Photoinduced processes in dendrimers
Dirksen, A.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 3

Ultrafast Photoinduced Electron Transfer across Hydrogen Bonds of a Self-Assembled Donor-Acceptor System

Abstract: The hydrogen-bonded complex H1-G2 consisting of a methyl viologen-functionalized barbiturate host (H1) (1-(N-(3,5-bis((6-tert-butylacetylamino-2-pyridyl)amino)carboxyl)phenylacetamide)-1'-methyl-4,4'-bipyridium; counterions: 2 BArf or 2 PF6) and a [Re(Br)(CO)3] [barbi-bpy] (barbi-bpy = 5-[4-(4'-methyl)-2,2'-bipyridyl]methyl-2,4,6-(1H,3H,5H)-pyrimidinetrione) complex as the guest (G2) has been characterized in acetonitrile using 1H NMR and diffusion ordered NMR spectroscopy (DOSY). From 1H NMR, the binding constant (Kass) was determined to be 4.3 \times 10^5 M^{-1} in acetonitrile. The average molecular radii of the separate species H1 (10.9 Å), G2 (7.6 Å), and PF6-H1-G2 (9.3 Å) were calculated from the diffusion coefficients determined with DOSY for an equimolar (2.5 mM) solution of PF6-H1 and G2. The rather large molecular radius of PF6-H1 alone was attributed to the formation of small aggregates of PF6-H1, which upon binding of the guest G2 dissociate. The photophysical properties of BArf-H1, G2, and BArf-H1-G2 have been studied in CH2Cl2 using time-resolved fluorescence and transient absorption spectroscopy. Fast electron transfer was observed in the host-guest complex BArf-H1-G2 (k_{fet} = 1 \times 10^{12} s^{-1} (lower limit); k_{fet,1} = 3.4 \times 10^{10} s^{-1} (higher limit); k_{het,2} = 4 \times 10^{7} s^{-1} (lower limit)) and a high binding constant could be determined (Kass \geq 2 \times 10^5 M^{-1}).

Chapter 3

3.1 Introduction

The assembly of supramolecular systems using non-covalent interactions, such as hydrogen bonds, ionic interactions, and hydrophobic interactions, is still an emerging field in modern chemistry. Molecular recognition is based on these interactions enabling the selective assembly of host and guest molecules in a predefined way, which can be applied for the detection of specific molecules or ions in solution or for the construction of very large nanostructures. Similar, but far more complex forms of supramolecular organization based on multiple non-covalent interactions are found in nature. This is for example the case in cytochromes (a class of heme-containing proteins), which are essential for processes such as photosynthesis and respiration. The specific organization of photoactive components in these systems is required to obtain high efficiencies for charge separation (long-range electron transfer). To gain more insight in electron transfer processes as they occur in nature and in photo-induced electron transfer (PET) in non-covalently linked systems in general, several supramolecular assemblies have been synthesized and studied.

Especially, hydrogen-bonding has been applied to create a variety of electron donor-electron acceptor dyads to study PET. In order to gain a good understanding of electron transfer processes within such an assembly and to determine the rates of the electron transfer reactions, a high binding constant between the host and the guest species is required. This can be achieved by using multiple hydrogen-bonding interactions between host and guest. Already in 1988 Hamilton et al. published a receptor that binds barbiturate and its derivatives via six hydrogen bonds. Subsequently, this receptor has been used to extract barbiturates from serum as a binding site in a model for enzyme catalysis, as a building block in supramolecular materials, and as a functionalized receptor in hydrogen bond-based photoactive assemblies. The association constant of the hydrogen-bonded complexes between the barbiturate receptor and barbiturates is in the order of $10^5$-$10^8$ M$^{-1}$ in chlorinated solvents and further optimization is possible via substitution of the receptor.

In previous studies focusing on PET across hydrogen bonds, the efficiency of the electron transfer was found depend strongly on the nature of the host-guest binding motive. In addition more subtle factors, such as configuration, linker orientation, and directionality play a key-role for the electron donor-electron acceptor interaction. The development of more flexible systems in which the distance between the electron-donor and the electron-acceptor is reduced and in which secondary interactions between donor and acceptor might help to pre-assemble the host-guest complex in a conformation optimal for electron transfer, may lead to systems where the electron transfer rates are very similar to or even faster than those found in the covalently linked systems.

In order to create an assembly able to perform PET, a suitable electron donor and electron acceptor must be part of the host and of the guest of the supramolecular system. [Ru(bpy)$_3$] and [Os(bpy)$_3$] derivatives have been studied intensively in electron and energy transfer processes, and also [Re(X)(CO)$_3$(bpy)] (X = Cl, Br, I) derivatives provide viable photoactive
components suitable for this purpose. \([\text{Re}(X)(\text{CO})_3(\text{bpy})]\) \((X = \text{Cl}, \text{Br}, \text{I})\) derivatives as electron donor in combination with various suitable electron acceptors, such as quinones and viologens.\(^{45-51}\)

Here we report a flexible supramolecular electron donor-electron acceptor system that can be assembled \textit{via} hydrogen bonds by using the barbiturate receptor and a barbiturate as complementary units. To enable comparison with systems containing a similar rhenium complex, which is covalently linked to a methyl viologen acceptor, such as the \([\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb})]^{2+}\) complex described by Vlcek, Jr. \textit{et al.},\(^{48,51}\) the barbiturate receptor is functionalized with a methyl viologen rendering the host \(\text{H1}\) and \([\text{Re(Br)(CO)}_3(\text{dmb})]\) \((\text{dmb} = 4,4'\text{-dimethylbipyridine})\) with a barbiturate moiety giving \([\text{Re(Br)(CO)}_3(\text{barbi-bpy})]\) \((\text{barbi-bpy} = 5-[4-(4'-\text{methyl})-2,2'\text{-bipyridyl}]\text{-methyl-2,4,6-}(1H,3H,5H)\text{-pyrimidinetione})\) as the guest \(\text{G2}\) (Scheme 3-1). Flexibility is introduced in the host-guest system by the \(\text{CH}_2\)-linkers between the electron donor and the substrate moiety and between the electron acceptor and the receptor moiety.

![Scheme 3-1. The assembly of \(\text{H1}\) and \(\text{G2}\) to form the host-guest complex \(\text{H1-G2}\) \((A = \text{Br/I, PF}_6, \text{BAr}_3)\).](attachment:scheme_3-1.png)

The photophysical properties of the components and of the assembly have been studied in dichloromethane. An efficient and fast electron transfer is observed upon excitation of the donor moiety \((\text{G2})\). The kinetics of the electron transfer process within the host-guest complex \(\text{H1-G2}\) were investigated in dichloromethane using time-resolved emission and transient absorption techniques. Our findings are discussed focusing on the relation between the conformation of the assembly \(\text{H1-G2}\) and the kinetics of the photo-induced electron transfer.
3.2 Results and Discussion

3.2.1 Synthesis and Characterization of Guest and Host Molecules

The host-guest system in this study is based on a barbiturate receptor, which forms a very strong host-guest complex based on six hydrogen bonds with barbiturate and its derivatives. The barbiturate receptor is functionalized with an electron acceptor moiety, namely a methyl viologen unit, according to Scheme 3-2. Compound 4, which was prepared according to literature procedures, was functionalized by reaction with bromoacetyl chloride and subsequent alkylation of 5 with a methyl viologen group, rendering H1.

\[ R = \text{CH}_3\text{Bu} \]

Scheme 3-2. The synthesis of X-H1 starting from the amine-functionalized receptor.

H1 was obtained as a halide salt, X-H1, and the halides were exchanged for PF\(_6^-\) by precipitation from water upon addition of a concentrated solution of NH\(_4\)PF\(_6\) in water giving PF\(_6^-\)-H1, which is soluble in acetonitrile. Furthermore, the halides were exchanged for \{B[3,5-(CF\(_3\))\_2C\(_6\)H\(_3\)]\_4\} (BARt\(^+\)) via extraction of X-H1 from the aqueous layer to a diethyl ether layer containing 1.8 equivalents of NaBARt, giving BARt-H1, which is soluble in less polar solvents such as dichloromethane.

\[[\text{Re}({\text{Br}})(\text{CO})_3(\text{barbi-bpy})]\] was used as a guest molecule and synthesized by refluxing \[[\text{Re}({\text{Br}})(\text{CO})_3]\] overnight with the barbituric acid-functionalized bipyridine ligand (barbi-bpy) in acetonitrile. Subsequent extensive washing with dichloromethane and pentane yielded the desired guest \[[\text{Re}({\text{Br}})(\text{CO})_3(\text{barbi-bpy})]\] (G2).

All compounds were characterized using \(^1\)H NMR, \(^1^3\)C NMR, and high-resolution FAB mass spectrometry. In addition ground state UV-Vis absorption and emission spectra were recorded for both BARt-H1 and G2 in dichloromethane.

3.2.2 Photophysical Properties of BARt-H1 and G2

The ground-state UV-Vis absorption spectrum of BARt-H1 shows an absorption maximum at 302 nm (\(\epsilon = 34000 \text{ M}^{-1}\text{cm}^{-1}\)) in dichloromethane (Figure 3-la), which is in good agreement with the absorption at 304 nm reported by Hamilton et al. for a barbiturate receptor. In addition a very
weak absorption around 400 nm was observed. Excitation in this weak absorption band at 400 nm results in a short-lived (< 3 ns) emission with a maximum at 560 nm (Figure 3-1a, inset).

![Absorption and emission spectra](image)

**Figure 3-1.** Absorption and emission spectra (inset; λ<sub>exc</sub> = 435 nm) of (a) BArf-H1 and (b) G2 in dichloromethane.

The ground-state UV-Vis absorption and emission spectra of G2 are very similar to those of [Re(Br)(CO)<sub>3</sub>(bpy)]<sup>54</sup>. It shows a characteristic metal-to-ligand charge transfer (MLCT) absorption band at 372 nm (ε = 1900 M<sup>-1</sup>cm<sup>1</sup>) (Figure 3-1b). The emission from the ³MLCT state has a maximum at 590 nm (Figure 3-1b, inset) with an excited state lifetime of 60 ns in dichloromethane.

### 3.2.3 Characterization of PF₆-H₁-G₂ in Acetonitrile-d₃ by <sup>1</sup>H NMR

Having fully characterized the separate components PF₆-H₁ and G₂, the assembly PF₆-H₁-G₂ was studied using <sup>1</sup>H NMR techniques in order to gain more insight in the structure of the host-guest complex in solution. Unfortunately, the solubility of the separate components, in particular that of G₂, was too low in chlorinated solvents to carry out a NMR titration. However, in acetonitrile the solubility and the binding constant were found to be sufficient to characterize the PF₆-H₁-G₂ assembly. Upon addition of PF₆-H₁ to G₂ three sets of proton signals appeared, one set originating from free PF₆-H₁, one from free G₂, and one from the assembly PF₆-H₁-G₂. The aromatic region of the free components, PF₆-H₁ and G₂, and of the host-guest complex PF₆-H₁-G₂ are displayed in Figure 3-2.

The appearance of distinct signals shows that the exchange between the free components and the host-guest complex is slow on a NMR timescale. Characteristic for the formation of the assembly PF₆-H₁-G₂ is the clear shift of the proton signals originating from H-5.5' of the bipyridine ligand from 7.52 and 7.51 ppm in free G₂ to 7.58 and 7.41 ppm in PF₆-H₁-G₂. From the ratio between the integrals of the peaks corresponding to free G₂ and those corresponding to
PF₆-H₁-G₂ adduct at different concentrations, the binding constant in acetonitrile-d₃ was calculated to be 4.3 × 10² M⁻¹.

![Figure 3-2](image)

**Figure 3-2.** ¹H NMR spectra (aromatic region) of PF₆-H₁, G₂ and PF₆-H₁-G₂ (2.5 mM in acetonitrile-d₃); characteristic NMR signals corresponding to the host-guest complex are marked (*).

### 3.2.4 Diffusion Ordered NMR Spectroscopy (DOSY)

DOSY is a NMR technique that has proven to be a valuable tool for the characterization of supramolecular complexes. Mixtures of compounds can be "separated" based on their difference in diffusion coefficients and information about the molecular radius of molecules or assemblies in solution can be obtained. The formation of a host-guest complex results in a significant decrease in the diffusion coefficients of both components and can be probed with DOSY.

![Figure 3-3](image)

**Figure 3-3.** A Stejskal-Tanner plot of the experimental peak areas of the proton signals corresponding to bpy-H₅,₅' of free G₂ (7.51 and 7.52 ppm) and of bound G₂ (7.41 and 7.58 ppm). The solid lines represent linear least square fits to the data (R > 0.99); the slope of the line corresponds to the diffusion coefficient D.
A DOSY experiment was performed for an equimolar (2.5 mM) solution of PF$_6$·H1 and G2 in acetonitrile-d$_3$. At these concentrations the free components as well as the host-guest complex are present at sufficient amounts for detection by NMR. A Stejskal-Tanner plot$^{57,58}$ of the H5.5'-bp signal both of free G2 and of the host-guest complex PF$_6$·H1-G2, shows that the peaks corresponding to the assembly PF$_6$·H1-G2 are at a lower diffusion coefficient as compared to the free components (Figure 3-3; the $b$ value corresponds to $\gamma^2\delta^2G^2(\Delta-\delta/3)^{57}$).

According to the Stokes-Einstein equation$^{59}$ the molecular radius of PF$_6$·H1, G2, and PF$_6$·H1-G2 are 10.9 Å, 7.6 Å, and 9.3 Å respectively. In separate DOSY experiments, i.e. in the absence of the other component, the molecular radii of PF$_6$·H1 and G2 were determined for comparison. These were found to be in good agreement with the molecular radii of the free components in the mixture, namely 10.1 Å vs. 10.9 Å for PF$_6$·H1, and 7.0 Å vs. 7.6 Å for G2. As expected the diffusion coefficient of PF$_6$·H1-G2 was lower than that of free G2. Surprisingly, the molecular radius of the assembly PF$_6$·H1-G2 (9.3 Å) was found to be smaller than that of free PF$_6$·H1 (10.9 Å), suggesting that PF$_6$·H1 forms aggregates at these concentrations. Indeed, a dilution study of PF$_6$·H1 using $^1$H NMR spectroscopy revealed that PF$_6$·H1 self-aggregates at the concentration of 2.5 mM. A broadening of the aromatic signals of the pyridine rings and a shift in the signals corresponding to the NH-groups within the binding motive are observed at concentrations higher than 0.5 mM. In addition, from DOSY a smaller molecular radius (9.2 Å) was calculated for PF$_6$·H1 measured at a concentration of 0.1 mM. From the reduction of the molecular radius going from free PF$_6$·H1 (10.9 Å) to the host-guest complex PF$_6$·H1-G2 (9.3 Å) it appears that the small aggregates of self-associated PF$_6$·H1, existing at a concentration of 2.5 mM, dissociate upon binding to G2.

3.2.5 Photophysical Study for BAr$_r$H1·G2

In order to gain more insight in the photophysical processes between BAr$_r$H1 and G2 in the host-guest complex BAr$_r$H1-G2 and to have a quantitative measurement of those processes, transient absorption (TA) spectroscopy has been performed. First, the transient absorption spectrum of G2 has been recorded (Figure 3-4). The spectral properties of G2 are similar to those previously reported for [Re(Br)(CO)$_3$(bpy)].$^{54}$ Adding 1 equivalent of BAr$_r$H1 to this solution new absorption bands are formed with maxima at 400 nm and 610 nm, respectively. By comparison with the TA spectrum of reduced viologen,$^{60}$ the new signals can be assigned to the radical cation of the methyl viologen moiety attached to the receptor (Figure 3-4). Since free BAr$_r$H1 does not give any TA upon excitation at 435 nm, excitation in the MLCT band of G2 results indeed in a photoinduced electron transfer from the excited metal complex to the methyl viologen moiety attached to the receptor within the laser pulse (2 ns FWHM).
The kinetics of the back electron transfer process were studied using single wavelength emission and single wavelength nanosecond TA measurements. Both the excitation and the probing occur at one wavelength only. To exclude bimolecular electron transfer processes in the kinetics measurements, a reference system was used consisting of a $5 \times 10^{-4}$ M solution of dimethyl viologen with 1 equivalent of G2 in acetonitrile. Excitation of the sample with 435 nm laser light with an energy of 4 mJ/pulse did not result in the formation of the radical cation of dimethyl viologen.

The measurements for pure solutions of BArF-H1, G2, and BArF-H1-G2 were performed under the same conditions (at $5 \times 10^{-4}$ M concentration) as used for the reference system. Traces have been recorded at $\lambda_{\text{probe}} = 600$ nm for emission and $\lambda_{\text{probe}} = 470$ nm for transient absorption. These wavelengths are typical for G2, since 600 nm is the maximum of the $^3$MLCT emission and 470 nm of the TA spectrum of the excited state. The traces recorded for G2 in the absence and in the presence of BArF-H1 are compared in Figure 3-5.

From the emission decay at 600 nm the lifetime of the $^3$MLCT state of G2 was determined to be 60 ns. The addition of 1 equivalent of BArF-H1 resulted in a quenching of more than 90 % of the G2 excited state. The lifetime of the excited state of G2 in BArF-H1-G2 is now reduced to < 3 ns. Assuming that the quenching of the excited state of G2 in the host-guest complex BArF-H1-G2 is 100 % efficient, the binding constant was calculated to be $\geq 2 \times 10^5$ M$^{-1}$.

Also the decay measured for the TA spectrum probed at 470 nm shows for G2 the lifetime of 60 ns originating from the $^3$MLCT state. In case of BArF-H1-G2 the intensity of the signal is reduced to less than 10 % of the original signal, supporting the observations in the emission lifetime measurements. The residual absorption originates from the radical cation of the methyl viologen moiety, which also has a weak absorption at 470 nm as can be noticed from Figure 3-4. The negative signal present in the transient absorption trace probed at 470 nm is the result of some
residual emission from BAr\textsubscript{f}-H1. The same negative trace is observed for the sample containing BAr\textsubscript{f}-H1 only.

![Graph showing emission decay and transient absorption traces](image)

**Figure 3-5.** The emission decay probed at 600 nm (a) and the transient absorption trace probed at 470 nm (b) for G2 and BAr\textsubscript{f}-H1-G2 (CH\textsubscript{2}Cl\textsubscript{2}; \(\lambda_{\text{exc}} = 435\) nm).

To further support that the excited state of G2 is quenched in BAr\textsubscript{f}-H1-G2 as a result of an electron transfer to the methyl viologen moiety, a TA trace is measured probing at 400 nm (Figure 3-6). This is in the maximum of the absorption of the reduced methyl viologen moiety.

![Graph showing transient absorption trace](image)

**Figure 3-6.** The transient absorption trace probed at 400 nm for BAr\textsubscript{f}-H1-G2 (CH\textsubscript{2}Cl\textsubscript{2}; \(\lambda_{\text{exc}} = 435\) nm).

The TA trace (\(\lambda_{\text{probe}} = 400\) nm) measured for BAr\textsubscript{f}-H1-G2, can only be the result of the formation of the reduced methyl viologen moiety. This proves indeed that an electron is transferred from (barbi-bpy\textsuperscript{−}) to the methyl viologen moiety. The trace shows a double exponential decay with one component of 25 ns (85\%\,) and one component of \(\sim 40\) \(\mu\)s (15\%). Both refer to the lifetime of the charge-separated state. The rate of the back electron transfer is \(4 \times \)
$10^7 \, \text{s}^{-1}$. The long-lived component is attributed to complex dissociation. The rate of the back electron transfer is in the same order of magnitude as in the covalently linked system \([\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb})]^2^+\) (dmb = 4,4'-dimethyl-2,2'-bipyridine; MQ$^+$ = N-methyl-4,4'-bipyridinium), where the methyl viologen is one of the ligands of the rhenium complex. In that case the lifetime of the charge-separated state was found to be 44 ns in 1,2-dichloroethane and < 4 ns in acetonitrile.\textsuperscript{51}

The forward electron process was monitored using femtosecond TA spectroscopy, exciting at 400 nm and probing at 625 nm, which is close to the maximum of the absorption of the reduced methyl viologen. Figure 3-7 shows the full TA spectra of G2 and of the host-guest complex BAr$_r$H1•G2 2.5 ps after the laser pulse (CH$_2$Cl$_2$; $\lambda_{\text{exc}} = 400$ nm).

![Figure 3-7](image)

**Figure 3-7.** The full TA spectra of G2 and of the host-guest complex BAr$_r$H1•G2 recorded 2.5 ps after the laser pulse (CH$_2$Cl$_2$; $\lambda_{\text{exc}} = 400$ nm).

A significant part (57 \%) of the 625 nm transient is formed instantaneously, i.e. within the instrument time resolution ($k_{\text{rel,1}} > 7 \times 10^{12} \, \text{s}^{-1}$). A slower rise then ensues of which the kinetics fit the equation $\Delta A = A_0^+ + A^+_1(1-\exp(-t/\tau_i))$, with a rise time $\tau_i$ of 400 fs (43 \%), indicating that the rate of the forward electron transfer ($k_{\text{rel,2}}$) is $2.5 \times 10^{12} \, \text{s}^{-1}$ (lower limit). So, the formation of the radical cation of the methyl viologen moiety occurs via two different processes (Figure 3-8a).

The rates of the forward electron transfer are very similar to those found for \([\text{Re}(\text{MQ}^+)(\text{CO})_3(\text{dmb})]^2^+\).\textsuperscript{48,51} Also in that case a significant part of the transient is formed within the laser pulse, followed by a slower rise with a rise time $\tau_i$ of 8 ps and 14 ps in acetonitrile and ethyleneglycol, respectively.\textsuperscript{48,51} The fastest component is attributed to direct excitation in the charge-separated state and the slower component to an intraligand (IL) transition, which concerns the transfer of an electron from the reduced bipyridine ligand (dmb$^-$) to the methyl viologen ligand.\textsuperscript{51} Since the slow component (400 fs) of the forward electron transfer is similar to the intersystem crossing from the $^1\text{MLCT}$ state of G2, which is formed instantaneously upon
excitation, to the $^3\text{MLCT}$ of $\text{G}_2$ (Figure 3-8a), the IL transition is likely to occur from the $^3\text{MLCT}$ state of $\text{G}_2$. Another possibility is that $\text{BAr}_7\text{H}_1\text{G}_2$ can have two different conformations in solution; one in which the methyl viologen unit is in very close proximity of $\text{G}_2$, and one in which the methyl viologen unit points away from $\text{G}_2$. In the first case the electron transfer is expected to be extremely fast, since the electron donor and the electron acceptor are in very close proximity of each other. In the latter case the electron transfer should be slower due to the larger distance between the electron donor and the electron acceptor.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-8.png}
\caption{The transient absorption trace probed at 625 nm (a) on a very short timescale (0 - 10 ps) and (b) on a longer timescale (0 - 800 ps) for $\text{G}_2$ and $\text{BAr}_7\text{H}_1\text{G}_2$ ($\text{CH}_2\text{Cl}_2$: $\lambda_{\text{exc}} = 400$ nm).}
\end{figure}

The formation of the charge separated state is followed by a bi-exponential decay with a lifetime corresponding to 29 ps (27\%) and 1.32 ns (23\%) (Figure 3-8b), and a subsequent decay to the ground state with a lifetime of 25 ns (50\%). The short-lived component of 29 ps is most probably due to the decay of the CT state, that is not yet stabilized by the solvent. The long-lived component of 25 ns is attributed to the solvent-stabilized CT state. The results are summarized in Scheme 3-3.

The kinetics of both the forward and the back electron transfer resemble closely the kinetics of the PET in $[\text{Re}($\text{MQ}$(+)(\text{CO})_3($\text{dmb}$)$])^2+$. The differences in kinetics of the PET found here and those found for $[\text{Re}($\text{MQ}$(+)(\text{CO})_3($\text{dmb}$)$])^2+$ can be attributed to the different solvents used. In general the rates of electron transfer processes depend strongly on the polarity of the solvent, which determines its ability to stabilize the charge-separated state.

The great similarities in the kinetics of the PET of the covalently linked system and the supramolecular system and the DOSY experiments imply that the distance between the methyl viologen moiety and $\text{G}_2$ is very small in $\text{BAr}_7\text{H}_1\text{G}_2$. Vlcek, Jr. et al. suggested that in the case of $[\text{Re}($\text{MQ}$(+)(\text{CO})_3($\text{dmb}$)$])^2+$ the electron transfer could proceed via a through-solvent tunneling mechanism. Since the through space distance between and the (barbi-bpy$^-$) donor and the
methyl viologen acceptor moiety can be significantly shorter than the through bond distance, the tunneling mechanism could provide a reasonable explanation for the ultrafast kinetics measured in dichloromethane for the hydrogen-bonded complex.

Scheme 3-3. Photoinduced electron transfer (PET) in BArf-H1·G2: a schematic representation of the species involved.

3.3 Conclusions

In this Chapter it has been demonstrated that ultrafast photoinduced electron transfer processes can occur between an electron donor and an electron acceptor, which are assembled via hydrogen bonds. The kinetics of the electron transfer in the hydrogen-bonded system, BArf-H1·G2, are similar to the electron transfer kinetics in the covalently linked system, [Re(MQ+)(CO)3(dmb)]2+. This emphasizes that the introduction of a reversible connection between the electron donor and the electron acceptor, which does not only imply a weaker connection, but also a longer through-bond distance between donor and acceptor, does not necessarily result in slower kinetics of the electron transfer processes as compared to the corresponding covalently linked system. The
overall conformation of the assembly, which may be such that the electron donor and acceptor are in close proximity of each other, proves to be of great importance for the electronic coupling between the donor and the acceptor. The design of the receptor, the substrate, the electron donor and acceptor, and the linkers used to attach the electron donor and acceptor to the recognition units are crucial for the final conformation and flexibility of the entire system. Especially, potential secondary interactions within the supramolecular system should be taken into account. Furthermore, a through-solvent electron transfer mechanism may promote an efficient electron transfer within the assembly. Since the charge separation is four orders of magnitude faster than the charge recombination, this type of systems could be an interesting building block in electron-transport chains. The electron donor-acceptor system presented in this Chapter is one of the few examples of hydrogen-bonded assemblies, for which the electron transfer kinetics resemble those of the covalently linked system. The supramolecular approach offers the possibility to make libraries of donor-acceptor couples to search for the most efficient combinations and to create even larger multi-component systems in which electron transfer processes can occur. This will certainly result in a larger variety and a greater complexity of hydrogen-bonded donor-acceptor systems in the future.
3.4 Experimental Section

3.4.1 Solvents and Starting Materials

All reagents used were obtained from available commercial sources and used without additional purification unless otherwise indicated. CH\textsubscript{2}Cl\textsubscript{2} was distilled from CaH\textsubscript{2} and THF from Na/benzophenone prior to use. Commercial deuterated solvents were used as received for the characterization of the compounds. Acetonitrile-d\textsubscript{3} was distilled from CaH\textsubscript{2} to 4Å molecular sieves prior to use for the binding study.

3.4.2 Synthesis

*Preparation of the Methyl Viologen-Functionalized Barbiturate Receptor.* 1-Methyl-4,4'-bipyridinium (iodide) was prepared according to a literature procedure.\textsuperscript{61}

\[
\text{5-Nitroisophtaloyl Dichloride (1).} \quad \text{A slurry of 5-nitroisophtalic acid (0.45 g, 2.14 mmol), 1 mL of chloroform, 10 mL of thionyl chloride, and 2 drops of DMF was heated at reflux under N\textsubscript{2} for 5h.} \quad \text{5-Nitroisophtaloyl dichloride was precipitated from the reaction mixture using n-hexane and was, after decanting of the solvents, directly used without further purification.}
\]

\[
\text{1,3-Bis[[(6-aminopyrid-2-yl)amino]carbonyl]-5-nitrobenzenee (2).} \quad \text{To a solution of 2,6-diaminopyridine (2.22 g, 20.3 mmol) and triethylamine (0.51 g, 5.04 mmol) in 100 mL THF was added dropwise a solution of (1) in 20 mL of THF at room temperature under N\textsubscript{2}.} \quad \text{The reaction mixture was stirred for 3h, after which the solvent was removed under reduced pressure. The residue was washed with water to remove the excess of 2,6-diaminopyridine and triethylamine hydrochloride. The crude product was purified further by crystallization from THF/n-hexane, yielding 0.44 g (1.11 mmol, 52\%) of (2) as a yellow powder.} \quad \text{\textsuperscript{1}H NMR (dmsso-d\textsubscript{6}): } \delta (ppm) = 5.86 (s, two NH\textsubscript{2}), 6.30 (d, J = 8.10 Hz, H\textsubscript{py}-3), 7.39 (d, J = 7.80 Hz, H\textsubscript{py}-5), 7.47 (t, J = 7.80 Hz, H\textsubscript{py}-4), 8.80 (s, H\textsubscript{ar}-2,H\textsubscript{ar}-6), 8.92 (s, H\textsubscript{ar}-4), 10.61 (s, two C\textsubscript{py} CONH).
\]

\[
\text{13C NMR (dmsso-d\textsubscript{6}): } \delta (ppm) = 102.0, 104.6, 125.6, 132.8, 135.9, 139.1, 147.9, 150.1, 158.7, 163.0.
\]

\[
\text{HRMS (FAB) calcd. for C\textsubscript{18}H\textsubscript{16}O\textsubscript{4}N\textsubscript{7} (MH\textsuperscript{+}): 394.1264, found 394.1274.}
\]

\[
\text{3,5-Bis[[6-tert-butylacetylamino-2-pyridyl]amino]carbonyl]-nitrobenzenee (3).} \quad \text{To a solution of (2) (0.59 g, 1.50 mmol) and 1.0 mL triethylamine in 50 mL of anhydrous THF was added dropwise tert-butylacetyl chloride (0.46 g, 3.05 mmol).} \quad \text{The reaction mixture was stirred overnight, after which the solvent was removed in vacuo.} \quad \text{The crude product was purified using column chromatography on Al\textsubscript{2}O\textsubscript{3} (neutral) with 95:5 v/v DCM/MeOH as the eluent.} \quad \text{Crystallization from THF/n-hexane yielded 0.58 g (0.99 mmol, 65.6 \%) of (3) as a slightly yellowish powder.} \quad \text{\textsuperscript{1}H NMR (dmsso-d\textsubscript{6}): } \delta (ppm) = 1.02 (s, C\textsubscript{1}(CH\textsubscript{3})\textsubscript{3}), 2.31 (s, CH\textsubscript{2}C\textsubscript{2}(CH\textsubscript{3})\textsubscript{3}), 7.84 (m, H\textsubscript{py}-3,H\textsubscript{py}-4,H\textsubscript{py}-5), 8.91 (s, H\textsubscript{ar}-4), 8.92 (s, H\textsubscript{ar}-2,H\textsubscript{ar}-6), 10.07 (s, two C\textsubscript{py}CONH), 10.96 (s, two C\textsubscript{ar}CONH).
\]

\[
\text{13C NMR (dmsso-d\textsubscript{6}): } \delta\]
Ultrafast Photoinduced Electron Transfer

3,5-Bis[[6-tert-butylacetylamino-2-pyridyl]amino][carbonyl]-aniline (4). To a stirred suspension of (3) (0.50 g, 0.85 mmol) and 10% Pd-C (0.08 g) in 25 mL of ethanol abs. 0.5 mL of hydrazine monohydrate was added. The reaction mixture was refluxed for 4h under N2. The catalyst was removed by filtration through a Celite path and washed with ethanol abs.. The solvent was removed in vacuo, yielding 0.46 g (0.83 mmol, 98%) of (4) as a bright yellow solid. 1H NMR (dmso-d6): & (ppm) = 1.01 (s, C(C(CH3)3), 2.30 (s, CH2C((CH3)3), 5.67 (s, NH2), 7.33 (s, H-ar-2,H-ar-6)), 7.68 (s, H-ar-4), 7.81 (m, H-py-3,H-py-4,H-py-5), 10.04 (s, two C-arCONH), 10.22 (s, two C-arCONH). 13C NMR (dmso-d6): & (ppm) = 29.7, 31.0, 49.2, 109.8, 110.2, 114.0, 116.4, 135.0, 140.1, 149.4, 150.3, 150.6, 165.9, 171.0. HRMS (FAB) calcd. for C30H36O6N7 (MH+): 590.2727, found 590.2746.

2-Bromo-N-(3,5-bis[[6-tert-butylacetylamino-2-pyridyl]amino][carbonyl])-phenylacetamide (5). To a solution of bromoacetyl chloride (234 mg, 1.32 mmol) in 10 mL of dry THF cooled at 0 °C was added dropwise, under vigorous stirring, a solution of (4) (0.49 g, 0.88 mmol) and 4-(dimethylamino)pyridine (50 mg, 0.41 mmol) in 20 mL of dry THF. After 2h the reaction mixture was quenched with H2O and extracted with 3 x 30 mL of CH2Cl2. The organic extract was washed with 3 x 10 mL of a saturated NaHCO3 solution, dried with anhydrous MgSO4, and concentrated under reduced pressure, yielding 0.53 g of (5) (0.78 mmol, 88.6%) as a white solid. 1H NMR (dmso-d6): & (ppm) = 1.02 (s, C(C(CH3)3), 2.31 (s, CH2C((CH3)3), 4.11 (s, CH2Br), 7.80 (m, H-py-3,H-py-4,H-py-5), 8.28 (s, H-ar-4), 8.35 (s, H-ar-2, H-ar-6), 10.00 (s, two C-pyCONH), 10.42 (s, two C-arCONH), 10.82 (s, C-arCONH). 13C NMR (dmso-d6): & (ppm) = 29.6, 30.2, 30.9, 49.1, 110.1, 110.4, 121.9, 122.3, 134.9, 139.1, 140.1, 150.0, 155.0, 165.0, 165.4, 170.9. HRMS (FAB) calcd. for C32H39N7O5Br (MH+) = 680.2196, found 680.2141; HRMS (FAB) calcd. for C32H39N7O58lBr (MH+) = 682.2182, found 682.2155.

1-(N-(3,5-Bis[[6-tert-butylacetylamino-2-pyridyl]amino][carbonyl])-phenylacetamide)-1’-methyl- 4,4’-bipyridium (Br- / I) (X-H1). 1-Methyl-4,4’-bipyridium (iodide) (184 mg, 0.619 mmol) was refluxed overnight with 1 equivalent of (5) (420 mg, 0.617 mmol) in acetonitrile. The halide salt was filtered from the cooled solution and washed with a small amount of acetonitrile, yielding 0.38 g of X-H1 (0.388 mmol, 62.6%) as a red-brownish powder. 1H NMR (dmso-d6): & (ppm) = 1.01 (s, C((CH3)3), 2.30 (s, CH2C((CH3)3), 4.46 (s, bpy-CH3), 5.87 (s, bpy-CH2), 7.79 (m, H-py-4), 7.84 (m, H-py-3,H-py-5), 8.33 (s, H-ar-4), 8.37 (s, H-ar-2,H-6), 8.82 (d, J = 5.50 Hz, H-py-3,H-py-5), 8.90 (d, J = 5.50 Hz, H-py-2,H-py-6), 9.34 (d, J = 5.50 Hz, H-py-3,H-py-5), 9.40 (d, J = 5.50 Hz, H-py-2,H-6), 9.98 (s, two
**Chapter 3**

C_{py} CONH), 10.46 (s, two C_{ar} CONH), 11.41 (s, C_{ar} CONH). \textsuperscript{13}C NMR (dms-o-d6): \( \delta \) (ppm) = 29.6, 30.9, 48.1, 49.1, 62.2, 110.1, 110.4, 122.0, 122.5, 126.1, 126.3, 134.9, 138.8, 140.2, 146.7, 147.5, 148.1, 149.4, 150.0, 150.5, 163.7, 164.9, 171.0. HRMS (FAB) calcd. for C_{43}H_{49}N_{6}O_{5}^{79}Br (MH\textsuperscript{+}-I): 852.3030, found 852.3044; HRMS (FAB) calcd. for C_{43}H_{49}N_{6}O_{5}^{81}Br (MH\textsuperscript{+}-I): 850.3040, found 850.3055.

1-(N-(3,5-bis[(6-tert-butylacetylamino-2-pyridyl)amino]carbonyl)-phenylacetamide)-1'-methyl-4,4'-bipyridium (2PF_{6}) (PF_{6}-H1). X-H1 (0.38 g, 0.388 mmol) was dissolved in water and then precipitated by adding a concentrated solution of NH_{4}PF_{6} in water to yield 296 mg (0.276 mmol, 72.6 \%) of PF_{6}-H1. \textsuperscript{1}H NMR (acetonitrile-d3): \( \delta \) (ppm) = 1.05 (s, C((CH_{3})_{3}), 2.26 (s, CH_{2}C((CH_{3})_{3}), 4.42 (s, bpy-CH_{3}), 5.58 (s, bpy-CH_{2}), 7.85 (m, H_{py}-3, H_{py}-4, H_{py}-5), 8.13 (s, H_{ar}-4), 8.26 (s, H_{ar}-2, H_{ar}-6), 8.42 (d, \( J = 7.00 \) Hz, H_{bpy}-3, H_{bpy}-5), 8.47 (d, \( J = 7.00 \) Hz, H_{bpy}-2, H_{bpy}-6), 8.55 (s, two C_{py} CONH), 8.87 (d, \( J = 7.00 \) Hz, H_{bpy}-3, H_{bpy}-5), 8.92 (d, \( J = 7.00 \) Hz, H_{bpy}-2, H_{bpy}-6), 9.09 (s, two C_{ar} CONH), 9.26 (s, C_{ar} CONH). \textsuperscript{13}C NMR (dms-o-d6): \( \delta \) (ppm) = 29.9, 31.8, 49.7, 50.8, 63.5, 110.6, 110.7, 123.1, 123.4, 127.7, 128.0, 136.6, 139.4, 141.6, 147.5, 148.3, 150.6, 150.9, 151.4, 152.0, 163.6, 165.7, 172.1. HRMS (FAB) calcd. for C_{43}H_{49}N_{6}O_{5}PF_{6} (MH\textsuperscript{+}-PF_{6}): 916.3498, found 916.3452.

Na[B[3,5-(CF_{3})_{2}C_{6}H_{3}]_{4}] (NaBARf) has been prepared according to a literature procedure.\textsuperscript{62}

1-(N-(3,5-bis[(6-tert-butylacetylamino-2-pyridyl)amino]carbonyl)-phenylacetamide)-1'-methyl-4,4'-bipyridium (2BARf) (BARf-H1). X-H1 (256.5 mg, 0.262 mmol) was dissolved in water and extracted with diethyl ether containing 1.8 equivalents of NaBARf (440.7 mg, 0.50 mmol). The diethyl ether layer was collected and the solvent was removed in vacuo to yield 0.56 g (0.224 mmol, 89.7 \%) of BARf-H1. \textsuperscript{1}H NMR (acetonitrile-d3): \( \delta \) (ppm) = 1.01 (s, C((CH_{3})_{3}), 2.29 (s, CH_{2}C((CH_{3})_{3}), 4.46 (s, bpy-CH_{3}), 5.81 (s, bpy-CH_{2}), 7.83 (m, H_{py}-3, H_{py}-4, H_{py}-5), 8.33 (s, H_{ar}-4), 8.37 (s, H_{ar}-2, H_{ar}-6), 8.80 (d, \( J = 7.00 \) Hz, H_{bpy}-3, H_{bpy}-5), 8.88 (d, \( J = 7.00 \) Hz, H_{bpy}-2, H_{bpy}-6), 9.32 (d, \( J = 7.00 \) Hz, H_{bpy}-3, H_{bpy}-5), 9.36 (d, \( J = 7.00 \) Hz, H_{bpy}-2, H_{bpy}-6), 9.95 (s, two C_{py} CONH), 10.45 (s, two C_{ar} CONH), 11.20 (s, C_{ar} CONH). \textsuperscript{13}C NMR (dms-o-d6): \( \delta \) (ppm) = 29.5, 29.5, 30.8, 48.1, 49.1, 110.2, 110.3, 117.6 (septet, \( ^{3}J_{13}C^{19}F \) = 3.77 Hz), 122.0, 124.0 (q, \( ^{2}J_{13}C^{19}F \) = 271.5 Hz), 126.3, 127.2, 128.5 (m, \( ^{4}J_{13}C^{11}B \) = 2.9 Hz, \( ^{2}J_{13}C^{11}F \) = 31.8 Hz), 134.0, 135.0, 138.7, 140.1, 146.7, 147.5, 148.2, 149.5, 149.9, 150.5, 161.0 (q, \( ^{2}J_{13}C^{11}B \) = 49.7 Hz), 161.0 (t, \( ^{2}J_{13}C^{10}F \) = 50.3 Hz), 163.6, 164.8, 170.9. HRMS (FAB) calcd. for C_{107}H_{74}N_{6}O_{3}PF_{2}F_{4}B (MH\textsuperscript{+}): 2497.5262, found 2498.5107. UV-Vis \( \lambda_{\text{max}} \) (r in \text{M}^{-1}\text{cm}^{-1}) (CH_{2}Cl_{2}): 302 nm (34000).

5-[4-(4'-Methyl)-2,2'-bipyridyl]methyl-2,4,6-(1H,3H,5H)-pyrimidinetrione (barbi-bpy) was prepared according to a literature procedure.\textsuperscript{62}
[Re(Br)(CO)$_5$(barbi-bpy)] (G2). A solution of [Re(Br)(CO)$_5$] (0.41 g, 1.01 mmol) and (barbi-bpy) (0.29 g, 0.93 mmol) in 50 mL of acetonitrile was heated at reflux under N$_2$ overnight. After the evaporation of acetonitrile and washing with pentane, ether and dichloromethane, 0.34 g (55.4%, 0.52 mmol) of G2 was obtained as a yellow powder. $^1$H NMR (acetonitrile-d$_3$): $\delta$ (ppm) = 2.57 (s, bpy-4'-C$_6$), 3.50 (d, $J = 5.0$ Hz, bpy-4-CH$_3$), 4.07 (t, $J = 5.0$ Hz, CH), 7.45 (d, $J = 5.5$ Hz, H$_{bpy}$-5'), 7.48 (d, $J = 5.5$ Hz, H$_{bpy}$-6), 9.02 (2xs, two NH). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ (ppm) = 21.6, 32.3, 49.8, 125.6, 125.7, 126.6, 126.7, 128.9, 129.2, 153.5, 153.6, 156.2, 156.5, 169.1, 172.5, 190.5, 198.5. IR (CH$_2$Cl$_2$): v(C=O) 2033 cm$^{-1}$ (s), 2023 cm$^{-1}$ (s), 1918 cm$^{-1}$ (s). HRMS (FAB) calcd. for C$_{19}$H$_{14}$O$_6$N$_4$BrRe (MH$^+$): 659.9637, found 659.9659. UV-Vis $\lambda_{max}$ ($\varepsilon$ in M$^{-1}$cm$^{-1}$) (CH$_2$Cl$_2$): 372 nm (1900).

3.4.3 Instrumentation

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian Inova500 at 499.86 and 125.70 MHz, respectively. Diffusion measurements were carried out on a Varian Inova500 equipped with a Performa II pulsed gradient unit able to produce magnetic field pulse gradients of about 30 Gcm$^{-1}$ in the z-direction. The DOSY experiments were carried out in a 5 mm inverse probe at 295 K. The magnetic field pulse gradients were of 1 ms duration followed by a stabilization time of 2 ms. The diffusion delay was set to 0.1 s. The magnetic field pulse gradients were incremented from 0 to 25 Gcm$^{-1}$ in ten steps and the stimulated spin echo experiment was performed with compensation for convection. The pulse sequence was developed by Evans and Morris (University of Manchester). Fast Atom Bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with Xe atoms with an energy of 3 keV. During the high-resolution FAB-MS measurements a resolving power of 10,000 (10 % valley definition) was used. UV-Vis absorption spectra were recorded on a diode-array HP8453 spectrophotometer at 293 K. Fluorescence spectra were recorded on a SPEX fluorometer. Full transient absorption spectra were obtained 10 ns after the laserpulse (1 frame, 50 accumulations, 4 ml/pulse) exciting with a 2 ns (FWHM) Coherent YAG laser (10 Hz repetition rate) at 435 nm and using an OMA detection system. Nanosecond flash photolysis emission kinetics was measured by irradiating the sample at 435 nm with a 2 ns (FWHM) Coherent YAG 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 Muller Electronik MSP05 pulsing unit giving pulses of 0.5 ms. 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. The absorption transients were plotted as $\Delta A = \log(I_0/I_t)$ versus time, where $I_0$ was the monitoring light intensity prior the laser pulse and $I_t$ the observed signal at delay time $t$. The femto second TA setup used to probe the processes occurring within 1
ns has been described previously. Details on the experimental set-ups used to study the photophysical processes presented in this Chapter are given in the Appendix of this Thesis.

3.4.4 Determination of the Association Constant ($K_{ass}$) of PF$_6$-H1-G2 in Acetonitrile-d$_3$

The association constant of PF$_6$-H1-G2 in acetonitrile-d$_3$ was calculated from the ratio between the integrals of proton signals corresponding to the free components and the assembly. Since the ratio between the free components and the complex depends on the concentration, solutions containing 2.5 mM, 1.0 mM, 0.5 mM and 0.1 mM PF$_6$-H1-G2 have been measured subsequently to obtain an accurate value for $K_{ass}$.

3.4.5 Determination of the Association Constant ($K_{ass}$) of BAR$_F$-H1-G2 in CH$_2$Cl$_2$

Time-resolved fluorescence measurements were performed for a solution containing 5 $\times$ 10$^{-4}$ M BAR$_F$-H1-G2 to determine the association constant in CH$_2$Cl$_2$. The association constant was calculated from the amount of G2 emission quenched in the presence of 1 equivalent of BAR$_F$-H1, assuming that the electron transfer from G2 to the methyl viologen moiety is 100% efficient.
3.5 References and Notes

    Soc. 2001, 123, 3655.
    1938.
    2000, 6, 3558.
40. Scandola, F.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A. In Electron Transfer in Chemistry
44. Yonemoto, E. H.; Saupe, G. B.; Schmehl, R. H.; Hubig, S. M.; Riley, R. L.; Iverson, B. L.;
57. Stejskal-Tanner equation: \( \ln(I/I_0) = -\frac{1}{2} \gamma^2 G^2 (\Delta - \delta^3) D \), where \( I \) is the peak area, \( I_0 \) is the peak area in the absence of gradients, \( \gamma \) the magnetogyric ratio of the observed nucleus, \( \delta \) is the gradient duration, \( G \) the strength of the gradient pulse in T/m, \( \Delta \) the diffusion time and \( D \) the diffusion coefficient.
59. The Stokes-Einstein equation: \( D = \frac{k_B T}{6 \pi n r} \), where \( D \) is the diffusion coefficient, \( k_B \) is the Boltzmann constant, \( T \) is the temperature in Kelvin, \( n \) is the viscosity of the solution, and \( r \) is the radius of the molecular sphere. The viscosity of neat acetonitrile-d₃ was used.