Photoinduced processes in dendrimers
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Appendix

I. Investigation of Photoinduced Processes

To study the photophysical properties of the compounds described in this Thesis as well as the photophysical processes occurring within a molecule or between different components of a supramolecular assembly, several steady state and time-resolved spectroscopic techniques have been applied. The photophysical processes studied in this Thesis are (i) the photoisomerization of methyl orange, which is an azobenzene derivative, (ii) electron transfer processes and (iii) energy transfer processes within via hydrogen bonds-assembled donor and acceptor components. The spectroscopic methods used to investigate the excited state dynamics will be described.

II. Time-Resolved Absorption Spectroscopy

Time-resolved absorption spectroscopy provides a powerful tool for obtaining valuable information about the nature and dynamics of excited states and short-lived photochemical intermediates. It relies on recording electronic absorption spectra of transient species (excited molecules or photoproducts) at selected time delays after the excitation pulse. The transient absorption trace can either be recorded over an extended wavelength range (full spectrum) or at a single wavelength. In the former approach the excitation pulse is followed by a white light pulse that is used for monitoring. In the nanosecond transient absorption set-up white light pulses are typically generated by a pulsed Xe lamp; in the (sub)pico-second transient absorption set-up this is achieved via non-linear optical processes, e. g. by focusing the laser pulse into a water containing cuvette or a sapphire crystal. The white light that is transmitted by the sample, is recorded by a spectrographic detection system, such as an optical multichannel analyzer (OMA) or a streak camera. Transient absorption spectra are generally obtained as difference spectra, showing the time-resolved absorption changes relative to the ground state absorption.

By recording the transient absorption signal at a single wavelength at different time delays after the excitation pulse, kinetic traces can be constructed that allow an accurate analysis of the dynamics of the excited states and primary photoproducts. Kinetic traces in the nanosecond time domain are usually obtained by replacing the spectrographic detection system with a monochromator-photomultiplier combination, in order to select the desired wavelength from the complete spectrum.

In this Thesis, transient absorption spectra and kinetic traces were recorded on the (sub)pico- and nanosecond timescale. The experimental details of the employed set-ups are described in the following paragraphs.
II. a Nanosecond Time-Resolved Transient Absorption Spectroscopy: Experimental Set-up

Nanosecond transient absorption (ns TA) spectra were obtained by irradiating the samples with 2 ns pulses (FWHM) of a continuously tunable (420 - 710 nm) Coherent Infinity XPO laser. The output power of the laser was typically less than 5 mJ/pulse at a repetition rate of 10 Hz. Samples in a 1 cm quartz cuvette (Hellma) exhibited an optical density of ca. 0.8 at the excitation wavelength. The probe light from a low-pressure, high-power EG&G FX-504 Xe lamp passed through the sample cell and was dispersed by an Acton Spectra-Pro-150 spectrograph, equipped with 150 g/mm or 600 g/mm grating and a tunable slit (1 - 500 μm), resulting in 6 or 1.2 nm maximum resolution, respectively. The data collection system consisted of a gated intensified CCD detector (Princeton Instruments ICCD-576EMG/RB), a programmable pulse generator (PG-200), and an EG&G Princeton Applied Research Model 9650 digital delay generator. With this OMA-4 set-up (Figure 6-1) I and I₀ values are measured simultaneously, using a double kernel 200 μm optical fiber.

Figure 6-1. A schematic representation of the nanosecond transient absorption set-up: 1 laser, 2 Xe lamp, 3 sample, 4 spectrograph, 5 CCD camera, 6 pulser, 7 computer.

Nanosecond flash photolysis emission kinetics were measured by irradiating the sample at 435 nm with a 2 ns (FWHM) Coherent Infinity XPO laser (10 Hz repetition rate). In case of the nanosecond flash transient kinetics a pulsed Xe-lamp perpendicular to the laser beam was used as probe light. The 450 W Xe lamp was equipped with a Müller Electronik MSP05 pulsing unit giving pulses of 0.5 ms. A shutter, placed between the lamp and the laser, was opened for 10 ms to prevent photomultiplier fatigue. Suitable pre- and postcut-off filters and bandpass filters were used to minimize both the probe light and the scattered light of the laser. The light was collected in an Oriel monochromator, detected by a P28 PMT (Hamamatsu), and recorded on a Textronic TDS3052 (500 MHZ) oscilloscope. The laser oscillator, Q-switch, lamp, shutter and trigger were externally controlled with a homemade digital logic circuit, which allowed synchronous timing. Kinetic traces were obtained after 32 accumulations. The absorption transients were plotted as ΔA = log(I₀/Iₜ) versus time, where I₀ was the monitoring light intensity prior to the laser pulse and Iₜ the observed signal at delay time t.
II. b (Sub)Picosecond Time-Resolved Transient Absorption Spectroscopy: Experimental Set-up

Ultrafast transient absorption measurements were performed on the set-up installed at the University of Amsterdam (Figure 6-2).²

![Figure 6-2](image_url)

**Figure 6-2. A schematic representation of the picosecond transient absorption set-up:** 1 Hurricane, 2 OPA-800 (pump), 3 chopper, 4 delay line, 5 white light generator, 6 sample, 7 CCD camera.

The laser system is based on a Spectra Physics Hurricane Ti-sapphire regenerative amplifier system. The optical bench assembly of the Hurricane includes a seeding pump laser (Mai Tai), a pulse stretcher, a Ti-sapphire regenerative amplifier, a Q-switched pump laser (Evolution) and a pulse compressor. The output power of the laser is typically 1 mJ/pulse (130 fs FWHM) at a repetition rate of 1 kHz. A full spectrum pump-probe set-up was employed, based on an optical parametric amplifier (Spectra-Physics OPA 800) as a pump, where the residual fundamental light (150 μJ/pulse) from the pump OPA was used for generation of white light, that was detected with a CCD spectrograph. The pump OPA was used to generate excitation pulses at 435 nm (fourth harmonic of the 1740 nm OPA signal beam). The output was typically 4 μJ/pulse. The white-light generation was accomplished by focusing the fundamental (800 nm) into a sapphire plate. The pump light was then passed over the 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 energy of the probe pulse was approximately $5 \times 10^{-3} \mu$J/pulse at the sample. The angle between the pump and the probe beam was typically 5-7°. The cuvette (2 mm, Spectrocell) with a sample solution inside was equipped with a electrically driven stirrer stick to avoid local heating and sample decomposition by the laser beams. For the white-light/CCD set-up, the probe beam was coupled into a 400 μm optical fiber after passing through the sample, and detected by a CCD spectrometer (Ocean Optics, PC2000). The chopper (Rofin Ltd., $f = 10$-20 Hz), placed in the excitation beam, provided $I$ and $I_0$, depending on the status of the chopper (open or closed). The excited state spectra were obtained by $\Delta A = \log(I/I_0)$. Typically, an averaging time of 3 seconds was used to obtain the transient spectrum at a particular time delay. Due to group velocity dispersion (GVD) in the cuvette a chirp of ca. 0.5 ps is observed between 460 and 700 nm.

The CCD spectrograph, the chopper, and the delay line were controlled by a computer. In-house developed LabVIEW (National Instruments) software routines were used for spectral acquisition.
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The nearly saturated solutions of the samples exhibited an optical density of ca. 0.3 at the excitation wavelength in a 2 mm cell, which was the maximum obtainable. The absorbance spectra were measured before and after the experiments. In all cases less then 10% photodecomposition was observed.

III. Emission Spectroscopy

Emission can be measured using either steady state or time-resolved techniques. One of the main advantages of measuring emission is that the sensitivity is much higher than transient absorption. The emission quantum yield and the excited state lifetime provide important information of this state and are related to the radiative and non-radiative rate constants. Multiple or non-exponential behavior can give information about the presence of several close-lying excited states.

Steady state fluorescence measurements were performed on a Spex 1681 fluorimeter, 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. Emission quantum yields of the new compounds \((s)\) were determined for optically diluted solutions, relative to an appropriate reference emitter \((r)\), according to the equation

\[
\Phi_s = \Phi_r \left( \frac{I_s}{I_r} \right) \left( \frac{A_r}{A_s} \right) \left( \frac{n_{D,s}^2}{n_{D,r}^2} \right)
\]

in which \(\Phi\) represents the emission quantum yield, \(I\) is the ingrated emission intensity, \(A\) the ground state absorbance at the wavelength of excitation, and \(n_D\) the refractive index of the solvent used. The subscripts \(s\) and \(r\) refer to the sample and the reference compound, respectively.

Several methods are currently available for time-resolved emission studies: (i) modulation methods such as differential phase fluorimetry, (ii) pulse sampling methods, e.g. flashphotolysis, and (iii) time correlated single-photon counting. For the nanosecond emission measurements described in this Thesis a similar set-up as used for the nanosecond transient absorption measurements was employed for measuring the nanosecond flash photolysis emission kinetics (single wavelength set-up), with the exception that the probe lamp was not used. Picosecond emission measurements were performed with single photon counting using a picosecond laser. The emission lifetimes were were calculated by exponential fitting of the emission intensity versus time.
Both the quantum yield of emission and the emission lifetime give information about the rates of radiative and non-radiative decay, according to the equations

\[ \Phi = \frac{k_r}{k_r + k_{nr}} \quad \tau = \frac{1}{k_r + k_{nr}} \]

in which \( \Phi \) is the quantum yield of emission, \( \tau \) the excited state lifetime, and \( k_r \) and \( k_{nr} \) the rates of radiative and non-radiative decay, respectively.

IV. References
