvents precluded their use.[31] ^{1}H NMR spectra (Table 1) and microanalysis of the isolated complexes indicated that for each of the NaI, NaSCN, $NaIO_4$ and $NaBPh_4$ complexes isolated from MeCN, a solvent molecule was included in the upper cavity and these complexes are denoted as NaX-**1**(A) (X = I^-, SCN^-, BPh_4^-, IO_4^-,). The $NaIO_4$ complex of **1** isolated from MeOH also had an upper-rim bound solvent molecule, denoted as $NaIO_4$-**1**(M). No encapsulated chloroform or dichloromethane complexes of **1** could be isolated. Sodium salt complexes of **1** have been widely reported in the literature[10-16,19-24] and ^{1}H NMR assignments in $CDCl_3$ were based on these reports. ((Table1)) There have been few reports on the variation of binding constants of metal cations by calixarenes with the nature of counter-anion in non-polar solution.[32] A paper by Pochini *et al*. investigated an anion effect on complexation of a calix-crown ligand in $CDCl_3$ with a series of ammonium salts with p-toluenesulfonate, chloride and picrate as counter anions.[33] Their results indicated that tightening the ion-pair (as evidenced by shifts in the NMR signals for tosylate and picrate anion upon complexation) weakened the complexation of the ammonium ion by the calix-crown ligand. The complexation induced shifts noted in our study would indicate that the ion-pair interaction at the lower-rim (as evidenced by ^{1}H NMR signals of the $OC\mathbf{H_2}COCH_2CH_3$ and $OCH_2COC\mathbf{H_2}C\mathbf{H_3}$ moieties and the methylene bridges) was relatively similar for all the anions except for tetraphenylborate. This may be an indication that ion-pairing with tetraphenyl borate was weakest for this anion, which is consistent with the "non-coordinating" nature of this ligand, or that the phenyl groups of the anion are having an additional shielding effect at the lower rim.

^{1}H NMR signals at 1.71 ppm, 1.50 ppm and 1.43 ppm in the NMR in the spectra of NaI-**1**(A), NaSCN-**1**(A) and $NaBPh_4$-**1**(A) respectively were assigned to encapsulated MeCN in the upper rim of the complexes. A small amount of MeCN was added to solutions of NaX-**1** and this confirmed that these peaks could be assigned to complexation induced shifts of upper-rim bound MeCN; in *d*-chloroform, MeCN is known to have a chemical shift of 1.98 ppm.[34] The exchange of free NaX-**1** to MeCN co-ordinated NaX-**1**(A) occurs rapidly and so over the NMR time scale an average chemical shift for MeCN is obtained. The integration of the **1**H NMR signals confirmed that the host:MeCN ratio was 1:1 in all samples and thus the extent of MeCN binding by NaX-**1** seemed to be anion-dependent. The stability constant for the formation of the MeCN encapsulated complex of NaSCN-**1**(A) has been calculated from titration data to be 31 M^{-1}.[25] Given the value of this stability constant, to ensure that all of the NaSCN-**1** present in solution also contained upper-rim bound MeCN, an excess of MeCN had to be added to the solution.[25] Solid sate studies have shown that an interaction between the calixarene and MeCN occurs possibly *via* a CH_3-π interaction where the methyl group of the MeCN is orientated toward the hydrophobic upper cavity resulting in a significant shielding effect on the alkyl hydrogens.[30,36] The presence of MeCN in the upper cavity of the complexes resulted in small downfield shifts in the *t*-butyl and aromatic signals for these complexes, relative to when MeCN was absent.

The presence of encapsulated MeCN and MeOH was also observed in $NaIO_4$-**1** complexes with a chemical shift of 1.47 ppm and 3.39 ppm respectively.[37] Free MeOH in $CDCl_3$ has a chemical shift of 3.64 ppm.[34] Although crystals of suitable quality have not been isolated for solid state structure analysis, a potassium complex of a calixarene tetraamide has been reported with a molecule of MeOH in its hydrophobic cavity.[38]

Photo-Decomplexation Studies of NaX-1

Our previous work had shown that irradiation of $NaBPh_4$:**1** in $CDCl_3$, generated products consistent with the photooxidation of the anion.[18] In this study, we monitored the fate of the other anions upon photoexcitation of the macrocyclic complexes. A low pressure mercury lamp operating at room temperature, emits primarily one band of radiation at 253.6 nm. Exposure of calixarene complexes to this wavelength leads to extensive photochemical reaction and breakdown of the host compound. However the output of low pressure mercury lamps includes a number of weak lines above 280 nm, including 289.4, 296.7, 302.2 and 312.26 nm. Figure 2

shows the absorption spectra of the calixarene host compound (**1)** and some of its complexes, together with the transmission characteristic of a typical pyrex NMR tube. ((Figure 2)) The pyrex NMR tube effectively cuts out all radiation at the main excitation wavelength of the lamp and is only 10% transmitting at 280 nm but increases thereafter. With the exception of the NaI complex the two main absorption bands of the calixarene varied little in position upon coordination of the different salts but varied somewhat in intensity. Table 2 gives the absorption data of free calixarene and its complexes at a number of wavelengths.((Table 2)) The unphotolysed samples of NaX-**1** had two main absorption bands at ca. 272 nm and 283 nm, characteristic of the complexed calixarene, the latter assigned to the $S_0 \rightarrow S_1$ transition of the aryl ether moiety.[39,40] The use of a glass filter (in the form of a pyrex NMR tube) effectively excludes the 254 nm radiation[41] and the remaining lines centred around 308nm are the primary wavelength of excitations and corresponds to the shoulder of the $S_0 \rightarrow S_1$ transition[41] and the anion centred absorptions. Photoexcitation of aryl ethers leads to the ejection of an electron from the arene excited (π,π^*) state and the formation of a radical cation. The subsequent activation of the aromatic ring is primarily at the *para* position but also at the *ortho* position.[42] In our case, a *t*-butyl and a methylene group occupy these two positions, and so the expected further reactions are inhibited. The other chromophoric species in solution are the counter anionic species i.e. the iodide, thiocyanate, or periodate ions that have weak absorptions at this wavelength (perchlorate ions have no absorption bands in this region).[43]

The results for irradiation of the complexes in $CDCl_3$ are presented in Table 3. The % decomplexation is calculated from the ^{1}H NMR spectra of the photolysed solution *via* integration of the aryl protons of the free and complexed species as distinct signals can be seen for both species in the spectrum. These results indicated a significant anion dependence on the extent of decomplexation with up to 85% decomplexation being achieved with BPh_4^- and SCN^- as anions but no decomplexation occurring for the sodium perchlorate complex and little for the periodate complex (14%). There was no apparent relationship between the extent of ion-pairing at the lower-rim and the extent of photodecomplexation, a factor we had previously thought to be important.[18] If fresh solutions of salt was added to the NMR tubes, full recomplexation of **1** occurred. The presence of encapsulated MeCN reduced the initial % photodecomplexation of the

tetraphenylborate and periodate complexes. In all cases at extended irradiation times, where MeCN was present in solution, recomplexation was seen to occur to some extent. ((Table 3))

Interesting decomplexation behaviour was noticed upon irradiation of NaX-**1**(A) complexes. Figure 3 illustrates the linear relationship between the amount of calixarene remaining complexed to a sodium cation and the chemical shift of MeCN peak (all three lines yielded R^2-values greater than 0.99) for three sodium complexes. The ordinate-intercept value of each of the graphs is approximately 2 ppm (δ of free MeCN in $CDCl_3$ is 1.98 ppm)[34] and thus it appeared that the photo-induced decomplexation of encapsulated MeCN was seen to directly correlate with the % decomplexation of cationic guest. As stated already an excess of MeCN in solution would be needed to ensure full 1:1 complexation of upper-rim MeCN.[25] However such an excess would mask any observed decomplexation of the bound MeCN and so all studies were carried out with NaX-**1**: MeCN ratio of 1:1. The slope of each graph is different indicating that the nature of the interaction of bound acetonitrile with the upper cavity was anion-dependent. The binding constants (log K_s) for calixarenes with neutral guests in the upper cavity have been measured in polar solvents and have been found to be usually at least 3 or more times less than the binding constants of the same calixarenes with cationic guests.[19-22] Whilst studies have been carried out to determine the binding constant for cationic species of **1** in MeCN,[19-22] the K_s for NaX-**1** with MeCN in the presence of different anions at the lower rim is now a feature of a further study by our group. ((Figure 3))

$NaIO_4$-**1** complexes with encapsulated solvent were also examined. After irradiation of $NaIO_4$-**1**(M), the MeOH peak shifted marginally downfield but again was found to be linearly dependent upon the extent of photo-decomplexation and a similar result was found for the corresponding $NaIO_4$-**1**(A) complex (Figure 4). Extrapolation of the graphs to 0% complexation yielded a chemical shift value of 3.64 ppm (chemical shift of MeOH in $CDCl_3$ is 3.49)[34] and a value of 2.32 ppm for the acetonitrile-encapsulated sample. ((Figure 4))

These studies clearly re-enforce the synergistic relationship between upper and lower-rim bound guests in calix[4]arenes.[25,33,36,44] In addition the *extent* of neutral guest decomplexation

depended on the identity of the counter anion at the lower rim, and the role of this anion in the decomplexation process was important to determine.

Photoreactivity of the counter anions of NaX-1

Potentiometric titration of aqueous extracts of the irradiated $CDCl_3$ solutions of NaI-**1** and NaI-**1**(A) (Table 4) indicated that the concentration of iodide was reduced upon irradiation but that reduction did not correlate exactly with the decomplexation of the calixarene. In fact, while most of the iodide had reacted after 10 minutes, partial complexation of the calixarene at this and later times, indicated the presence of another anion in solution. UV/Vis analysis indicated that tri-iodide was produced, presumably from the intial reaction of iodine radicals to form iodine followed by further reaction with iodide to form tri-iodide.[45] Chloride was also detected in reasonable concentrations (Table 4). A white precipitate isolated from the photolysed solutions was identified as NaCl. If a fresh source of counter anion, in the form of **t**-butyl ammonium iodide, was added to the NMR tubes full recomplexation of **1** occurred, indicating that sodium was still present in its cationic form. ((Table 4))

Replicate 1ml samples of chloroform were irradiated for up to 90 minutes, under the same conditions described above, and in each case no chloride was detected.[46] Solutions of **1** in $CDCl_3$**,** irradiated for 60 minutes, showed no degradation of the calixarene. However potentiometric titration showed that chloride was present in these solutions but at a significantly reduced level (1.69 ±0.04 mM) than that recorded following irradiation of the sodium complexes of **1** as shown in Table 4. In a separate series of experiments the non-chromophoric *t*-butyl ammonium iodide (TBAI) was irradiated for timed intervals and analysed by both ^{1}H NMR and potentiometry. After just 15 minutes no iodide could be detected in solution and chloride, in an equivalent amount to that of iodide initailly present, was detected [Figure 5(a)]. The presence of tri-iodide in these solutions was confirmed by UV/VIS spectroscopy. The results confirmed that chloride can be produced from the direct photo-oxidation of the anion and to a lesser extent from irradiation of the ligand itself. ((Figure 5))

GC and GC-MS analysis, of the irradiated $CDCl_3$ solutions of both the calixarene and TBA complexes, showed that the primary organic products formed were deutero-dichloromethane and

-dichloroiodomethane ($CDCl_2I$) and traces of deutero-1,1,2,2-tetrachloroethane. It is known that reduction of chloroform generates short-lived radical anions which eject chloride immediately upon formation.[47] The generated radicals can undergo disproportionation and recombination processes as well as further attack on solvent and this is evidenced by the photoproducts identified above. In all cases the photolysis by-products were present in much larger quantities for experiments carried out on the complexes rather than the free ligand.

UV irradiation on metal coordination complexes where iodide is present either as an axial ligand or as a counter anion leads to the generation of an $I^{\cdot}$ radical, with concomitant reduction of the solvent by charge transfer to solvent (CTTS).[48-56] When I^- and NCS^- are the axial ligands, dimerization of the $I^{\bullet}$ and $SCN^{\bullet}$ radicals was found to be an efficient secondary process. For those studies carried out in chlorinated solvents generation of iodide radicals has resulted in the production of chloride from chlorinated solvents.[52,53]

The pattern of destruction of counter anion and production of chloride can be seen again in the irradiation of NaSCN-**1** and NaSCN-**1**(A) (Figure 6). Quantitative FT-IR results indicated that irradiation of the NaSCN-**1** solutions resulted in the concentration of thiocyanate anions falling to undetectable levels after 30 minutes. However, the complex was once again noted by ^{1}H NMR to be only partially decomplexed over the same time period. The main anion present from photolysis of thiocyanate solutions, detected by potentiometry, was again chloride anion and NaCl could be recovered as a precipitate from solution. The NMR spectrum recorded after irradiation is consistent with the a small amount of complex being present as NaCl-**1**.[18] Elemental sulphur precipitated out of solution and was identified by microanalysis. ((Figure 6))

Irradiation of *t*-butyl ammonium thiocyanate (TBASCN) over 60 minutes in $CDCl_3$ also showed the destruction of the SCN anion, though at lower levels than recorded for NaSCN-**1** (Figure 5(b)). GC-MS analysis of both of these irradiated solutions showed the formation of mainly deuterated dichloromethane as a photo-product of the solvent.

Irradiation of thiocyanate complexes in non-aqueous solvents leads to production of thiocyanate radicals which can then form sulphur and cyanide anion. [49,52,54] The proposed reaction is:

(1) $SCN^- + h\nu \rightarrow SCN^{\cdot} + e^-_{solvated}$

(2) $SCN^- + h\nu \rightarrow S + CN^-$

followed by complex reactions in which cage recombination and further reactions with SCN^- are central:

(3) $SCN^- + SCN^{\cdot} \rightleftharpoons (SCN)_2^{\cdot -}$

(4) $2\ (SCN)_2^{\cdot -} \rightarrow (SCN)_2 + 2\ SCN^-$

(5) $S + SCN^- \rightarrow S_2 + CN^-$

(6) $2\ SCN^{\cdot} \rightarrow (SCN)_2$

Elemental sulphur was recovered following photolysis of NaSCN-**1** and TBASCN, but there was no evidence for the presence of cyanide from auto-titration or FT-IR studies. The cyanide anion itself can be further photolysed to the cyano-radical, which can oxidise the solvent or form cyanogen gas.[54]

Based on these results, and shown in Scheme 1, is the proposed mechanism for the decomplexation process. Irradiation of NaX-**1** in $CDCl_3$ results in the generation of two excited species, a radical aryl cation and the direct oxidation of the counter anionic species. This excitation results in a charge transfer to solvent with the subsequent generation of a number of photoproducts of both the solvent and anion. Athough a radical aryl cation may be generated initially; abstraction of an electron from the bound anion or solvent is likely to have occurred quickly, as no photoproducts of the host compound are detected. Given the results with TBAX salts, together with the non-reaction of a perchlorate salt calixarene complex, it is likely that generation of a radical from the anion predominates. The generation of a radical from the anion leads to the break-up of the ion-pair and the subsequent expulsion of the sodium cation. This cation remains available for re-complexation if a suitable counter anion, such as chloride, is present**.** The products of iodide oxidation were ultimately triiodide and iodine, sulphur was isolated from irradiated thiocyanate solutions and chloride ion was generated from the CTTS to the solvent in both cases. The poor solubility of sodium chloride in chloroform, even in the

presence of the macrcocycle, precluded full recomplexation. The NMR spectrum recorded after irradiation shows the complex peaks to be at slightly shifted positions relative to the initial complex and these positions are consistent with the complex being present as NaY-**1** ($Y = I_3^-$, Cl^-). While photoproducts of the solvent, including the deuterated forms of 1,1,2,2-tetrachloroethane, dichloromethane and dichloroiodomethane, could be detected by GC-MS, there were no detectable photoproducts by NMR or GC-MS, of the macrocycle itself. ((Scheme 1))

Irradiation of NaX-1 in Other Deuterated Solvents

The % decomplexation of NaI-**1** and NaSCN-**1** were recorded after irradiation in CD_3OD, CD_3CN and CD_2Cl_2 (Figure 7). No decomplexation of the complexes occurred in CD_3OD or CD_3CN. While ion pairing is minimised in these solvents it should also be noted that these solvents are not easily reduced by CTTS. The extent of decomplexation of both complexes was significantly less in CD_2Cl_2 and both autotitration and IR measurements indicated that, while destruction of the anions had occurred, it was to a far lesser extent than in $CDCl_3$. Although the extent of ion-pairing would be similar for these solvents, this difference in reactivity is thought to reflect the relative ease of reduction of these solvents [chloroform, -1.67 V ($E_{1/2}$) vs. dichloromethane -2.33 V ($E_{1/2}$)][57] ((Figure 7)) resulting in the formation of chloride as well as other photoproducts.

Electrochemical studies

In a recent paper by Arrigan *et al.* the electrochemical oxidation of **1** in acetonitrile was investigated.[58] They found that the reversible one-electron oxidation of the aryl ether occurred but that upon complexation with a sodium cation this electrochemical oxidation proved more difficult (the counter anion in these studies was perchlorate). The electrochemical oxidation of the anions in $CDCl_3$, as TBAX salts and as the complexes NaX-**1,** was examined by cyclic voltammetry. The results indicated that the iodide, thiocyanate and tetraphenylborate anions in the form of the TBAX salts had oxidation potentials at 0.86, 1.2 and 0.85 V respectively. In the corresponding calixarene NaX-**1** complexes, these oxidation potentials were recorded at 0.55 V ($X = I^-$), 0.95 V ($X = SCN^-$) and 0.80 ($X = BPh_4^-$) respectively. Thus complexation with the calixarene lowers the oxidation potential of the anion which is consistent with the anion being effectively shielded from the bound cation. The relative ease of electrochemical oxidation of the

anions was approximately in the same order as their photochemical oxidation (taking irradiation results after 15 minutes in Table 2, which is before equilibrium is reached).

Conclusion

This study involved the irradiation of a series of sodium salt complexes of **1** and found that the extent of decomplexation of the complexes varied as a function of the anion. The lower the oxidation potential of the anion the greater the extent of initial decomplexation, with iodide, thiocyanate and tetraphenyl borate complexes being easily decomplexed and the expected non-reaction of perchlorate. Addition of fresh solutions of anion (in the form of *t*-butyl ammonium iodide/thiocyanate etc.) allowed full recomplexation to occur, indicating that the integrity of both the cation and macrocycle were maintained during irradiation. However potentiometric studies of the inorganic species in solution indicated that there was not a linear correlation between photooxidation of the anion and decomplexation of the calixarene. Photolysis of the anions resulted in the production of other anionic species which could allow recomplexation to occur to some extent. The overall % decomplexation measured was found to be determined by the amount of NaCl-**1** and NaX-**1** (X = product anion e.g. I_3^-) present *in solution* at the end of the experiment. The enhanced stability of acetonitrile encapsulated complexes was only observed for tetraphenylborate and periodate complexes.

This work also identified the relationship between the photooxidation of the counter anion at the lower rim of the calixarene with the upper rim complexation of a neutral guest. It is clear that the presence of a complexed cation in the lower rim greatly enhances the upper rim encapsulation of the solvent, so much so that when the cationic guest is expelled from the lower rim the upper rim guest is subsequently expelled. This is consistent with the earlier work of Stibor who found that the complexation of acetonitrile by **1** was greatly enhanced by the presence of a sodium cation at the lower rim.[25] Thus the possibility for a novel control mechanism for the complexation of neutral guest at the upper rim of calixarenes, by choice of lower rim counter anion or level of irradiation, has been identified. Importantly, the photoreaction of the non-chromophoric TBA salts followed similar patterns to the calixarene complexes suggesting that controlled photodecomplexation of bound guests by other macrocyclic systems such as cryptands or resorcinarenes should be possible. The development of high level control of switching systems is

obviously desirable and this system offers potential as an analogue switching device for the control of complexation of neutral species. A number of factors are important to ensure that decomplexation occurs and occurs to a predetermined level including the irradiation time, the nature of the solvent, the nature of the counter anion and the nature of the calixarene itself. The dependence of the binding constants at the upper and lower rim as a function of the nature of the counter-anion is currently being investigated.

Experimental Section

Complexes of *p-tert*-Butylcalix[4]arene Tetraethyl Ester

This calixarene was synthesised and supplied as pure from Prof. M. A. McKervey, Queen's University Belfast and from Loctite (Irl) Ltd. All salts used in this study were supplied by Sigma-Aldrich and were dried overnight at 110^0C prior to use. The following solvents were used in this study: HPLC MeCN, HPLC MeOH (Riedel de Haan); and HPLC chloroform, HPLC dichloromethane, d_3-MeCN, *d*-chloroform, d_4-dichloromethane and d_4-MeOH (Aldrich). Anhydrous chloroform was supplied by Sigma-Aldrich. Hydrogen, air, nitrogen and helium and were supplied by Air Products.

The complexes were prepared by mixing equimolar amounts of ligand and salt (typically 0.5 mmol) in ~50 ml of MeCN, chloroform or MeOH overnight in the dark. The solvent was allowed to evaporate naturally and passing a stream of N_2 over the complex dried the isolated salt. Full complexation was verified from ^{1}H NMR and FTIR data. Micro-analytical data, recorded at the micro-analytical laboratory at the National University of Ireland, Dublin, showed that complexes that contained solvent within the upper cavity contained 1:1 mole ratios of solvent to complex in all cases.

Spectroscopic Techniques

Solutions of the analytes were typically 10^{-4} mol L^{-1}. UV-Vis spectra were recorded using a double beam Shimadzu 160A Spectrophotometer. Their spectra were measured using a 10 mm

path-length quartz cells. Infrared spectra were recorded using a *Nicolet* Impact 410 FTIR Spectrometer and the spectra processed on an attached PC using Omnic v.3.1a software. NMR spectra were recorded using a JEOL 300 MHz FT-NMR spectrometer. Typically 20 mg of analyte was dissolved in 0.5 ml of a deuterated solvent and placed in a precision pyrex NMR tube.

Irradiation Procedure

The photolysis lamp used in this study was a Pen-Ray 5.5 Watt low-pressure cold cathode mercury vapour lamp with a 150 V (60 Hz) power supply. An external transformer was added to enable direct use of the mains power supply (220 V, 50 Hz). Previous irradiation studies with this lamp showed that a UV filter needed to be used in order to avoid ligand decomposition.[18] This filter was simply a glass NMR tube into which the irradiation sample was placed. Typically 1ml of a 4.5 mmol solution of a complex in an appropriate solvent was placed into a Pyrex NMR tube. Another 1ml aliquot of the irradiation sample was placed in the dark during the irradiation time as a reference sample. Before irradiation the solution was degassed for ~10 minutes to remove any dissolved oxygen from the sample.

Potentiometric Titration

A 1 ml aliquot of a 4 mM irradiated solution, in chloroform or dichloromethane, was washed with 5 ml ultra-pure water in order to extract all water-soluble inorganic species from the organic solvent. The aqueous layers were collected and transferred to a 50 ml plastic beaker where 2 ml of 2 M HNO_3 was added. The volume in the beaker was made up to ~25 ml with doubly distilled water. The solution was then titrated with 0.01 M $AgNO_3$ using a *Metrohm* 702 SM Titrino autotitrator with a *Metrohm* 703 Ti stand. The end point was determined potentiometrically using a combined silver ring electrode.

GC-MS Analysis

A GC method was developed using a Shimadzu GC system incorporating a GC-14A gas chromatograph fitted with an FID detector and a Supelco SBP-5 fused silica capillary column

(15m x 0.20mm, 0.20μm film thickness). Spectra were obtained from a Shimadzu C-R5A integrator. Samples were introduced to the GC via a Hamilton 10μl syringe. A GC-MS method was developed using a Shimadzu GC system incorporating a GC-17A gas chromatograph, fitted with an FID detector and a Supelco SBP-5 fused silica capillary column (30m x 0.25mm, 0.25μm film thickness), and a QP-5000 mass spectrometer. Spectra were obtained using the 'Class-5000' software package, and samples were introduced to the system via a Shimadzu AOC-20i auto injector.

Electrochemical Analysis

A CHI630A Electrochemical Analyser was used with a Pt wire as the auxillary electrode, a Ag/Ag^+ non-aqueous reference electrode, and a glassy carbon working electrode. A 0.1M solution of *t*-butylammonium hexafluorophosphate in chloroform was used as the electrolyte. 0.1M solutions of *t*-butylammonium thiocyanate and iodide were prepared in chloroform, and the solution to be analysed contained 6 ml of the electrolyte + 1 ml of the individual anion solutions. A 1 mmol solution of *t*-butylammonium tetraphenylborate was prepared in the electrolyte and was analysed undiluted. All solutions were degassed using nitrogen for 10 minutes prior to analysis. The technique used was CV, sweeping in a positive direction, looking at oxidation between 0 and 1.8V, and the reverse as far as –0.6V. The scan rate was 0.1V/s, four segments were carried out (two full sweeps forward and reverse from –0.6 to 1.8V), and the sensitivity was 2×10^{-5}A/V.

Acknowledgments

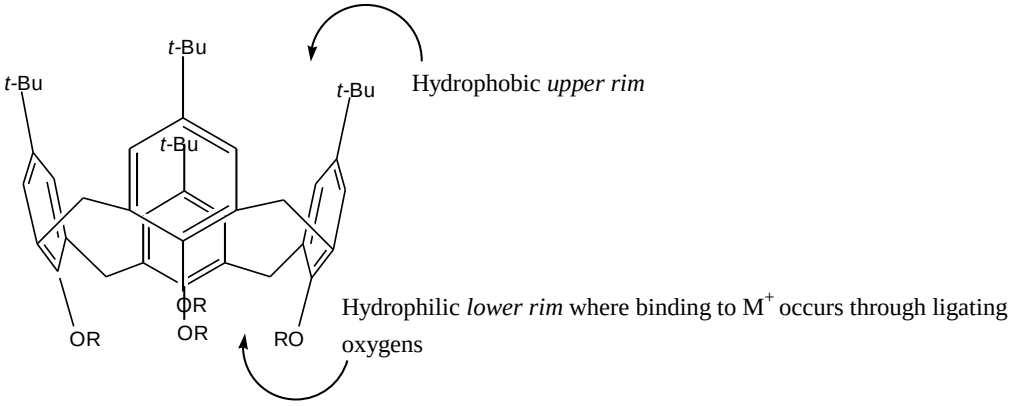
We would like to thank Prof. MA McKervey and Loctite Ireland Ltd. for calixarene samples used in this work, and BA Murray and J. McGinley for useful discussions. We would also like to thank EM Dempsey and T McCormac for use of the electrochemical analyser. DT would like to thank Enterprise Ireland for financial assistance. CMcK would like to thank the Postgraduate R&D Skills programme (Technological Sector Research, Strand I) and the Ph.D continuation fund of IT Tallaght for funding.

REFERENCES

1. F. Vögtle, D. Udelhofen, S. Abramson, B. Fuchs, *J. Photochem. And Photobiol. A.* **2000**, *131*, 41-48.
2. M. Sukwattanasinitt, R. Rojanathanes, T. Tuntulani, Y. Sritana-Anant, V. Ruangpornvisuti, *Tetrahedron Lett.* **2001**, *42*, 5291-5293.
3. T. Saji, I. Kinoshita, *J. Chem. Soc., Chem. Commun*. **1986**, 716.
4. A.M. Allegier, C.S. Slone, C.A. Mikin, L.M. Liable-Sands, G.P.A. Yap, A.L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 550.
5. W. Devonport, M.A. Blower, M.R. Bryce , L.M. Goldenberg, *J. Org. Chem.* **1997**, *2*, 885.
6. H. Graubaum, F. Tittelbach, G. Lutze, K. Gloe, M. Mackrodt M. *J. Prakt. Chem*. **1997**, *339*, 55.
7. S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa, O. Manabe, *J. Am. Chem. Soc*. **1980**, *102*, 5860-5865.
8. B. Pipoosananakaton, M. Sukwattanasinitt, N. Jaiboon, N. Chaichit, T. Tuntulani, *Bull. Korean Chem. Soc.* **2000**, *21***,** 867-874.
9. B. Pipoosananakaton, M. Sukwattanasinitt, N. Jaiboon, N. Chaichit, T. Tuntulani, *Tetrahedron Lett.* **2000**, *41*, 9095-9100.
10. V. Balzani, F. Scandola, In *Supramolecular Photochemistry*, T.J. Kemp (ed) Ellis Horwood series in physical chemistry, England, **1991**.
11. F. Arnaud-Neu, E. Collins, M. Deasy, G. Ferguson, S.J. Harris, B. Kaitner, A.J. Lough, M.A. McKervey, E. Marques, B.L. Ruhl, M.J. Schwing-Weill, E.M. Seward, *J. Am. Chem. Soc.* **1989**, *111*, 8681.
12. G. Barrett, B.S. Creaven, S. Harris, B. Lynch, M.A. McKervey, M. Ryan, *Anal. Proc*. **1993**, *30***,** 150.
13. B.S. Creaven, M. Deasy, J.F. Gallagher, J. McGinely, B. Murray, *Tetrahedron* **2001,** 8883-8887.
14. *Comprehensive Supramolecular Chemistry*, Vol 1, Gokel GW(ed), Pergamon Press, **1997**.
15. J.W. Steed, J. Atwood, *Supramolecular Chemistry*, Wiley & Sons, **2000**.
16. *Calixarenes, a Versatile Class of Macrocyclic Compounds*, J. Vincens, V. Bohmer (eds), Kluwer, Dordecht, **1991**.
17. G. Barrett, B.S. Creaven, B.Lynch, D.Corry, B. Johnston, M.A. McKervey, *J. Chem. Soc., Chem. Commun.* **1995**, 363.
18. M. Pitarch, A.Walker, J.F. Malone, M.A. McKervey, B.S. Creaven, D. Tobin, *Gazetta Chimica Italiana*, **1997,** *127*, 717.
19. A.F. Danil de Namor, N. Apaza de Sueros, M.A. McKervey, G. Barrett, F. Arnaud Neu, M.J. Schwing-Weill, *J. Chem. Soc., Chem. Commun*. **1991**, 1546.
20. A.F. Danil de Namor, M.A. Gil E, Llosa Tanco, D.A. Pancheo Tanaka, L.E. Pulcha Salazar, R.A. Schulz, J. Wang, *J. Phys. Chem.* **1995**, *99*, 16776.
21. M.A. McKervey, F. Arnaud Neu, M.J. Schwing-Weill, in *Comprehensive Supramolecular Chemistry*, Gokel GW(Ed) Pergamon Press, **1997**, Vol 1, p. 537.
22. Y. Israël, C. Detellier, *J. Phys. Chem. B* **1997**, *101*, 1897-1901.
23. R. Ungaro, A. Pochini In *Topics in Inclusion Phenomena. Calixarenes, A Versatile Class of Macrocyclic Compounds*, J. Vicens, V. Bohmer (eds) Kluwer Academy: Dordecrht, **1990.**

24. M.A. McKervey, M.J. Schwing-Weill, In *Topics in Inclusion Phenomena. Calixarenes, A Versatile Class of Macrocyclic Compounds*, J. Vicens, V. Bohmer (eds) Kluwer Academy: Dordecrht, **1990**.
25. S. Smirnov, V. Sidorov, E. Pinkhassik, J.. Havlicek, I. Stibor, *Supramol. Chem.* **1997**, 187-196.
26. C.D. Gutsche, *Aldrichimica Acta*, **1995**, 3.
27. C.D. Gutsche, B. Dhavan, K.H. No, R. Muthukrish, *J. Amer. Chem. Soc.* **1981**, 3782.
28. G.D. Andreeti, R. Ungaro, A. Pochinni, *J. Chem. Soc. Chem. Commun.* **1979**, 1005.
29. M. Coruzzi, G.D. Andreeti, V. Bocchi, A. Pochinni, R. Ungaro, *J. Chem. Soc.Perkin Trans.* **1982**, 1133.
30. M.A. McKervey, E. Seward, G. Ferguson, B.L.Ruhl, *J. Org. Chem.* **1986**, 3581.
31. In addition the high extinction coefficeint of some of these solvents, at the wavelengths of excitation, precluded their use.
32. A quantitative measure of the strength of interaction between a host and guest species is provided by the stability constant. However, the determination of association constants in media of low dielectric constant, particularly chloroform, is complicated by the phenomenon of ion-pairing in this solvent and measured constants do not refer to well-characterised thermodynamic processes
33. A. Arduini, W.M. McGregor, D. Paganuzzi, A. Pochini, A, Secchi, F. Ugozzoli, R. Ungarro, *J. Chem. Soc.Perkin Trans.* **1996,** 839-846.
34. M.E. Gottlieb, V. Kotlyar, A. Nudelman *J. Org. Chem.* **1997,** *62*, 7512-7515.
35. W. Xu, R.J. Puddephat, L. Manojlovic-Muir, K.W. Muir, C.S. Frampton, *J. Incl. Phenom. and Molec. Recogn.* **1994**, *19*, 277.
36. A. Arduini, G. Giorgi, A. Pochini, A. Secchi, F. Ugozzoli *Tetrahedron* **2001**, 2411-2417.
37. Although elemental analyses of the $NaIO_4$-**1** complexes were satisfactory, dissolution in $CDCl_3$ showed these compounds to be only about 95% complexed.
38. A. Arduini, E. Ghidini, A. Pochini, R. Ungaro, G.D. Andreeti, F. Ugozzoli, *J. Inclusion Phenom.* 1988, **6**, 119.
39. A. Gilbert and J. Baggott, *Essentials of Molecular Photochemistry*, Blackwell Scientific Publications, Oxford, 1991.
40. A. Gilbert In *Photochemistry in Organic Synthesis*, J.D. Coyle (ed) The Royal Society of Chemistry, Special Publication No 57, **1986**, 278.
41. The 254 nm line of the photolysis lamp is the more intense and experiments conducted without a glass filter resulted in the expected production of numerous organic decomposition products as a result of the photochemical reactivity of the aryl ether and ester moieties at this wavelength. Extensive photoreaction leading to decomposition of the calixarene did not occur.
42. F. Galindo, M.A. Miranda, R. Tormos *J. Photochem. and Photobiol. A*: **1998**, *117*, 17-19.
43. All of the salts studied were were soluble only in their complexed form in $CDCl_3$, but solutions of the salts in MeOH determined that they did have weak excitaion spectra above 280 nm.
44. A.F. Danil de Namor, R.M. Cleverly, M.L. Zapata-Ormachea *Chem. Rev*., **1998**, *98*, 2495-2525.
45. UV/Vis spectra of the unphotolysed NaI-**1** complexes were recorded and had two main absorption bands at 274 nm and 283 nm. In the irradiated complexes a new peak at 368 nm was observed which was concomitant with the destruction of iodide and was assigned as an I_3^- absorption band by comparison with an authentic sample. Quantification of tri-iodide proved difficult due to the dilution effect on the equilibrium position between poly-iodide and monomeric iodide species in solution. Dilution to record UV/Vis spectra was necessary in order to compare NMR, UV/is and potentiometric readings on the same sample.While halides can form polyatomic species the likelihood of this

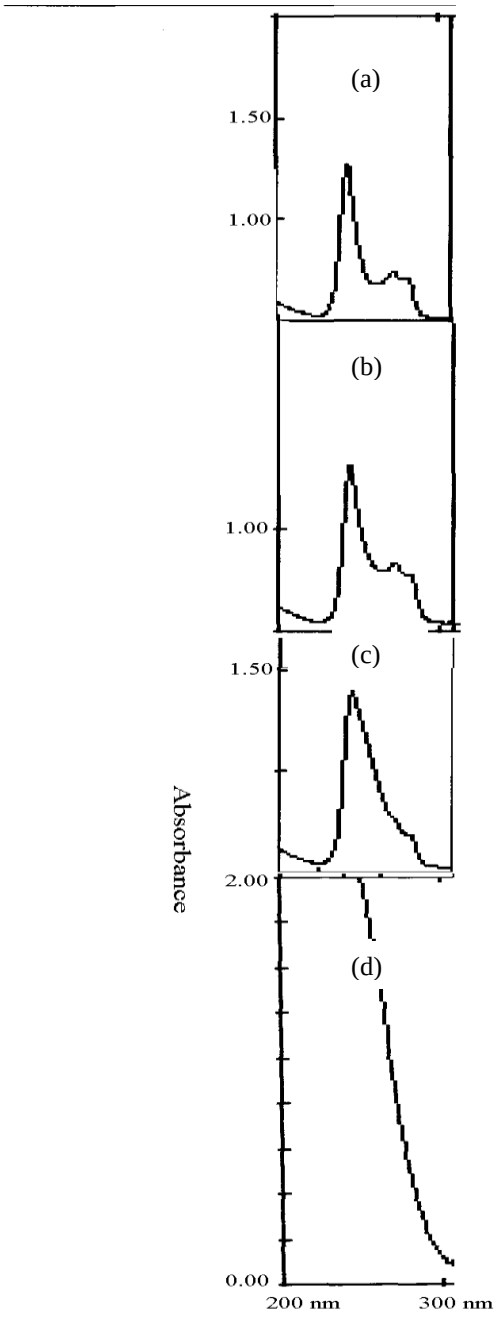
occurring depends on the size of the counter cation and higher species than I_3^- are unlikely to occur with sodium cations in aqueous solution. However dilution in non-aqueous solution does affect the equilibrium between iodide, iodine and triiodide.
46. Photochemical studies in chlorinated solvents are generally avoided because of the known generation of chlorine radicals in such solvents (albeit at different wavelengths to those used in this study). Extensive photo-irradiation of chloroform and dichloromethane did not result in the production of any detectable photoproducts under the conditions used in these studies.
47. J. Grimshaw, J.S. Ramsey, *J. Chem. Soc. Perkin Trans 2,* **1975**, 215.
48. T. Donohue *Lanthanide Actinide Res,* **1985**, *1,* 89.
49. T. Imamura, T. Jin, T. Suzuki, M. Fujimoto, *Chem. Lett.* **1985,** *6,* 847.
50. F. Pina, M, Maestri, *Inorg. Chem.* **1988**, *142,* 223.
51. J. Muchova, V. Holba *Collect. Czech. Chem. Commun.* **1984,** *49,* 398.
52. A. Vogler, H. Kunkely *Inorg. Chem.* **1982**, *21*, 1172.
53. A. Vogler, H. Kunkely, *Agnew. Chem.***1982**, *94,* 217.
54. S.A. Vinogradov, K.P. Balashev, G.A.Shagisultanova, *Koord. Chim.* **1984**, *10,* 399.
55. D.M. Dooley, B.M. Patterson, *Inorg. Chem.***1982**, *21*, 4330.
56. B. Kraut, L. Vincze, S. Papp, *Acta Chim. Hung.* **1986**, *122,* 203.
57. A.J. Fry *Synthetic Organic Electrochemistry 2nd Ed* Wiley-Interscience Publication, New York,**1989.**
58. A. Paillerer, D.W.M. Arrigan. *Electrochemistry Communications,* **2001**, *3,* 24-27.



R = $CH_2COOCH_2CH_3$

Figure 1: Structural formula of calixarene **1** indicating how it can bind guests.

Figure 2: UV/Vis absorbance spectra recorded in $CDCL_3$ of (a) uncomplexed calixarene (**1**), (b) NaSCN-**1**(A) (c) NaI-**1**(A) and (d) a pyrex NMR tube. Concentrations of complexes and calixarene approximately 1 x 10^{-5} M.



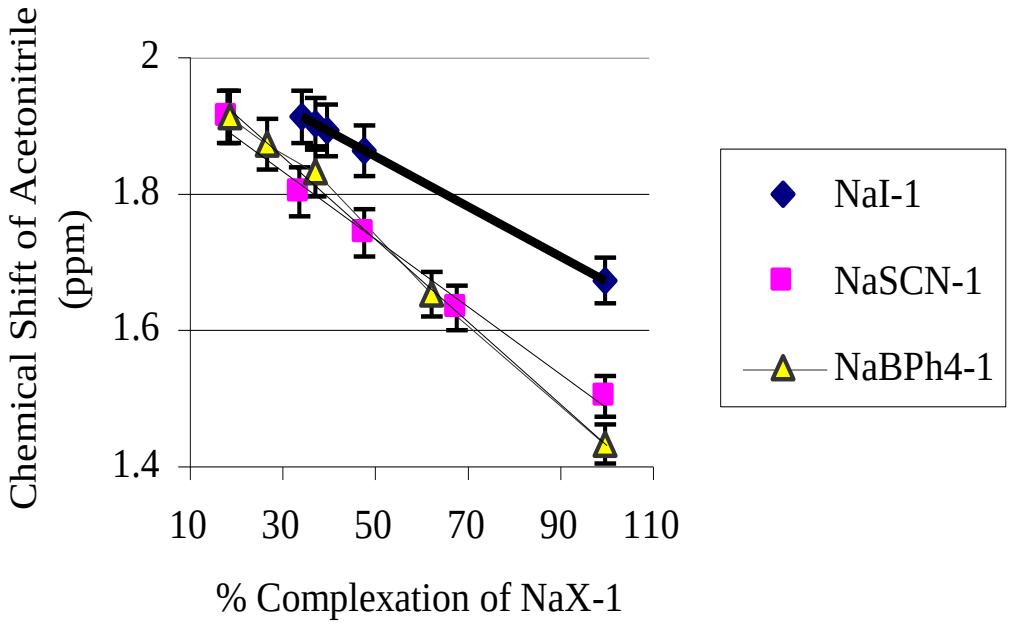


Figure 3: The relationship between the % complexation of NaX-**1** (X= SCN^-, BPh_4^-, I^-) and the chemical shift of upper-rim bound acetonitrile.

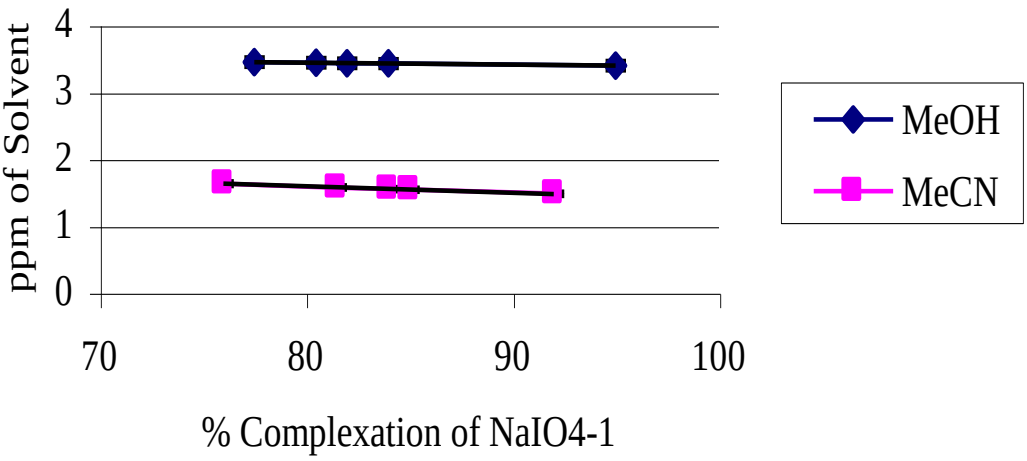
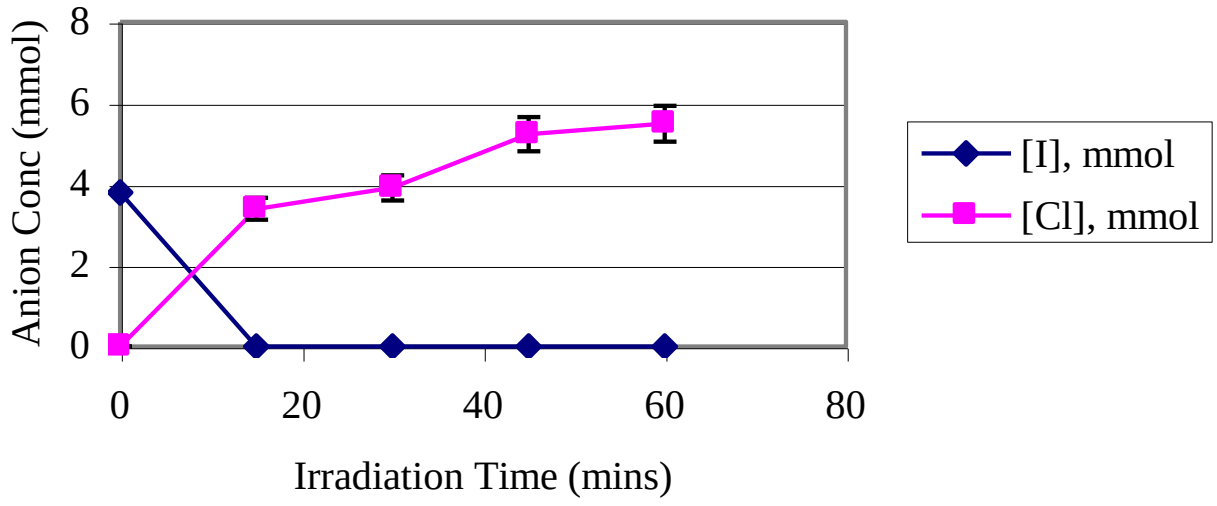
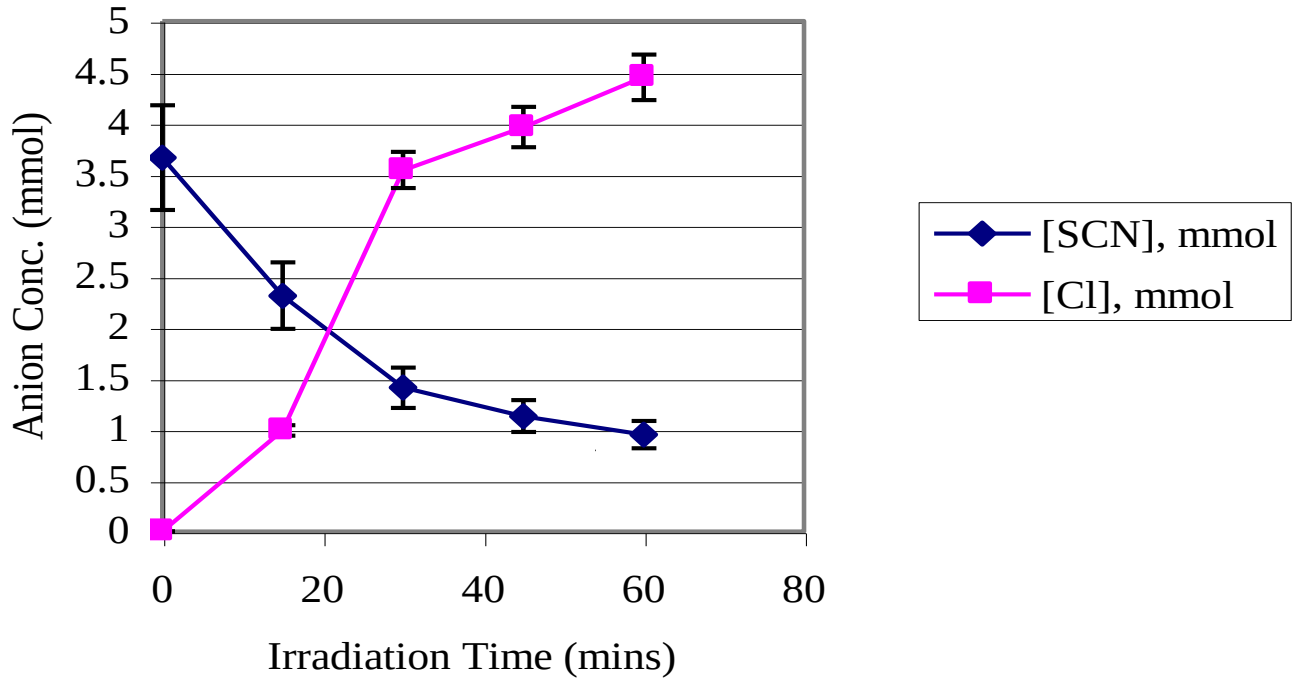


Figure 4: The relationship between the % complexation of $NaIO_4$-**1**(S) (S= MeOH , MeCN) and the chemical shift of S.

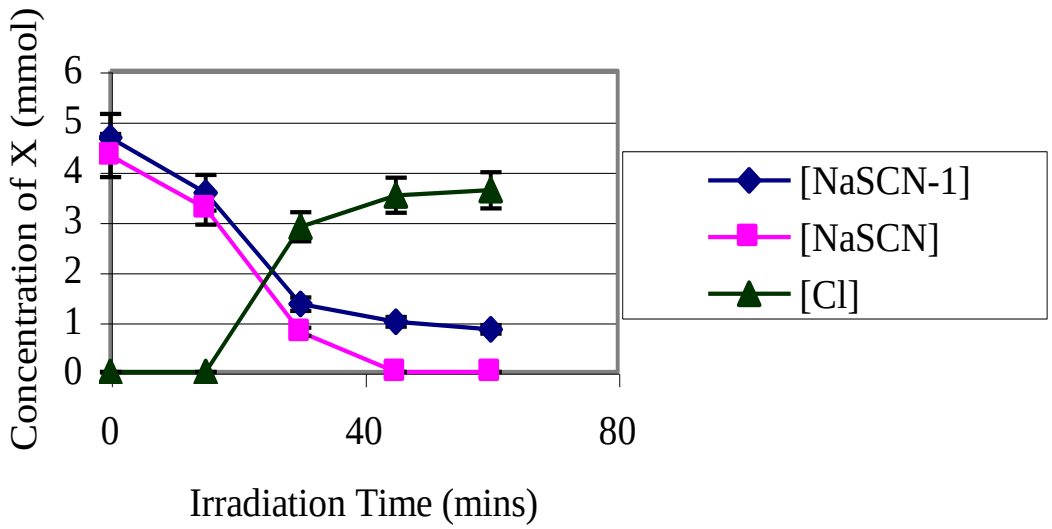


(a)

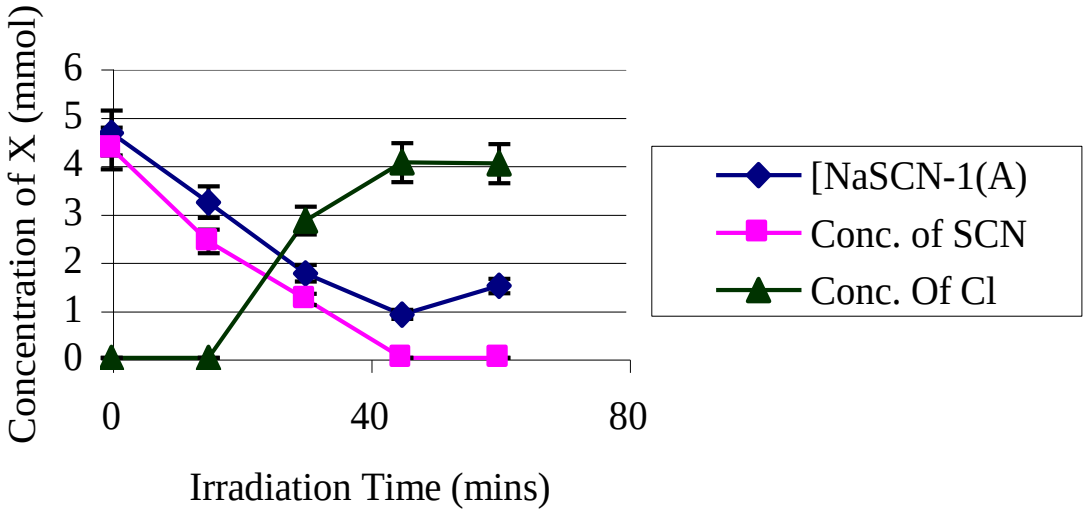


(b)

Figure 5: Plots of (a) concentrations (mmol) of iodide and chloride anions following photolysis of TBAI at 15 minute intervals (average of 3 experiments) (b) concentrations (mmol) of thiocyanate and chloride anion following photolysis of TBASCN at 15 minute intervals (average of 3 experiments).



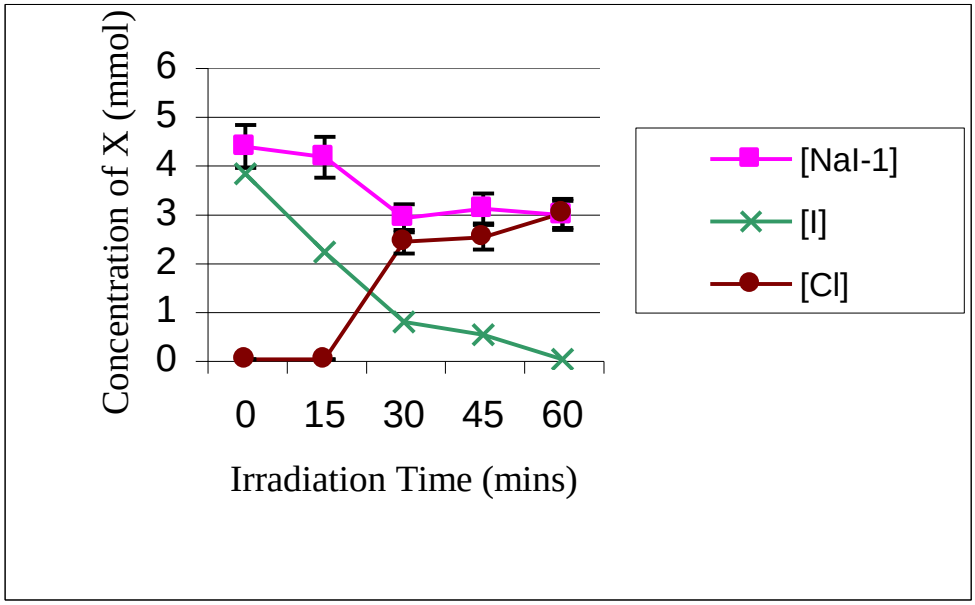
(a)



(b)

Figure 6: Relationship between the concentration of (a) NaSCN-**1** and (b) NaSCN-**1**(A) and chloride and thiocyanate concentrations at various irradiation times. Errors are estimated based on six replicate measurements.

(a)



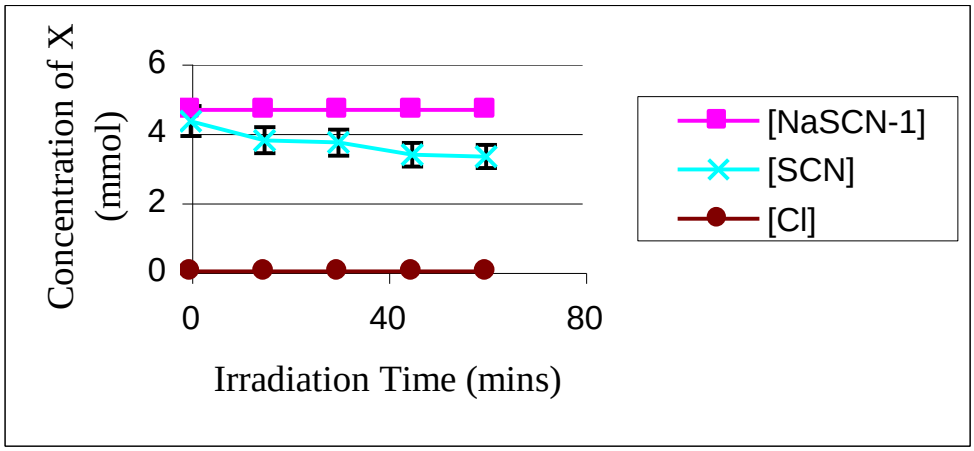


Figure 7: Variations in the concentration of NaX-**1** (X = SCN^-, I^-), and Cl^- upon photolysis of NaX-1 in CD_2Cl_2. (average of 6 replicate experiments)

Table 1: ^{1}H NMR chemical shift data for NaX complexes of **1** (X = I^-, SCN^-, BPh_4^-, ClO_4^-, IO_4^-) isolated from different solvents.(A) and (M) indicate encapsulated acetonitrile and ethanol respectively. All spectra were recorded in $CDCl_3$.

Functional Group	**^{1}H NMR Chemical Shifts for NaX-1 (ppm)**									
	Free Ligand	NaI-**1(A)**	NaI-**1**[(i)]	NaSCN-**1**(A)	NaSCN-**1**[(i)]	$NaBPh_4$-**1**(A)	$NaBPh_4$-**1**[(i)]	$NaClO_4$-**1**[(i)]	$NaIO_4$-**1**(A)	$NaIO_4$-**1**(M)
t-Butyl	1.07	1.17 (s)	1.14 (s)	1.15 (s)	1.14 (s)	1.16 (s)	1.14 (s)	1.14 (s)	1.15(s)	1.14 (s)
$OCH_2\mathbf{CH_3}$	1.27	1.41 (t)	1.42 (t)	1.42 (t)	1.42 (t)	1.38 (t)	1.35 (t)	1.43 (t)	1.41 (t)	1.41 (t)
Solvent [(ii)]		1.71(s)		1.50 (s)		1.43 (s)			1.47 (s)	3.39 (s)
$\underline{CH_2}$ Bridge										
$\mathbf{H_B}$	3.19	3.42 (d)	3.40 (d)	3.40 (d)	3.40 (d)	3.36 (d)	3.34 (d)	3.38 (d)	3.40 (d)	3.40 (d)
$\mathbf{H_A}$	4.85	4.25 (d)	4.24 (d)	4.25 (d)	4.25 (d)	4.19 (d)	4.18 (d)	4.26 (d)	4.26 (d)	4.26 (d)
$O\mathbf{CH_2}CH_3$	4.21	4.39 (q)	4.38 (q)	4.38 (q)	4.38 (q)	4.32 (q)	4.33 (q)	4.38 (q)	4.38 (q)	4.38 (q)
$O\mathbf{CH_2}C{=}O$	4.8	4.48 (s)	4.47 (s)	4.48 (s)	4.48 (s)	4.42 (s)	4.42 (s)	4.48 (s)	4.48 (s)	4.48 (s)
Aromatic-**H**	6.77	7.16 (s)	7.12 (s)	7.13 (s)	7.12 (s)	7.12 (s)	7.11 (s)	7.12 (s)	7.13 (s)	7.12 (s)

(i) Complexes isolated with no encapsulated solvent
(ii) Solvent is encapsulated in complex

Table 2: UV/Vis absorbance data for host compound, **1**, and its NaI, NaSCN and $NaIO_4$ complexes in $CDCl_3$.

Compound	**λ (nm)**	**ε ($cm^{-1}mol^{-1}$) x10^3**
1	275	3.49
	281	3.54
	308	0.06
NaI-**1**(A)	272	4.73
	282	2.90
	308	0.25
NaI-**1**	272	4.71
	282	3.15
	308	0.28
NaSCN-**1**(A)	273	3.51
	282	3.41
	308	0.49
NaSCN-**1**	273	3.55
	282	3.44
	308	0.50
$NaIO_4$-**1**(A)	274	3.00
	283	2.58
	308	0.12
$NaIO_4$-**1**(M)	273	2.94
	282	2.59
	308	0.11

Table 3: % Decomplexation of NaX-**1** complexes (typical concentration 4.5 mmol), before and after irradiation in $CDCl_3$ as determined by ^1H NMR spectroscopy (average of 6 replicate experiments). Complexes with encapsulated MeCN and MeOH are indicated by NaX-**1**(A) or NaX-1(M) respectively.

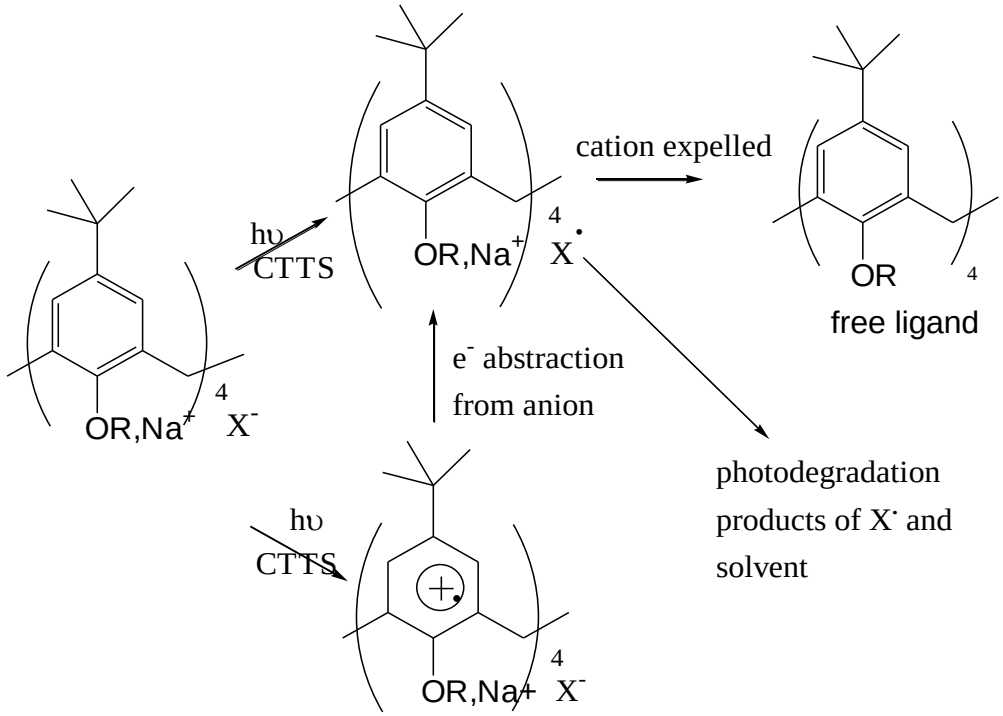
% Decomplexation of NaX-**1** complexes									
Irradiation Time (minutes)	NaI-**1**(A)	NaI-**1**	NaSCN-**1**(A)	NaSCN-**1**	$NaBPh_4$ -**1**(A)	$NaBPh_4$ -**1**	$NaClO_4$-**1**	$NaIO_4$-**1**(A)	$NaIO_4$-**1**(M)
0	0%	0%	0%	0%	0%	0%	0%	0%	0%
15	56±5%	55±6%	31±2%	25±1%	30±3%	44±9%	0%	7%	9%
30	64±2%	67±2%	62±4%	67±5%	65±5%	82±5%	0%	6%	16%
45	62±3%	65±2%	81±2%	81.5±3%	81±2%	87±1%	0%	10%	14%
60	53%	65%	68±3%	83.5±1%	72±3%	86±1%	0%	16%	14%

Table 4: Autotitration results for NaI-**1** complexes before irradiation, and after irradiation for 10[*] and 45[#] minutes. Results are average of six replicate experiments.

	Complexed Calixarene (%)	Complexed Calixarene (mM)	Uncomplexed Calixarene (mM)	Iodide Concentration (mM)	Chloride Concentration (mM)
NaI-**1**	100	8.76	0	8.56	*N/D*
	74[*]	6.47±0.65	2.29±0.8	5.5±1.5	0.92±1
	36[#]	3.05±0.14	5.70±.0.14	N/D	6.63±0.5
NaI-**1**(A)	100	8.76	0	8.64	*N/D*
	66[*]	5.74±0.2	3.02±0.2	3.16±0.6	N/D
	38[#]	3.38±0.2	5.38±0.21	N/D	6.53±0.3

N/D = not detectable

Scheme 1: Proposed decomplexation mechanism for the sodium salt complexes of **1**. Encapsulated solvent is omitted for clarity



R=$CH_2OCOCH_2CH_3$

$X=I^-$, SCN^-, BPh_4^-