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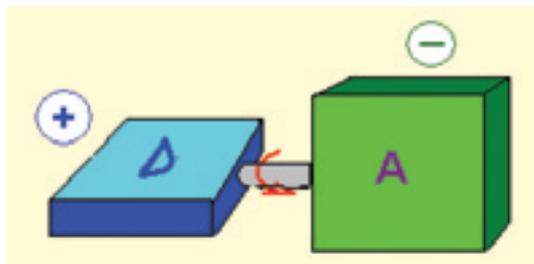
PHOTOCHEMISTRY

Highlighting Excited Molecules

From Photochemical Mechanisms to Application as Fluorescent Probes

The field of photochemistry covers all processes which involve chemical changes brought about by absorption of visible or ultraviolet radiation. The major difference between thermal and photochemical reactions originates from the difference in electron distribution in ground and photoexcited states of a molecule. This can lead to a complete alteration of the chemical behavior. – The dissipation of the excess energy of an excited species mainly occurs via radiative and nonradiative transitions. Fluorescence and phosphorescence are the two types of radiative transitions where an excited species passes from the excited state to the ground state with the emission of a photon. The photoexcited states that are involved in fluorescence decays usually have very short lifetimes ($< 10^{-6}$ s). Nonradiative transitions can be viewed as chemical reactions combining reaction paths on ground- and excited state surfaces. – Advanced steady-state and time-resolved spectroscopic methods in combination with systematic variations of properties of the surrounding medium, such as the polarity of the solvent or the temperature, can be applied as important tools to elucidate details of the mechanism of the relaxation of photoexcited states.

Fig. 2
TICT-systems can emit dual fluorescence: The system shown here is dimethylaminobenzonitrile (DMABN), the prototype TICT system [6]. The short wavelength band corresponds to the precursor excited state (E) reached directly by the absorption process, while the long wavelength band corresponds to emission from the excited product state (P) formed along the TICT reaction coordinate (twisting, electron transfer; in some cases, further degrees of freedom are necessary to circumnavigate the lower cone of a »conical intersection«, see Fig. 3).

One of the most important phenomena of excited states are charge transfer processes that can lead to the formation of partially or fully charge separated species. In addition, we can distinguish between several other types of excited state relaxations that involve the motion of molecular moieties. Depending on the type of this motion, they require a specific (reaction) volume in order that they can occur. The surrounding medium (vacuum, solvent, synthetic or biopolymer)

a flexible chain, can form an excited dimer by diffusive motion. They can be applied for probing of microviscous properties of fluid solvents and oils [2].

F-probes that are based on charge transfer in combination with twisting of molecular moieties can be divided into two subgroups: They can either respond to photoexcitation with structural flattening (MICT in Fig. 1) or with further twisting towards an ideal perpendicular excited-state structure (TICT in Fig. 1).

F-probes based on MICT are most useful in environments where high fluorescence quantum yields (i.e. high probe sensitivities) are required. They probe the micropolarity of the environment whereas TICT-probes are highly sensitive with respect to small changes of both viscosity and polarity, since substantial intramolecular twisting occurs that is connected with a huge change of the dipole moment. In both cases the local charge and dipole moment distribution of the surrounding medium is reflected in the spectral position of the fluorescence F-probes (Fig. 2 and 3). Moreover, TICT-related probes are very sensitive to the complexation of the D moiety with metal ions, which makes them powerful F-probes for environmental, medical and biological purposes. Using such probes, e.g. the intracellular Ca^{++} flow in single heart cells can be displayed in real time [3].

Fig. 1
A system consisting of connected donor D and acceptor A can relax towards a perpendicular conformation with full charge separation as shown (Twisted Intramolecular Charge Transfer = TICT) if certain energetic conditions are fulfilled (e.g. DMABN in Fig. 2). If these are not fulfilled (e.g. in biphenyl), the system relaxes to more planar conformations in the excited state, due to the increased mesomeric interaction between both subsystems. A certain degree of charge transfer is often involved as well (Mesomeric Intramolecular Charge Transfer = MICT). The typical TICT-probe starts from a planar or partially twisted ground state geometry, and on its way towards the perpendicular conformation in the excited state it creates a huge dipole moment due to a complete separation of charges between D and A. For reviews see [4, 5].

plays a crucial role and can significantly influence the degree of these intramolecular motions, i.e. the smaller the reaction volumes required the more easily these reactions can occur. This is the basis for employing such compounds as »fluorescent probes« (F-probes), in combination with their charge transfer properties. F-probes are useful to characterize the surrounding medium in terms of microviscous and micropolar properties.

DEWAR-type F-probes are connected with a relatively small folding (e.g. anthracene towards DEWAR-anthracene) and need only small reaction volumes enabling their ability to probe solid polymers like plexiglass (PMMA) [1]. F-probes that are based on the twisting motion of two molecular subgroups against each other generally require a larger reaction volume. The largest volumes are needed for EXCIMER-type F-probes, where two molecular subgroups, connected by
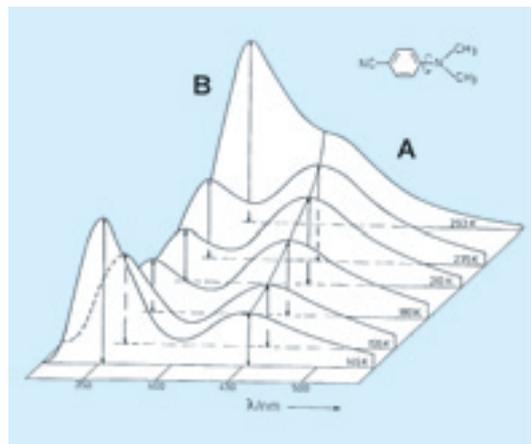
Fluorescent Probes based on Charge Transfer and Conformational Relaxation as Useful Microscopic Reporters

A) Unique Architecture of Dendrimers – Probing of a Gradient of Solvent Density

Dendrimers are perfectly branched synthetic macromolecules having numerous chain ends all emanating from a single core. These novel structures are envisioned to be used as model systems that will impact sensor technology, light-emitting diodes, photocata-
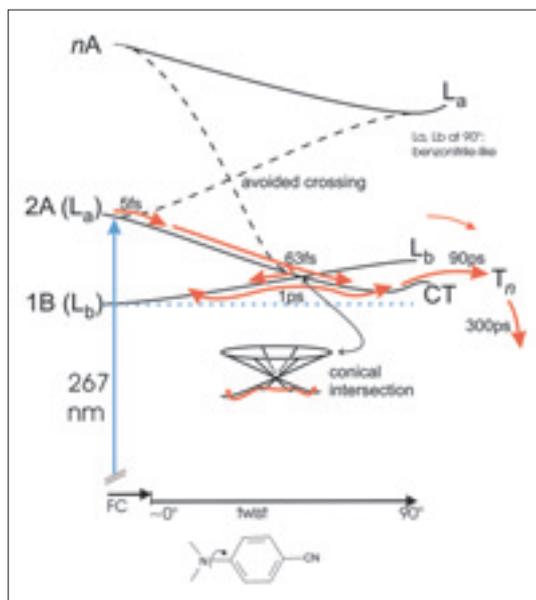
Schematic view of the conical intersection in DMABN and of the reaction sequence involved in a gas phase experiment [7]. By 267 nm excitation, the planar molecule E is excited to S_2 (L_a) hich reacts by ultrafast kinetics to the twisted TICT-conformation (P, CT state) and back to E(S_1, L_b). Femtosecond laser spectroscopy is used to follow such fast chemical motions. Transitions from top to bottom through the conical intersection cone (usually termed a photochemical funnel), as well as reaction paths on the lower surface circumventing this cone are modern views of many highly relevant primary photochemical processes, such as the vision process (see below).

Photochemie

Photochemische Reaktionen sind die Quelle allen Lebens auf der Erde: Mit Hilfe der Photosynthese wandeln die Pflanzen und einige Bakterien Sonnenlicht in chemische Energie um, die Basis unserer Nahrung ist. Auch der Sehprozess ist eine photochemische Reaktion. Man kann diese Reaktionen in verschiedene Klassen einteilen, von denen die Isomerisierungsreaktionen und die Elektron-Transfer-Reaktionen die bekanntesten sind. Bei Isomerisierungsreaktionen bewegen sich Molekülteile gegeneinander, was einen gewissen Platz erfordert. Dies kann dazu dienen, mit Hilfe mechanistischer Untersuchungen einen tieferen Einblick in den Reaktionsablauf zu gewinnen: Hier kommen Modellmoleküle zum Einsatz, sowie ultraschnelle spektroskopische Methoden. Einige Beispiele (TICT-Moleküle, fluoreszierende Umgebungssonden, mechanistische Studien zum Sehprozess) werden hier näher dargestellt.

lysts or light harvesting antennas in biomimetic photosynthetic systems. [for reviews see 8 and 9]

The goal of our long-term project is to synthesize spherical dendrimers with covalently linked dye molecules that can undergo photoinduced vectorial long-distance electron transfer between the centre and the periphery. The possible polarity gradient that results from the unique inner structure of dendrimers will be used to support the driving force for the charge transfer of suitable combinations of electron donor and acceptor (Fig. 4).

In this project pyrene based F-probes covalently linked to selected generations of dendrimers are applied to investigate the polarity gradient that can result from a generation specific solvent density in the interior of these spherical polymers (Fig. 5).

In a first approach, we have developed pyrene-based probes with acceptor substituted aryl groups to study their excited state properties. Strong solvatochromic effects indicate that a substantial charge transfer takes place after excitation and geometrical relaxation on the excited state surface. Multiple fluorescence signals have been observed for certain ranges of solvent polarity. They indicate how small structural variations of the basic pyrene chromophore by additional aryl groups and additional substituents introduce substantial changes of the fluorescence properties. The multiple fluorescence originates from changing contribution of different excited states involved (Fig. 6): In case of Ib, in highly polar solvents, the relaxation on the excited state surface occurs towards planarization via the formation of a MICT state, in contrast to the behaviour of photoexcited Ic where the pyrene and biphenyl moiety undergo further twisting (TICT formation) [10, 11].

As a result, spectral and kinetic parameters of the fluorescence of Ib and Ic dramatically change with the ability of the solvents to stabilize the excited states enabling these compounds to act as highly sensitive F-probes to detect the solvent density inside of dendritic structures (Fig. 6).

In the next step, dendrimers have been synthesized with incorporated aryl pyrenes as probes and volume dummies in those generations that do not carry the probes in order to maintain the same sterical and chemical microenvironment in each generation (Figs. 7 and 8).

The solvatochromic properties of the incorporated probes in comparison to the free probe molecules in
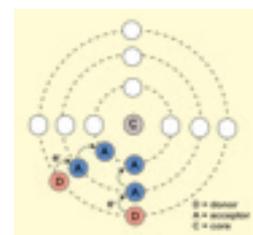

Fig. 4
The ET concept in dendrimers: Multiple photoinduced electron transfer between the incorporated electron donor and acceptor moieties can occur by selective excitation of the donor chromophore. In case of acceptor groups in more than one generation sequential electron transfer can be expected to occur. The driving force for the electron transfer is provided by a graduated acceptor strength or a generation specific stabilization of the resulting anion radical due to a gradient in the solvent density.
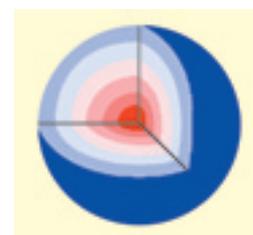

Fig. 5
A possible gradient in the solvent density inside a dendrimer is illustrated, the red colour indicates a high and the blue colour a low solvent density.
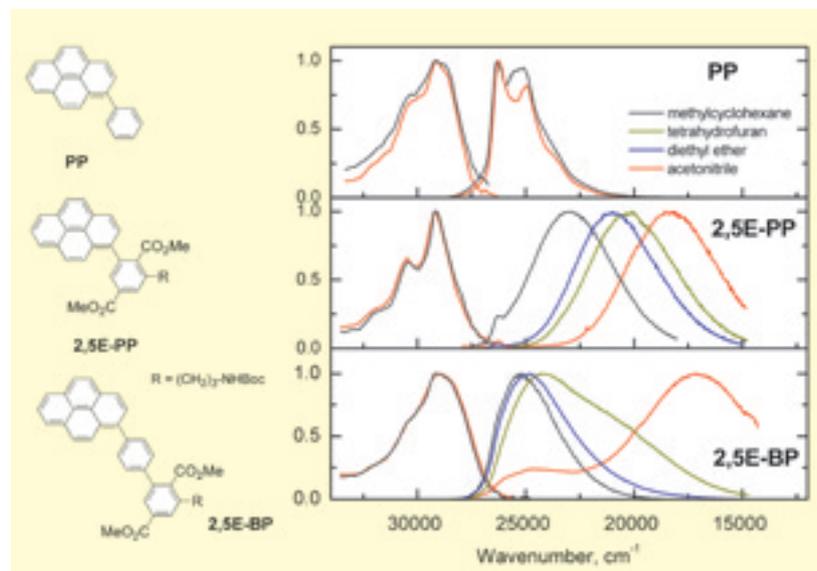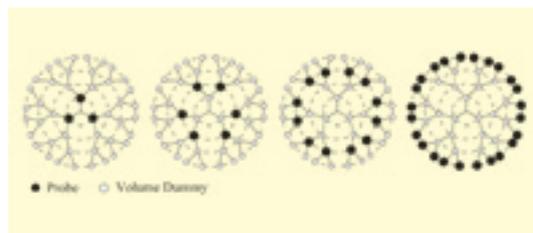
Fig. 7
The probe-dummy concept to detect generation-specific solvent effects. F-probes (solid circles) that can be selectively excited are incorporated in one specific generation and volume dummies (open circles) in all other generations to maintain the structure of the entire dendrimer.

solution and possible interchromophoric interactions in the dendrimers have been investigated. The fluorescence spectra of the dendrimers such as in Fig. 8 show a significant blue shift of their maxima compared to the spectra of the free samples indicating a lower solvent density inside the dendrimer or a limited geometrical relaxation of the incorporated probes.

B) The Primary Process of Vision and what we can Learn from Model Compounds and Fluorescent Probes
Our eyes contain a dye PRSB (Fig. 9) which reacts like a Chameleon: it changes its colour in response to the surrounding medium. This is the basis for the three different rhodopsin pigments which are contained in the cones of our retina: blue, green and red, and which are necessary for our colour vision.

Colour vision can therefore be studied along three different lines:

i) By using theoretical models which describe the effect of different charge distributions on the absorption spectrum and help to understand the observed colour changes and allow to predict new »artificial vision« molecules;
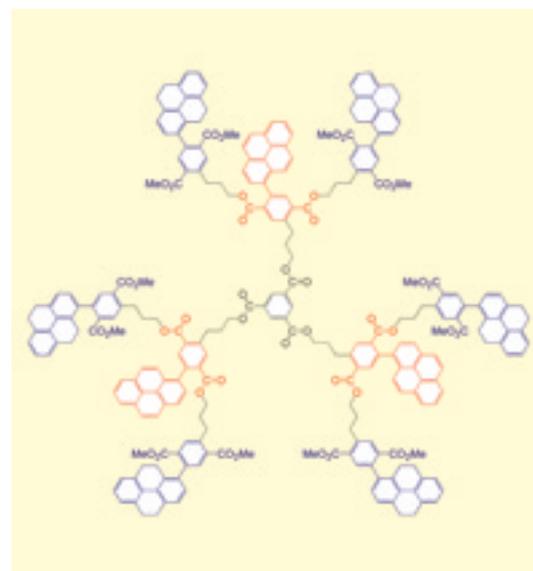
Fig. 8
Prototype of a dendrimer with incorporated F-probes (red) in the first and volume dummies (blue) in the second generation with dendrimer specific effects on the fluorescence properties of the probe molecule in comparison to the free probe in solution.

ii) By experimentally studying model compounds of PRSB which possess intrinsically different charge distributions;

iii) By trying to probe the electric field inside the proteins of the different colour visual cones directly by using F-probes.

Regarding points i) and ii), the »Polymethinic Theory« [13] is most suited for understanding and prediction. The strongest redshift in absorption is expected if the positive charge is evenly distributed, which is the case e.g. in symmetric cyanine dyes (Fig. 10). Therefore, the symmetric charge distribution is called the cyanine limit (CL). Recent theoretical advances [14, 15] indicate that not only PRSB can be understood by this model, but also many laser dyes like DCM and DCS (Fig. 11). At the same time, a relationship exists between the CL and the location of conical intersections which are important for the primary process of vision (twisting around bond 11–12) and excited-state photochemistry in general. Using selectively bridged model compounds, this relationship can be studied experimentally (see Figs. 11 and 12) [16, 17]: In DCS (situated in Fig 10 on the left-hand-side (b) of the CL), the resonance structure shown is the most relevant one for the ground state, with a double bond in the centre. In the excited state, bond orders reverse, hence the most
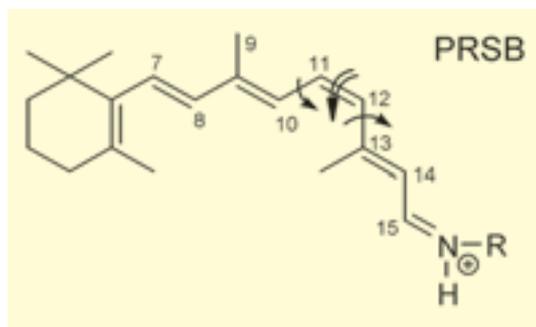
Fig. 9
Rods and the different colour cones of our eyes contain the same dye: Protonated Retinal Schiff Base (PRSB), but its colour (i.e. its absorption spectrum) can be different. Recent x-ray structural determinations of the rhodopsin protein of different colour cones indicate that the positive charge residing on PRSB is distributed in a different manner, more localized for the blue pigment, more extended for the red one. Thus, charge distribution and colour are intimately linked. The charge distribution in PRSB is generated by the surrounding protein: relatively small changes of the amino acid sequence generate different electrical fields around PRSB and thus determine its charge distribution. The primary photochemical reaction leads to bond twisting around 11-12, possibly supported by involving also the adjacent single bonds (so-called Hula-Twist mechanism [12]).

reactive bond leading to twisting is the central bond (this leads to trans-cis isomerization in both DCS and DCS-B24). In DPD, situated at the right-hand-side (c) of the CL, the central double bond and the adjacent single bonds do not behave as expected from the resonance structure shown: The photochemically most reactive bonds are the two »single« bonds (twisting and transition from S1 to S0 through the conical intersection (COI) in this case leads back to the starting material), whereas the double bond is »reluctant« to twist. The consequence: unbridged DPD (a close relative of the laser dye DASPMI) is completely photostable (every molecule undergoes the photoreaction, but no new product can be formed), and trans-cis isomerization around the »double« bond can only be observed if both »single« bonds are bridged as in DPD-B24 [16, 17].

Regarding point iii) of the above list of possible approaches, TICT-probes could be used for directly probing the electric field created by ions and dipoles of the protein matrix of different colour visual pigments. Especially useful would be dual fluorescent probes related to DMABN (Fig. 2), but these suffer from their short absorption wavelength which interferes with the absorption of the protein itself. Nevertheless, using such TICT probes in rhodopsin has led to valuable conclusions and opened the way to further development,
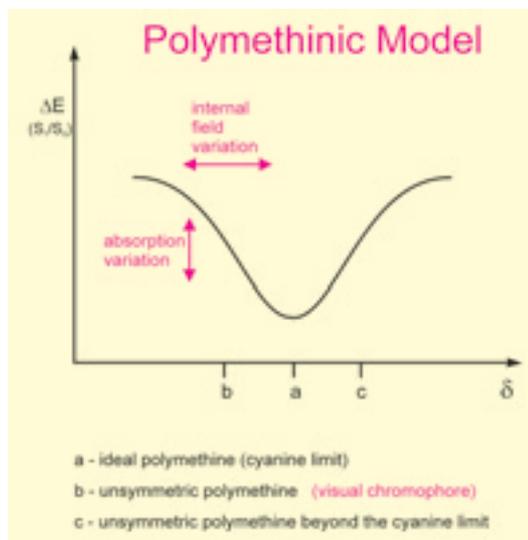

Polymethinic Model

a - ideal polymethine (cyanine limit)
b - unsymmetric polymethine (visual chromophore)
c - unsymmetric polymethine beyond the cyanine limit

DCS   DCS-B 24   DPD   DPD-B 24

in the direction of »vectorial fluorescent probes«, i.e. F-probes which can sense the direction of a charge or dipolar field in the environment [18, 19].

C) Developing Metal Ion Fluorescent Probes

Fig. 13 shows two examples of the principle of metal ion F-Probes [19]: Complexation of the dye with a suitable metal ion most easily occurs in the crown ether ring. The lone pair of the amino nitrogen of the ring is involved in this binding, and therefore the donor-acceptor character of the dye becomes weaker, i.e. it changes its position on the CL-axis in Fig. 10. This normally shifts both absorption and emission to the blue. In suitable cases, it also closes TICT-reaction channels. In this case, the dye shows strong »fluorescence enhancement«, i.e. it is dark (without fluorescence) in the absence of the metal ion and indicates its presence by strong fluorescence.

It would be highly desirable to develop ion-specific F-probes and even bifunctional ones: a bifunctional F-probe would possess two different binding sites (e.g. two crowns specifically binding to different ions) and would indicated the absence or presence of these ions by different colour and changes of the intensity. F-probes

Fig. 10
Schematic representation of the consequences of polymethinic theory: The smallest S_0–S_1 energy gap ΔE occurs for the compound with a symmetric charge distribution (cyanine limit CL). In the left- and the right-hand-side vicinity of the CL, small variations in the charge distribution asymmetry, induced by substituents (for model compounds) or by the protein matrix (for the vision process) cause strong changes in ΔE and thus the colour of the dye.
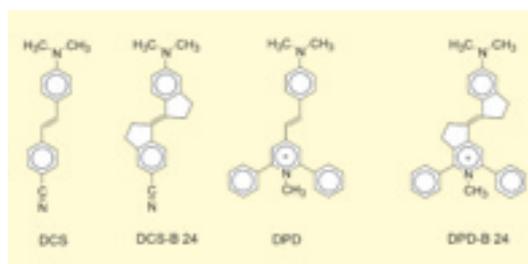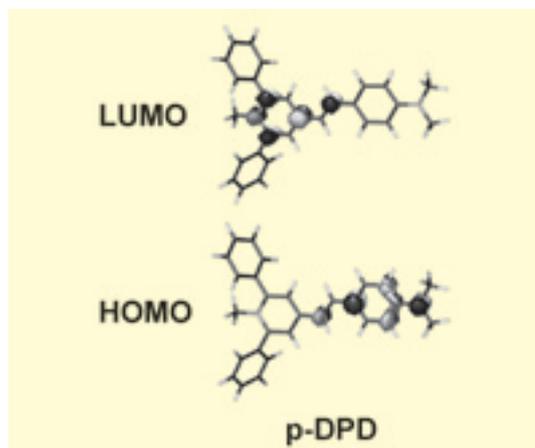
Fig. 11
Two closely related dye families, usable as model compounds for the vision process, which differ strongly in the way in which the pi-electrons are distributed in the ground state: In DCS, the acceptor unit (benzonitrile) is sufficiently weak such that HOMO and LUMO are weakly polarized: On excitation, only a partial charge separation occurs. For DPD, where the acceptor is the much stronger pyridinium group, HOMO and LUMO are strongly polarized (Fig. 12), and excitation leads to a much stronger shifting of electron density from D to A. Both theory and experiments related to the model compounds DCS and DPD indicate that these are situated at different sides of the CL.

Fig. 12

Frontier molecular orbitals of DPD. The highest molecular orbital (HOMO) is rather localized on the donor anilino unit, and the LUMO on the pyridinium ring. In the related stilbenoid compound DCS with a weaker acceptor, HOMO and LUMO are much less localized and overlap more strongly.

Fig. 13

If a fluorophore can complex to metal ions as in the two aza-crown-ether derivatives of DMAN shown here [20], the photochemical reaction properties are altered resulting in strong changes of the dual fluorescence.

with dual fluorescence would have the additional advantage of higher precision and insensitivity towards unwanted perturbations from other sources. Such F-probes could be used in environmental control for detecting and quantifying traces of heavy atoms
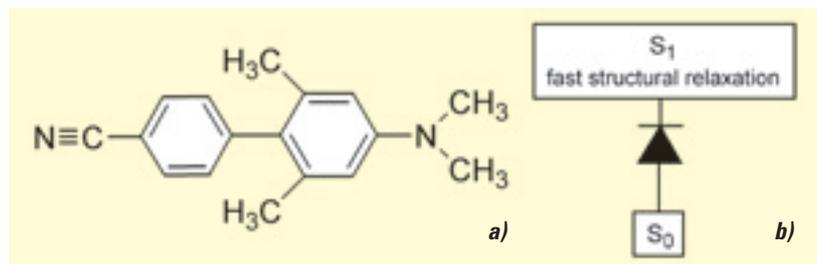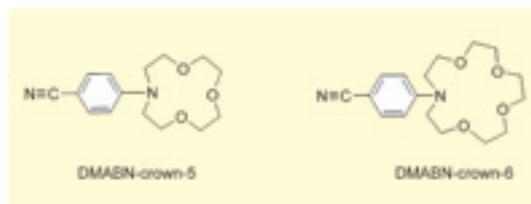

Fig. 14

The biphenyl derivative in a) acts like a molecular photodiode (b): Allowed (i.e. efficient) access from ground to excited state, but forbidden return from S_1 to S_0. The key for understanding is a structural relaxation in the excited state, leading from a more planar conformation (E, around 60° twist) to a highly twisted TICT conformation (P, around 90° twist with strongly enhanced dipole moment). In medium polar solvents, both E and P are populated and show bright fluorescence, and their equilibration can be shown by ps-methods [21]. It is expected that complexation to metal ions changes the properties of E and P in a different way.

(iron, mercury etc) in waste water. They could also be used in principle for visualizing not only the Calcium flow but also that of Sodium or Potassium in single living cells.

Presently, we try to develop such F-probes basing on the known dual fluorescent TICT-property of the biphenyl shown in Fig. 14.

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Coworkers in 2002/2003
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