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I. INTRODUCTION: Supramolecular chemistry and light

The complexity of physicochemical processes that can be resulted from the interaction of light with “matter” depend on the degree of organization of the receiving “matter”. The elementary form of organization is that of a small number of atoms in a molecule. The interaction of photons with molecules can trigger simple changes, such as the modification of the molecular structure (isomerization), which can be applied for various purposes. Solar energy for instance can be converted into, and also stored in the form of chemical energy by transforming a molecule in its higher energy isomer, or laser beams can write bits of information into materials composed of photochromic molecules.

A considerably higher level of organization is the “assembly of a discrete number of molecular components to yield supramolecular species.” Supramolecular organization can be attained by various types of intermolecular forces. By linking together molecular components by coordination or covalent bonds, coulombic interactions, hydrogen bonds, etc. it is possible to put together prefabricated molecular components that carry the desired light-related properties: absorption spectrum, excited state lifetime, luminescence spectrum, excited state redox properties, and so on. As a result of this, it is possible to design “structurally organized and functionally integrated systems” (photochemical molecular devices capable of collecting and using the energy and information input of photons to perform complex functions such as light harvesting, charge separation, conversion of light into electrical energy, data processing and storage.

Interrogation of a supramolecular species by photons can be used to design other types of functions (sensing systems, logic devices) and can also yield important (sometimes unique) pieces of information on the environment of the supramolecular species and the degree of reciprocal perturbation of the various components. This, in turn, may help to extend and refine current theories of chemical reactivity and spectroscopy, with a positive feedback on the design of more valuable supramolecular systems. In this work our goal has been to study some of these newly designed and
synthesized systems. With the application of several techniques of optical stationary and time-resolved spectroscopy we aimed to identify the qualities essential for the specific application of the molecule or supramolecular system as a photochemical device. Among these qualities special attention has been paid to molecular recognition, deactivation processes of electronically excited states and to isomerisation processes.

**I.1. Molecular and supramolecular devices**

The concept of molecular devices (MD) was first introduced by Jean Marie Lehn. He defined MDs as “structurally organized and functionally integrated chemical systems, which are based on specific components, arranged in a suitable manner and may be built into supramolecular devices”.

The specific function performed by the molecular device is the result of the integration of the elementary operations executed by the individual components. There are photonic, electronic or ionic devices depending on whether they operate with (accept or donate) photons electrons or ions. This defines fields of molecular and supramolecular photonics, electronics and ionics.

Two basic types of components may be distinguished:

1. *active components*, that perform a given operation (accept, donate, transfer) photons, electrons or ions.

2. *structural components*, that participate in the build up of the supramolecular architecture and in the positioning of the active components, in particular through recognition processes.

A basic feature of this type of molecular systems is that the components and the devices that they constitute “should perform their functions at the molecular and supramolecular levels as distinct from the bulk material”. Incorporation of molecular devices into supramolecular architectures yields functional supermolecules or assemblies (such as layers, films, membranes etc.)
According to Lehn’s original definition, molecular and supramolecular devices are formed from covalently and non-covalently linked components, respectively. Contrarily, based on Steed’s, Atwood’s and Balzani’s approach the latter category may also include covalently bound systems. According to their definition: “covalently built devices made up of distinct but interacting components, retaining at least in part their identity as if they were bound together in a non covalent fashion, could also belong to the supramolecular domain”.¹⁶ This means a significant extension of the basic definition of supramolecular species and their view is becoming more and more accepted especially in the field of supramolecular photochemistry. It is also applied for all supramolecular devices discussed throughout this thesis.

I.2. Supramolecular photochemistry — molecular and supramolecular photonic devices

The formation of supramolecular entities from photoactive components may be expected to perturb the ground-state and excited-state properties of the individual species, giving rise to novel properties that define a supramolecular photochemistry¹,⁶.

Of all the ways in which to construct a supramolecular device, the use of photochemically active components is, perhaps, the most versatile. Light-induced processes are of fundamental importance in biochemical devices such as plant photosynthetic membranes.

Light-absorbing components (chromophores) are readily available and lend themselves to extensive synthetic modification, and light is readily introduced to a system that is in a variety of physical states (e.g. solid, liquid or gas) or media (solutions in various solvents). Light may be used to induce events such as charge separation, to initiate catalysis, to interrogate a system in sensing applications, or to induce changes in the state of a bistable device (switching).

Incorporation of photochemically active components within a supramolecular complex may be expected to modulate the photochemical behaviour of the chromophore(s), leading to a number of interesting and potentially useful effects such as energy migration, photoinduced charge
separation, perturbations of optical transitions and polarisabilities, modification of ground- and excited-state redox potentials, photoregulation of binding properties, selective photochemical reactivity etc. Numerous types of devices may thus be imagined and created.

I.3 Fundamentals of photochemistry

The photophysical and photochemical features of supramolecular entities provide a vast area of investigation processes occurring at the level of both intramolecular and intermolecular organization. They may depend on recognition events and then occur only if the correct selective binding of the complementary active components takes place.

In principle, supramolecular photonic devices require a complex organization and adaptation of the components in space, energy, and time, leading to the generation of photosignals by energy transfer (ET) or electron transfer (eT), substrate binding and chemical reactions.

The fundamental processes needed for the execution of the specific light related functions are the following:

**Absorption:**
When a molecular chromophore is irradiated with electromagnetic radiation of a wavelength corresponding to the energy required to promote an electron to an accessible electronic excited state, energy is absorbed resulting in the promotion of an electron from a ground-state molecular orbital to an excited one with higher energy.

**Deactivation processes:**
Electronically excited states have only a short lifetime. In general, several processes are responsible for the energy dissipation from the excited state. One of these is known as primary charge separation. The energy of the excited state can either be dissipated as heat to the solvent (nonradiative decay), emitted radiatively (luminescence), or used to carry out a chemical reduction.
**Fluorescence:** luminescence involving direct radiative decay, in which the electron returns to the ground state from a singlet excited state. Fluorescent emissions are usually of lower energy than the absorbed energy because the electron is promoted into a vibrationally excited state from which it relaxes nonradiatively before fluorescing back to the electronic ground state. This is the reason why many fluorescent dyes are able to absorb high-energy UV light and fluoresce in the visible region.

If the electron undergoes a change of spin state (intersystem crossing), then it accesses the triplet manifold of excited states. The triplet excited state, once formed, is long-lived and may undergo vibrational relaxation to a lower energy level before relaxing slowly and emitting another kind of luminescence, termed **phosphorescence**, of a lower frequency to the absorbed light or dissipating energy via nonradiative process.

In the presence of an external electron acceptor (low-lying empty orbital on an adjacent molecule or component), the excited-state electron may reduce the acceptor chemically, resulting in spatial charge separation. Eventual recombination is accompanied by emission of light of a different frequency, or by emission of heat. Finally, the energy from the excited state may be transferred to an external acceptor without electron transfer. This is termed **energy transfer (ET)**. The resulting secondary excited state may then relax with emission of luminescence, again of a lower frequency to the original absorption. This process is the beginning of an energy transfer cascade as in photosynthesis.

The results of photoexcitation may be divided into three broad categories:\(^{16}\):

1. Re-emission of the absorbed energy as light (fluorescence or phosphorescence).

2. Chemical reaction of the excited state
   (secondary charge separation, isomerisation, dissociation).

3. Nonradiative vibrational relaxation of the excited molecule dissipating energy to the solvent.

Among the molecular and supramolecular devices described in this thesis all 3 operations will be exemplified. Within the context of supramolecular devices
discussed in the later sections, the re-emission of the radiation by luminescence is of key interest in some of the described calixarene based sensing and signalling molecules and supramolecular devices. Moreover, another key area of our investigations is the phenomenon of photoinduced electron transfer (see section I.5.).

I.4. Photosensitive molecular receptors

Substances that change color or change fluorescence in response to a change in their environment have been known and have been put to various human uses for thousands of years. For such ancient examples for their applications are the various indicator compounds used for measuring acidity and basicity. Receptor molecules bearing such or similar photosensitive indicator groups may display marked modifications in their photophysical properties on the binding of substrate species, leading to changes in their light absorption (e.g., colour generation) or emission features and allowing their detection by spectroscopic measurements \(^{17,18,19,20,21,22,23,24}\). They represent molecular devices for substrate-selective optical signal generation and for optical reading-out of recognition processes. Such photo-chemosensors make possible the development of sensitive analytical methods for the detection of specific substrates\(^{25}\). These chromoionophores (or luminoionophores) respond to the binding of metal ions \(^{17,18,19,20,21,22,23,24}\) or other small molecules and may be of much interest as analytical tools as well as for environmental applications and for the study of ionic changes in biological processes\(^{24}\). Receptor molecules introduced in section I.4.1. combine the strong and selective complexing ability of calixarenes with the intense absorption properties of the indophenol photosensitive group. Similar molecules, like azophenol \(^{26,27,28,29,30,31}\), spirobenzopyran \(^{32,33,34,35}\), anthracene \(^{20,36,37}\) or coumarin \(^{38,39,40}\) display marked changes in absorption and fluorescence on complexation of alkali-metal cations or protonation, thus acting as fluorescent signalling systems (that may involve photoinduced electron transfer quenching \(^{22,23,36,41}\), for instance in a very selective colorimetric assay of lithium in serum \(^{27,42,43}\). Photoresponsive substances derived from other types of receptors like spherands \(^{44}\) present related properties. Fluorescent sensors may also be derived from cyclodextrins \(^{45}\).

Photoresponsive receptor molecules present features that allow the development of molecular recognition dependent optrodes \(^{25,46,47}\), optical sensors for
the continuous monitoring of specific substrates in organisms, in the environment, etc. Among those we will investigate a group of chromogenic calixarenes and calixoresorcinarene capable of binding selectively to small neutral molecules or ions. In these supramolecular devices the signaling operation will be executed either by the receptor molecule (indophenol coupled calixarenes) or the change in the absorption or luminescence properties of the substrate molecule, bound to the sensor device (calixresorcinarene Nile-blue complex) will be detected.

I.4.1. Calixarene host molecules

Calixarenes are condensation products of para-substituted phenols and formaldehyde that mainly consist of 4, 6 or 8 phenolic units and, following cyclodextrins and crown ethers, represent the third form of supramolecules that can be used as enzyme mimics, phase transfer catalysts and host molecules for metal ions and neutral molecules.

I.4.1.1 Indophenol coupled chromogenic calixarene hosts – photoactive supramolecular devices for the detection of ions and aliphatic amines

In the research group of István Bitter various sets of chromogenic calixarene molecules have been synthesized and as part of a cooperative effort tested in our laboratory as potential supramolecular devices for selective recognition and optical signalling. In my present work two new chromogenic calix[4]arene derivatives \( \text{CXa,b} \) (Scheme 1) – prepared recently – and for comparison a calix[4]binaphto(crown) ether \( \text{CXc} \) have been studied to elucidate their recognition properties toward aliphatic amines and various alkali and alkali earth metal ions. The interaction between the chromogenic hosts and amine guests was associated and monitored with the coloration of the system due to the presence of indophenol indicator moiety inserted into the calixarene core.
Scheme 1. The studied chromogenic calyx[4]arene (CXa, CXb) and calix[4]binaphto(crown) ether (CXc) host molecules


The calixarene core in forming supramolecular complexes can play two different roles. In the majority of ionophores the macrocyclic skeleton is merely a lipophilic matrix of appropriate conformation holding the properly designed coordination sphere where the ionic guest can be bound through non-covalent interactions.\(^{55}\) (Some exceptions are known where cation-π interactions between the guest - a soft cation\(^{56}\) or an organic ammonium ion\(^ {57}\) – and the calixarene core take part in the binding process. The situation is quite different with organic guests, which can penetrate into the calixarene cavity, forming a great variety of inclusion complexes. Of these, the calixarene complexes with ‘fluorescent probes’ – aromatic hydrocarbons and fluorescent dyes – have received a special attention, the properties
of which can be very efficiently studied in dilute solutions by combining UV-Visible absorption and fluorescence spectroscopic methods.

The first papers in this field have been published by Shinkai and co-workers\textsuperscript{58, 59, 60, 61}, who demonstrated that such experiments provide invaluable information about the nature of the host-guest interaction and about the ring-size selectivity of the host in these systems. Following these works there has been a growing interest in this research area, as an important part of the investigation of various types of nanocavities. The fluorescent guests studied in supramolecular structures with calixarene (calix[4]arene, calix[6]arene, calix[8]arene and calix[4]resorcinarene) derivatives were 2-anilino-naphthalene\textsuperscript{58}, 8-anilino-1-naphthalenesulfonate anion\textsuperscript{59, 61}, pyrene\textsuperscript{60, 62}, pyrene-modified N-alkyl-pyridinium cations\textsuperscript{63, 64} 2-(2'-hydroxyphenyl)-4-methylloxazole\textsuperscript{65} and the cationic dyes Auramine O\textsuperscript{66}, Brilliant Cresyl Blue\textsuperscript{67} and Acridine Red\textsuperscript{68}.

A great number of dyes, including some of the dyes mentioned above, have a basic and at least one (singly) protonated form. As had been pointed out by Shinkai et al.\textsuperscript{69}, the interaction between these indicator dyes and calixarene based supramolecular receptors in protic solvents can be described by a complicated reaction scheme, in which the proton transfers from the solute to the free and complexed forms of the basic guest are taken into account. They applied the scheme for the analyses of systems formed by p-sulfonated calixarene hosts and indicator dye guests, the latters with a neutral and a cationic form (Phenol Blue, Anthrol Blue)\textsuperscript{69} or with a monocationic and a dicationic form (4[(4-dimethylamino)styryl]-1-methylpyridinium iodide)\textsuperscript{70}, in aqueous solutions.

Besides the proton transfer between such dye guests and the solvent molecules, an additional type of proton transfer may take place between the guest and the host, if the host comprises dissociable protons. In the present work we have studied the role of the latter process in a model system. We have chosen tetraundecyl-calix[4]resorcinarene (RA in Scheme 3) as a host with dissociable protons and Nile Blue, as a dye guest existing in a basic and in a protonated form (NB and NBH\textsuperscript{+} in Scheme 3).
Scheme 2. tetraundecyl-calix[4]resorcinarene

Scheme 3. Protonated and neutral isomer of Nile blue A
The conversion of NB to NBH$^+$ and vice versa in various types of solvents was the subject of a thorough spectroscopic study by Douhal.$^{71}$ The characteristics of the $S_0\rightarrow S_1$ transition and of the following deactivation of NBH$^+$ in polar solvents is known in detail from previous time-resolved spectroscopic measurements$^{72,73,74}$ and quantum chemical calculations.$^{75}$ It is also known that calixresorcinarene RA forms stable hydrogen-bonded complexes with strongly polar guests like sugars and these complexes are soluble in apolar solvents.$^{76}$ Nile Blue is a versatile oxazine dye with many applications in analytical chemistry, photoscience, materials science and molecular biology.

1.5. Photoinduced electron transfer devices

As already described in the previous sections, light absorption markedly affects the electronic properties of chromophores and thus they may induce intra- or intermolecular electron transfer processes in supramolecular assemblies. Light induced electron transfer is a process in which an electron is transferred from an electron donating species (D) to an electron accepting species (A). Prior to electron transfer one of the components is excited with light$^{77}$:

\[
D + A \xrightarrow{\text{hv, excitation}} D^* + A \\
D^* + A \xrightarrow{\text{electron transfer}} D^{••} + A^•
\]

By this simple sequence, energy of light is converted into electrochemical energy. Subsequent to the electron transfer dipolar species is created, consisting of the radical cation of the donor (D$^{••}$) and the radical anion of the acceptor (A$^{-}$). The photogeneration of charge-separated species by photoinduced electron transfer (PeT) is of interest for initiating several functionalities of supramolecular devices (e.g., natural and artificial photosynthesis) and for the transfer of photosignals (e.g., through a membrane). In the photosynthetic reaction center two consecutive steps
of electron transfer is followed and accomplished by a proton coupled electron transfer process by which energy of light is converted into an electrochemical proton gradient, by which the biological synthesis of energy rich molecules like ATP (adenosine triphosphate) is driven. Studying this process in well defined artificial systems may lead to further insight into the first events of the biological processes that are responsible for a major part of the energy on earth\textsuperscript{77}. Not only is all the energy in all "food and feed" on earth derived from the light induced conversion of carbon dioxide and water into carbohydrates, also all the energy in fossil fuels like oil, natural gas and coal was initially fixed by phototrophic organisms.

Thus numerous artificial systems of this type have been extensively studied in many laboratories from the photochemical point of view and as models of natural photo-synthetic centres \textsuperscript{78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91}, especially in order to achieve very fast charge separation \textsuperscript{92, 93, 94, 95} and slow recombination, for instance in multiporphyrin complexes \textsuperscript{95}. In this respect, organized supramolecular devices have been used to separate the D and A components and influence the rates of forward and reverse electron transfer processes so as to yield long lived charge-separated states \textsuperscript{91}. Our present work has been concerned with photoinduced charge separation in calixarene – fullerene assemblies, which is discussed in the following section.

I.5.1. Calixarene-C\textsubscript{60} assemblies

Fullerenes in general form inclusion complexes with aromatic macrocycles and indeed calixarenes such as p-t-butylcalix[6]arene and p-t-butylcalix[8]arene may be used in the large scale separation of C\textsubscript{60} and C\textsubscript{70} from the toluene solution of the complex soot mixture formed by carbon arc vaporization of graphite.\textsuperscript{96, 97} 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.\textsuperscript{98} Ikeda et al. demonstrated that calixarenes with preorganized cone conformation and a proper inclination of the benzene rings can interact with C\textsubscript{60}, even without a deep inclusion of the fullerene host in the calixarene cavity.\textsuperscript{99} The thermodynamics of the complex formation between fullerene and various calixarene
derivatives indicate that both solvophobic effect and \( \pi-\pi \) interactions are major driving forces for the association process. 100

Despite the fundamental scientific importance and potential applications of fullerene-calixarene supramolecular devices, very few information is available on the interaction between their constituents in the electronic excited state. Islam et al. have studied the excited state properties of \( C_{60} \) incorporated into a cationic homooxacalix[3]arene in aqueous solution. 101 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. 102 The encapsulation of \( C_{60} \) in the cavity of \( p\text{-}\text{tert}\text{-}\text{butyl-calix[8]arene} \) 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.

Our general aim has been to elucidate how calixarenes influence the kinetics of the photoinduced processes of \( C_{60} \). 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. 103 104 105 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 \( C_{60} \).

**I.6. Nonlinear optical materials and supramolecular devices**

Molecules exhibiting nonlinear optical (NLO) behavior are known for a variety of applications, including frequency doubling of laser light, electrooptical switching devices and optical communication. Organic and inorganic substances presenting a large electronic polarizability are likely to display marked optical nonlinearities that depend primarily on molecular features, but novel effects should arise on going to the supramolecular level. 120, 121, 122

Nonlinear optical (NLO) properties are considered to result from both the in-
trinsec characteristics of the molecules and from their arrangement in a material (solid, powder, monolayer or multilayer film). An intermediate stage should also be taken into account, that of the supermolecules, where the association of two or more components may yield more or less pronounced NLO effects. Thus, three levels of non-linear optical properties may be distinguished corresponding to the molecule, the supermolecule and the material. The molecular level involves intramolecular effects and structures, whereas at the supramolecular level intermolecular interactions and architectures appear together with collective effects in the material. Incorporation into supramolecular arrangements may perturb the electronic properties of individual molecules and impose a specific orientation, namely by recognition induced self-organization.

The design of molecules, supermolecules and materials presenting NLO activity involves molecular and supramolecular engineering. At the molecular level, a high polarizability, leading to large quadratic and cubic hyperpolarizability coefficients, is sought. At the supramolecular level, it is necessary to achieve a high degree of organization, such as found in molecular layers, films, liquid crystals, the solid state, which may be generated by molecular recognition and inclusion complex formation. Both features are required for materials to display pronounced second order NLO effects; the structure must also be non-centrosymmetric, due either to the molecular components themselves or to their arrangement in the condensed phase. Besides, centrosymmetric species present third order but no second order NLO properties. In addition, bulk characteristics such as stability, preparation, processing and mechanical features will determine the practical usefulness of a given material.

Of special interest are push–pull aromatic compounds bearing a donor group on one end and an acceptor on the other (see section I.6.1.). Push–pull nitropirimidine N-oxide derivatives are highly polarizable. They display intramolecular charge transfer and marked second-harmonic generation. Molecular recognition-dependent optical changes produced by indicator ligands could lead to selective control of non-linear optical properties. Molecular electron donor-acceptor complexes may present NLO effects since they possess polarized ground states and undergo intermolecular charge transfer on excitation. It is possible to finely tune their polarization, polarizability, extent of charge transfer, absorption bands, etc., by many variations in basic structural types as well as in substituents. It is clear that combining the
1.6.1. Nitropyridine N-oxides - building blocks of supramolecular optically nonlinear materials

The nonlinear optical properties of nitropyridine N-oxide molecular crystals have been extensively studied since the early 80-s. It has been found that in these materials the observed large nonlinearities are directly related to the asymmetric π electron system, and they can be assisted by intramolecular charge transfer (ICT) processes, leading to further - two or three orders of magnitude - amplification of this feature, compared to aliphatic molecules of the same size. For building such molecular crystals, suitable for nonlinear optical devices, an essential characteristic is the high first order molecular hyperpolarizability. When optimizing this feature, primarily the push-pull property of the N-oxide and the effect of the functional groups on the charge transfer process are to be considered. The additional substitution of the pyridine ring may also result in the cancelling of the molecules centrosymmetry which would permit any nonlinear optical behaviour. Uncovering the intramolecular dynamic processes that may interfere destructively with the basic charge transfer mechanism from the N-oxide group to the nitro group would be also desirable.

Similar nitramino substituted pyridine N-oxides have been also prepared and their crystal structure have been determined. The unsubstituted molecule has been also applied for probing the hydrogen bond donor ability of solvents.

In this work we report on the intramolecular photoinduced processes and their influences on the electronic and optical properties of a newly synthesised nitropyridine N-oxide derivative: 2-butylamino-6-methyl-4-nitropyridine N-oxide (NPO) (Scheme 4). Our proposed model is based on an intramolecular proton transfer, followed by weak fluorescence and several nonradiative deactivation processes.
II. Objectives

The study and application of supramolecular devices form a vast and emerging field of chemical research. The main objective of this thesis work has been the investigation of a series of newly designed and synthesized systems bearing photochemical functions. With the application of several technique of optical stationary and time resolved spectroscopy we aimed to identify the properties
essential for the specific application of the molecule or supramolecular system as photochemical devices. Among those characteristics, special attention has been paid to molecular recognition, deactivation processes of electronically excited states and to isomerisation processes.

One of the major parts of our work has focused on the study of calixarene based molecular and supramolecular systems. The complex forming properties of three new calix[4]arene derivatives of cone conformation, supplied with indophenol indicator groups have been studied by UV/Vis spectroscopy in different solvents in the presence of alkali/alkali earth metal ions and aliphatic amines. In these compounds the dicarboxamide bridges with one or two adjacent chromogenic indophenol units form the binding site for cations and significant changes of their UV/Vis spectra are expected upon complexation. We studied the basic characteristics of complex formation in order to investigate the possibility of their applications as photoactive supramolecular sensor devices.

Another part of our work has focused on the interactions between a calixarene host comprising dissociable protons, and an organic dye guest existing in a neutral base and in a protonated form. These interactions have been studied on model systems obtained by dissolving Nile Blue base and tetraundecyl-calix[4]resorcinarene in two apolar solvents, dichloromethane and toluene. Steady state absorption, fluorescence spectroscopy and fluorescence lifetime measurements were applied as experimental methods. A common field of the applications of this dye in more complex apolar environments. Nile Blue salts (and in particular, the salts of its lipophilised derivatives) are employed as indicator dyes in optical sensors with hydrophobic polymer matrices; or when they are applied in photodynamic therapy studies, as special photosensitizers which localize in the lysosome of tumor cells.

We have studied the light related interactions of \( p-t \)-butyl-calix[n]arenes with \( C_{60} \). 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. The main goal of this part of our work has been to elucidate, how calixarenes influence the kinetics of the photoinduced processes of \( C_{60} \).

Besides our studies with calixarene supramolecular systems, we performed ultrafast time resolved experiments on 2-butylamino-6-methyl-4-nitropyridine N-
oxide. Our aim has been to study the intramolecular photoinduced processes and their influence on the electronic and optical properties of this newly synthesized molecule with potential applications in ONL molecular devices. As it serves as an excellent model compound for studying the effects of the interaction between an N-oxide group and an amino substituent in the ortho position, we aimed to study the suspected tautomerization process resulting from a proton transfer between these groups in the ground and/or excited electronic states.

* 

The experimental work carried out in the scope of this thesis have been conducted at three laboratories, as part of a broader cooperative effort of the spectroscopy research group of the Department of Physical Chemistry at the Budapest University of Technology and Economics for the development of new photoactive molecular and supramolecular devices. The major part of the work has been accomplished at the Photochemistry laboratory of the Chemical Research Center of the Hungarian Academy Sciences and at the Department of Physical chemistry of the Budapest University of Technology and Economics. In addition a part of our dynamic studies has been completed at the van’t Hoff Institute of Molecular Sciences at the University of Amsterdam.

* 

III. Experimental

III.1. Materials and sample preparation

III.1.1. Calixarene host molecules

The investigated calixarene host molecules are partly of commercial origin (p-t-butyl-calix[n]arenes) or synthesized by István Bitter and coworkers at the Budapest University of Technology and Economics.

*Calix[4]arenes*

The preparation of the calix[4]arenes was performed by the oxidative treatment of the respective bridged derivatives\textsuperscript{130} with 4-amino-3-cresol according to
literature procedures. For the spectroscopic experiment $5 \times 10^{-5}$ mol dm$^{-3}$ solutions of ligands were prepared with different solvents. An aliquot (50 µl) of amine (about $5 \times 10^{3}$-fold excess) was added into 3 mL solutions of the ligand.

**Tetraundecyl-calix[4]resorcinarene**

Tetraundecyl-calix[4]resorcinarene RA (Scheme 3) was prepared by István Bitter and coworkers through the cyclooligomerisation of resorcinol and dodecanal as described in the literature.

**p-t-butyl-calix[n]arenes**

$p$-tert.-butyl-calix[n]arenes (BCXn) were purchased from FLUKA (>99 %) and used without further purification.

**III.1.2. Guest molecules**

**Nile blue**

Nile Blue A perchlorate was purchased from Fluka and used as received. Its basic form, NB, was prepared by precipitating it from the aqueous solution of NBH$^+$-perchlorate with NaOH, extracting with CH$_2$Cl$_2$ and evaporating the solvent.

**Aliphatic amines**

All aliphatic amines, used as guest molecules have been purchased from Sigma Aldrich and used as received. The concentration of ethylamine in the stock solution was determined by HPLC technique, adopting the method of Forlay-Frick et al., developed originally for the determination of some amino acid derivatives (such as selenomethionin) and of some antibiotics. The HPLC measurements were carried out on a Millipore Waters 3000 equipment connected with a Supelco LC-18-08 column (with the length of 25 cm and the diameter of 5 mm) and a Millipore Waters 470 scanning fluorescent detector. The eluent contained 90% (v/v) acetonitrile and 10% (v/v) water, and 2% (v/v) of phosphoric acid was added to acidify the solvent mixture. The system was calibrated with a series of propyl-amine ethanol
stock solutions of known concentration, assuming that the sensitivities of the system for ethylamine and propyl-amine are identical.

**Alkali and alkali earth metal ions**

Alkali and alkali earth metal ions, as guest molecules were used in the form of their bromide salts (≥98% purity), purchased from Fluka and applied without further purification.

**Buckminsterfullerene (C₆₀)**

C₆₀ (99.9%), was purchased from SES Research Co. and used without further purification. Our samples containing ca. 10⁻⁴ M C₆₀ were purged with nitrogen.

**III.1.3. Solvents and additives**

All organic solvents prior to use (HPLC grade, Aldrich) were dried over molecular sieve 4A (Aldrich). 2,4,6-Trimethylpyridine (TMP) and pyridine (Py) (Aldrich) were distilled before use. Samples containing ca. 10⁻⁴ M C₆₀ were purged with nitrogen.

**III.1.4. NPO**

NPO (see scheme 4, section 1.6.1. was prepared by Anna Szemik-Hojniak at the Faculty of Chemistry of the University of Wroclaw in Poland. It was obtained by the mixing of equimolar amounts (0.01 M) of 2-chloro-4-nitro-6-methyl pyridine N-oxide and butylamine in 40 cm³ volume of ethanol. The mixture was then refluxed for 4 hours, ethanol was evaporated, water added and precipitate was filtered off. Recrystalization from petroleum ether gave a 76% of the product (2-butylamino-6-methyl-4 nitropyridine N-oxide) (mp. 98°C). Its purity was checked by GC / MS method. Elemental analysis shows its composition as follows: Calculated (%): C-54.77; H-6.90; N-16.43. Found (%): C-55.01; H-6.88; N-16.57.
III.2. Experimental methods

III.2.1. Steady state UV/Vis and fluorescence spectroscopy

In Budapest, UV/Vis absorption spectra were recorded using a GBC Cintra 10E double beam, and a Perkin–Elmer Lambda 2S single beam diode array spectrophotometer. The fluorescence emission spectra were taken by using a Perkin-Elmer LB50 spectrofluorimeter. For the measurements 1 cm quartz cell (Hellma) was used.

In Amsterdam, electronic absorption spectra were also recorded in a quartz cuvette (1 cm, Hellma), using a Hewlett-Packard 8453 diode array single-beam spectrophotometer (190 - 1100 nm range). Continuous-wave emission spectra were obtained on a Spex Fluorolog 1681 spectrometer, equipped with a Xe arc light source, a Hamamatsu R928 photomultiplier tube detector and double excitation and emission monochromators. Emission spectra were corrected for source intensity and detector response by standard correction curves.

III.2.2. Time resolved techniques

III.2.2.1. Time correlated single photon counting – fluorescence lifetime measurement

Single Photon Counting (SPC) is an analytical (statistical) technique based upon the ability to detect and count individual quanta, or photons, of light to measure the luminescence decay of a sample. The time profile of the decay is determined by measuring the time difference between the excitation of the sample and the detection of the emitted photon (from the sample) by the photomultiplier.

With our calixarene based systems (with relatively high fluorescence yield) the measurements have been carried out in Budapest at the photochemistry laboratory of the Chemical Research Center of the Hungarian Academy of Sciences (CRC) on a home built setup using diode laser excitation light source. The 404 and 632 nm exciting pulses were provided by two Picoquant diode lasers, with pulse duration of...
60 and 90 ps, respectively. The emission was collected at a 90 degree angle through an Oriel 0.25 m monochromator, located in front of a Hamamatsu H5783 photosensor module. The output signal was connected to a Picoquant Timeharp 100 computer board module (channel width 36 ps). Data were analyzed by a non-linear least-squares deconvolution method.

Figure 1. Operation of the diode laser excited, single photon counting instrument. (PQTH: Picoquant Timeharp electronics, ……: electronic signal, _______: optical signal)

Following a large number of flashes, the time dependence of the fluorescence intensity $I(t)$ is loaded and stored in the memory of the analyser computer board module. Since the values of the half widths of the excitation flashes and the fluorescent lifetime are the same order of magnitude, the observed time dependence can be obtained from the convolution of the instrument’s $H(t)$ “response” function, (characteristic to the time resolution) and the samples real decay function $G(t)$:

$$I(t) = \int_0^t G(t-t')H(t')dt'$$

(1)

$H(t)$ was measured by the use of a light scattering dummy sample: a quartz cuvette filled with distilled water. By knowing $H(t)$ and $I(t)$, $G(t)$ can be calculated through an iterative deconvolution.\textsuperscript{134}

For samples with relatively low fluorescence yield such as our nitropyridine N-oxide molecules the above technique is not applicable and higher laser intensity of excitation is needed. These measurements have been carried out on a setup\textsuperscript{135}
operated by the van't Hoff Institute of Molecular Sciences in the University of Amsterdam. The complete SPC setup (Figure 2) has been fully described in a paper. 

Figure 2. Schematic representation of the time-correlated single photon counting set-up: 1. mode locker, 2. Ar$^+$-ion laser, 3. dye laser, 4. cavity dumper, 5.
A mode-locked Ar-ion laser (Coherent 486 AS Mode Locker, Coherent Innova 200 laser) was used as the excitation source (laser pulses of ca. 80 ps at 514.5 nm with a repetition rate of 76 MHz) to pump a DCM dye laser (Coherent model 700). A cavity dumper (Coherent 7200) was mounted on the synchronously pumped dye laser to decrease the repetition rate from 76 MHz to 3.8 MHz and to increase the energy per pulse (25 nJ/pulse, 1 ps duration). The laser light was frequency doubled through a 6 mm thick BBO crystal resulting in an excitation wavelength of 305 to 350 nm. A dichroic mirror separates the frequency-doubled laser beam (excitation beam) from the fundamental. The fundamental beam was split into two beams: one beam was led to a photodiode producing the "stop" signal, whereas the other was led to an autocorrelator for the measurement of the pulse shape. A microchannel plate photomultiplier (Hamamatsu R3809) was used as detector. The instrument response (17 ps FWHM) was recorded using the Raman scattering of a doubly deionised water sample. Time windows of 5 - 50 ns could be used (1.25 - 12.5 ps/channel). The recorded traces were deconvoluted with the system response and fitted to an exponential function using the Fluofit (PicoQuant) program.

III.2.2.2. Transient absorption techniques

III.2.2.2.1. Flash photolysis

Flash photolysis experiments were performed at CRC in Budapest on various calixarene-fullerene assemblies in order to gain information on the kinetics of the energy discipation processes during the quenching of the triplet excited state. A home built setup was used (Figure 3) with a Nd-YAG laser (Continuum Surelight) excitation light source, giving 5 ns pulses at 532 nm. Absorption was detected perpendicular to the laser light using a 450W xenon lamp, an Oriel 0.25m 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 ~10 mJ in order to minimise the contribution of the triplet-triplet annihilation.

![Diagram of flash photolysis setup]

Figure 3. Flash photolysis setup. •••••• : electronic signal, ——— — : optical signal

### III.2.2.2. Ultrafast transient absorption measurements

Ultrafast transient absorption measurements were carried out on the set-up installed at the University of Amsterdam (Figure 4).

#### III.2.2.2.1. (Sub)Picosecond time-resolved transient absorption spectroscopy: Experimental setup
Figure 4. Schematic representation of the sub-picosecond transient absorption setup: 1. Hurricane, 2. OPA-800, 3. delay line, 4. white light generator, 5. Berek polarizer, 6. chopper, 7. sample, 8. CCD camera.\textsuperscript{135}

The laser system, employed in the ultrafast transient absorption experiments are based on a Spectra-Physics Hurricane Titanium Sapphire regenerative amplifier system\textsuperscript{137}. The optical bench assembly of the Hurricane included a seeding laser (Mai Tai), a pulse stretcher, a Ti:Sapphire regenerative amplifier, a Q-switched pumped laser (Evolution) and a pulse compressor. The output of the laser is typically 1 mJ/pulse (130 fs FWHM) at a repetition rate of 1 kHz. Two different pump-probe setups were used (see figure 4): (i) a full spectrum setup based on an optical parametric amplifier (Spectra-Physics OPA 800) as pump, with the fundamental light (2 µJ/pulse) being used for white light generation, which was detected with a CCD spectrograph; (ii) single-wavelength kinetics measurements based on two OPAs, one of them being used as pump and the other as probe, and an amplified Si-photodiode for detection. For both setups the OPA (1) was used to generate excitation pulses at 400 nm (fourth harmonic signal of the OPA or idler). The output power was typically 4 µJ/pulse.
The pump light was passed over a delay line (Physik Instrumente, M-531DD) that provides an experimental time window of 1.8 ns with a maximal resolution of 0.6 fs/step. The white light generation was accomplished by focusing the fundamental (800 nm) into a H₂O flow-through cell (10 mm, Hellma). For the single-wavelength measurements, the polarization of probe light was controlled by a Berek Polarization Compensator (New Focus). The energy of the probe pulses was ca. 5 x 10⁻³ µJ / pulse at the sample. The angle between the pump and probe beams was typically 5-7°. The cylindrical cell (d = 1.8 cm; 1 mm, Hellma), with a solution of the sample, was placed in a homemade rotating ball bearing (1000 rpm), avoiding local heating by the laser beams.

For the white light / CCD setup, the probe beam was coupled into a 400 µm optical fiber after passing the sample, and detected by a CCD spectrometer (Ocean Optics, PC2000). Typically, 2000 excitation pulses were averaged to obtain the transient absorption at a particular time. A chirp of < 1 ps was observed between 425 and 700 nm. For the single wavelength kinetic measurement, an amplified Si photodiode (Newport, 818 UV / 4832-C) was used. The output of the Si photodiode was connected to an AD-converter (National Instruments, PCI 4451, 205 kS/s), enabling the intensity measurement of each separate pulse. Typically, 500 excitation pulses were averaged to obtain the transient absorption at a particular time. The CCD spectrograph, chopper, Si-photodiodes, AD-converter and delay line were controlled by a computer. In-house developed LabVIEW (National Instruments) software routines were used for spectral acquisition, and single line measurements over a series of different delay settings. The total instrument rise time of the ultrafast spectrometer was ca. 300 fs. The solutions of the samples were prepared to have an optical density of ca. 0.8 at the excitation wavelength in a 1 mm cell. The absorbance spectra of the solution were measured before and after the experiments. No photodecomposition was observed.

III.2.5. Cyclic voltammetry

For the electron transfer studies in this thesis, it was necessary to determine the redox properties of the C₆₀-calixarene complexes in order to determine the driving forces involved in the processes. For this reason cyclic voltametric studies were
performed. The measurements have been carried out on an OMNI-101 Cypress Systems microprocessor controlled potentiostat instrument. Graphite working and platinum auxiliary electrodes were immersed into the sample and a silver wire immersed into KCl/AgCl solution served as reference. 0.1 M tetrabutyl-ammonium-hexafluorophosphate conducting salt was added to the benzonitrile sample solutions which were previously purged with nitrogen. All measurements were performed at room temperature and for calibration purposes we used ferrocene (with well defined redox potential 138 139

IV. Calculations

IV.1. Calculation of ground state equilibrium constants from absorption spectra

The complex formation constants for the studied calixarene-amine systems ($K_c$), were determined by the method of Benesi and Hildebrand 140. An example for the detailed procedure of the calculation method is described in section V.1.1. Moreover, in more complex cases, such as our NB-RA systems iterative procedures have been applied (see section V.1.3.)

IV.2. Ground state stoichiometry from absorption spectra

The stoichiometry of the complexes were determined by the continuous variation (Job’s) method141. The principle idea of this method is recording the absorbance of a series of solutions in which the mole fraction $X$ of the ligand (L) is varied from 1 to 0 as shown in Fig 5, while the total number of moles of L and the guest molecule M is held constant. The dependence of the solution absorbance on the molar ratio of M and L analytical concentrations is used to determine the molar ratio l/m for the reaction mM + Ll = MmLl.

The mole fraction yielding the maximum absorbance $X_m$ is related to the stoichiometric ratio in the complex by:

$$ l/m = X_m / (1-X_m). \hspace{1cm} (1) $$
Figure 5. The continuous variation (Job’s) method for the determination of the stoichiometry of complex formation. In curve 1 the maximum absorbance is observed when the mole fraction of ligand equals the mole fraction of ligand in the complex. If dissociation of the complex is significant, the behaviour shown in curve 2 is observed and extrapolation of the linear portion can be used to locate the position of the maximum more accurately. It is assumed that only the complex absorbs at the monitored wavelength.  142

IV.3. Calculation of fluorescence lifetime and the quenching coefficient

The SPC data processing was carried out by Picoquant Fluofit software, using a non linear least squares deconvolution technique. For the fitting the program applied one or two exponential functions:

\[ y = C_1 \times e^{-\frac{t}{\tau_1}} + C_2 \times e^{-\frac{t}{\tau_2}} \]  

(2)
which gave the values of $\tau_1$ and $\tau_2$ lifetimes and $C_1, C_2$ preexponentials. By using a Marquart algorithm, the residuals and the $\chi^2$ quality factor of the fitting was calculated by

$$r(t_i) = \frac{[I_{m}(t_j) - I_{sz}(t_j)]}{\sqrt{I_{m}(t_j)}}$$

(3)

and

$$\chi^2 = \frac{1}{N - P} \sum_{i=1}^{N} \frac{[I_{m}(t_j) - I_{sz}(t_j)]^2}{I_{m}(t_j)}$$

(4)

functions, where $N$: number of data measured, $P$: number of parameters fit, $I_{m}(t_0)$: the value measured in channel $I$, $I_{sz}(t_0)$: the calculated value in channel $I$. Acceptable results of fitting were those with equal distribution of residuals and with $\chi^2$ values less than 1.2.

Some additives can have quenching effect leading to shortening of the fluorescence lifetime($\tau$):

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[H]$$

(5)

where $\tau_0$ is the fluorescence lifetime in the absence of quencher, $k_q$ represents the rate constant of the quenching process, $[H]$ denotes the concentration of the quencher. Plotting $\tau^{-1}$ vs. $[H]$ results in a linear function where the slope gives the rate constant of the dynamic quenching.

IV.4. Quenching kinetics of triplet C$_{60}$

The time evolution of the triplet C$_{60}$ absorbance at 750 nm was strictly single exponential if triplet lifetime was shorter than ca. 4$\mu$s in the presence of quencher. The traces corresponding to the long lived triplet excited C$_{60}$ ($A(t)$) were analysed
taking into account the second-order disappearance of the triplet via triplet-triplet annihilation, fitting the following function to the experimental data:\(^{143}\)

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

(7)

where \(A_0\) is the initial absorbance, \(l\) is the optical path, \(\varepsilon_T\) 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.

V. Results and discussion

V.1. Calixarene based photosensitive receptor devices

V.1.1. Recognition of amines by indophenol coupled chromogenic calixarenes

The supramolecular recognition properties of our calixarenes \(\text{CXa, CXb and CXc}\) (see Scheme 1) have been monitored through the changes in the UV/Vis spectra upon their coordination to the host molecule. The common feature of the spectra of ligands (\(\lambda_{\text{max}} = 520–534\) nm) in the presence of amines is the appearance of a new band in the region of 652–667 nm (see Figure 6). The quantitative evaluation of the spectral changes by Job’s method (see section IV.2.) applying various molar ratios indicated the formation of an adduct with 1:1 stoichiometry. The application of the method of Benesi and Hildebrand is shown in Figure 6. The upper part (A) shows a series of spectra with the same initial concentration of calixarene \(\text{CXa}\) and with various initial concentrations of di-n-propyl-amine. The lower part (B) shows the Benesi-Hildebrand plot. Similar diagrams were also obtained for other calixarenes and amines.
Figure 6. (A) Absorption spectra of 1-di-n-propyl-amine systems in ethanol. Concentrations: \((C_{Xa})_0=5 \times 10^{-5}\) M in each solution, \((C_{amine})_0=(a)0\) M, (b) \(2.7 \times 10^{-3}\) M, (c) \(5.5 \times 10^{-3}\) M, (d) \(8.2 \times 10^{-3}\) M, (e) \(2.7 \times 10^{-2}\) M, (f) \(7.2 \times 10^{-2}\) M. (B) Benesi-Hildebrand plot of the absorbance values at 664 nm.

The complex formation constants obtained this way are presented in Table 1. As will be shown, they suggest the formation of internal supramolecular complexes in the concentration range of these dilute solutions, and do not seem to be related to the acid-base equilibria governing the composition of systems with higher calixarene and amine concentrations, studied by NMR measurements in Ref. 53.
Table 1. The equilibrium constants of the complex formation of the ligands CXa,b,c with different aliphatic amines in ethanol and DMSO ([2]: according to Kubo)

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ethyl-amine</th>
<th>n-Propyl-amine</th>
<th>n-Butyl-amine</th>
<th>t-Butyl-amine</th>
<th>3-Amino-propanol</th>
<th>Di-n-propyl-amine</th>
<th>Triethyl-amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>CXa</td>
<td>436.3</td>
<td>46.4</td>
<td>18.7</td>
<td>138.7</td>
<td>250.6</td>
<td>77.2</td>
<td>39.8</td>
</tr>
<tr>
<td>CXb</td>
<td>234.7</td>
<td>78.7</td>
<td>62.6</td>
<td>109.8</td>
<td>258.2</td>
<td>27.2</td>
<td>16.2</td>
</tr>
<tr>
<td>CXc</td>
<td>951.8</td>
<td>103.9</td>
<td>155 (95.9 [2])</td>
<td>1090 [2]</td>
<td>123.4</td>
<td>71.2</td>
<td>18.4</td>
</tr>
<tr>
<td>CXb in DMSO –</td>
<td>87.7</td>
<td>71.3</td>
<td>107.9</td>
<td>67.7</td>
<td>–</td>
<td>24.5</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. The equilibrium constants of the complex formation of the ligands CXa,b,c with different aliphatic amines in ethanol and DMSO ([2]: according to Kubo)
As can be seen, the equilibrium constants for primary amines are generally higher than those obtained for dipropylamine and for triethylamine. This supports the formation of supramolecular complexes in these dilute solutions, since the basicity of the three types of amines in the opposite order, therefore, one would expect an opposite trend for the equilibrium constants in simple acid–base reactions.

The most significant effects that seem to control the stability of the amine-calixarene complexes are: (i) the numbers of hydrogen atoms in the amino group and (ii) steric effects. It is exactly true for calixcrown CXc (see Scheme 1) where the order of $K_c$ values is in accordance with the reaction model suggested by Kubo et al. According to this model the complexation of CXc starts with the protonation of the amine guest by one of the hydroxyl groups in the calixarene host, resulting in the formation of an ammonium ion, which is simultaneously bound by the neighbouring crown ring through hydrogen bonds. The complex, therefore, is stabilized by the ionic indophenolate-ammonium cation interaction and by the hydrogen bonds with the oxygen donor atoms in the crown ether moiety. Consequently, primary amines can form the most stable complexes (three hydrogen bonds), while tertiary amines are hardly bound. In addition, the complex stability is also affected by steric factors. In the series of $n$-primary amines the complex stability decreases with increasing chain length of the alkyl group. At the same time, the highest $K_c$ was measured for t-butylamine, which might be due to an additional binding factor via Me-π interaction between the t-Bu group and the naphthalene ring.

Considerations discussed above are not completely valid for capped calixarenes CXa,b. (see Scheme 1) As can be seen in Table 1, the complex formation constants for primary amine complexes (except for ethylamine complexes) are substantially lower than those for CXc, indicating a much weaker binding. Besides, the order of the $K_c$ values is not strictly controlled by the order of the amines. These differences may be attributed to the structural differences between CXc and CXa,b, respect of the indicator group and the binding site (see Scheme 1). The indophenol with moieties to compounds CXa,b exist in a stable endo-quinoide tautomeric form, which means that the phenolic OH group is far from the binding site, whereas both OH groups of CXc are close to the cavity. Consequently, the model of binding in case of CXa,b should be modified.
Two consecutive processes are assumed (Figure 7): (i) first the protonation of amine by one of the exophenolic OH- resulting in exo-calix ion-pair (acid-base equilibrium, $K_1$), (ii) rapid tautomerisation of the indophenolate resulting in the formation of an endo/exo-quinoide structure followed by stabilizing the ammonium cation via H-bonds (complexation, $K_2$).
Figure 7. Scheme of the equilibria assumed
In this respect a question emerges: which electron donating groups in the carboxamide cap can accept the ammonium protons? Since the carbonyl groups are oriented out of the cavity \(^53\), there remain the phenolether oxygens (and the quinone carbonyl of the other indophenol unit in \(\text{CXa}\)) to accept protons. Considering the tetrahedral geometry of the ammonium cation, in principle, primary amines can form both internal (A) and external (B) supramolecular complexes. Structure A comprising three H-bonds should be more stable than complex B where only two H-bonds are used for the stabilization. Obviously, the two kinds of complexes can be in equilibrium with each other in which the proportion of the individual forms strongly depends on the bulkiness of the substituents. In the internal complexes (A), a severe steric repulsion should be accounted between the apical substituent of the amine and the upper part of the bridging unit.

Of the amine series, the smallest ethylamine gave by far the highest \(K_c\) values with \(\text{CXa}\) (even so with the sterically more crowded \(\text{CXb}\)), which may be attributed to the formation of such an internal complex, although we have no structural evidences to support it. From steric reasons, the other amines with ligands \(\text{CXa}\) and \(\text{CXb}\) can form at most external complexes (B) of much lower stability (two hydrogen bonds). Since the two coloration processes cannot be separated spectroscopically (the different indophenolate–ammonium ion-pairs can not be distinguished), they appear as a single equilibrium where \(K_1\) (acid–base equilibrium) and \(K_2\) (complexation) may be involved in the measured constants with unknown proportions. Due to the weak interactions, their contribution to the \(K\) values can be comparable and thus deeper insight into the structural feature of complexes cannot be obtained.

It should be pointed out, however, that the presence of hydroxyl group in 3-aminopropanol increases the equilibrium constant of complex formation with carboxamide bridged ligands \(\text{CXa,b}\) compared to that of propylamine, but not in the case of the crown bridged calix[4]arene \(\text{CXc}\). Additional interaction between the carboxamide oxygen and the hydroxyl group (in the amine) may occur resulting in a significant enhancement of complex stability. In contrast, the hydroxyl group does not seem to interact with the etheric oxygens of \(\text{CXc}\).

In order to compare the complex formation in a protic and in an aprotic solvent, analogous measurements have been carried out with \(\text{CXb}\)-amine systems in dimethylsulfoxide. As apparent from Table 1, in the majority of cases, the equilibrium
constants obtained with the same amine in the two solvents do not differ significantly. However, much lower stabilities were obtained with 3-aminopropanol in DMSO than in ethanol. This observation is in accord with the more polar and nucleophilic character of DMSO, which much easily disrupt the intramolecular OH· · ·OC bond than the less polar and self-solvated ethanol.

In conclusion, the results indicate that calix[4]arenes capped by diamide bridges form strongly polar supramolecular complexes with various types of amines. Of the calixarenes studied, \textbf{CXb} may be worth testing as part of an analytical sensor device for the optical detection of aminoalcohols.


We have also investigated the possibility of using \textbf{CXa} and \textbf{CXb} molecules (see section 1.4.1.1) as photoactive sensor devices for the detection of alkali and alkali earth metal ions in organic solvents (MeCN, acetone, ethanol). Table 2 shows the absorption maxima of ligands \textbf{CXa}, \textbf{CXb} and different alkali/alkali earth metal bromides in the absence and in the presence of triethylamine in the visible region.
Table 2. Absorption maxima (nm) of ligands CXa–b in the presence of different salts

<table>
<thead>
<tr>
<th></th>
<th>CXa</th>
<th></th>
<th>CXb</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Acetone</td>
<td>MeCN</td>
<td>EtOH</td>
<td>Acetone</td>
</tr>
<tr>
<td>LiBr</td>
<td>528</td>
<td>518</td>
<td>527</td>
<td>653  ○</td>
</tr>
<tr>
<td>LiBr +</td>
<td>651</td>
<td>667</td>
<td>663</td>
<td>652  ○</td>
</tr>
<tr>
<td>Et3N</td>
<td></td>
<td></td>
<td>534</td>
<td>fading</td>
</tr>
<tr>
<td>NaBr</td>
<td>516</td>
<td>521</td>
<td>528</td>
<td>516</td>
</tr>
<tr>
<td>NaBr +</td>
<td></td>
<td>675</td>
<td>663</td>
<td>666</td>
</tr>
<tr>
<td>Et3N</td>
<td>513</td>
<td>518</td>
<td>529</td>
<td>519</td>
</tr>
<tr>
<td>KBr</td>
<td>518</td>
<td>517</td>
<td>527</td>
<td>515</td>
</tr>
<tr>
<td>KBr +</td>
<td></td>
<td>674</td>
<td>660</td>
<td>674</td>
</tr>
<tr>
<td>Et3N</td>
<td>519</td>
<td>519</td>
<td>528</td>
<td>516</td>
</tr>
<tr>
<td>CaBr₂</td>
<td>639</td>
<td>640</td>
<td>527</td>
<td>722  ○ fading 687  weak</td>
</tr>
<tr>
<td>CaBr₂ +</td>
<td>○</td>
<td>○</td>
<td>620</td>
<td>○ fading 687 weak</td>
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<tr>
<td>Et3N</td>
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<tr>
<td>MgBr₂</td>
<td>516</td>
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<tr>
<td>MgBr₂ +</td>
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<td>Et3N</td>
<td>517</td>
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</table>

○ = precipitation.

Triethylamine as a weak base is capable of facilitating the deprotonation of the OH group of the ligands. (But as the last row of Table 2 shows, triethylamine itself forms complexes with CXa and CXb in some solvents.) In apolar solvents, no complex formation was observed in the case of CXa but the spectra of calixarene CXb was different; in the presence of both lithium ion and base, plateaux occurred over a wide visible region providing evidence of weak complex formation. Li⁺ without base was complexed efficiently only by ligand CXb in acetonitrile, while Ca²⁺ was bound under similar conditions by calixarene CXa in acetone and acetonitrile and by CXb in acetone and ethanol. In conclusion, CXb has been found to have a strong and selective complex forming ability and after quantitative measurements it may be of value in optical sensor devices.
V.1.3. **Supramolecular complex formation between Nile Blue and tetraundecylcalix[4]resorcinarene**

**Steady state behavior**

Solutions of **NB** and **RA** (see Scheme 2 and Scheme 3) prepared with various solvents were mixed and the interactions between the two solutes were monitored by comparing the UV-visible absorption spectra of the pure components to those of the mixtures. Dissolving **NB** in protic solvents (water, alcohols), equilibrium mixtures of **NB** and **NBH⁺** were obtained, before adding any **RA** to the solutions. In these solvents, as well as in aprotic, polar solvents, like acetonitrile, no change in the spectrum upon the addition of **RA** was observed. In aliphatic, aromatic and chlorinated hydrocarbons the mixing was followed by substantial changes in the spectrum. Of the latter systems, the toluene- and dichloromethane solutions were studied in detail. Absorption and fluorescence spectra of pure **NB** and of pure **NBH⁺** perchlorate were taken, then the spectra of **NB** (2⋅10⁻⁶ M) in the presence of various amounts of **RA** (from 5⋅10⁻⁷ to 4⋅10⁻⁵ M) were recorded in the two solvents.

Absorption and fluorescence spectrum characteristics of the solutions of pure **NB**, of pure **NBH⁺** perchlorate, and of the mixtures with the highest **RA** excess are summarized in Table 3.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solute composition [M]</th>
<th>Absorption spectrum</th>
<th>Fluorescence spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[NBH⁺]₀ [NB]₀ [RA]₀</td>
<td>λ_max [nm] (ε [M⁻¹cm⁻¹])</td>
<td>λ_max [nm] (relative fluorescence intensity)</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2⋅10⁻⁶</td>
<td>647 (97 400)</td>
<td>505 to 660 (505 to 1160)</td>
</tr>
<tr>
<td></td>
<td>2⋅10⁻⁶</td>
<td>505 (45 200)</td>
<td>579 (886)</td>
</tr>
<tr>
<td></td>
<td>2⋅10⁻⁶ 4⋅10⁻⁵</td>
<td>649 (96 500)</td>
<td>595 (36) 666 (103)</td>
</tr>
<tr>
<td>Toluene</td>
<td>2⋅10⁻⁶</td>
<td>627 (-)</td>
<td>645 (43)</td>
</tr>
<tr>
<td></td>
<td>satd. soln.ᵃ</td>
<td>627 (-)</td>
<td>645 (43)</td>
</tr>
<tr>
<td></td>
<td>2⋅10⁻⁶</td>
<td>490 (36 800)</td>
<td>544 (271)</td>
</tr>
<tr>
<td></td>
<td>2⋅10⁻⁶ 4⋅10⁻⁵</td>
<td>647 (55 900)</td>
<td>567 (9) 658 (20)</td>
</tr>
</tbody>
</table>

Variations of the absorption and fluorescence spectra of NB with the amount of added RA are displayed in Figure 8 and 9, respectively.

Figure 8. Absorption spectra of Nile Blue base (NB) – tetraundecyl-calix[4]resorcinarene (RA) mixtures (a) in dichloromethane and (b) in toluene. Initial concentrations: \([NB]_0 = 2\cdot10^{-6} \text{ M}\) in each solution, \([RA]_0 = (A) \text{ 0}, (B) 1\cdot10^{-6}, (C) 2\cdot10^{-6}, (D) 3\cdot10^{-6}, (E) 4\cdot10^{-6}, (F) 6\cdot10^{-6}, (G) 8\cdot10^{-6}, (H) 1.2\cdot10^{-5}, (I) 1.6\cdot10^{-5}, (J) 4\cdot10^{-5} \text{ M}.\)
Figure 9. Fluorescence emission spectra of the NB - RA mixtures (a) in dichloromethane, excitation wavelength ($\lambda_{\text{ex}}$) = 505 nm; (b) in dichloromethane, $\lambda_{\text{ex}}$ = 585 nm; (c) in toluene, $\lambda_{\text{ex}}$ = 490 nm; (d) in toluene, $\lambda_{\text{ex}}$ = 585 nm. Initial concentrations are the same as in Fig. 8.

They indicate that Nile Blue exists at least in five different forms in these systems: (i) unreacted NB, (ii) a supramolecular complex consisting of a neutral host and a neutral guest NB-RA, (iii) a supramolecular complex of ionic nature, $\text{NBH}^+\cdot\text{RA}^-$, (iv) complexed cation $\text{NBH}^+\cdot\text{RA}$ and (V) uncomplexed cation $\text{NBH}^+$. The presence of these species in the solutions have been confirmed through calculating the equilibrium constants for the occurring reactions, and also by the fluorescence decay experiments, the details of which will be given later.

The location of the absorption band belonging to Nile Blue base is not sensitive to the addition of RA to the solutions. The formation of NB-RA is indicated primarily by the fluorescence measurements. The fluorescence band of the base is shifted gradually to higher wavelengths with increasing RA content. In case of CH$_2$Cl$_2$ solutions the maximum of this band, $\lambda_{\text{max}}$, is located at 579 ± 2 nm in the spectra of all systems with initial RA concentrations [RA]$_0$ = 0 - 8·10$^{-6}$ M, then it is
shifted gradually to 595 nm observed at $[RA]_0 = 4 \cdot 10^{-5}$ M, the highest applied excess of the host. In toluene, e.g. the corresponding band, appearing at 544 nm in the absence of RA, shows a clear shift to higher wavelengths even at low RA contents, it appears at 560 nm in the spectrum of the solution with $[RA]_0 = 8 \cdot 10^{-6}$ M. As can be seen in Figure 9, the shape of the band, too, changes in the same interval (the shoulder gradually disappears). This is followed by a further moderate shift to 567 nm, as $[RA]_0$ is increased to $4 \cdot 10^{-5}$ M. These results suggest that NB-RA is more stable in an apolar medium, like toluene.

Reliable absorption and fluorescence spectral data for pure NBH$^+$ (in form of its perchlorate salt) could be obtained only in dichloromethane. The solubility of this salt is very low in toluene and the absorption spectra indicate that a part of the dissolved cations are instantly deprotonated.

The absorption features arising from free NBH$^+$, and from its complexed forms, NBH$^+$-RA and NBH$^+$-RA$^-$ strongly overlap, thus, they can not be easily separated in the absorption spectra.

The absorption feature with a single maximum around 650 nm, becoming dominant at high RA concentrations, has been assigned to NBH$^+$-RA. As can be seen in table 3, $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ values for the complexed and uncomplexed cations in dichloromethane are very close. The corresponding data for the toluene solutions can not be directly compared, because of the aforementioned poor solubility of NBH$^+$ perchlorate in this solvent.

The presence of NBH$^+$-RA$^-$, a supramolecular structure of ionic nature is indicated by the appearance of two overlapping bands with maxima around 585 nm and 645 nm in the absorption spectra in Figure 8. The intensities show that in both solvents the concentration of this species rapidly increases with the amount of the added RA upto $[RA]_0 = 4 \cdot 10^{-6}$ M, the addition of further RA to the systems leads to the conversion of this product into NBH$^+$-RA. The range of the visible absorption of NBH$^+$-RA$^-$ clearly shows the cationic character of its Nile Blue moiety, and through that the ionic nature of the whole supramolecular structure. NBH$^+$ perchlorate dissolved in polar or amphiphilic solvents has a single absorption band in the visible range ($\lambda_{\text{max}} = 635$ nm in water, 628 nm in ethanol, 627 nm in 1-butanol, 624 nm in chloroform).144
In contrast, in 1-chloro-naphthalene the absorption band ($\lambda_{\text{max}} = 646$ nm) has a shoulder on the lower wavelength side,\textsuperscript{145} the relative intensity of which does not change with the concentration,\textsuperscript{71} thus, it does not seem to be related to aggregation. Instead, the splitting may be a consequence of the imperfect solvation of the oppositely charged ions. Nile Blue may be present in forms of tight ion pairs in this rather apolar solvent, in other words, the electrostatic interaction between the NBH$^+$ cation and the perchlorate anion is expected to be stronger in 1-chloronaphthalene than in more polar solvents. The electrostatic forces may be even stronger between the NBH$^+$ and RA$^-$ moieties of the ionic complex in the systems studied, where the solvent molecules are unable to weaken the electrostatic part of the host-guest interactions, what may be the reason for the splitting observed in the spectra in Fig. 8.

As can be seen in Figure 9b, the fluorescence of the supramolecular systems in toluene is very weak, when they are irradiated at 585 nm, where the free and the two complexed forms of NBH$^+$ cation absorb strongly. This confirms that the NBH$^+$ cations are present dominantly in the complexed forms, as NBH$^+$-RA and NBH$^+$-RA$^-$.

Probably, neither of the complexes exhibit a detectable emission in toluene, the weak fluorescence of the solutions with high RA excess may arise from a small amount of free cations.

The dichloromethane solutions show fluorescence, when irradiated at the above wavelength. The intensity increases with the concentration of RA in the systems, but even in cases of high RA excess, where the absorption spectra indicate that almost the whole amount of NB is converted to protonated species, it remains weaker by one order of magnitude than that of pure NBH$^+$ salts. This suggests that there is only a small amount of strongly fluorescing free NBH$^+$ cations in these systems, and - in contrast to the toluene solutions – the complexation of the cations in forms of NBH$^+$-RA$^-$ and NBH$^+$-RA, results in a dramatic reduction of fluorescence, but not in a complete quenching. A substantial reduction of the fluorescence intensity have been reported for the majority of supramolecular systems studied so far, with cationic dye guests and calixarene hosts comprising dissociable protons\textsuperscript{63, 64, 67, 68}, but there are also examples, where such systems exhibit a fluorescence enhancement.\textsuperscript{65, 66}

The applied absorption and fluorescence spectroscopic methods do not provide much information about the type of inclusion of the complexes formed by NB and RA. The inclusion of dye molecules by calixarene receptors can be studied efficiently.
by measuring the shifts in the $^1$H NMR spectra of the dye moieties upon the addition of calixarenes, as was shown in two papers by Shinkai et al.$^{69,70}$ The solubility of their hosts, guests and complexes in D$_2$O was high enough for such measurements.

We made an effort to carry out similar experiments by measuring the $^1$H NMR spectra of NB, of NBH$^+$ (perchlorate salt), of RA and of NB-RA mixtures in two solvents—CDCl$_3$ and CD$_2$Cl$_2$—in which the UV/Vis spectra indicate complex formation. These experiments clearly indicated the proton transfer from RA to NB, but did not give reliable information concerning the inclusion type structure of the complex. In CDCl$_3$ the solubility of NBH$^+$-perchlorate is too low for NMR measurements, in CD$_2$Cl$_2$ the solubility of RA is too low to prepare mixtures which contain at least the ‘ionic’ complex NB$^+$ RA$^-$ in higher concentration.

Reactions and equilibrium constants

In the majority of studies on supramolecular systems the formation of a single supramolecular product is observed, when the stoichiometry of the complex can be justified, and the association constant can be determined with the help of a simple Benesi-Hildebrand plot of the absorbance values or of the fluorescence intensities (see section V.1.1). Since the spectra revealed the existence of three different supramolecular complexes in our systems, this route could not be followed. Instead, various schemes with parallel and consecutive reactions have been set up and tested by checking if the values obtained for the equilibrium constants for the individual reactions are independent of the composition. The equilibrium concentrations of the reactants and of the products have been determined from the absorption spectra. The alternative route, the calculation of the equilibrium concentrations from the self-absorption corrected fluorescence intensities, seemed very difficult, when it was realized that the fluorescence lifetimes follow the complex formation in a complicated manner. The spectral data of twelve solutions in each solvent have been taken into account: the solution of pure NB, NB with $[R]_0 = 4 \cdot 10^{-5}$ M - its spectrum has been taken as the spectrum of NBH$^+$-RA – and ten further NB solutions with various amounts of added RA from $[RA]_0 = 5 \cdot 10^{-7}$ to $3 \cdot 10^{-5}$. The concentration of the free NBH$^+$ cations has been taken as zero and it has been assumed that the absorption
coefficients for the four forms of Nile Blue, $\varepsilon_{NB}(\lambda)$, $\varepsilon_{NB\cdot RA}(\lambda)$, $\varepsilon_{NBH^+\cdot RA^-}(\lambda)$, and $\varepsilon_{NBH^+\cdot RA}(\lambda)$, are independent of the composition.

Applying Beer’s law for such a system, the spectrum – the absorbance of a sample in a cell with light-pass $\ell$ - can be expressed as a sum of the contributions from the components, which are present in their equilibrium concentrations:

$$A(\lambda) = \left\{ \varepsilon_{NB}(\lambda) \cdot [NB] + \varepsilon_{NB\cdot RA}(\lambda) \cdot [NB\cdot RA] + \varepsilon_{NBH^+\cdot RA^-}(\lambda) \cdot [NBH^+\cdot RA^-] + \varepsilon_{NBH^+\cdot RA}(\lambda) \cdot [NBH^+\cdot RA] \right\} \cdot \ell \quad (9)$$

The absorption spectrum of $NB\cdot RA$ has been taken to be identical with that of $NB$ for the ten systems involved in the analysis, which seems to be a reasonable assumption at least for the dichloromethane solutions, where the effect of the added $RA$ is small even on the fluorescence behavior. The spectrum of $NB^+\cdot RA^-$, a component available only in equilibrium mixtures, has been obtained at the end of an iterative substraction of the bands representing $NB$ (together with $NB\cdot RA$) and $NBH^+\cdot RA$. The result of this procedure is illustrated in Figure 10, showing the contributions of the components to the spectrum of two selected systems: one in dichloromethane and one in toluene.
Figure 10. Resolution of the absorption spectra of a NB – RA mixture in (a) dichloromethane and (b) in toluene. Initial concentrations: $[\text{NB}]_0 = 2 \cdot 10^{-6}$ M, $[\text{RA}]_0 = 4 \cdot 10^{-6}$ M (1 : NB; 2 : RA)

The analysis has led to the conclusion that our systems are governed by three reactions. The weakly bound and the ionic complexes are formed in the simultaneous processes

$$\text{NB} + \text{RA} \rightleftharpoons \text{NB} \cdot \text{RA} \tag{10}$$

and

$$\text{NB} + \text{RA} \rightleftharpoons \text{NBH}^+ \cdot \text{RA}^- \tag{11}$$

The ionic complex is protonated then in a subsequent step:
The experimental spectra do not provide direct information about reaction (11). As can be seen in Fig. 8., at lower RA concentrations the formation of the ionic complex – reaction (12) – predominates in dichloromethane and this is the only observable reaction in toluene. As the concentration of RA is increased, the ionic complex is gradually protonated and in systems with large RA excess NB is converted almost completely into NBH$^+\cdot$RA.

Thermodynamically the systems can be characterized by the apparent equilibrium constants $K_1$, $K_2$, and $K_3$ belonging to reactions (11), (12) and (13), respectively

$$K_1 = \frac{[NB \cdot RA]}{[NB][RA]}, \quad \text{(13)}$$

$$K_2 = \frac{[NBH^+ \cdot RA^-]}{[NB][RA]}, \quad \text{(14)}$$

and

$$K_3 = \frac{[NBH^+ \cdot RA][RA^-]}{[NBH^+ \cdot RA^-][RA]}, \quad \text{(15)}$$

Denoting the fractions of NB converted to NB$\cdot$RA and to NBH$^+\cdot$RA$^-$ by $\alpha$ and $\beta$, respectively, and the fraction of NBH$^+\cdot$RA$^-$ is converted to NBH$^+\cdot$RA by $\gamma$, the equilibrium concentrations of the products and the reactants are

$$[NB \cdot RA] = [NB]_0 \cdot \alpha, \quad \text{(16)}$$

$$[NBH^+ \cdot RA^-] = [NB]_0 \cdot \beta \cdot (1 - \gamma), \quad \text{(17)}$$

$$[NBH^+ \cdot RA] = [RA^-]_0 = [NB]_0 \cdot \beta \cdot \gamma, \quad \text{(18)}$$
\[ [\text{NB}] = [\text{NB}]_0 \cdot (1 - \alpha - \beta), \quad (19) \]
\[ [\text{RA}] = [\text{RA}]_0 - [\text{NB}]_0 (\alpha + \beta \cdot \gamma). \quad (20) \]

As a first estimation, the value of \( \alpha \) (and of \( K_1 \)) has been taken zero, and the values for \( K_2 \) and \( K_3 \) have been calculated from the concentrations available from the resolved spectra. In case of the dichloromethane solutions, the values obtained for \( K_2 \) and \( K_3 \) have been independent of the composition, what seems to confirm that \( K_1 \) has a small value in this solvent. In contrast, the figures obtained for \( K_2 \) and \( K_3 \) have shown a small, but systematic variation with the amount of the added \text{RA}. The equilibrium constants for the latter systems have been computed in an iteration process, in which \( K_2 \) and \( K_3 \) have been calculated using values for \( \alpha \) for the ten systems corresponding to various assumed values for \( K_1 \), as long as \( K_2 \) and \( K_3 \) became independent of the composition of the mixtures.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( K_1 ) ([10^3 \text{ M}^{-1}])</th>
<th>( K_2 ) ([10^3 \text{ M}^{-1}])</th>
<th>( K_3 ) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>-</td>
<td>7.5±1.3</td>
<td>0.012±0.003</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.0±0.5-</td>
<td>98±8</td>
<td>0.023±0.005</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>2.8±0.5</td>
<td></td>
<td>0.34±0.06</td>
</tr>
</tbody>
</table>

Table 4. Equilibrium constants for reactions in Nile Blue base - tetra-undecyl-calix[4]resorcinarene systems

The calculated equilibrium constants are presented in Table 4. As can be seen, the association constants, particularly that for the formation of \( \text{NB}^+\cdot\text{RA}^- \) in toluene, are significantly larger with \( 10^2 - 10^4 \) order of magnitude than the values typical of organic guest – calixarene systems. 59, 61, 64, 66, 67, 68, 70, 146

Such high equilibrium constants were obtained for the complexation of pyrene by water soluble calixarenes in aqueous solutions. 59, 61

It seems plausible that the \( \text{NBH}^+ \) cations, solvatophobic in apolar solvents (like pyrene is solvatophobic in water), form very stable complexes with \( \text{RA}^- \) anions. The solubility of this complex in apolar media is due partly to the zero net charge,
partly to the isolation of the oppositely charged functional groups by the aromatic rings and the long aliphatic chains.

In order to study the behavior of the system in a saturated and in a chlorinated aromatic hydrocarbon, analogous experiments have been carried out in \( n \)-heptane and in chlorobenzene. In the former solvent, in which the solubility of RA is poor, the simultaneous formation of the “neutral” (NB•RA) and the “ionic” (NB⁺•RA⁻) complexes could be observed in slow heterogeneous reactions by measuring the absorption and fluorescence spectra repeatedly. In chlorobenzene the system behaved in a similar manner as in dichloromethane. The equilibrium constants for reactions (12) and (13) have been evaluated, their values are also presented in Table 4.

**Dynamic behavior - fluorescence lifetimes**

The dynamic behavior of the systems were studied by time correlated single photon technique (see section III.2.2.1). In order to separate the fluorescence emissions of the pure and/or complexed forms of NB base from that of the pure and/or complexed forms of the NBH⁺ cation, the exciting pulses were produced by two semiconductor lasers, operating at 404 nm (in the absorption range of the former species) and at 632 nm (in the absorption region of the latter species); and the emission monochromator was set to wavelengths 545 nm and to 660 nm, close to the fluorescence maxima of neutral and cationic forms of Nile Blue, respectively. Most of the decay curves show a single exponential character. The exceptions are those obtained by exciting the cationic species in dichloromethane, which have been found biexponential, with two strongly different amplitudes. The (dominant) fluorescence lifetimes (\( \tau_F \)) obtained with the two different excitation and observation wavelengths are presented in Table 5.
<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solute composition [M]</th>
<th>Fluorescence lifetimes [ps]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[NBH(^+)](_0)</td>
<td>(\lambda_{ex} = 404) nm (\lambda_{ab} = 545) nm</td>
</tr>
<tr>
<td></td>
<td>[NB(_0)]</td>
<td>(\lambda_{ex} = 632) nm (\lambda_{ab} = 660) nm</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>(2 \cdot 10^{-6})</td>
<td>2910</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 2( \cdot 10^{-6})</td>
<td>1260</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 4( \cdot 10^{-6})</td>
<td>1240</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 8( \cdot 10^{-6})</td>
<td>1270</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 1.6( \cdot 10^{-5})</td>
<td>1280</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 3( \cdot 10^{-5})</td>
<td>1270</td>
</tr>
<tr>
<td>Toluene</td>
<td>(\sim 6 \cdot 10^{-8})</td>
<td>3210</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6})</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 2( \cdot 10^{-6})</td>
<td>380</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 4( \cdot 10^{-6})</td>
<td>390</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 8( \cdot 10^{-6})</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 1.6( \cdot 10^{-5})</td>
<td>470</td>
</tr>
<tr>
<td></td>
<td>(2 \cdot 10^{-6}) 3( \cdot 10^{-5})</td>
<td>550</td>
</tr>
</tbody>
</table>

\(^a\) Estimated errors within ±5%

**Table 5. Fluorescence lifetimes of Nile Blue base and of Nile Blue cation in pure solvents and in Nile Blue base – tetra-undecyl-calix[4]arene supramolecular systems**

Values for \(\tau_F\) for NB have not been found in the literature. The observation that the addition of RA does not influence the rate of fluorescence decay in
dichloromethane—$\tau_F$ has a constant value of 1260 ± 20 ps—is in accord with the result of the steady-state experiments: reaction (11) does not play an important role in this solvent. In contrast, the lifetimes measured at 545 nm in toluene provide further evidence for the formation of NB•RA. The value for $\tau_F$ is 390 ps for pure NB and 550 ps for complex NB•RA, the latter measured at the highest applied excess of RA. The decay curves of the solutions with lower RA concentrations have seemingly also a single-exponential character with lifetimes between the two above values, in other words, the lifetimes of the two co-existing species cannot be obtained separately in the fitting procedure. (Model calculations by Gardini et al.\textsuperscript{147} demonstrated that the correct values for two relatively close fluorescence lifetimes may not be obtained from the analysis of the decay curves arising from the two coexisting species, instead a single exponential function may give a satisfactory fit.) Fluorescence lifetimes for cation NBH$^+$ in various sets of solvents were already reported in earlier studies.\textsuperscript{72,73,148,149,150} Its lifetime decreases with increasing solvent polarity, from $\sim$3100 ps measured in chloroform to $\sim$400 ps measured in water. Our result for the dichloromethane solution practically coincides with the $\tau_F$ value of 2900 ps reported in Refs. 149, 150. Lifetimes for NBH$^+$-salts dissolved in an apolar solvent such as toluene have not been found in the literature, the value in Table 5 fits the trend observed for decreasing solvent polarity. The fluorescence of Nile Blue in the presence of RA in toluene was very weak when the 632 nm laser was applied for excitation, which did not allow reliable measurement of the fluorescence lifetimes of the cationic species in this solvent.

In accordance with the steady-state spectra in Figure 9, much stronger fluorescence was observed when the dichloromethane solutions were excited with this laser, which allowed recording of the above mentioned decay curves with double exponential character. As can be seen in Table 5, the value of $\tau_F$ belonging to the dominant component decreases with increasing concentrations of the calixresorcinarene up to $[\text{RA}]_0 = 8 \times 10^{-6}$ M, and it remains unchanged at higher RA concentrations. Its lowest value of $\sim$2100 ps can be assigned to NBH$^+$•RA. The longer decays observed at lower RA contents may be associated with the presence of free NBH$^+$ cations in low concentrations. The relative amplitude of the minor component increases with the concentration of RA up to $[\text{RA}]_0 = 4 \times 10^{-6}$ M, and shows an opposite trend above this value, suggesting that it originates from the ionic complex
The amplitude of this component is too small for accurate determination of the respective lifetime. Its estimated value is ~800 ps.

As pointed out in our former study, the fluorescence decay of cation NBH$^+$ has an intramolecular and an intermolecular channel. The predominant intramolecular process is probably the conversion of the electronic excitation energy into the excitation of the diethylamino group. The intermolecular channel is of significance in protic solvents, as it is associated with a fast excited state proton transfer. In the case of NB$^+$RA, the longer decay of the complex, compared to that of pure NB, may be due to the rigidifying of the diethylamino group by the hydrogen bonds between the host and the guest. In contrast, in NBH$^+$RA and particularly in NBH$^+$RA$^-$, the decay of the excited NBH$^+$ moiety becomes faster than that of the uncomplexed NBH$^+$ cation, possibly via proton transfer from the guest.

### V.2.1. Interaction of triplet C$_{60}$ with p-tert.-butyl-calix[n]arenes and their complexes with pyridine derivatives – a photoinduced electron transfer device

An overview of the processes taken into account in the analysis of the experimental results is presented in scheme 5.

$$
\begin{align*}
3\text{C}_60 & \overset{k_0, k_{TT}}{\longrightarrow} \text{C}_60 \\
\text{C}_60 + \text{BCX}_n & \overset{k_1}{\longrightarrow} \text{C}_60 \cdot \text{BCX}_n \\
3\text{C}_60 + \text{BCX}_n & \overset{\phi_R \cdot k_1}{\longrightarrow} \text{C}_60 - \text{BCX}_n + \text{H}^+ \\
& \quad (1 - \phi_R) \cdot k_1 \rightarrow \text{C}_60 + \text{BCX}_n
\end{align*}
$$

Scheme 5.

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
**Quenching of triplet C\textsubscript{60}**

Triplet C\textsubscript{60} quenching by BCX\textsubscript{n}-s has been studied in four solvents of various polarities: benzonitrile, CH\textsubscript{2}Cl\textsubscript{2}, chlorobenzene and toluene. Immediately after the laser flash the well-known characteristic absorption of triplet C\textsubscript{60} appeared\textsuperscript{151}, whose decay was followed at 750 nm, the maximum of the triplet-triplet absorption band. Addition of BCX\textsubscript{4} or BCX\textsubscript{8} did not alter the \textsuperscript{3}C\textsubscript{60} lifetime, because no complex formation occurred for the former compound, and the binding of BCX\textsubscript{8} did not affect the energy dissipation processes from the triplet state. In contrast, increasing amounts of BCX\textsubscript{6} gradually accelerated the triplet deactivation in benzonitrile and CH\textsubscript{2}Cl\textsubscript{2}.

The variation of the pseudo-first-order decay rate constant (k) as a function of BCX\textsubscript{6} concentration is shown in Figure 11.
Figure 11. Pseudo-first order rate constants for triplet C\textsubscript{60} quenching vs. BCX6 concentration in benzonitrile (•), CH\textsubscript{2}Cl\textsubscript{2} (■), chlorobenzene (▲) and toluene (▼).

As can be seen, there are linear dependencies in benzonitrile and dichloromethane, clearly demonstrating that triplet C\textsubscript{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 $k_1=(1.7\pm0.3)\times10^9$ M\textsuperscript{-1}s\textsuperscript{-1} and $(3.1\pm0.4)\times10^7$ M\textsuperscript{-1}s\textsuperscript{-1} in benzonitrile and CH\textsubscript{2}Cl\textsubscript{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\textsubscript{60}-BCX6 system, applied to the study of dynamic quenching, have also shown that in dichloromethane the initial absorbance of triplet C\textsubscript{60} gradually decreases with increasing calixarene concentration. E.g., a
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 C₆₀ upon the addition of BCX6 is shown in Figure 12.

![Figure 12](image)

**Figure 12.** (upper part) Variation of the absorbance at 445 nm vs. BCX6 concentration; line represents the best fit of eq. 2.

(lower part) Alteration of the absorption spectrum of C₆₀ on addition of BCX6 in CH₂Cl₂. Insert: details of the spectral evolution in the 395-435 nm range.
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:

\[
A = A_0(1+K_1\cdot[\text{BCX6}]\cdot\varepsilon_C/\varepsilon_F)/(1+K_1\cdot[\text{BCX6}]) \tag{21}
\]

where \(A_0\) is the absorbance in the absence of \(\text{BCX6}\), \(K_1\) the association constant for the \(\text{C}_{60}-\text{BCX6}\) complex, \(\varepsilon_C/\varepsilon_F\) denotes the ratio of the molar absorption coefficients for the complexed and free forms of \(\text{C}_{60}\). The non-linear least-squares fit of this function to the experimental data has yielded \(K_1=110\pm10\text{M}^{-1}\) in \(\text{CH}_2\text{Cl}_2\). A comparison of this value to the one reported in toluene \(^{152}\) (\(K_1=230\text{M}^{-1}\)) 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 \(\text{C}_{60}\) is detected on the addition of \(\text{BCX6}\) 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 \(\sim10^{-4}\text{M}\) \(\text{C}_{60}\) and 7.5 mM \(\text{BCX6}\) concentrations about 45\% of \(\text{C}_{60}\) is complexed by the calixarene. This value agrees with the extent of the triplet yield diminution suggesting that the excitation of \(\text{C}_{60}-\text{BCX6}\) complex does not lead to triplet formation. The electron transfer within the singlet-excited complex is so rapid in \(\text{CH}_2\text{Cl}_2\) 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 \(\text{BCX6}\) concentrations, where ground state complexation is precluded. \(\text{C}_{60}\) readily binds to \(\text{BCX6}\) in toluene, but the triplet yield for the complex remains the same as that of the free \(\text{C}_{60}\). 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 C₆₀, time-resolved transient absorption spectra have been recorded in benzonitrile (Figure 13).

![Graph showing transient absorption spectra](image)

Figure 13. Time-resolved absorption spectra in benzonitrile solution of 10⁻⁴ M C₆₀ + 0.14 mM BCX6 immediately (■) and 9 μs after the laser flash (▲). Insert: decay of C₆₀⁻ anion radical absorption at 1080 nm.

The spectrum appearing concomitant to the laser pulse corresponds to the triplet-triplet absorption of C₆₀. 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 C₆₀⁻ anion radical on the basis of general agreement with previous spectroscopic results.¹⁵³
It is well-established that the radical cations of phenols are strongly acidic, e.g. the pKₐ value of the 4-tert-butyl derivative is -7 in DMSO. The incipient cation radicals, formed in the electron transfer from phenols to triplet excited molecule, lose a proton, rapidly leading to phenoxy radical. Results of laser flash photolysis and time-resolved EPR experiments have confirmed the formation of phenoxy radical and C₆₀⁻ anion radical also in the photoreduction of C₆₀ by hydroquinone. Similar behaviour is expected when a macrocyclic phenol, BCX₆ is used as electron donor. Based on the absorption spectra of phenoxy, 4-methylphenoxy and 4-tert butylphenoxy radicals, the absorption of the phenoxy type radical formed from the calixarene (BCX₆⁻) 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 C₆₀⁻ and BCX₆⁻.

Yield of radical ion formation

The insert in Figure 13 presents a typical transient absorption of C₆₀⁻ anion radical recorded at 1080 nm and the result of the nonlinear least-squares fit assuming second order decay kinetics. Using ε(C₆₀⁻) = 18300 M⁻¹cm⁻¹ for the molar absorption coefficient of C₆₀⁻ at 1080 nm, k₂ = 5.9×10⁹ M⁻¹cm⁻¹ is obtained for the second-order rate constant of C₆₀⁻ consumption, very close to the diffusion-controlled limit.

The absorbance at 1080 nm grows at the same rate as the triplet decays (Figure 14A) indicating that the triplet state is the precursor of C₆₀⁻.
Figure 14. Absorption-time profiles in the presence of 0.5 mM BCX6 in benzonitrile. A, at 750 and 1080 nm; B, at 500 nm.

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 ($\Delta A(C_{60}^{-})$) of $C_{60}^{-}$ 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 C₆₀ can be expressed as

\[
\Phi_R = \frac{\Delta A_0(\text{C}_6^\bullet \text{−})}{\Delta A_0(\text{C}_6^3)} \times \frac{\varepsilon(C_6^3)}{\varepsilon(\text{C}_6^\bullet \text{−})} \times \frac{k_1 \cdot [\text{BCX6}]}{k_0 + k_1 \cdot [\text{BCX6}]} \tag{22}
\]

where \(k_0\) denotes the rate constant of triplet deactivation in the absence of additive. \(\Delta A_0(\text{C}_6^3)\) and \(\Delta A_0(\text{C}_6^\bullet \text{−})\) represent the initial absorban ces of the respective species, \(\varepsilon(C_6^3)\) and \(\varepsilon(\text{C}_6^\bullet \text{−})\) are their molar absorption coefficients.

The absorbance changes have been measured in 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 C₆₀ can be detected selectively (see Fig. 3). Taking 16100 M⁻¹cm⁻¹ and 18300 M⁻¹cm⁻¹ for the molar absorption coefficient of \(3\text{C}_6\) and \(\text{C}_6^\bullet \text{−}\), respectively at the above wavelengths, \(^{151}\) the results of several experiments have provided \(\Phi_R = 0.48\pm0.04\) for the radical yield.

(ii) The transient absorbance at 500 nm, where the contributions of the two species are commensurable, allowed the determination of \(\Phi_R\) from a single decay curve. The molar absorption coefficients at this wavelength\(^{151}\) are \(\varepsilon(3\text{C}_6) = 3200\) M⁻¹cm⁻¹ and \(\varepsilon(\text{C}_6^\bullet \text{−}) = 2600\) M⁻¹cm⁻¹. As an average of the values calculated from several decay curves, \(\Phi_R = 0.42\pm0.04\) has been obtained, in a fair agreement with the result given above.

Based on the two types of independent measurements, we suggest \(\Phi_R = 0.45\pm0.07\) for the radical yield from triplet reaction in benzonitrile.
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 6.

\[
\begin{align*}
\text{ TMP + BCXn } \xrightarrow{K_2} & \quad \text{TMP\cdot BCXn} \\
\text{ } \xrightarrow{k_q} & \quad C_{60}^+ + \text{BCXn}^- + \text{TMPH}^+ \\
3C_{60} + \text{TMP} \cdot \text{BCXn} \xrightarrow{k_q} & \quad C_{60} + \text{TMP} \cdot \text{BCXn}
\end{align*}
\]

Scheme 6.

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 $k_q$.

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 Figure 15, where the pseudo-first-order triplet decay rate enhancement, $k'_q \cdot k_0$, normalized with respect to total calixarene concentration, $[\text{BCXn}]_0$, is plotted against TMP concentration.
Figure 15. Effect of calixarene structure on the TMP induced $^3$C$_{60}$ quenching in CH$_2$Cl$_2$ (▲) 2.5×10$^{-4}$M BCX8, (●) 6×10$^{-4}$M BCX6, (■) 2×10$^{-3}$M BCX4.

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$^{96,97,152}$ 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 BCXn. Molecular dynamic simulations and UV absorption spectroscopic experiments carried out by Schlachter et al.$^{152}$ 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.$^{160}$ The hydrogen-bonding
expedites electron transfer because of two main reasons: (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.105

The saturation character of the curves in Figure 15 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 BCXn is complexed. For the relative enhancement of the decay rate constant of triplet C_60, in the presence of calixarene BCXn and TMP – the latter in large excess – the formula

\[ \frac{k' - k_0'}{[BCXn]_0} = k_q \frac{K_2 \cdot [TMP]_0}{1 + K_2 \cdot [TMP]_0} \]  

(23)

can be derived. In equation (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-BCXn complex, \( K_2 \) is the equilibrium constant for the formation of the TMP-BCXn complex. 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 6.
Table 6. Equilibrium constants of complex formation and rate constants of triplet C₆₀ quenching by BCXₙ-pyridine type complexes

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Base</th>
<th>BCX₈</th>
<th></th>
<th></th>
<th>BCX₆</th>
<th></th>
<th></th>
<th>BCX₄</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$k_q 10^9$ M⁻¹ s⁻¹</td>
<td>$K_{2}^{kin}$</td>
<td>$K_{2}^{abs}$ M⁻¹</td>
<td>$k_q 10^9$ M⁻³ s⁻¹</td>
<td>$K_{2}^{kin}$</td>
<td>$K_{2}^{abs}$ M⁻¹</td>
<td>$k_q 10^9$ M⁻³ s⁻¹</td>
<td>$K_{2}^{kin}$</td>
</tr>
<tr>
<td>PhCN</td>
<td>TMP</td>
<td>25±3</td>
<td>11±2</td>
<td>8.5±3</td>
<td>quenched without additive</td>
<td>low solubility</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Py</td>
<td>19±3</td>
<td>0.3±0.2</td>
<td>0.2±0.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>TMP</td>
<td>21±3</td>
<td>1.1±0.3</td>
<td>0.5±0.2</td>
<td>22±3</td>
<td>1.5±0.3</td>
<td>1.0±0.3</td>
<td>6.1±0.6</td>
<td>1.1±0.3</td>
</tr>
<tr>
<td></td>
<td>Py</td>
<td>concave</td>
<td>a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhCl</td>
<td>TMP</td>
<td>1.5±0.9</td>
<td>0.5±0.2</td>
<td>0.8±0.3</td>
<td>16±2</td>
<td>1.3±0.2</td>
<td>1.3±0.2</td>
<td>low solubility</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Py</td>
<td>concave</td>
<td>concave</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PhCH₃</td>
<td>TMP</td>
<td>low solubility</td>
<td>9.1±0.8</td>
<td>3.8±0.5</td>
<td>3.7±0.9</td>
<td>low solubility</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Py</td>
<td>concave</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
a effect is too small to determine
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 ($K_{2}^{\text{abs}}$) – also given in Table 6 agree closely with the corresponding values obtained from kinetic measurements ($K_{2}^{\text{kin}}$).

When we use a less basic additive, pyridine (Py), which possesses weaker hydrogen-bonding power \(^{161}\), both the binding equilibrium constant and the reaction rate enhancement are much smaller compared with the effect of TMP. It is apparent from Figure 16 that even the form of the pyridine concentration dependence is entirely different in CH$_2$Cl$_2$ and chlorobenzene.
Figure 16. Reaction rate enhancement on addition of TMP (A) and pyridine (B) in benzonitrile (●), CH$_2$Cl$_2$ (■) 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.

**Cyclic voltammetry**

With the corresponding BCXn compounds we performed cyclic voltammetric measurement. Our results shown on Figure 17 demonstrate that BCX6 can be oxidized at a lower potential than BCX4 or BCX8. Hence, this can also explain why BCX6 reacts spontaneously - without the help of pyridine additives - with C_{60}^3.

![Figure 17. Cyclic voltammograms of calixarenes in CH₂Cl₂ (0.1M TBAPF6 supporting electrolyte, Ag-AgCl reference electrode, glassy carbon working electrode, Pt counter electrode, sweep rate 100 mV/s).](image-url)
Isotope effect

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. Figure 18 clearly shows that the deuterated complex reacts much slower ($k_H/k_D = 1.53 \pm 0.17$).

![Graph showing deuterium isotope effect on the reaction rate increase](image)

**Figure 18.** Deuterium isotope effect on the reaction rate increase $10^{-4} \text{ M } C_{60} + 10^{-3} \text{ M BCX8}$ in benzonitrile containing $0.5 \text{ M CH}_3\text{OH (●)}$ or $0.5 \text{ M CH}_3\text{OD (▲)}$.

Based on the marked isotope effect, we conclude that the reaction proceeds via 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. Similar reaction mechanisms were found when hydrogen-bonded complexes of simple phenols with pyridine derivatives served as electron donors.\textsuperscript{103, 104, 105}
V.3. Ultrafast dynamics of 2-butylamino-6-methyl-4-nitropyridine N-oxide (NPO) – a candidate for NLO materials

Steady state spectra and quantum chemical calculations

Previous experimental evidences of UV spectroscopy,\textsuperscript{162,163} NMR\textsuperscript{164} and quantum chemical calculations\textsuperscript{165, 166, 167} suggest that the first and second excited states of pyridine N-oxides are a charge transfer on the $^1L_b$ state,\textsuperscript{168} respectively, and the direction of the CT is dependent on the type of substituents attached to the pyridine ring.\textsuperscript{169, 170} The steady state absorption and fluorescence emission spectra of NPO, obtained in acetonitrile are shown in Fig. 19.

![Figure 19. Normalised absorption and fluorescence spectra of 2-butylamino-6-methyl-4-nitropyridine N-oxide in acetonitrile (solid curves) and cyclohexane (dashed curves).](image)

We notice that the Stokes shift is rather solvent dependent, reaching a value of about 8000 cm$^{-1}$ in acetonitrile. The absorption spectrum, on the other hand, shows only a minor polarity dependence. The fact that the excitation spectrum (not shown here) and the absorption spectrum overlap in polar aprotic solvents corroborates the hypothesis that in these solvents only one ground state species exists. In apolar solvents such as cyclohexane, in contrast, it is found that the excitation spectrum does
not coincide with the absorption spectrum, which strongly suggests that there are two or more co-existing ground state species present. The conclusion that in polar aprotic solvent only one species exists in ground state is further reinforced by the observation that the shape of the absorption and fluorescence spectrum does not show any concentration dependence, which can be ascribed to the strong electrostatic interaction between the solute and solvent molecules in polar solvent.

The results of the quantum chemical calculations of Mihály Kállay, Wybren Jan Buma are in line with the experimentally recorded absorption and emission spectra. The considered isomers correspond to local minima both on the ground and on the excited-state potential energy surfaces (PESs). The relative energies of the ground and excited-state isomers are compiled in Table 7. All methods predict that for the ground state the amino-H isomer is more stable than the other tautomer by 30-60 kJ/mol. The calculations reveal that the S₁ state is dominated by the HOMO → LUMO configuration for both isomers. This transition results in a significant charge transfer from the pyridine ring in the direction of the nitro-group, as well as from the amino group (NH-Bu) to the ring. Excited-state relaxation does not alter the character of the excited state. For the S₁ state a reversal of the stability of the two isomers occurs; now the N-O-H isomer is found to be lower in energy by 10-20 kJ/mol. To obtain insight into the vibrational effects on the relative order of the first excited state of the two isomers, the zero-point energies (ZPEs) have been calculated in the case of the ground state using the harmonic frequencies. Since the effect of the ZPEs on the calculated energy differences is about 1 kJ/mol, it is irrelevant to the current study and can be ignored.
Table 7. Energy difference (kJ/mol) between the two tautomeric (N-O.....HN and N-O-H.....N) forms of 2-butylamino-6-methyl-4-nitropyridine N-oxide for ground and first excited state. \(^a\) Primed and unprimed labels refer to the N-O.....HN and N-O-H.....N species, respectively.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Ground state (E(S_0') - E(S_0)^a)</th>
<th>Excited state (E(S_1') - E(S_1)^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF/CIS</td>
<td>6-311++G**</td>
<td>32</td>
<td>-22</td>
</tr>
<tr>
<td>MP2</td>
<td>6-311++G**</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>(TD-)DFT</td>
<td>def-TZVP</td>
<td>54</td>
<td>-9</td>
</tr>
</tbody>
</table>

Table 8 reports the calculated vertical absorption and emission transition energies. The performance of the CIS method is rather poor, while the DFT transition energies are in excellent agreement with the experimental results. Comparison of the calculated and experimental vertical excitation energies strongly suggests that excitation takes place from the amino-H isomer, in agreement with the calculated stabilities of the two tautomeric forms in the ground state. The calculated and experimental fluorescence wavelengths reveal that emission occurs predominantly from the N-O-H isomer.
Table 8. Calculated transition wavelengths (nm) for vertical absorption and emission of the two tautomeric forms of 2-butylamino-6-methyl-4-nitropyridine N-oxide.

<table>
<thead>
<tr>
<th>Method</th>
<th>Basis</th>
<th>Absorption</th>
<th>Emission</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>N-O.....HN</td>
<td>N-O-H.....N</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S₀ → S₁⁺</td>
<td>S₀' → S₁⁺'*</td>
</tr>
<tr>
<td>CIS</td>
<td>6-311++G**</td>
<td>261</td>
<td>302</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>def-TZVP</td>
<td>428</td>
<td>511</td>
</tr>
<tr>
<td>Exp.</td>
<td>TZVP</td>
<td>402</td>
<td>450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>630</td>
</tr>
</tbody>
</table>

**Time-resolved experiments**

Figure 20 shows typical fluorescence transients detected at various emission wavelengths. When detecting at the blue side of the emission band, e.g., 510 nm, a fast decrease followed by a slow decay is observed, while detection at long wavelengths, e.g., 580 nm, shows the appearance of a corresponding fast rise. The curves can be well fitted with a bi-exponential function. The long component of ~150 ps is independent of the probing wavelength, and has a relative amplitude that is increasing towards longer detection wavelengths. This component can be well assigned to the lifetime of the equilibrated emissive state. Apart from the long component, the fits find a short component on the order of a few ps. An accurate determination of this component is more difficult because of the instrument response of ~16 ps. Results of the fits are summarized in Table 9. As a further attempt to determine the ultrafast dynamics, femtosecond transient absorption experiments have been performed.
Figure 20. Fluorescence decay curves at various wavelengths as measured by time-correlated single photon counting in acetonitrile.

<table>
<thead>
<tr>
<th>Emission wavelength (nm)</th>
<th>$\tau_1$ (ps)</th>
<th>$a_1$</th>
<th>$\tau_2$ (ps)</th>
<th>$a_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>5</td>
<td>89.1</td>
<td>149</td>
<td>10.9</td>
</tr>
<tr>
<td>530</td>
<td>7</td>
<td>66.5</td>
<td>151</td>
<td>33.5</td>
</tr>
<tr>
<td>580</td>
<td>3</td>
<td>-87.6</td>
<td>156</td>
<td>100</td>
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<tr>
<td>640</td>
<td>8</td>
<td>-19.3</td>
<td>157</td>
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</tr>
<tr>
<td>700</td>
<td>12</td>
<td>-19.1</td>
<td>150</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 9. Fits of the fluorescence transients of 2-butylamino-6-methyl-4-nitropyridine N-oxide dissolved in acetonitrile to a bi-exponential function $I(\lambda,t) = a_1(\lambda) e^{-t/\tau_1(\lambda)} + a_2(\lambda) e^{-t/\tau_2(\lambda)}$ convoluted with the instrument response. The sum of positive amplitudes is taken as 100.
Figure 21. Transient absorption spectra of 2-amino-6-methyl-4-nitropyridine N-oxide in acetonitrile obtained after excitation at 420 nm. Figure (a) shows spectra for short pump-probe delays: 0 ps (→), 0.4 ps (→), 0.5 ps (→), 0.6 ps (→), 1.0 ps (→), 2.2 ps (→), 6.2 ps (→); Figure (b) shows the spectra for longer delay times: 0 ps (→), 20 ps (→), 50 ps (→), 100 ps (→), 200 ps (→), 300 ps (→), 800 ps (→).
Femtosecond transient absorption spectra are shown in Figure 21. After excitation at 420 nm, two broad absorption bands around 400 nm and 650 nm emerge almost instantaneously (Figure 21a), accompanied by a bleaching around 420 nm. Subsequently, another absorption band around 530 nm appears, which rises with a time constant of ~0.6 ps. Simultaneously a broad stimulated emission band emerges between 650 and 800 nm that rises with the same time constant. After the initial spectral dynamics the whole spectrum decays (Figure 21b) at a rate matching the emissive lifetime of the excited state determined in the TC-SPC experiments (~150 ps). This picture becomes more clear when we look at individual transients, for example at 740 nm (inserts in Figure 21). The transient at 740 nm is composed of two components: an positive absorption signal with an ultrashort decay time below 100 fs as determined by fitting the transient, and a negative, stimulated emission signal that grows in with a time constant of ~0.6 ps (Figure 21a) and subsequently decays with ~150 ps (Figure 21b).

The presence of an absorption band centred around 650 nm with an ultra-short lifetime is at odds with the intramolecular charge transfer model that has been widely accepted for the parent molecule 4-nitropyridine N-oxide. Our quantum chemical calculations indicate that the S₁ state of the present amino-substituted derivative has significant charge transfer character, giving rise to a dipole moment in the excited state that is significantly different from that of the ground state. The change in dipole moment upon excitation would result in a solvent reorganization effect when the molecule is dissolved in a polar solvent such as acetonitrile, and would manifest itself in the time-resolved absorption spectrum as a dynamic Stokes shift. Our experiments show, in contrast, that the initially excited species evolves on an ultrafast timescale into another species with distinctly different absorption and emission characteristics. Following the results of the quantum chemical calculations, we attribute this species to the tautomer of the molecule. In this picture the absorption band centred around 650 nm is ascribed to excited-state absorption from the S₁ state of the amino-H isomer. Depopulation of this state by proton transfer leads to the population of the excited state of the N-O-H isomer.

The time-resolved spectra show that it takes about 0.6 ps for our molecular system in acetonitrile to reach its equilibrium in the excited state. Since the reorganization of acetonitrile is known to occur on the same time scale, we assign this process to the salvation dynamics of acetonitrile. The associated dynamic Stokes shift
was indeed observed in the picosecond fluorescence decay measurements, \textit{i.e.}, a fast fluorescence decay, limited by the instrument response, appears when detecting on the blue side of the emission band and a corresponding rise is observed when detecting at the red side of the emission band. A similar shift is, however, not directly visible in the femtosecond transient absorption experiments. The apparent lack of a dynamic Stokes shift in these experiments can be ascribed to the richness of the transient absorption spectrum, which comprises the excited state absorption, ground state bleaching, and stimulated emission of two species. The overlap of these bands obstruct the distinct appearance of a spectral shift. For example, the stimulated emission of the N-O-H isomer can only be observed between 650 and 800 nm due to the strong broad absorption band centred at 530 nm. From the picosecond fluorescence decay measurements we have established that the dynamics observed for detection wavelengths longer than 580 nm are very similar, \textit{i.e.}, no spectral shift is seen in this wavelength range.

We thus conclude that in a polar aprotic solvent photoexcitation of 2B6M leads to intramolecular charge redistribution and that the excited, charge-transferred molecules leave the Franck-Condon region almost exclusively via proton transfer in less than 100 fs. The highly polar excited state of the proton transferred species is subsequently subject to solvent reorganization, prior to relaxation to the ground state. The scheme of the dynamic processes is presented in Figure 22.
A final point worth noticing is that dissipative vibrational relaxation processes are not observed in the transient absorption spectrum. After photoexcitation molecules will experience vibrational energy relaxation to reach an equilibrium distribution, unless only the lowest vibrational levels are selectively excited, which is generally not the case in the condensed phase. During this process excess vibrational energy is transferred to the solvent and the molecule relaxes to the lowest vibrational levels, which is detected as a shift of the emission and/or absorption band. The absence of a spectral shift on the picosecond time scale for 2B6M in acetonitrile implies that many vibrational modes are involved in the relaxation process and/or that the relaxation process is too fast to follow, similar to what is observed for Coumarine 153. For the latter molecule vibrational excitation relaxation out of the higher energy modes was shown to be ultra-fast (~30 fs), and the effect of subsequent dissipative relaxation of
the thermalized vibrational energy on the time-resolved (sub-picosecond) fluorescence spectra negligible.

VI. Conclusion

In this work new photochemically active organic molecules and supramolecular complexes have been investigated by the purpose of finding new functionalities and evaluating existing ones for their possible application as components of photoactive molecular and supramolecular devices.

A major part of our work has targeted the study of calixarene based supramolecular assemblies, with the aim of investigating their possible applicability as photoabsorptive supramolecular sensor devices. The complexation properties of new chromogenic calix[4]arenes with aliphatic amines and alkali/alkali earth metal ions have been studied by UV/Vis spectroscopy. The structural features responsible for basic qualities, such as the stability of the supramolecular complex and selectivity of the host molecule have been investigated. These systems have been found to be effective in the selective binding of ions and the optical signalling of the complex formation.

The interactions between a calixarene host comprising dissociable protons, and an organic dye guest existing in a neutral base and in a protonated form, have been also studied on model systems obtained by dissolving Nile Blue base (\textit{NB}) and tetraundecylicalix[4]resorcinarene (\textit{RA}) in two apolar solvents, dichloromethane and toluene. Steady state absorption and fluorescence spectroscopy and fluorescence lifetime measurements were applied as experimental methods. We aimed to identify the supramolecular products and to determine the equilibrium constants for the reactions occurring in this model system may be helpful in the analysis of many related systems, where proton transfer between the host and the guest may take place. In addition, knowledge of the properties of the Nile Blue-calixresorcinarene complexes in apolar solvents may be interesting in relation to the applications of this dye in more complex apolar environments. This is the case when Nile Blue salts (and in particular, the salts of its lipophilised derivatives) are employed as indicator dyes in optical sensors with hydrophobic polymer matrices; or when they are applied in photodynamic therapy studies, as special photosensitizers which localize in the lysosome of tumor cells.
Another part of our studies with calixarene systems has focused on the the interaction of buckminsterfullerene (C_{60}) with calix[n]arene host molecules. Due to the wide absorption spectra in the visible range, C_{60} may serve as light collector component (antenna) in the buildup of photoactive supramolecular devices. Following the photoexcitation, a highly efficient deactivation path is the photoreduction of triplet excited C_{60} by phenol derivatives such as calixarenes. 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}.

Finally, we performed ultrafast time resolved experiments on 2-butylamino-6-methyl-4-nitropyridine N-oxide

By femtosecond transient absorption and picosecond time-resolved emission experiments, as well as quantum chemical calculations has elucidated the electronic and structural dynamic processes occurring after excitation of 2-butylamino-6-methyl-4-nitropyridine N-oxide in polar, aprotic solvents. In such solvents it has been concluded that the molecule is exclusively in one conformation. We have shown that upon excitation an intramolecular charge redistribution occurs that triggers proton transfer. This proton transfer process takes place on a time scale shorter than 100 fs. It is concluded that the excited state dynamical processes, such as solvation and vibrational cooling, occur in the proton transfer tautomer.

VII. Summary

New findings and scientific achievements:


1.1. It has been found that among the studied calixarene host molecules C_{Xb} shows the greatest complex forming ability with alkali/alkali earth metal ions and it is selective for Li^+, Ca^{2+} in polar solvents.

1.2. The equilibrium constants of the complex formation of the ligands C_{Xa,b,c} with different aliphatic amines in ethanol and DMSO has been determined. For primary
amines they are higher, than those obtained for dipropylamine and for triethylamine which has stronger basicity. This serves as a direct indication of the formation of supramolecular complexes.

1.3. The most significant effects controlling the stability of the amine-CXc complexes, are, the numbers of hydrogen atoms in the amino group and steric effects. The complex, therefore, is stabilized by the ionic indophenolate-ammonium cation interaction and by the hydrogen bonds with the oxygen donor atoms in the crown ether moiety. Consequently, primary amines can form the most stable complexes (three hydrogen bonds), while tertiary amines are hardly bound.

1.4. The complex stability is also found to be affected by steric factors as in the series of n-primary amines the complex stability decreases with the increasing chain length of the alkyl group. The highest stability constant was measured for t-butylamine, which might be due to an additional binding factor via Me-π interaction between the t-Bu group and the naphthalene ring.

1.5. In the case of the interaction of CXa and CXb with aliphatic amines the complex formation constants are substantially lower than those for CXc, indicating a much weaker binding.

1.6. With CXa and CXb the order of the Kc values are not strictly controlled by the order of the amines. These differences may be attributed to the structural differences between CXc and CXa,b, in respect of the indicator group and the binding site. The indophenol moieties of compounds CXa,b exist in a stable endo-quinoide tautomeric form, which means that the phenolic OH group is far from the binding site, whereas both OH groups of CXc are close to the cavity.


2.1. It has been established that the equilibrium composition of the NB - RA systems is controlled predominantly by three reactions:
(1) formation of the weakly bound complex NB\textbullet RA;  
(2) simultaneous formation of the tightly bound ionic species with zero net charge \( \text{NBH}^+\text{•RA}^- \) (\( \text{NBH}^+\text{•} = \) protonated form of NB, \( \text{RA}^- = \) monophenolate form of RA);  
(3) protonation of the latter product in a subsequent step yielding \( \text{NBH}^+\text{•RA} \).

2.2. The equilibrium constants for these reactions have been determined from the absorption spectra by an iterative procedure: the high value of the equilibrium constant for reaction (2) in toluene (9.8 \( \times \) 10\(^6\)) is in accordance with the strongly solvatophobic nature of cation \( \text{NBH}^+ \) in this solvent.

2.3. The fluorescence lifetime of neutral base NB increases whereas that of its protonated form, NB\text{H}^+, markedly decreases upon complexation. These effects have been interpreted in terms of intra- and intermolecular decay channels.

3. Photoinduced electron transfer in calixarene-C\textsubscript{60} exciplexes

3.1. We established that in benzonitrile triplet C\textsubscript{60} is readily quenched by \( p.\text{-tert.-butyl-calix[6]arene} \) (BCX\textsubscript{6}) in electron transfer forming C\textsubscript{60}\textsuperscript{−} radical anion with a yield of 0.45±0.07.

3.2. The rate constant of the electron transfer process was found to be strongly dependent on the solvent polarity:
- In CH\textsubscript{2}Cl\textsubscript{2}, excitation of the C\textsubscript{60}–BCX\textsubscript{6} 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\textsubscript{60}–BCX\textsubscript{6} complex. P.-tert.-butyl-calix[n]arenes consisting of 4 or 8 phenolic units (BCX\textsubscript{4}, BCX\textsubscript{8}) were unreactive with both the singlet and triplet excited C\textsubscript{60}.

3.3. The addition of bases (trimethylpyridine or pyridine) forming hydrogen bonded adducts with calixarenes accelerated significantly the electron transfer to triplet C\textsubscript{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.

3.4. 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.

4. Ultrafast dynamics of 2-butylamino-6-methyl-4-nitropyridine N-oxide (NPO)

We have unraveled the effects of the amino substituent in the ortho position on the excited state dynamics of NPO by studying the picosecond fluorescence kinetics and femtosecond transient absorption and by performing quantum chemical calculations.

4.4.1. The S\(_1\) state of the NPO molecule has significant charge transfer character and shows a large (~8000 cm\(^{-1}\)) static Stokes shift in acetonitrile.

4.4.2. Analysis of the experimental and the theoretical results leads to the conclusion that the intramolecular charge transfer upon photoexcitation triggers in polar, aprotic solvents an ultra-fast (<100 fs) intramolecular proton transfer between the amino and the N-O group in the excited state of the molecule. The electronically excited N-OH tautomer is subsequently subject to solvent relaxation and decays with a lifetime of ~150 ps to the ground state.
References

General references to section I.


J. L. Atwood, Comprehensive Supramolecular Chemistry, Pergamon, 1996.


List of references

1 V. Balzani and F. Scandola, Supramolecular Photochemistry, Ellis Horwood, Chichester, 1991
8 V. Balzani, Tetrahedron, 1992, 48, 10443
11 A. Slama-Schwok, M. Ottolenghi, D. Avnir, Nature 355, 240-242
16 J. W. Steed, J. L. Atwood, Supramolecular chemistry, John Wiley & Sons, 2000
17 M. Takagi and K. Ueno, Topics Curr. Chem. 1984, 121, 39
20 J.-P. Desvergne, F. Fages, H. Bouas-Laurent and P. Marsau, Pure Appl. Chem. 1992, 64, 1231
63 M. Inouye, K. Hashimoto and K. Isagawa, J. Am. Chem. Soc., 1994,
64 K. N. Koh, K. Araki, A. Ikeda, H. Otsuka and S. Shinkai, 
65 I. Garcia-Ochoa, M.-A. D. Lopez, M. H. Vinas, L. Santos, 
897.
8, 309.
67 Y. Zhang, T. H. Pham, M. S. Pena, R. A. Agbaria and I. M. Warner, 
6227.
Jpn.*, 1997, 70, 2131
1101.
73 A. Grofcsik, M. Kubinyi and W. J. Jones, *J. Mol. Struct.*, 1995, 348, 
197.
250, 261.
75 A. Grofcsik, M. Kubinyi, A. Ruzsinszky, T. Veszprémi and 
76 K. Kobayashi, Y. Asakawa, Y. Kikuchi, H. Toi and Y. Aoyama, 
77 R. Williams, PhD thesis, UVA, Amsterdam, 1996
78 D. Gust and T. A. Moore, Topics Curr. Chem. 1991, 159, 103;
79 D. Gust, T. A. Moore, A. L. Moore, A. N. Macpherson, A. Lopez, J. M.
Ma, L. J. Demanche, S.-C. Hung, D. K. Luttrull, S.-J. Lee and P. K. Kerrigan, J.
Am. Chem. Soc. 1993, 115, 11141;
82 S. V. Lymar, V. N. Parmon and K. I. Zamarasev, Topics Curr. Chem. 1991, 159, 1;
83 Photoinduced Electron Transfer, (Eds.: M. A. Fox and M. Chanon), Elsevier,
1978, 75, 1;
85 N. Sutin, J. Photochem. 1979, 10, 19
86 J. D. Petersen, Coord. Chem. Rev. 1985, 64, 261
89 Photoinduced Electron Transfer, Topics Curr. Chem. 1990, 156; 1990, 158; 1991,
159; 1992, 163; 1993, 168.
90 M. Calvin, Acc. Chem. Res. 1978, 11, 369
91 J. R. Norris, Jr., and D. Meisel, Photo-chemical Energy Conversion, Elsevier, New
York, 1989 (84-hez tartozik)
Svec, Pure Appl. Chem. 1992, 64, 1319;
93 M. R. Wasielewski, Chem. Rev. 1992, 92, 435;
94 J.-C. Chambron, A. Harriman, V. Heitz and J.-P. Sauvage, J. Am. Chem. Soc. 1993,
115, 6109;
95 J.-C. Chambron, S. Chardon-Noblat, A. Harriman, V. Heitz and J.-P. Sauvage,
96 J. L. Atwood, G. A. Koutsantonis and C. L. Raston, Nature,
1994, 368, 229.
1992, 111, 531.
99 A. Ikeda, Y. Suzuki, M. Yoshimura and S. Shinkai, Tetrahedron,
1998, 54, 2497.
100 6 (a) S. Shinkai and A. Ikeda, Gazz. Chim. Ital., 1997, 127, 657; (b)


110 A. M. Glass, Science 1984, 226, 657;


120 J.-M. Lehn in [100], Vol. 2, p. 215;
121 J.-M. Lehn in [109], p. 436.
135 Steve Welter, Phdthesis, UVA, Amsterdam, 2005.
1999, 103, 8834.


