

Charge Injection into Organic Semiconductors

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Introduction

The observation of efficient electroluminescence in organic semiconductors a decade ago gave new momentum to the field of organic optoelectronics. Organic light emitting diodes (OLEDs) are currently under intensive development in both academia and industry for applications in flat panel displays.¹ The first commercial product, a car stereo display, was introduced in the market three years ago by Pioneer. Last year, Philips opened an OLED pilot plant, while Motorola recently announced that it will begin introducing OLED displays in cell phones as early as next year. Today, almost every major consumer electronics company and a lot of smaller start-up companies in the United States and overseas have experimental programs in OLED development.

This renewed interest in organic semiconductors due to OLEDs has had beneficial effects in other organic-based devices too. Organic thin film transistors have recently reached performance similar to that of amorphous silicon transistors,² while organic solar cells are reaching energy conversion efficiencies exceeding 1%, a five orders of magnitude increase since the early 70s.³ Many believe that these advances are signaling the beginning of the era of "plastic electronics", an era where inexpensive, organic-based electronic components will become available. IBM is currently running a TV commercial that shows a futuristic supermarket in which electronic tags placed on every item ensure completely automated checkout. Inexpensive electronic components will change the face of our world as we know it.

Essential for the operation of all organic optoelectronic devices is the process of charge injection (or extraction) from metal electrodes into the organic semiconductor. In OLEDs, the efficiency of charge injection is the single most important factor in determining the efficiency.⁴ Efficient charge injection is also very important for good performance in organic thin film transistors.² Despite the importance of charge injection at the metal/organic interface, we know very little about the fundamentals of this process. This is mainly because of two reasons. First, knowledge from inorganic semiconductors cannot be directly translated to the case of organic materials due to the different nature of charge transport in the latter. Second, in the majority of device studies, the process of charge injection cannot be easily separated from the process of charge transport. In addition to the technological importance, understanding the process of charge injection is a fundamental problem that is too beautiful to ignore.

Measuring Charge Injection

As with traditional semiconductors, a metal/organic contact can be Ohmic or current-limiting. In the former case the contact supplies adequate current to satisfy the demands of the organic layer, while in the latter it creates a bottleneck in the current flow. A figure-of-merit is the injection efficiency η :

$$\eta = J_{\text{INJ}}/J_{\text{SCL}} \quad (1)$$

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From the Executive Director

D. C. Neckers, Executive Director, Center for Photochemical Sciences, Bowling Green State University

We're about to hold the 15th Annual Advisory Board meeting of the Center for Photochemical Sciences. For the first time we have invited our alumni to the meeting. At last count at least 10 will be joining us. This will be one week after I've been in Moscow to accept an Honorary UNESCO Professorship from Mendeleev University. (See article on page 6.) And it is almost to the day ten years after the time that then University President Paul Olscamp invited me to join him "on a trip to Russia."

Nothing has satisfied me more than being part of the changing face of international relationships during the last part of the 20th century. Interestingly, more of our alumni did their undergraduate education in formerly communist countries than in the US, Canada, Japan or Europe. Because our Ph.D. program was new in 1989, we opened our doors to them with highly profitable consequences for them and for our Center. We didn't plan it or design it to happen this way. It just did. All we were doing was working with our students, one by one—Natasha Tarasova and her colleagues at Mendeleev and my colleagues and I at the Center for Photochemical Sciences. By doing so we have been at the forefront of the newly emerging associations, friendships, alliances, and partnerships between the individuals and groups in the former Soviet states and the US. We did what teachers anywhere try to do—give their students opportunities to succeed, according to their abilities, at the highest levels in their professions.

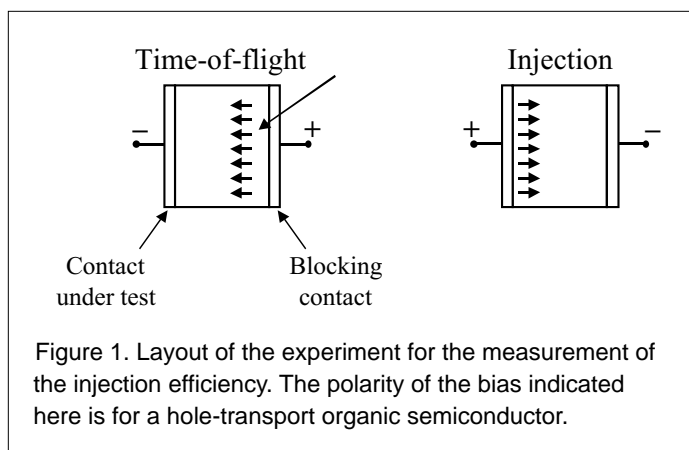
Our scientific worlds have undergone extraordinary change in the last decade. Email has replaced the letter and the phone call. Everything we now get is on-line where it's cheaper to store, and easier for students to access—*Chemical Abstracts*, *Journal of the American Chemical Society*, *Tetrahedron Letters*, and *Journal of Physical Chemistry*. As fuel prices rise, can one anticipate internet meetings to replace international travel, miserably crowded planes and far too expensive center city hotels?

We're a long way from being of one world, but one has to feel that the changes of the last decade have done a great deal to bring us closer to that. I'm looking forward, very much, to being named Honorary UNESCO Professor at Mendeleev. For the memories of a prior day, and for the changes that I've seen in my lifetime in science, it is an appointment I shall forever cherish.

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where J_{INJ} is the density of the net current injected by the contact and J_{SCL} is the space charge limited current density. For the case of trap-free materials (which we know how to synthesize thanks to advances in electrophotography⁵), J_{SCL} is given by the Mott-Gurney law:⁶

$$J_{\text{SCL}} = (9/8) \cdot \epsilon \cdot \epsilon_0 \cdot \mu \cdot V^2 / L^3 \quad (2)$$

where ϵ_0 is its dielectric constant, μ is the charge carrier mobility, assumed here to be field independent, V is the applied voltage and L is the thickness. By definition, $\eta=1$ for an Ohmic contact and $\eta < 1$ for a limiting contact.

The injection efficiency can be measured with a technique developed by Abkowitz et al.⁷ A variation of this

technique, which is appropriate for monopolar materials (where only one of the carriers is mobile), is shown in Figure 1. The polarity of the applied bias in the figure is appropriate for a hole-transport material. First, the mobility of the carriers in the organic is measured with a time-of-flight experiment⁵ and the space charge limited current is calculated according to eq 2. Second, the polarity of the applied bias is reversed and the current injected from the contact under test is directly measured.

For the time-of-flight experiment, a non-injecting (“blocking”) contact ensures a negligible dark current. A strongly absorbed pulse of light excites a thin sheet of carriers inside the organic, just underneath the blocking contact. The transient photocurrent is measured as this sheet of carriers drifts towards the opposite electrode. The photocurrent drops to zero as soon as the carriers arrive at the opposite electrode. The mobility is calculated from the time it takes the carriers to transit the sample.

The injection efficiency at the metal/organic interface is a complex function of many parameters. The interface energetics play an important role, as carriers might have to overcome an energy barrier to be injected into the organic. The composition and the morphology at the interface play an important role too, as they can have an effect on the interface energetics. Systematic studies that carefully isolate and measure the influence of each parameter are very important for understanding the injection process. Generally, organic materials form well-defined contacts: A variety of studies find that the energy barrier at the metal/organic interface scales with the difference of the appropriate energy levels of the metal and the organic,⁸⁻¹² indicating the absence of energy level pinning. This is reflected in the process of charge injection: Recent measurements of the hole injection efficiency in an organic semiconductor show that η increases with the work function of the injecting electrode.⁷

In addition to forming well defined interfaces, organic semiconductors offer unique degrees of freedom that can be used to probe the fundamentals of the injection process. Consider, for example, tetraphenylene diamine doped polycarbonate (PC:TPD), which is one of the most well studied organic semiconductors. The mobile species is holes, which move by hopping among TPD molecules. By varying the relative concentration of TPD into PC, one can change the hole mobility by several orders of magnitude without disturbing the interface energetics. We have used this degree of freedom to explore the dependence of injection on mobility. As an injecting electrode we used Indium Tin Oxide (ITO), which is commonly used in OLEDs.

Experimental results are shown in Figure 2. The injection efficiency was measured at a constant electric field in six samples with a TPD concentration ranging from 30 to 100%. The mobility is varied for three orders of magnitude, yet the injection efficiency remains constant at about 3%. Therefore, ITO forms a current limiting contact with PC:TPD, regardless of the mobility.

The above results may appear surprising at first. One might expect that the number of carriers that “boil-over” from the contact into the organic per unit time is solely determined by the energy barrier at the interface and it is therefore fixed. If the bulk is slow (low mobility), these carriers will be enough to sustain a space charge limited current. As the bulk gets faster, the injection efficiency should drop. The fact that η is independent of mobility means that the injected current (J_{INJ}) depends on the transport properties of the organic. An explanation for this behavior is given below.

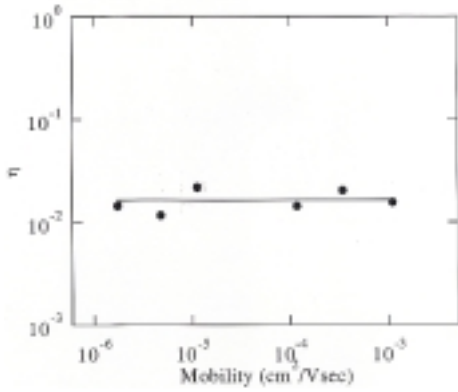


Figure 2. Injection efficiency of the ITO/PC:TPD contact as a function of mobility in PC:TPD. Each data point corresponds to a different sample, with a different concentration of TPD. The solid line is a guide to the eye.

....And a Bit of Theory

Extending existing injection models developed for crystalline materials to treat injection at the metal organic interface is not straightforward. This is because charge transport in organic semiconductors takes place not by free propagation in extended states but rather by hopping between localized states. The recent interest in metal/organic interfaces has prompted the development of a variety of new models, which are reviewed in reference 1. Here we outline the features of a simple model that predicts a mobility dependent injection.

Since mobilities are low in organic materials, it is to be expected that surface recombination of injected carriers will play a very important role in determining the current at the interface.¹³ The net injected current density J_{INJ} will be equal to:

$$J_{INJ} = J_{MO} - J_{OM} \quad (3)$$

where J_{MO} is the current density injected from the metal to the organic and J_{OM} is the backflow (recombination) current density.

Scott and Malliaras¹⁴ developed a simple model based on the premise that surface recombination at the metal/organic is a field-enhanced diffusion process, entirely analogous to Langevin bimolecular recombination in amorphous semiconductors. This allows for a straightforward calculation of the surface recombination current density, J_{OM} , which, for zero field, is found to be equal to:

$$J_{OM} = 16 \cdot \pi \cdot \epsilon \cdot \epsilon_0 \cdot (kT)^2 \cdot \mu \cdot n_0 / e^2 \quad (4)$$

where μ is the mobility and n_0 is the charge density at the interface. Using detailed balance ($J_{MO} = J_{OM}$ at zero field), J_{MO} is equal to:

$$J_{MO} = 16 \cdot \pi \cdot \epsilon \cdot \epsilon_0 \cdot (kT)^2 \cdot \mu \cdot N_0 \cdot \exp(-\phi_B / kT) / e^2 \quad (5)$$

where N_0 is the density of states in the organic and ϕ_B is the Schottky energy barrier. Note that the above equation can be rewritten in terms of an effective Richardson constant, which, for typical parameters for the organic, is four orders of magnitude smaller than the free electron value.¹⁴

The above equations are for the zero field case. Taking the field dependence of surface recombination and barrier lowering into account, we can calculate the net injected current density:

$$J_{INJ} = 4 \cdot \psi^2 \cdot N_0 \cdot e \cdot \mu \cdot E \cdot \exp(-\phi_B / kT) \cdot \exp(f^{1/2}) \quad (6)$$

where ψ is a slowly varying function of electric field and the exponential in the square root of electric field, $f = e^3 \cdot E / (4 \cdot \pi \cdot \epsilon \cdot \epsilon_0 \cdot (kT)^2)$, represents the usual Schottky barrier lowering effect. Here the mobility is assumed to be independent of the electric field. The three currents are plotted in Figure 3 for $\phi_B = 0.55$ eV. It can be seen that J_{MO} and J_{OM} are of comparable magnitude, indicating that surface recombination does indeed play a major role in determining the net injected current.

The model gives a rather good prediction for the electric field dependence of η . In Figure 4, experimental data for the sample with 60% TPD in PC are compared to calculated values for barrier heights of 0.50 and 0.55 eV. The model reproduces the dip and the subsequent increase of η with electric field. Moreover, the predicted barrier height is within the expected range.¹⁵ The actual electric field dependence of η is a bit steeper, probably due to the electric field dependence of the mobility in PC:TPD.

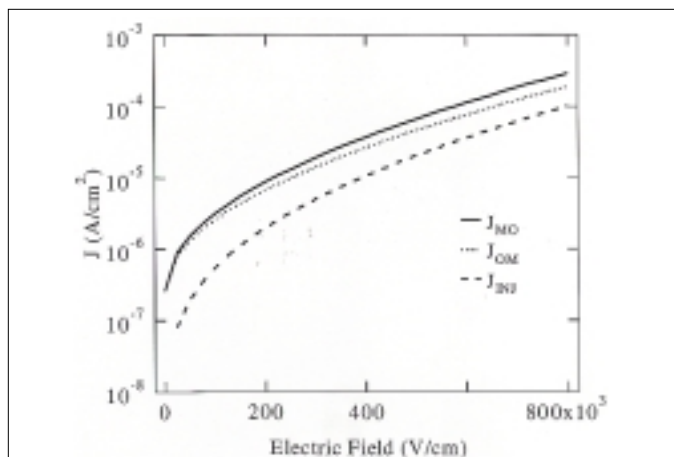


Figure 3. Electric field dependence of the currents at the metal/organic interface for $\mu=5 \cdot 10^{-5} \text{ cm}^2/\text{V}\cdot\text{sec}$ and $\phi_B=0.55 \text{ eV}$.

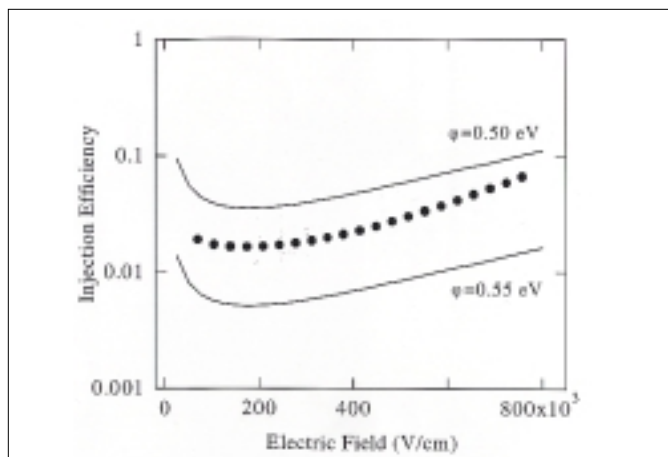


Figure 4. Electric field dependence of the injection efficiency of the ITO/PC:TPD contact for a sample containing 60% TPD in PC. The solid lines are the predictions of the theory for $\phi_B=0.50$ and 0.55 eV .

Conclusions

The field of organic optoelectronics is currently enjoying a golden era. Organic light emitting diodes are on the threshold of commercialization, while other organic-based devices are being developed at an incredible pace. All these devices rely on efficient charge injection from metal electrodes. At this point, however, our fundamental understanding of the charge injection process is very limited. Understanding this process will allow us to optimize metal/organic interfaces and increase device performance.

Organic semiconductors have undergone several years of development for applications in electrophotography and are now available with tailored, well-defined charge transport properties. An important lesson we learned from all these years of development is that organic semiconductors are **model systems** for the study of a wide variety of charge transport phenomena. We can and we should capitalize on this knowledge to explore the properties of metal/organic interfaces. There is a lot of beautiful science to be done!

Acknowledgements

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About the Authors

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D. C. Neckers Awarded Honorary Professorship

On October 11, 2000, Dr. D. C. Neckers, Executive Director of the Center for Photochemical Sciences, received an honorary professorship in the UNESCO Associated Center of Chemical Science and Education at Mendeleev University of Chemical Technology of Russia. The Center at Mendeleev was organized four years ago and is a part of an international network of UNESCO associated centers with locations in Great Britain, France, Poland, the Czech Republic, South Africa, Kenya, Estonia, and Belorussia. The purpose of the network is to innovate chemical education in the world through new means and curricula developments, to improve the public appreciation of science (chemistry, in particular), and increase the involvement of educators in sustainable development worldwide.

Dr. Neckers was awarded the professorship in recognition of his outstanding contributions to the development of the United States-Russian cooperation in university level chemical education. Prof. Natalia Tarasova, Chair of the Department for the Problems of Sustainable Development, stated, "In these difficult times for Russian science Dr. Neckers saved several dozens of gifted students for the sake of global development of science by admitting them to the Ph.D. program at Bowling Green State University thus allowing them opportunities they never would have had in Russia."

Neckers was recognized at the International Conference "Chemical Education and Sustainable Development" where he gave a plenary talk on "Globalization and University Level Chemical Education". The conference was organized under the auspices of IUPAC, UNESCO, Russian Academy of Sciences, Russian Chemical Society, Ministry for Industry, Science and Technology of Russia, Ministry for Education of Russia, and Mendeleev University of Chemical Technology of Russia. About 500 educators, representatives of UNESCO Associated Centers worldwide among them, attended.

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Photochemical and Photophysical Processes in the Design of Holographic Recording Materials

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Introduction

Any light-induced change in a material has the potential to provide for optical recording of patterns. Ultimately, the photoinduced process must produce a change in either the material's absorbance, refractive index, or light scattering properties. If the changes can be spatially localized in the material at the micrometer scale, the process is suitable for holographic recording.¹ This article will catalog most of the primary and secondary photoinduced processes that have been used for holographic recording. Some of the ways that the photoinduced processes impact recording characteristics will be illustrated. First, however, an introduction to holographic recording will be provided.

A hologram is a faithful recording of an "object" beam (which may or may not carry an image) such that the object beam can be restored from the hologram by proper illumination. Figure 1 illustrates the recording process: the object beam and a plain reference beam, both coherent and from the same laser, are directed onto a recording material. The two beams interfere constructively and destructively, such that some regions in the material are brightly illuminated while others are dark, giving an interference pattern. Through photochemical and/or photophysical processes, the absorbance and/or refractive index of the bright regions is altered (sometimes requiring post-exposure developing steps), and the hologram is recorded. When the hologram is illuminated with the reference beam alone, the object beam is fully or partially restored through diffraction. To an observer, a holographic image looks three-dimensional because the restored object beam appears just as if it had come from the object, not from a two-dimensional projection of the object like one obtains in a photographic image.

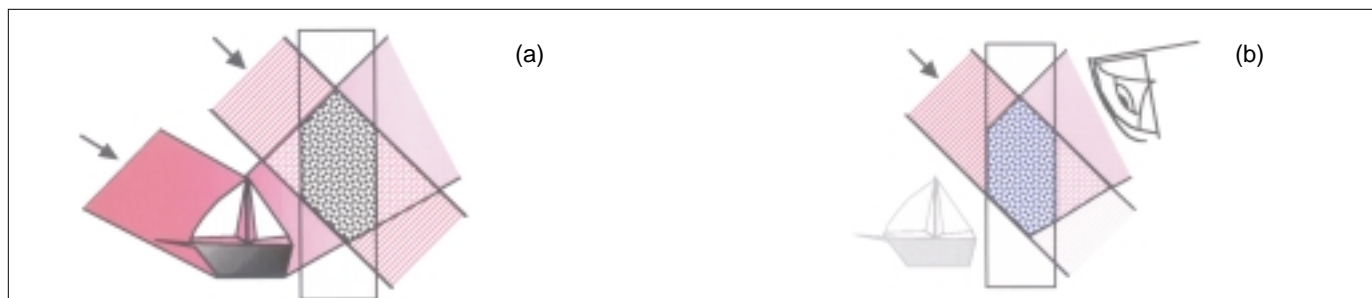


Figure 1. A hologram is written (a) by overlapping an object and a reference beam at a film of recording media, resulting in micron-sized bright and dark regions within the film, represented in white and black. Through photoinduced chemical and physical processes, the intensity pattern is recorded as a refractive index and/or absorbance pattern, represented in white and blue in (b). The hologram is read by diffraction of the reference beam, causing the full or partial restoration of the object beam. To an observer, the three-dimensional object appears to be in its original position.

Simple but very useful holograms may also be obtained when the object beam does not carry an image. If the object and reference beams are both collimated plane waves, one obtains a grating interference pattern with a sinusoidally varying intensity (Figure 2). The characteristics of the grating (spacing and orientation) can be easily controlled by adjusting the angles of incidence. Such gratings can be used as optical elements to diffract laser beams. Holographic optical elements that perform other functions, such as focusing or defocusing a diffracted beam, can also be made by using an appropriate object beam in the recording step (Figure 3).

As noted, holographic recording materials can rely on amplitude effects (absorbance or scattering), phase effects (refractive index), or a combination. Phase effects are generally preferable, since much higher diffraction efficiencies (percentage of light that the hologram diffracts) are possible, even up to 100%. A pure amplitude hologram can be 7% efficient at best.² Also, holograms that rely on absorbance are more prone to undergo photodegradation.

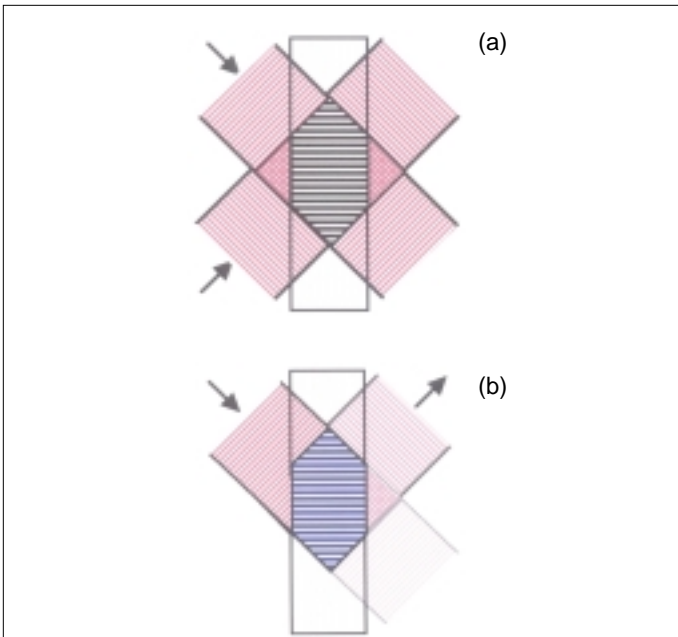


Figure 2. Illumination of a film with intersecting laser beams (a) results in a sinusoidal intensity grating, represented in white and black. The resulting refractive index and/or absorbance grating, represented in white and blue (b), can then diffract all or part of one of the writing beams into the former path of the other.

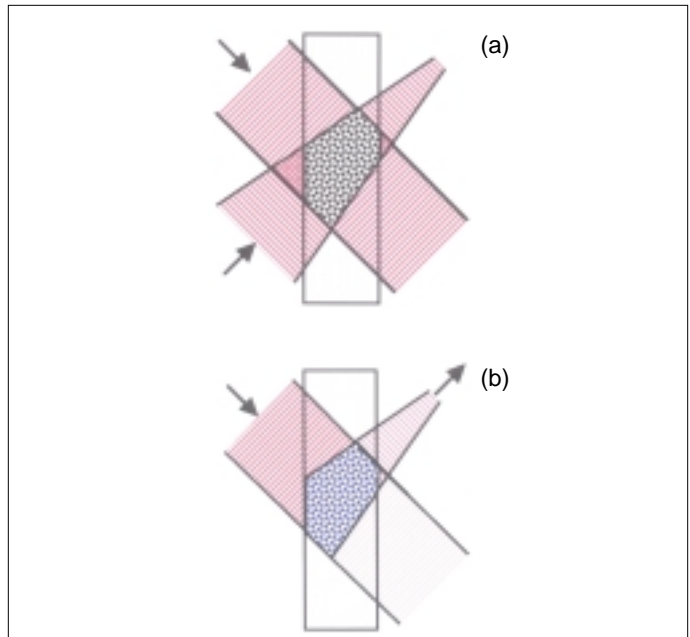


Figure 3. Holographic optical elements that focus light can be written (a) and read (b) in analogy to simple gratings. (The interference pattern, no longer a grating, is not represented accurately in the figure.)

Even though several types of recording media are available for holography, and a great many more candidate materials have been reported in the literature, there is a great need for media that offer new and better properties for holographic recording. While progress in holographic processing and storage of computer data, for example, has and continues to present many types of hurdles, the rate-limiting hurdles have generally related to material capabilities.³ This article takes a look at available and reported recording media from a perspective somewhat different than the usual one based upon material capabilities, examining instead the primary and secondary light-induced events that lead to recording. From this perspective, one can gain insight into which processes offer the best prospects for further advances in different capabilities.

Catalog of Photoinduced Physical Processes

The primary and secondary processes that account for recording in the vast majority of holographic media are depicted in Figure 4. The first thing a photochemist might note about this figure is that photochemistry seems to

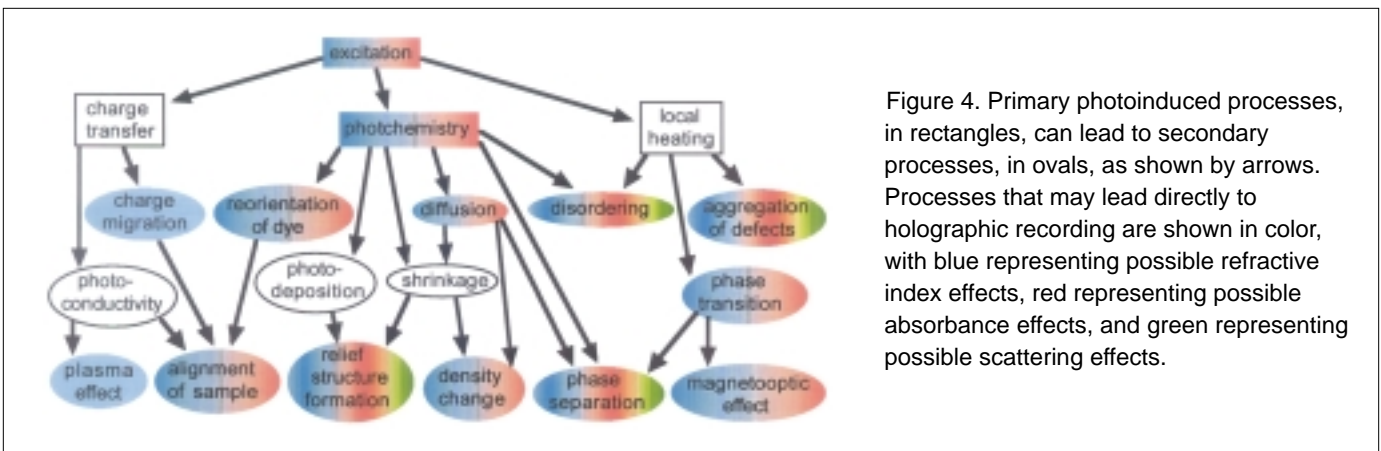


Figure 4. Primary photoinduced processes, in rectangles, can lead to secondary processes, in ovals, as shown by arrows. Processes that may lead directly to holographic recording are shown in color, with blue representing possible refractive index effects, red representing possible absorbance effects, and green representing possible scattering effects.

represent a relatively small portion of the figure. Actually, many types of photochemistry are lumped together here, and this category will be dissected in the next section. However, it is true that many physical processes can and do lead to holographic recording. Indeed, some of the most promising strategies for reversible recording make use of photoprocesses that produce no chemical changes in the recording medium, though reversible photochemistry does play an important role in many of these. Note also that charge transfer, a primary photochemical process, is considered separately here due to its potentially non-localized nature and its ability to cause several types of secondary physical effects.

Photochemistry, taken generally as conversion of reactants to products, can have multiple direct and indirect effects on the optical properties of a material. Obviously, reactants and products can have different absorbances and refractive indices, leading to direct effects. Photochemistry can also lead to shrinkage, as usually happens with polymerization, leading to changes in density and therefore optical properties. Shrinkage can also lead to surface relief structures.⁴ Photoinduced disordering of an ordered phase can also occur if the reactants and products have different shapes.⁵ When photochemistry occurs in one region but not in a neighboring region, the resulting concentration gradients lead to diffusion, which can then lead to other effects. These include density variations⁶ (with or without shrinkage) and phase separation.⁷ Diffusion can also serve to reduce or eliminate the differences between regions, leading to a “washing out” of the hologram. (This process has been used to measure diffusion constants.⁸) Photochemistry can also lead to photodeposition of surface relief structures.⁹

The first primary photophysical process that should be mentioned is excitation, since it leads to all other primary and secondary processes in the figure. It is listed separately, however, because an excited state indeed has a different absorbance and refractive index than the ground state, leading to recording, albeit transient. Some recording strategies depend on secondary absorption by excited states.¹⁰

Local heating in the region of the chromophore through internal conversion and other processes has been used in many recording strategies. A common secondary effect of local heating is the introduction of disorder, which can be especially pronounced if the material undergoes a phase transition.¹¹ The refractive index of ordered and disordered phases is typically very different. If the material is highly viscous, such as a polymer below its glass transition temperature, then the photoinduced disorder and the hologram can be permanent with optional erasing by annealing. In some materials, particularly inorganic crystals, local heating can lead to a migration and aggregation of defects, and this has also served as the basis for holographic recording.¹² In magnetooptic recording, local heating above the Curie point allows a change of the ferromagnetic alignment upon cooling through the influence of an external magnetic field. Though commercial magnetooptic devices use bit storage, holographic recording has been demonstrated.¹³ Local heating is the basis for many holographic recording media that are sensitive in the infrared.¹⁴

Just as light can cause disorder, it can cause order as well. Photosensitive reorientation of chromophores, most often azobenzene dyes, has been proposed to occur through *trans-cis-trans* isomerization cycles.¹⁵ The selectivity comes from the fact that the dye's transition dipole moment lies along one axis, and light that is polarized perpendicular to this axis is not absorbed. Therefore, each molecule will absorb the polarized light until, through photoisomerization, it becomes rotated into an orientation that no longer absorbs. Photosensitive reorientation is generally used in media that will amplify the orientation effects, such as liquid crystalline polymers¹⁵ or amorphous oligomers or polymers.¹⁶ The director of a dye-containing liquid crystal can thus be rotated, causing a very large change in refractive index. In dye-containing amorphous polymers, the reorientation caused by polarized light can lead to ordered regions in the initially disordered material.¹⁶ Chiral chromophores that undergo photoisomerization have also been shown to serve as “chiroptical switches” for the alignment of cholesteric liquid crystals and polymers.¹⁷

Charge transfer can lead to a number of physical effects useful for recording. In some materials, photoinduced charge transfer leads to photoconductivity, which can directly affect refractive index through the plasma effect.¹⁸ In the presence of an applied electric field, photoconductivity will cause a significant change in the local fields, which in turn can cause alignment changes in an electrooptic component such as a liquid crystalline material.¹⁹ Migration of charges with or without an applied field also leads to local field changes through the formation of a space charge field. If the material contains a liquid crystal or other electrooptic component, the refractive index will be affected differently in the different regions. The migration of charges through the material can itself have aligning or disordering effects, apart from the space charge field effects. These various mechanisms related to charge migration can all be put under the heading of photorefractivity, an area of much recent work.²⁰ The use of photoconductive substrate layers has also found extensive use, including in commercial thermoplastic media²¹ and in switchable liquid crystalline media.²²

Catalog of Photochemical Processes

Since reactants and photoproducts generally have different optical properties, any photochemical reaction is potentially useable for recording. Especially useful for reversible holograms are photochromic reactions, allowing photocontrol over the reaction in both directions.²³ However, the sensitivity of a recording material based on molecular property effects that require one or more photons for each molecular change will necessarily be low. Therefore, many photochemical recording strategies couple the chemistry with one or more of the physical effects noted above, serving to amplify the molecular effects. In some cases, secondary chemical processes provide amplification. The most common photochemical reactions used in holographic imaging are shown in Table 1.

Table 1. Photochemical Processes for Holographic Recording

Photoprocess	Holographic Media
Charge transfer	Photorefractives Silver halide Photochromic semiconductor Thermoplastics
Polymerization and crosslinking	Photopolymers Switchable liquid crystalline Dichromated gelatin Photoresists (negative)
Isomerization	Photochromics Azobenzene alignment Chiroptical switches Bacteriorhodopsin
Cycloaddition	Cinnamates
Depolymerization	Photoresists (positive)

explains why so many recording strategies are based upon photopolymerization.²⁶ Polymerization is also popular because it can also lead to many different physical amplification effects, including diffusion, shrinkage, phase separation, and disordering. Furthermore, the product is a stable solid with usually excellent optical properties. Photopolymer materials like those available from DuPont rely principally upon diffusion for their refractive index changes.²⁷ As polymerization occurs, diffusion of monomer occurs from the dark regions to the bright regions. After exposure, including a recommended uniform fixing exposure, the entire film is polymerized, but the bright regions are more dense and therefore have a higher refractive index.

Crosslinking during polymerization is often important, and in some media crosslinking of an existing polymer is the basis of the recording process. For example, in dichromated gelatin, a popular holographic material, gelatin strands are photochemically crosslinked, which limits the swelling ability of the gelatin.²⁸ (The actual photochemistry that leads to this particular crosslinking reaction is complex and not well understood.) Photopolymerization and crosslinking are also important in negative photoresist media, in which unexposed material is washed away during development, giving a surface relief structure.²⁹

Photopolymerization has been used to advantage in the production of electrically switchable holograms with liquid crystals. My group has reported the photopolymerization of liquid crystalline monomers to form switchable holographic gratings.³⁰ In the bright regions, the highly crosslinked polymer retains the initial order of the nematic monomer, resulting in almost no change in refractive index upon polymerization. However, upon application of an electric field, the mobile monomeric regions are selectively reoriented, resulting in a large refractive index change and strong diffraction. By repeatedly switching the field off and on, the hologram is also switched off and on. Another

Charge transfer processes were discussed in the last section, but an important example was left out. Silver halide materials, similar to photographic film but more finely grained, are among the oldest media for holography.²⁴ They are still very popular, partly due to their very high sensitivity. The primary photoreaction is a reduction of silver halide to silver metal, and a tremendous amplification occurs in the chemical development step. Even silver halide grains that contain only a few silver atoms are fully reduced in development, while grains with below-threshold exposure are not reduced and then washed away.

Charge transfer is also important in photochromic insulator or semiconductor materials.²⁵ Light of different wavelengths serves to transfer electrons between band gap traps (defects) that have different energies. The optical properties of the material depend upon which of the traps are occupied, leading to a recording effect.

Photoinitiation of free radical or cationic chain processes is another means for achieving chemical amplification, and this partly

strategy to make a switchable hologram, reported on by Sutherland and other groups,³¹ starts with a mixture of unreactive liquid crystal and a non-liquid crystalline monomer. As the monomer polymerizes in the bright regions, more monomer diffuses from the dark regions and the liquid crystal is pushed toward the dark regions. In the dark regions, the liquid crystal phase-separates into droplets. The result, a holographic polymer-dispersed liquid crystal (H-PDLC), can also be switched off and on with an applied electric field.

Photoisomerization is another important process for holographic recording. Already mentioned are azobenzene dyes, which undergo photoselective orientation, and chiroptical switches. Photochromic dyes, such as spiropyrans,³² fulgides,³³ and stilbenes,³⁴ undergo isomerizations that change their optical properties. These isomerizations can also be used to control liquid crystal alignment. Bacteriorhodopsin, a photochromic protein whose complex photocycle involves *cis-trans* isomerization, exhibits a very low level of degradation after a great many cycles.³⁵

Photocycloaddition reactions, particularly [2+2] reactions of cinnamates, have also been used for recording.³⁶ These reactions have been shown to provide surface relief structures due to shrinkage.

Positive photoresists are materials whose structure is degraded by exposure, allowing exposed regions to be washed away.³⁷ These materials make use of photodepolymerization or photoetching reactions. The surface relief structures obtained from photoresists (positive or negative) can be filled with liquid crystals to produce switchable holograms.³⁸ Alternatively, they can be coated with aluminum, producing a die master that can be used to make thousands of embossed copies.³⁹ This process accounts for most of the holograms we see around us (on credit cards, magazines, etc.).

Much of this article has dealt with processes that can amplify a primary photoinduced effect. However, some applications do not require a large diffraction efficiency but do require large storage densities. For these applications, photochemical hole-burning is an attractive option.⁴⁰ When a chromophore is imbedded in a glassy matrix, its absorption band becomes inhomogeneously broadened, such that different frozen-out conformations have different absorption spectra. Any bleaching photochemical process (possibly reversible) carried out with monochromatic light will then burn a hole in the absorption spectrum. Therefore, multiple holograms may be written in the same spot of film just by changing the wavelength (called wavelength multiplexing).

Conclusions

The fact that so many photochemical and photophysical processes have been used for holography can be attributed to two reasons. First, essentially any chemical or physical change in a material is accompanied either directly or indirectly by changes in optical properties. Second, the performance of a given material in holographic recording depends on so many different characteristics that simultaneous optimization of all is impossible. These characteristics include phase vs. amplitude recording, sensitivity, efficiency, resolution, latency, erasability, speed, development steps, fixing steps, stability, switchability, wavelength response, multiplexing strategies and capacity, temperature range, distortion, etc. For different applications, different characteristics are most important, and the media must be optimized for these. The enormous variety of recording mechanisms then becomes very useful, allowing great flexibility for this optimization.

For example, for an application that requires high efficiency, high sensitivity, the ability to read quickly after writing, long-term stability, and low distortion, many recording strategies are eliminated. Media that require post-exposure chemical processing, such as silver halide, dichromated gelatin, and photoresists, would not allow quick reading. The high efficiency and sensitivity requirements suggest that some form of amplification is necessary. Photopolymerization methods are attractive for this reason, as well as for their long-term stability. However, the low-distortion requirement may limit the choices to photopolymers that exhibit low shrinkage, since shrinkage can lead to distortion of the holograms as well as amplification.⁴¹

Concerning the development and optimization of holographic recording media, an important point is that holographic experiments themselves provide rich data about the primary and secondary photoinduced processes that lead to hologram formation.^{3,42} With this built-in probe and the seemingly limitless possibilities for application of photochemical and photophysical processes to holographic recording, new materials and strategies as well as variations on existing ones will undoubtedly continue to appear!

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About the Author

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Michael A. J. Rodgers Receives Award in Photochemistry

The Inter-American Photochemical Society has just announced that Dr. Michael A. J. Rodgers, Center for Photochemical Sciences, Bowling Green State University, is the winner of the 2001 I-APS Award in Photochemistry. The award recognizes "outstanding contributions in photochemistry over the past decade." Dr. Rodgers' selection is based upon his development and applications of fast kinetic methodology to the study of photochemical and photobiological processes.

I-APS President Frederick D. Lewis said, "While this award is based on contributions made during the past decade, the selection committee was clearly impressed by the breadth and depth of your contributions to the photochemical field during your career."

Dr. Rodgers will present the Award Lecture at the I-APS Conference to be held in Cordoba, Argentina, May 20-25 2001. This is the second year in a row a member of the Center for Photochemical Sciences has won this coveted award. Dr. D.C. Neckers was the 2000 award winner.

Supramolecular Dynamics of Guest Complexation to Cyclodextrins

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Introduction

Supramolecular systems are formed from individual components held together by non-covalent interactions. The paradigm of supramolecular chemistry is that functions performed by these systems are different from the sum of the functions achieved by the individual components.¹⁻² The aim is to create new and unique functions that are not accessible in molecular chemistry. The synthesis of a variety of complex structures has driven the development of supramolecular chemistry. Traditionally, new systems are characterized by structural methods and thermodynamic techniques. However, full characterization of each system requires its dynamics (kinetics) to be understood. Dynamic information can not be derived from thermodynamic or structural studies and requires kinetic measurements. In supramolecular chemistry dynamic aspects have received only limited attention because many of the processes are fast (sub-millisecond) and require fast kinetic techniques. Although a great amount of insight has emerged from the traditional structural approach, the design and synthesis of functional supramolecules led in many cases to disappointing performance because dynamic aspects were neglected. Therefore, the understanding of the dynamics is the key to comprehend supramolecular function.

We have systematically studied the dynamics of supramolecular systems. Initially we chose cyclodextrins (CDs) as host molecules because of their simplicity. CDs are cyclic molecules with D-glucose units (6, 7 or 8 for α -, β - and γ -CD) that form host-guest complexes with a variety of inorganic and organic molecules.³⁻⁹ Although the thermodynamic characterization of guest binding to CDs has been extensively reported,⁷⁻⁹ there is only limited information on the dynamics of guest complexation to CDs.^{4,10-30} The scope of this review is centered on our studies with CDs. Reference will also be made to work done by others that directly relates to our investigations.

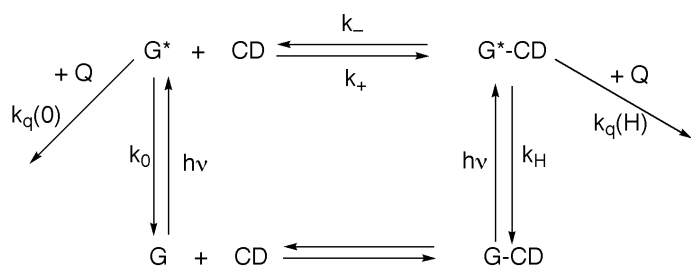
Theoretical Background

The equilibrium constants and binding stoichiometries for CD complexes have to be known before the complexation dynamics is investigated. Determination of these parameters is done by fluorescence, absorption or NMR experiments and relies on well-established methodology.³¹

Dynamic studies require real-time kinetic measurements. Time-resolution faster than milliseconds can be obtained by using a chemical that has a lifetime of the same order of magnitude as the dynamic processes being studied. Reactive intermediates, such as excited triplet states or radicals are useful for these studies.

The complexation dynamics of an excited state to CD is shown in Scheme 1. The complexation dynamics can be followed directly when the excited state has a different molar absorptivity in water than within the CD, and the equilibrium constants for the excited and ground states are different. The kinetic scheme is analogous to that for excimer formation.³² When k_0 and k_H are significantly smaller (≤ 100) than the entry and exit processes, the fast decay can be approximated to equation 1.^{19,33}

$$k_{\text{obs}} = k_- + k_+ [\text{CD}] \quad (1)$$

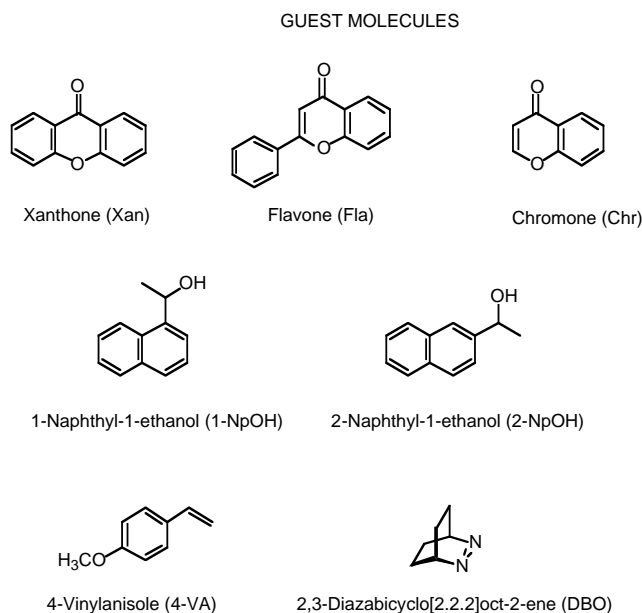


Scheme 1

Unfortunately, the use of the direct methodology is limited to a few molecules. In most cases a quenching methodology, where the quencher resides primarily in the aqueous phase ($k_q(0) > k_q(H)$, Scheme 1), is employed to obtain the k_+ and k_- values. Provided the decay of the excited state is first-order at all quencher concentrations the observed rate constant is given by:^{19,28,29,34}

$$k_{\text{obs}} = k_{\text{H}} + k_{-} + k_{\text{q}}(\text{H})[\text{Q}] - \frac{k_{-}k_{+}[\text{CD}]}{k_{\text{o}} + k_{\text{q}}(\text{O})[\text{Q}] + k_{+}[\text{CD}]} \quad (2)$$

A detailed discussion on how changes in the relative rate constants affect the plots of k_{obs} versus $[\text{Q}]$ can be found elsewhere.¹⁹ Briefly, the plots of k_{obs} versus $[\text{Q}]$ are curved and at high quencher concentrations a linear relationship is achieved. Since the parameter k_{-} appears in the linear and in the non-linear terms of equation 2, this rate constant is usually recovered with a higher degree of precision than the entry rate constant.



Scheme 2

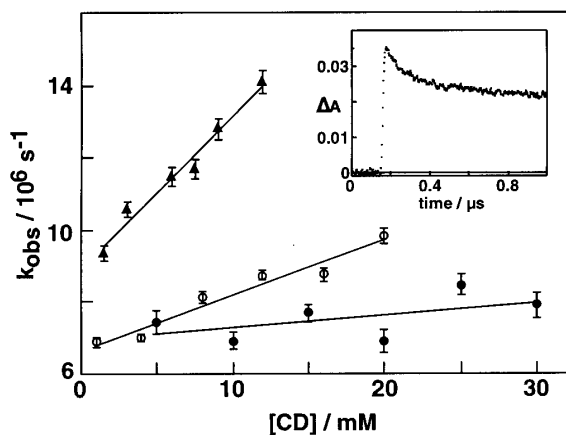


Figure 1. Dependence of the initial rate constant (k_{obs}) for the relaxation kinetics of triplet xanthone complexed to β -CD (\blacktriangle , upper line), Hp- β -CD (\circ , middle line) and γ -CD (\bullet , lower line) on the CD concentration. Error bars correspond to those from the fitting of experimental data to the sum of two exponentials. The inset shows the decay of triplet xanthone at 620 nm when complexed to 15 mM Hp- β -CD. (Adapted with permission of The Royal Society of Chemistry; Liao, Y.; Frank, J.; Holzwarth, J. F.; Bohne, C. *J. Chem. Soc., Chem. Commun.* **1995**, 199-200.)

Dynamics of CD Complexes With 1:1 (Guest:CD) Stoichiometry

Excited triplet xanthone (Scheme 2) is a suitable probe to follow its complexation with CDs, because the triplet-triplet absorption maximum shifts with solvent polarity,^{35,36} and the triplet state has a higher dipole moment and basicity than the ground state. Therefore, the excitation of xanthone leads to a non-equilibrium situation and the triplet relocates from the CD cavity to the water.¹⁰ The rate constant for the fast decay (inset Figure 1) of the biphasic kinetics depends on the CD concentration (Figure 1). The k_{+} and k_{-} values were obtained using equation 1 (Table 1, $K_{\text{T}} = k_{+}/k_{-}$).²⁰ The equilibrium constants for the triplet are significantly smaller than the equilibrium constants for the xanthone ground state (Table 1). This result shows that ground and excited-state guests can have very different complexation dynamics and the k_{+} values, that are sometimes difficult to measure, can not be estimated from K_{G} and the excited state k_{-} values. In the present example such an estimate would be in error by more than one order of magnitude.

Xanthone is located at the rim of the CD without penetrating deeply into the cavity.³⁷ The similar k_{-} values observed for β -, γ - and Hp- β -CD indicate that xanthone is located in a similar position in the CD complexes because the exit process is not very much affected by the CD structure. A greater sensitivity to the CD structure was observed for the entry rate constants, suggesting that complex formation is influenced significantly by the CD structure. The ratio between K_{G} and K_{T} was larger for Hp- β -CD (90) than for β -CD (23). Understanding how to increase this ratio has an impact when designing CD supramolecules to be used for targeted photorelease of guests. A high ratio for the equilibrium constants due to a decrease of k_{+} will decrease the re-trapping probability by the CD of the photoreleased guest.

Barra showed that D_2O does not change the ground state equilibrium constants between xanthone and β -CD, but decreases the triplet equilibrium constant (Table 1).¹¹ Most of the solvent effect is on the decrease of the entry rate constant. The xanthone ground state entry rate constant determined in laser-temperature jump experiments is the same as measured for the excited state, whereas the exit rate constant is ca. 25 smaller for the ground state.²⁰ Since a constant k_{+} value was observed, the rate limiting

step for complex formation can not be related to the desolvation of xanthone. The isotope effect observed for the k_+ is suggestive that the rate limiting step is the desolvation of the CD cavity. However, this interpretation is not consistent with the lack of a solvent effect on the K_C values and the experiments available at this time can not be completely reconciled.

Table 1. Equilibrium constants for ground and excited state guest molecules with cyclodextrins and entry and exit rate constants for the excited states for complexes with 1:1 complexation stoichiometry.

Guest	CD	$K_C / 10^3 M^{-1}$	$K_T / 10^3 M^{-1}$	$k_+ / 10^8 M^{-1} s^{-1}$	$k_- / 10^6 s^{-1}$	Method ^a	Reference
Xan	β	1.1 ± 0.2	0.048 ± 0.013	4 ± 1	8.4 ± 0.7	D	20
	β		0.09 ± 0.01	11 ± 1	12 ± 1	Q	30
	β/D_2O	1.07 ± 0.05	0.0116 ± 0.0009	0.88 ± 0.06	7.6 ± 0.1	D	11
	γ	0.22 ± 0.03	< 0.004	< 0.3	7.3 ± 0.5	D	20
	Hp- β^b	1.8 ± 0.1	0.020 ± 0.004	1.4 ± 0.3	7.1 ± 0.4	D	20
Chr	β	0.24 ± 0.04	0.14 ± 0.05	30 ± 10	21 ± 1	Q	30
Fla	β	1.09 ± 0.08	0.55 ± 0.35	24 ± 12	4.4 ± 1.8	Q	30
1-NpOH	β	0.50 ± 0.08^d	0.98 ± 0.54^e	4.7 ± 1.9	0.48 ± 0.18	Q	12
2-NpOH ^c	β	1.8 ± 0.2^d	1.6 ± 1.1^e	2.9 ± 1.6	0.18 ± 0.07	Q	12
4-VA ^{**}	α	0.11 ± 0.03			> 10	Q	40
	β	0.70 ± 0.03			> 10	Q	40
DBO	α	0.05 ± 0.01		1.9		D	22
	β	1.1 ± 0.3		4.0		D	22
	γ	0.006 ± 0.003		0.8		D	22

^aD = direct spectroscopic method, Q = quenching methodology; ^bHp- β -CD corresponds to hydroxypropyl- β -CD; ^cdata for the CD complex with 1:1 stoichiometry; ^dequilibrium constants determined in the presence of 0.5 M Na_2SO_4 ; ^ecalculated from the k_+ and k_- values in reference 12.

To date xanthone is the only guest molecule for which the entry and exit rate constants can be obtained using a direct kinetic measurement. The dynamics of xanthone complexation to β -CD was studied using the quenching methodology (Figure 2, Table 1), so that the exit/entry rate constants could be compared to those obtained for other guests.³⁰ The quenching methodology overestimates both rate constants, but this effect is more pronounced for the entry rate constant. Although the rate constants determined in the direct measurements are more precise, the values obtained in the quenching experiments should be used for comparison with other guests.

Chromone, flavone and xanthone are ketones of different sizes, but all contain the 4H-pyran-4-one moiety. These molecules were used to compare the effect of guest size on the complexation dynamics with β -CD.³⁰ The quenching plots were curved in the presence of β -CD (Figure 2). The degree of deviation of the quenching plots from the linear plot acquired in water provides an indication on how fast the entry/exit dynamics is and on how well the guest is protected from the quencher in solution. The larger the deviation (e.g. flavone compared to chromone) the slower the complexation dynamics (Table 1) and/or the larger the protection efficiency from quenching. The fast dynamics for chromone (Table 1) is related to the fact that the CD cavity does not provide a tight fit for this small molecule. The entry rate constant for triplet flavone is somewhat larger than for xanthone, whereas its exit rate constant is significantly smaller. Consequently, the reduction of K_T compared to K_C is smaller for flavone than for xanthone. We proposed that this difference is due to the incorporation of the phenyl ring of flavone in the CD cavity, which acts like an anchor retarding the exit.³⁰ This example shows that appending moieties that are not related to the functionality of the guest can be employed to fine tune the complexation dynamics.

The complexation dynamics of 1-naphthyl-1-ethanol (1-NpOH) and 2-naphthyl-1-ethanol (2-NpOH) with β -CD was studied to determine how the shape of the guest influences the entry/exit processes.¹² 1-NpOH forms a weaker complex with β -CD than 2-NpOH,¹² because it is a bulkier molecule and cannot penetrate as deeply into the CD cavity.³⁸ This different geometry has an effect on the k_- values in that they are larger for 1-NpOH than 2-NpOH

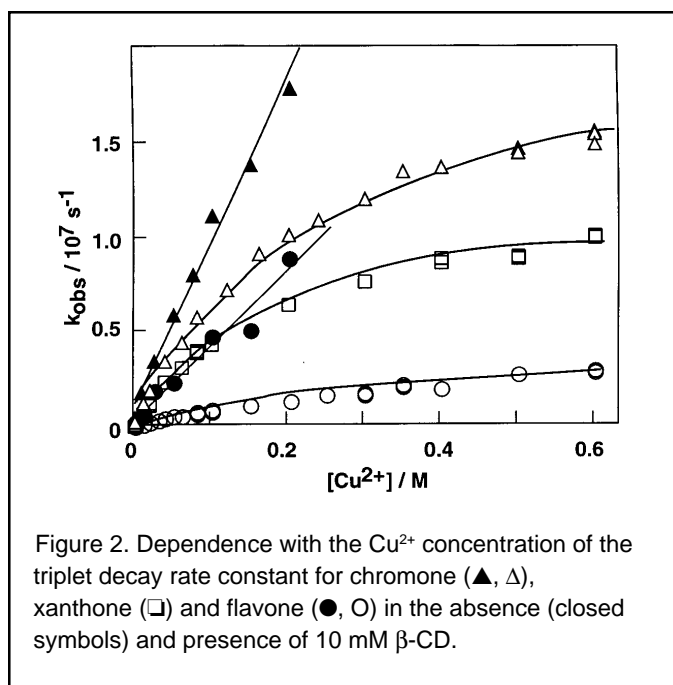


Figure 2. Dependence with the Cu^{2+} concentration of the triplet decay rate constant for chromone (\blacktriangle , \triangle), xanthone (\blacksquare , \square) and flavone (\bullet , \circ) in the absence (closed symbols) and presence of 10 mM β -CD.

(Table 1). The k_{-} values for both NpOHs are of the same order of magnitude as previously determined for the naphthalene/ β -CD complex.¹⁷ Slower processes were also observed for larger naphthalene derivatives or when the solvent contained 10% acetonitrile.^{28,29} The dynamics for both NpOHs is much slower than measured for xanthone (Table 1). The original interpretation for the lower K_T value for xanthone was that its triplet has a π, π^* configuration and a higher dipole moment.^{10,11,20} This interpretation can not be correct because the NpOH triplets also have a π, π^* configuration and a fast exit would be expected if the cause was a change in dipole moment. In the case of xanthone, the large difference for the equilibrium constants that triggers the relocation is probably related to the increased basicity of the excited state when compared to the ground state ($\text{p}K_a(\text{G}) = -4.1$, $\text{p}K_a(\text{T}) = 3$).³⁹

The effect of forming a charged organic guest within the cavities of α - and β -CD was studied by photogenerating styrene radical cations (e.g. 4-vinylanisole) through photoionization.⁴⁰ No curvature was observed in the quenching plots, suggesting that exit of the radical cations

is fast (< 100 ns). This result has implications when CDs are used as protecting agents for drugs that show phototoxicity and are known to form ionic intermediates.⁴¹⁻⁴³ Any attempt to stabilize these drugs by complexation with CDs may be fruitless if exit of the charged reactive intermediate is fast.

The probe 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) has a very long fluorescence lifetime ($< 1 \mu\text{s}$) and the excited singlet state is quenched by an "aborted" hydrogen transfer.⁴⁴ The fluorescence of DBO can be used to study its complexation dynamics of supramolecular systems in a similar fashion as described above for excited triplet states. In the case of α -, β - and γ -CD, Nau and Zhang showed that the quenching rate constant by CDs for the excited singlet DBO formed in the aqueous phase corresponds to the entry rate constant of the DBO into the CD cavities (Table 1).²² Once the excited DBO enters the CD cavity, it is deactivated by the reaction with the internal glycosidic C-H bonds. This deactivation happens before the excited DBO has a chance to exit into the aqueous phase. The development of DBO as a probe for supramolecular dynamics is a significant advance, because DBO can be used to measure entry rate constants with a higher precision than obtained from the quenching methodology. The order of the k_{+} values for excited singlet DBO binding to CDs parallels the K_{eq} values for the ground state, suggesting that for the tighter complexes the entry process is faster. However, the k_{+} values are less sensitive to the CD structure than the ground state equilibrium constants, indicating that some selectivity for the exit rate constant of ground state DBO probably exists ($k_{-}(\beta) < k_{-}(\alpha) < k_{-}(\gamma)$).

Effect of Co-Solvents on the Complexation Dynamics of Guests With CDs

The addition of alcohols or surfactants can affect both the entry and exit rate constants for the binding of naphthalenes and pyrene with CDs.^{17,25} We studied the effect of alcohol addition on the exit rate constants of triplet xanthone from β - and γ -CD complexes.²¹ Linear, branched and cyclic alcohols form complexes containing the CDs and xanthone. The equilibrium constants for these ternary complexes are smaller for β -CD, but larger for γ -CD, when compared to the K_{eq} values in the absence of alcohols. However, for both CDs the exit rate constants for triplet xanthone are smaller for the ternary complexes than for the xanthone/CD complexes. This result shows that trends observed for equilibrium constants can not be extrapolated to effects on the complexation dynamics. The magnitude of the decrease of the k_{-} values was not very sensitive to the structure of the alcohols. We proposed that the slow down of the exit was due to the formation of a protective layer at the rim of the CDs by preferential solvation of the CD entrances with alcohol molecules.²¹ The dynamics of xanthone binding to CDs in the presence of alcohols is much faster than that observed for pyrene and naphthalenes.^{17,25} This difference could be due to the structure of the host-guest complex. Xanthone is complexed at the rim of the CD,³⁷ whereas naphthalene derivatives are included in the β -CD cavity,³⁸ and in the case of pyrene a 1:2 (guest:CD) complex was shown to be formed in addition to the 1:1 complex.⁴⁵

Dynamics of CD Complexes With More Than One CD

CDs can form complexes with more than one host molecule. Very little is known about the dynamics of these higher order complexes. 2-NpOH forms 1:1 and 2:2 complexes with β -CD. The latter leads to excimer emission and its equilibrium constant is higher (3000 M^{-1}) than for the 1:1 complex (Table 1).¹² The triplet decay of 2-NpOH in the presence of quencher (Mn^{2+}) was not mono-exponential and the long lived component was assigned to the triplet 2-NpOH in the protected 2:2 complex. In addition, a broadening was observed for the NMR signals of 2-NpOH in the presence of β -CD. These results led to an estimate of 10^3 s^{-1} for the dissociation rate constant of the 2:2 complex. This value is much slower than observed for the 1:1 complex ($1.8 \times 10^5 \text{ s}^{-1}$).¹² In the case of styrene radical cations, 1:2 (guest:CD) complexes were observed in the presence of α -CD. The exit of these charged guests is faster than 100 ns.⁴⁰ The reasons for the very slow dynamics in the case of 2-NpOH and the fast dynamics in the case of charged guests is not yet understood and will require further investigations.

Conclusions

Time-resolved photophysical techniques are well suited to investigate the dynamics of supramolecular systems as our detailed description involving CDs have shown. Furthermore, this type of methodology can be employed for more complex systems. Some of the future challenges are to measure the mobility of guests between different sites in a supramolecular system and to obtain more detailed information on the many dynamic events over short distances, which lead to the global exit and entry rate constants measured to date. The knowledge gained on the dynamic processes will be useful for the rational development of supramolecular function, and photophysical techniques will play a key role in these studies.

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