

## 6 Light-induced charge Separation over Distances of 5, 10 and 15 Å in Water- and Solvent- filled Yoctowells

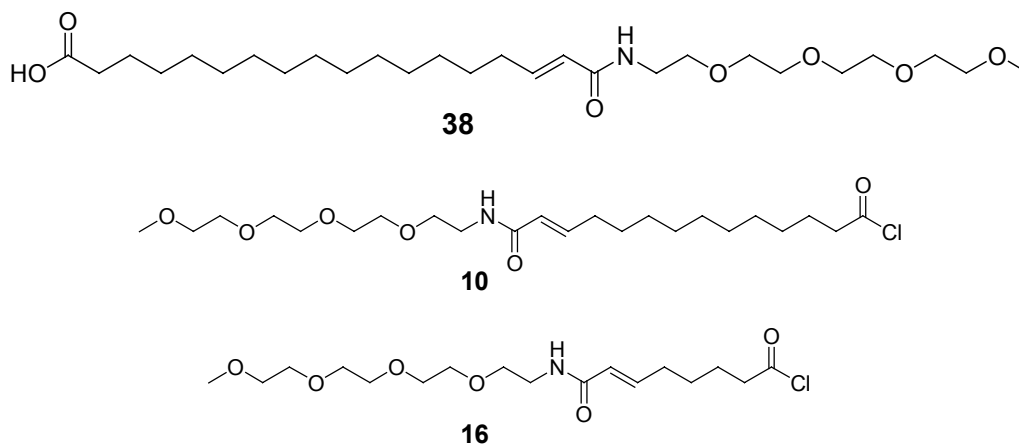
### 6.1 Introduction

Porphyrin-based yoctowells in rigid lipid monolayers<sup>23-25</sup> provide the unique possibility to study photo induced electron transfers in isolated face-to-face or orthogonal non-covalent complexes. Aggregation of the redox pairs is impossible, because the complexes are entrapped in solid wells. Furthermore the distance between the donor at the well's bottom and the loosely attached acceptor can be varied in a range of about 4-10 Å with an accuracy of  $\pm 1$  Å. The fluid in the wells can be water or any other solvent, which does not break amide hydrogen bonds.<sup>109</sup> We studied charge separation between a zinc porphyrin and a *bis*-iminoquinone, which were situated face-to-face in distance of 5, 10 and 15 Å. Solvents of different polarity were used to dissolve the carrier particles and to fill the yoctowells. An orthogonally placed tetrapyridinium ligand to the zinc porphyrinate was also investigated.

## 6.2 Heterodimers with in the yoctowells

### 6.2.1 Preparation of yoctowells on aminated silica particles

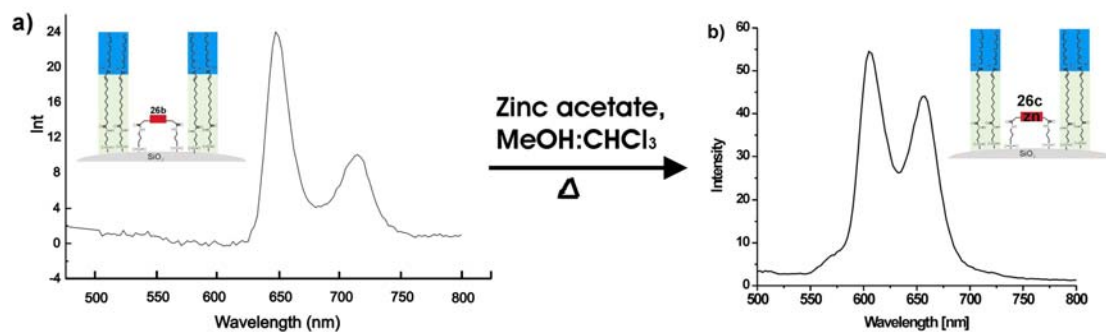
The aminated silica colloidal particles was washed 4 times with anhydrous ethanol and dry  $\text{CH}_2\text{Cl}_2$  by repeated centrifugation, dispersion, and ultrasonification. Then, obtained silica particles were dissolved in of dry  $\text{CH}_2\text{Cl}_2$  containing dry triethylamine. With vigorous stirring, then was added  $\text{CH}_2\text{Cl}_2$  solution of activated meta-tetracarboxy with ethylchloroformate **26b** was added dropwise. After the mixture was stirred for 2 h, the solution of bola (scheme1) **10** or **16** or **38** in  $\text{CH}_2\text{Cl}_2$  were given. The resulting suspension was stirred in the dark overnight. The membrane coated nanoparticles were isolated by repeated centrifugation, dispersion.



**Scheme 1**

### Preparation of silicate particles with zinc porphyrin (**26c**) at the bottom

It is known that zinc porphyrins form stable cation radicals, whereas free base porphyrins do not.<sup>113</sup> For this purpose we had changed our bottom free base porphyrin **26b** to zinc porphyrin **26c**. A silica particles containing yoctowells were dispersed in methanol :chloroform (1:1), after dispersion equimolar amount by weight zinc acetate was added and refluxed these particles for 4 hrs with slow stirring. After completion of conversion nanoparticles were isolated by repeated centrifugation, dispersion, and ultrasonification using methanol (three times) and chloroform (two times) to remove excess zinc acetate (Figure 6.1b).

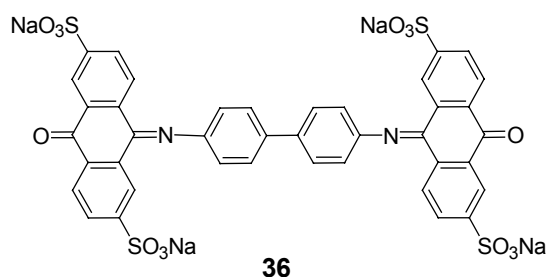


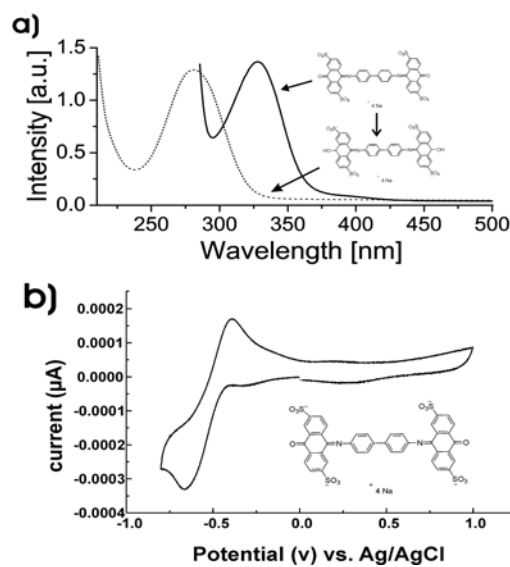
**Figure 6.1** Fluorescence of (a) free base porphyrin **26b** converted to (b) zinc porphyrin **26c** at the bottom of the yoctowells.

### 6.2.2 Functionalization of walls of yoctowells

Amino groups were introduced on the wall of yoctowells by Michael addition of methylamine to the trans double bond of bolaamphiphile having length 15 Å for bola **38**, 10 Å for bola **10** and 5 Å for bola **16** on silica particles. Briefly, gaps-coated silicate particles prepared above were dispersed in 10 mL of an aqueous solution of methylamine (10 mM). After the mixture was stirred for 2 h, the silica particles were collected by centrifugation and washed several times using Milli-Q water.

A ring of methylammonium groups was then fixed at the walls of the wells at a distance of 5, 10 and 15 Å with respect to the bottom zinc porphyrin **26c**. This ring was used to attach the four negative sulfonate groups of the *bis*-iminoquinone **36**, which was prepared from benzidine and anthraquinone sulfonate for this purpose we perform a schiff base method. It has same diameter of 22 Å as the bottom porphyrin **26c** and a reduction potential of -550 mV vs an Ag/Ag(I) electrode reduction and re-oxidation spectra UV/vis (Figure 6.2), which is comparable to other iminoquinones.<sup>114</sup> It was water- stable for at least 3 days at pH 6-9.



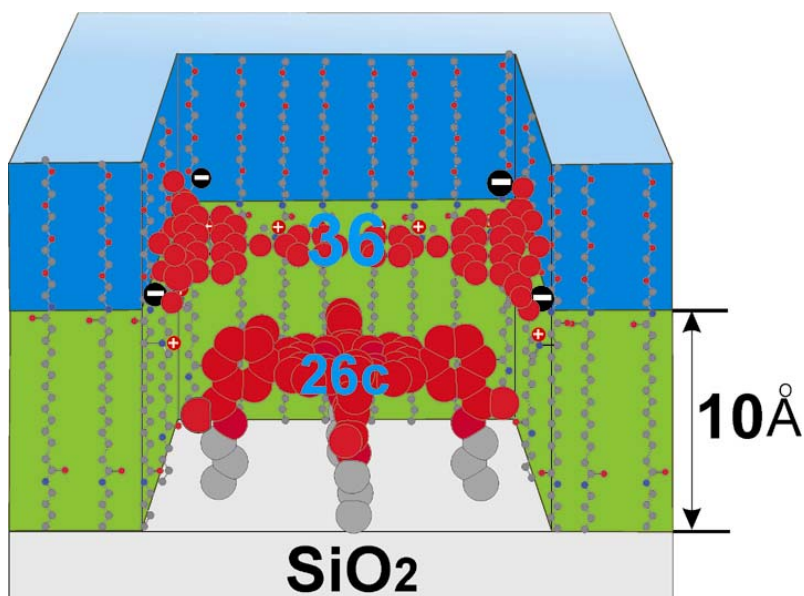


**Figure 6.2 UV/vis** (a)  $10^{-4}$  M solution of bis-iminoquinone (dark line) *bis*-iminohydroquinone after reduction with NaBH<sub>4</sub>(dotted line); **and CV** (b) Cyclic voltmeter (cv) of bis-iminoquinone  $-550$  mV vs an Ag/Ag(I).

We applied acceptor as a *bis*-iminoquinone for light induced charge transfer reaction applying fluorescence decay measurements with the help of Prof. Röder.

### 6.2.3 Construction of porphyrin (26c)-*bis*-iminoquinone (36) heterodimer within the yoctowells

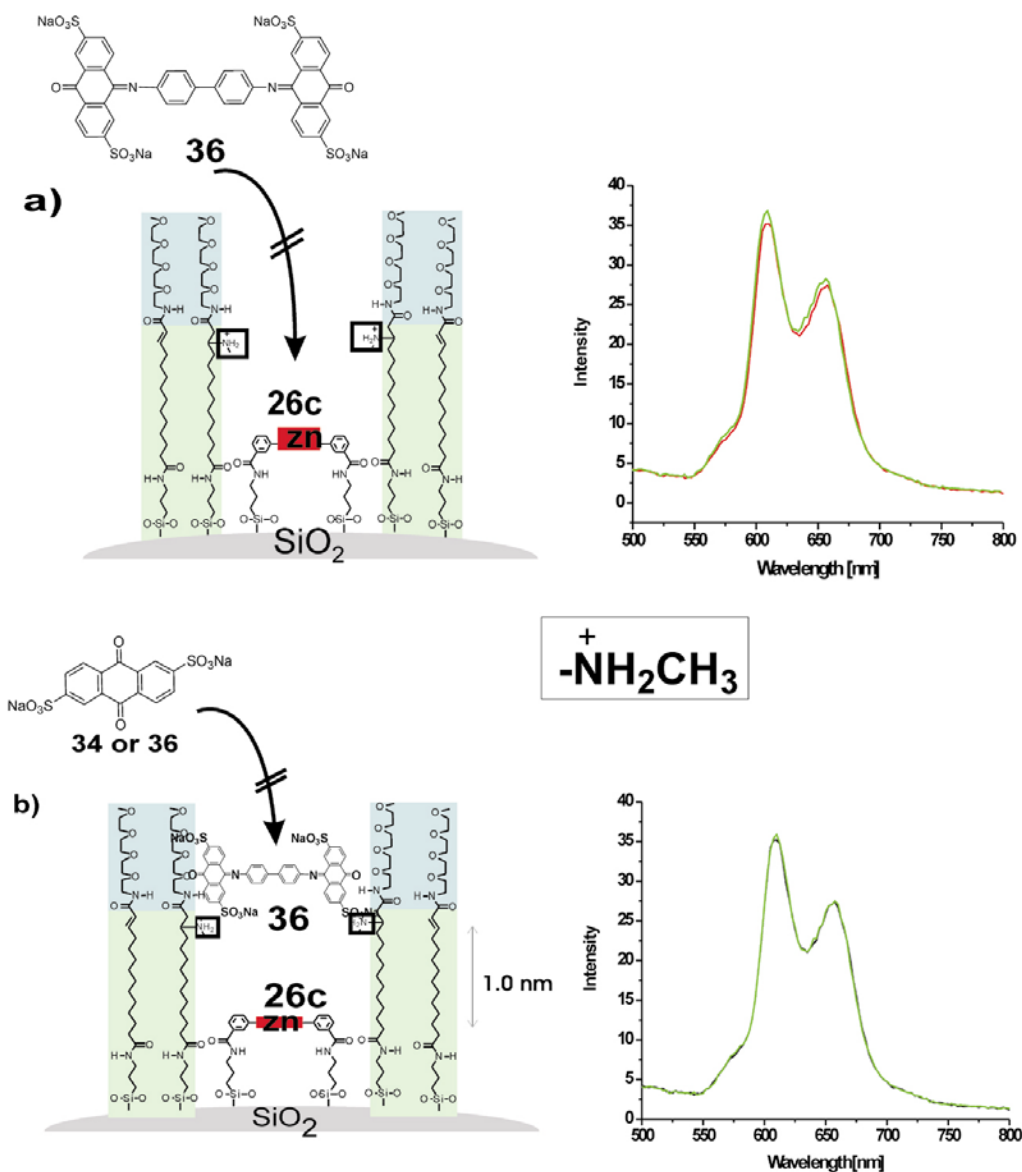
Porphyrin-iminoquinone heterodimers (Figure 6.3) separated by a defined distance were established on silica particles as follows. Silica particles (0.5 g) with amino functionalized gaps were dispersed in 5 mL of Milli-Q water, and *bis*-iminoquinone **36** (0.1 mg) was added. The reaction mixture was stirred for 30 min and kept in the dark overnight. Silica particles with porphyrin-iminoquinone heterodimers were obtained after washing with Milli-Q water three times to remove excess iminoquinone (see model 6.3) and finally applied for singlet state charge transfer reaction.



**Figure 6.3** Model of the yoctowell with a porphyrin **26c** bottom and an iminoquinone **36** at the top of the rim.

### Confirmation of heterodimers by fluorescence quenching experiments

Fluorescence quenching of zinc porphyrin **26c** by addition of  $10^{-4}$  M quinone disulfonate **34** and *bis*-iminoquinone **36** after Michael addition of methylamine to the double bonds facing the gap does not lead to fluorescence quenching of the bottom zinc porphyrin **26c**. Addition of a large excess of *bis*-iminoquinone **36** or quinone **34** to the porphyrin-covered sample with *bis*-iminoquinone **36** does not lead to fluorescence quenching of the bottom zinc porphyrin (figure 6.4a), *bis*-iminoquinone **36** covers close the gap reversibly. 2,6-Disulfonatoanthraquinone **34** was attached only loosely to this ring, but the exactly fitting *bis*-iminoquinone **36** was tightly bound (figure 6.4b). Two different dyes have thus been immobilized at a defined sub-nanometer distance in an aqueous medium.



**Figure 6.4** Fluorescence quenching of zinc porphyrin **26c** by addition of (a)  $10^{-6}$  M quinone disulfonate **34** and (b) *bis*-iminoquinone **36** after Michael addition of methylamine to the double bonds facing the gap. (b) Addition of a large excess of *bis*-iminoquinone **36** or quinone **34** to the porphyrin-covered sample does not lead to fluorescence quenching of the bottom zinc porphyrin **26c**. Thus, *bis*-iminoquinone **36** closed the gap reversibly at distances of 6, 10 and 15 Å.

After conformation of the heterodimers by fluorescence quenching experiments we applied these silica colloidal particles with heterodimers within the yoctowells to the excited fluorescence decay of the bottom zinc porphyrin **26c** in the absence or presence of *bis*-iminoquinone **36** at a distance of 15 Å , 10 Å and 5 Å on the amino silicate

particles with noncovalent porphyrin-iminoquinone heterodimers within the yoctowells. The excited singlet state of **26c** was therefore produced with 200-fs pulses at 428 nm, and its decay time was measured. The blank experiments without the distant iminoquinone showed two typical times of decay of ~2.4 ns and 0.7 ns, which we always found on the silicate particles.

*meso*-(*m*-Tetrabenzoic acid) porphyrin **26b** was first bound to aminated particles<sup>74</sup> and walled in with oligoethyleneglycol-acid chloride bolaamphiphile **10, 16 and 38**. Two parallel running hydrogen bond chains rendered the walls impermeable to water and amines,<sup>28</sup> the OEG head groups dissolved the particles in water, ethanol and chloroform-ethanol 10:1. Then these particles were refluxed in methanol/chloroform mixture with zinc acetate after 4 hrs collected particles with centrifugation and washed several times with methanol to remove excess zinc acetate and yielded yoctowells on silicate particles with zinc porphyrin at the bottom **26c**. The terminal double bond with different distances was then aminated on the water-dissolved particles with methylamine to produce a ring of methylammonium groups in water, acetonitrile and ethanol and of methylamine groups in chloroform/ethanol at the rim of the yoctowells. This ring was used to attach the sulfonate groups of the dimeric iminoquinone **36**, which was prepared from benzidine and anthraquinone disulfonate. *Bis*-iminoquinone has the same diameter of 22 Å as the bottom porphyrin **26c** and a reduction potential of -550 mV vs. an Ag/Ag(I) electrode, which is comparable to other iminoquinones.<sup>114</sup> It was water-stable for at least 3 days at pH 6-9.

### 6.3 Results and discussion

These silica colloidal particles with heterodimers (figure 6.3), for the fluorescence decay measurements of the bottom porphyrin **26c** in the absence or presence of *bis*-iminoquinone **36** at a distance of 15 Å, 10 Å and 5 Å on the amino silicate particles with noncovalent porphyrin-iminoquinone heterodimers within the yoctowells in water at pH 7-8. These particles were then dissolved in water, ethanol, acetonitrile or chloroform/ethanol 10:1 and investigated by laser pulse fluorescence excitation and fluorescence decay measurements.

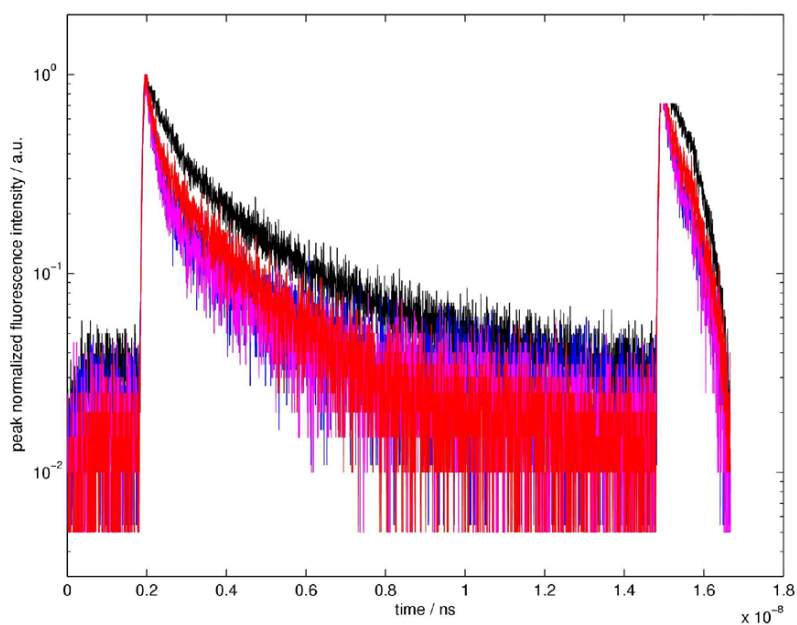
**Fluorescence decay measurements:** were carried out using the method of time-resolved single photon counting with equipment containing an SPC300 (Becker & Hickl) with a multichannel plate (Hamamatsu) and a Czerny-Turner monochromator (Oriel) on the detection pathway with the help of Prof. Röder and her co-workers. Details of the experiments procedure can be found in page no. 147.

It was found that fast electron transfer reaction (decay time ~ 100-200 ps) only occurred if the bottom porphyrin was zinc complex **26c** and if the *bis*-iminoquinone **36** was present at the rigid. Free base porphyrin (figure 6.1a) shows no effect in presence or absence of *bis*-iminoquinone **36**. It is known that zinc porphyrins form stable cation radicals, whereas free base porphyrins do not.<sup>113</sup> The necessity of the presence of iminoquinone **36** also clearly implies an electron transfer process for the 100-200 ps decay (Table 2).

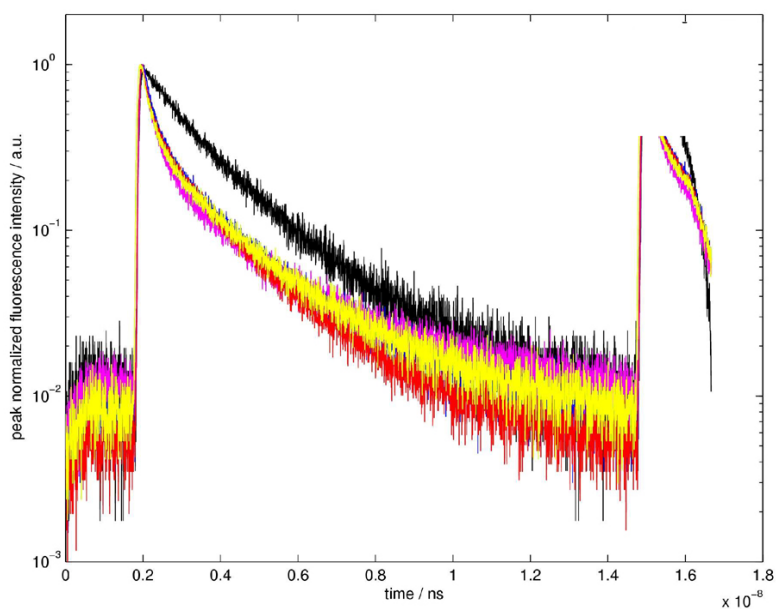
The results of Table 2 show that the 6 Å transfer is only slightly faster than over the distances of 10 Å and 15 Å. The 250 ps decay in the absence of *bis*-iminoquinone 5 Å yoctowell is probably caused by the amino groups at the rim (Figure 6.5). The excited zinc porphyrin is reduced to the anion radical with relatively low efficiency and the electron transfer from the amine to the zinc porphyrinsate is also slower by a factor of →two as compared to the porphyrin → iminoquinone transfer. A plot show linearity (Figure 6.8-6.9). Furthermore three solvents of different dipole moments (CHCl<sub>3</sub>: 1.0 D; H<sub>2</sub>O :1.8 D; CH<sub>3</sub>CN : 3.8 D) all give about the same decay times, which indicates that



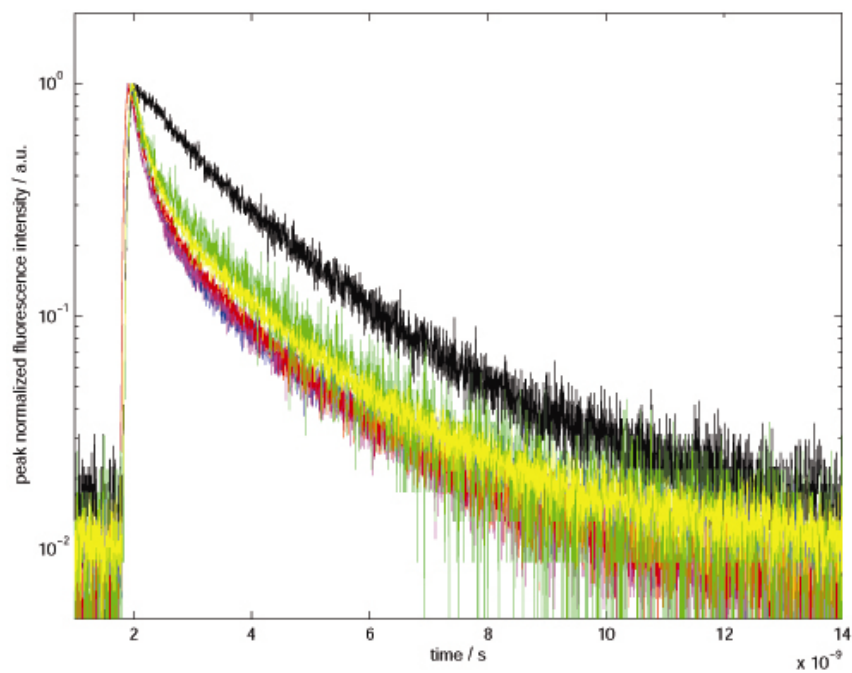
even the long way of 10 Å to 15 Å does not differentiate between dipole moments (figure 6.8 and 6.9). The medium has obviously very little effect.



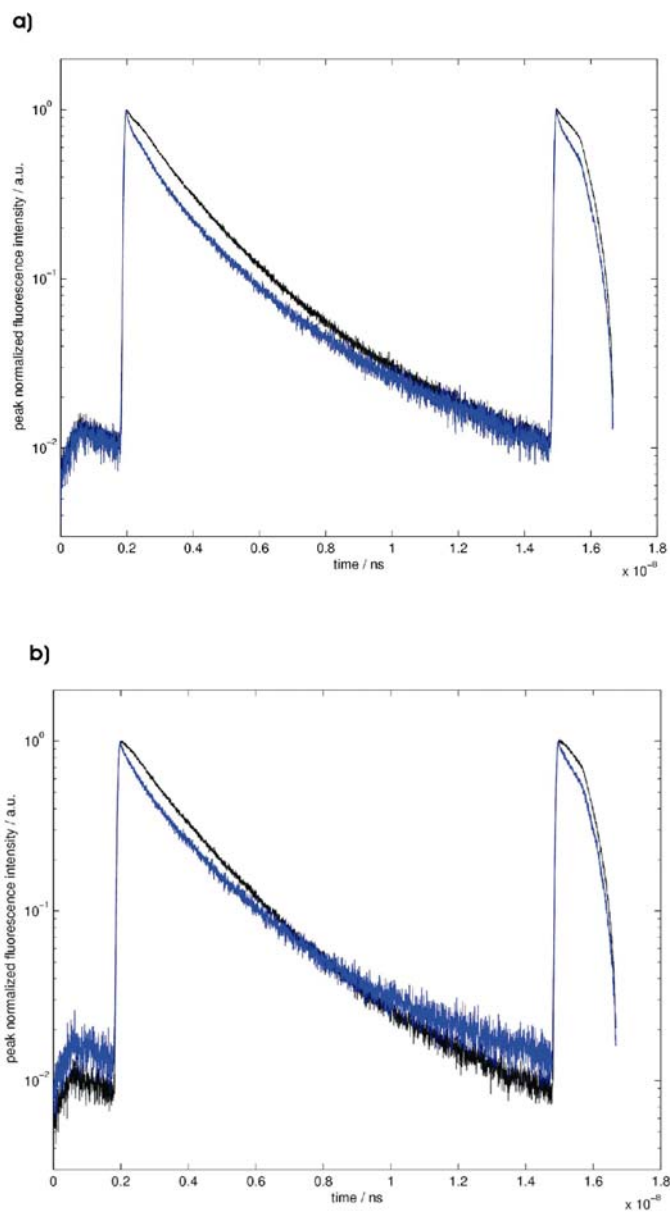
**Figure 6.5** Plot of distance-decay time in water at 5 Å without *bis*-iminoquinone (black) and with *bis*-iminoquinone **36** and excited at bottom zinc **26c** porphyrin [other four curves (red, blue, yellow and orange)].



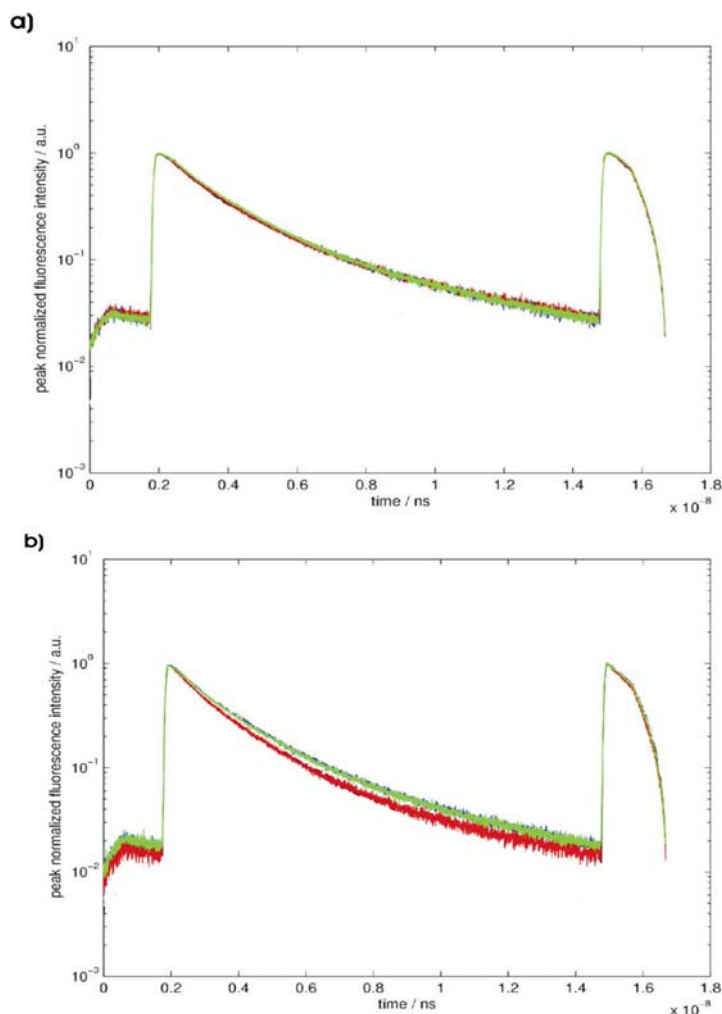
**Figure 6.6** Plot of distance-decay time in water at 10 Å without *bis*-iminoquinone (black) and with *bis*-iminoquinone **36** and excited at bottom zinc **26c** porphyrin (red, yellow, orange, blue).



**Figure 6.7** Plot of distance-decay time in water at 15 Å without *bis*-iminoquinone (black) and with *bis*-iminoquinone **36** and excited at bottom zinc **26c** porphyrin (green, red, blue, yellow).



**Figure 6.8** Plot of decay time with two different solvent at 10 Å distance a)  $\text{CHCl}_3$  b) EtOH without bis-aminoquinone (black) and with *bis*-iminoquinone **36** and excited at bottom zinc **26c** porphyrin (blue)



**Figure 6.9** Plot of decay time with two different solvent at 15 Å distance with *bis*-iminoquinone **36** and excited at bottom zinc **26c** porphyrin in a) acetonitrile b) chloroform : ethanol (10:1)

Covalent porphyrin-quinone systems in face-to-face orientation have only studied in organic solvents. Concentrations were, however, high enough to execute pump-probe transition absorption spectroscopy of the zinc porphyrin cation radical. Charge separation constants of 0.6 ns were reported for a 3 Å separation between zinc porphyrinate and quinone and 3.1 ps for 5.5 Å separation. 3 Å is sub-Vander Waals and implies strong  $\pi\pi$  interactions in the charge separated state,<sup>111</sup> 5.5 Å is comparable to our 5 Å nanowell. The electron transfer in the covalent system is about forty times faster than the fluorescence decay measured by us. Fluorescence decay times measured in different solvents for two covalent zinc porphyrin-quinone conformers with distances of 6.5 and 8.5 Å gave, however, comparable time constants of 0.63 ns in acetonitrile and ethanol

and 0.79 ns in chloroform.<sup>112</sup> Covalent systems are thus as insensitive to solvent changes as the non-covalent in the yoctowells. The 250 ps decay in the 5 Å-deep well in the absence of quinone **36** is probably caused by an electron transfer from the amino groups at the well's rim to the excited porphyrin. This is not observed in the presence of the quinone and does not occur at all at distance of 10 Å and 15 Å. Anion formation by addition of an electron to the excited state of the zinc porphyrinate **26c** is thus slower than the loss of an electron and it only occurs over a small distance.

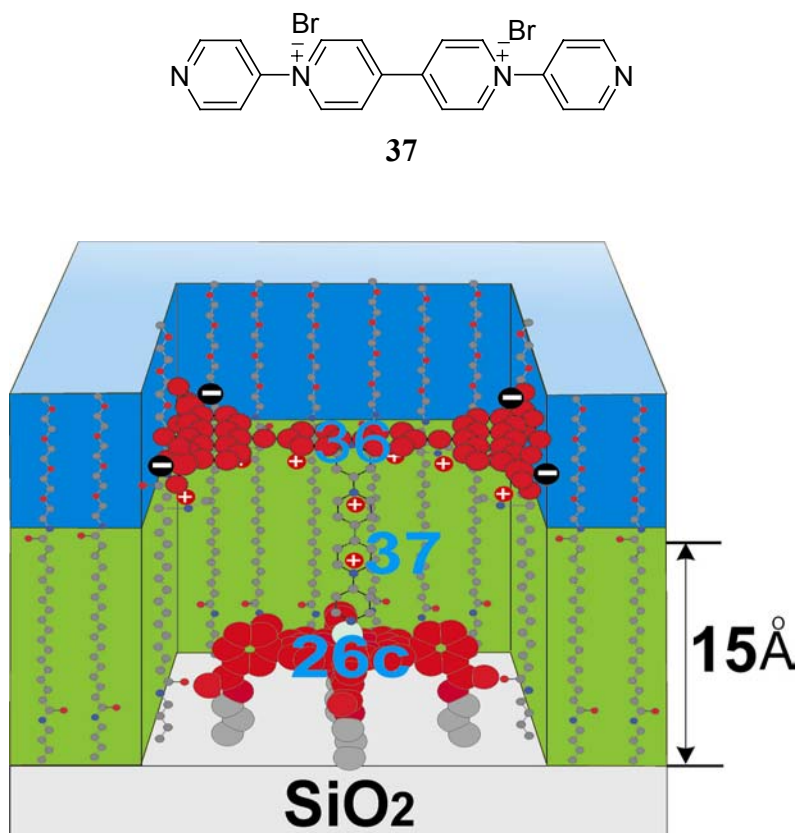
**Table 2.** Decay times of zinc porphyrin **26c** excitation in the (a) absence of *bis*-iminoquinone **36** and in the (b) presence of *bis*-iminoquinone **36** at various distances and in four different solvents.

Solvents	5 Å	10 Å	15 Å
<b>Water</b>			
a)	0.25; 1.03; 3.43	---; 0.56; 1.99	---; 0.75; 2.18
b)	0.13; 0.63; 3.43 0.14; 0.79; 3.33 0.12; 0.24, 1.85	0.15; 0.78; 2.95 0.16; 1.00; 2.66 0.16; 0.98; 2.66 0.16; 0.79; 2.08	0.19; 1.02; 2.90 0.17; 1.04; 2.84 0.17; 0.93; 2.52 0.17; 1.67; 1.92
<b>Ethanol</b>			
a)	--	--; 0.94; 2.25	--
b)	--	0.28; 1.19; 3.36	--
<b>Chloroform</b>			
a)	--	--; 0.92; 3.43	--
b)	--	0.23; 1.19; 3.36	0.28; 1.58; 6.01 0.28; 1.54; 6.56 0.28; 1.57; 6.12
<b>Acetonitrile</b>			
b)	--	--	0.32; 1.61; 7.20 0.35; 1.63; 7.27 0.36; 1.63; 7.18

All times are in the 'ns'

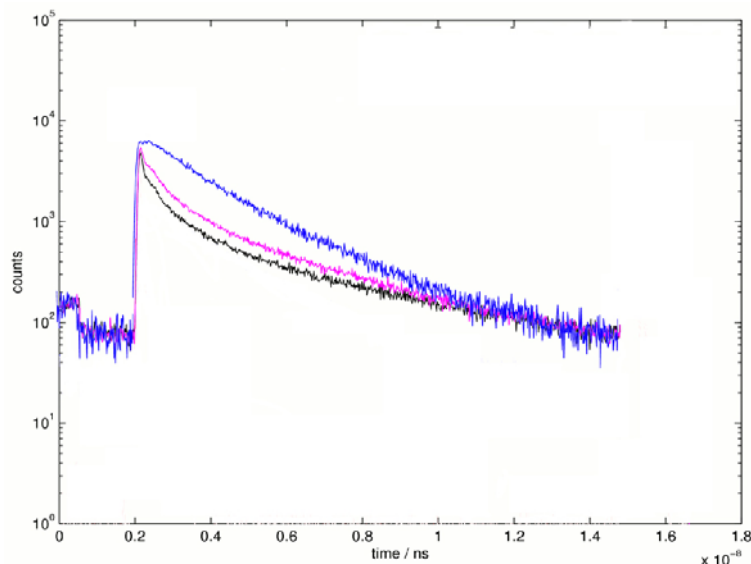
We also fixated the tetrapyrroline rod **37**, as a spacer with a central viologen unit to the bottom zinc porphyrin in 15 Å distance within the yoctowells model figure 6.10.

The tetrapyrroline with a central viologen unit was synthesized according to a literature procedure.<sup>110</sup>



**Figure 6.10** Model of the axial acceptor tetrapyrroline **37** and *bis*-iminoquinone **36** at the top of the rim on zinc porphyrin **26c** donor at the bottom.

The viologen unit also acts a electron sink about the same recombination rate as the porphyrin-quinone pair. The final transfer to the top *bis*-iminoquinone **36** was, however, relatively slow. It was found that in presence of tetrapyrroline rod **37** fast electron transfer reaction gave 0.155 ns decay, when we attached *bis*-iminoquinone **36** above the tetrapyrroline rod, the electron transfer relatively slow 0.29 ns (Table 3, figure 6.11).



**Figure 6.11** Plot of decay time of 15 Å yoctowell a) absence of tetrapyrrodine (blue) b) presence of tetrapyrrodine (black) c) with top of *bis*-iminoquinone **36** (red) and excited at bottom zinc **26c** porphyrin.

**Table 3.** Decay times of zinc porphyrin **26c** excitation in absence and presence of tetrapyrrodine **37** and finally in presence of *bis*-iminoquinone **36**.

Sample	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)	relative amplitude (%)
15 Å nanowells on aminated silica without tetrapyrrodine spacer.	4.188	1.511	----	31.5 : 68.5
15 Å nanowells on aminated silica with tetrapyrrodine spacer <b>37</b> .	5.658	0.938	0.155	57 : 31 : 12
15 Å nanowells on aminated silica with tetrapyrrodine spacer <b>37</b> and top <i>bis</i> -iminoquinone <b>36</b> .	5.133	1.292	0.295	50 : 34 : 16

In the yoctowells, an amorphous rigid water volume separates the redox pair. Modification of the site of the double bond site allows variations of the distance between electron donor and acceptor in steps of 2.5 Å. This limit is caused by the requirement that the number of CH<sub>2</sub> groups between the two secondary amide groups must be even. Therefore, two CH<sub>2</sub> groups must be added or subtracted in the separating chain. The concentration of both porphyrins **26b** and **36** was about 10<sup>-6</sup> M and not sufficient for

transient absorption spectroscopy with our equipment. We used therefore transient emission spectroscopy. Surprisingly, no effect was observed in absence *bis*-iminoquinone **36** at a 15 Å and 10 Å distance. Essentially the same decay times of ~2.4 and 1.0 ns were observed with and without *bis*-iminoquinone **36** in all three distances. A similar biphasic behavior has been reported for porphyrin monolayers, which were separated by lipid monolayers from the gold surface of nanoparticles.<sup>90</sup> The results of Table 2 show that the 5 Å transfer is only slightly faster than over the distances of 10 Å and 15 Å. The 250 ps decay in the absence of *bis*-iminoquinone **36** 5 Å yoctowell is probably caused by the amino groups at the rim (Figure 6.5).

A new, faster, and very efficient decay mechanism with a decay time of 0.12- 0.14 ns only appeared, when the *bis*-iminoquinone **36** was attached at a distance of 5 Å (Figure 6.5). When *bis*-iminoquinone **36** present at 10 Å and 15 Å we observed efficient decay mechanism is slowed down as compared to 5 Å, in the rang 0.15 ns for 10 Å (Figure 6.6) and 0.18-0.19 ns for 15 Å (Figure 6.7). The system shows (heterodimers within the yoctowells) electron transfer reaction with distance independent probably because of the water-filled gaps is so high that a distance not make sense. A time of 130 ps is in agreement with rates of electron transfers in the slowest literature model systems.<sup>91,92</sup> This slowness could correspond to the unexpected finding, that the potential barrier for electron tunneling<sup>93,94</sup> in the water-filled gaps electron transfer reaction is slightly dependent on dielectric constant, which may be expected in non-organized, aqueous systems.<sup>101</sup> The electron transfer reaction seems to be distance independent, the electron travels perhaps along the hydrophobic walls like proton were shown to do.<sup>115</sup>



## 6.4 Conclusion

It is known that zinc porphyrins form stable cation radicals, whereas free base porphyrins do not. For this purpose we had changed our bottom free base porphyrin **26b** to zinc porphyrin **26c**. The acceptor having same size of the bottom porphyrin which was successively synthesized from benzidine and anthraquinone sulfonate for this purpose we perform by Schiff base method *bis*-iminoquinone **36**. Porphyrin-*bis*-iminoquinone heterodimers separated by a 5 Å, 10 Å and 15 Å defined distance was established on silica particles was confirmed by fluorescence quenching experiments. We applied these yocotwells with acceptor as a *bis*-iminoquinone for light induced charge transfer reaction applying singlet state photo spectrometer. A new, faster, and very efficient decay mechanism with a decay time of 0.12- 0.14 ns only appeared, when the *bis*-iminoquinone **36** was attached at a distance of 5 Å. When *bis*-iminoquinone **36** present at 10 Å and 15 Å we observed efficient decay mechanism is slowed down as compared to 6 Å, in the rang 0.15 ns for 10 Å and 0.18-0.19 ns for 15 Å. The electron transfer reaction seems to be distance independent, the electron travels perhaps along the hydrophobic walls like proton were shown to do. A time of 120 for 5 Å and 180 ps for 15 Å is in agreement with rates of electron transfers in the slowest literature model systems. The electron transfer reaction is slightly dependent on dielectric constant , which may be expected in non-organized, aqueous systems.