Asymmetric Electron Transfer from a Chiral Ruthenium Complex Donor to an Atropisomeric Chiral 2,2'-Bipyridine Acceptor[†]

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We report asymmetric light-induced electron transfer (ET) in water in the system (Λ)-Ru(methylvinylbipyridine)₃²⁺/(+)- and (-)-1,1'-tetramethylene-2,2'-bipyridine-3,3'-dicarboxylic acid at pH \geq 5 (zwitterionic form). This reaction is activation controlled; ΔG° was made nearly zero by manipulation of molecular structure, pH, and solvent. Then *reverse* ET to the excited donor occurs which renders the quenching reaction asymmetric. The asymmetry of ET is small as expected for high-DK solvents. From our results we infer that chiral recognition takes place in a diastereometric exciplex.

1. Introduction

The phenomenon of reaction asymmetry appears when the rates of the reaction of a chiral agent, say R, with the two enantiomers R and S of the chiral reagent differ. We define reaction asymmetry by

$$\kappa = k_{\rm R-S} / k_{\rm R-R} \tag{1}$$

Asymmetric photoreactions in solution¹ may be induced by different means: by circularly polarized light (direct photochemistry),² by a chiral sensitizer via energy transfer,^{3,4} or via electron transfer⁵ (ET). Inevitably, somewhere in the reaction an element of diastereomerism is obvious or hidden. The asymmetry for direct photochemistry is limited and determined by the difference of the absorption coefficients for right and left circularly polarized light. This is not so for sensitized photoreactions: the asymmetry may be smaller or larger than for direct photochemistry.⁴ Indeed, the highest asymmetry of a photoreaction hitherto reported is that of $\kappa = 7.9$ for an example of ET in nonpolar solvents at -10 °C.⁵

Asymmetry in a photoreaction requires that somewhere along the reaction coordinate an intimate contact between agent and reagent occurs in order that the chiral information may be transmitted. Thus long-range dipole-dipole (Förster) energy transfer is not expected to produce asymmetry in a sensitized reaction, whereas triplet-triplet energy transfer is effective.^{3,4} In view of this rationale the magnitude of asymmetry of Irie's quenching of binaphthyl by chiral amines⁵ seems surprising, but it has been attributed to exciplex formation in nonpolar solvents, in polar solvents like acetonitrile no asymmetry is found. On the other hand, exciplex formation need not lead to asymmetry in an ET reaction: we have studied a chiral hexahelicene/amine system⁶ where we saw exciplex emission even in polar solvents like MeOH, but no asymmetry of emission quenching. These findings prompted us to take a closer look to ET and to use asymmetry as a probe in the ET reaction.

We have set out to study a modification of one of the most intensively investigated systems for light-induced electron transfer in water, $Ru(bpy)_3^{2+}/methylviologen^{2+}$. We used 4-methyl-4'-vinyl-2,2'-bipyridyl (mvbpy) as a ligand for a chiral

Ru-complex 1 as a donor and chiral atropisomeric bridged quaternized 2,2'-bipyridine-3,3'-dicarbonic acids 2 and 3 in their racemic and enantiomeric forms as acceptors and other structurally related quaternized 2,2'-bipyridinium compounds 4-8 for comparison of the electrochemical properties.⁷



We found that ET is normally not asymmetric in an aqueous medium, but that with the use of the knowledge about ET, conditions can be found where asymmetry can be introduced in ET reactions. From our results we infer that enantiodifferentiation occurs in an exciplex.

2. Experimental Section

2.1. Syntheses. Synthetic work was very time consuming, especially the purification and resolution of the materials. A detailed description of the procedures is found in ref 7.

4-Methyl-4'-vinyl-2,2'-bipyridine (mvbpy). 4,4'-Dimethyl-2,2'-bipyridine was reacted (a) with lithium diisopropylamide (LDA) and chloromethyl ether (ClCH₂OCH₃)⁸ to give 4-methyl-4'-(2-methoxyethyl)-2,2'-bipyridine from which methanol was cleaved by means of potassium *tert*-butylate. Purification proved lengthy; finally column chromatography on a mixture of SiO₂/Florisil as an adsorbent and a mixture of THF, dioxane, and petroleum ether as an eluent yielded pure material. (b) A more convenient method was found to be the reaction of

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^{*} Abstract published in Advance ACS Abstracts, August 15, 1995.

dimethylbipyridine with LDA and formaldehyde⁹ to give 4-methyl-4'-(2-hydroxyethyl)-2,2'-bipyridine. This compound was purified on basic alumina (activity IV) by a gradient elution of ethyl acetate/ether (1:1) \rightarrow ethyl acetate. Elimination of water was achieved by sublimation from ground NaOH at 130 °C in vacuo,⁹ the pure material was characterized by MS and NMR spectra.

 $Ru(mvbpy)_3^{2+}$ (1) was prepared in analogy to the procedure of Palmer and Piper¹⁰ and purified on a Sephadex LH-20 column with MeOH. The NMR signals are those of mvbpy, with slightly different chemical shifts. PF₆⁻ and ClO₄⁻ salts were used for electrochemical experiments.

The N,N'-bridged-dialkylated 2,2'-bipyridines (4-6) were prepared by reaction of 2,2'-bipyridine with an excess of the corresponding dibromide.¹¹

2,2'-Bipyridine-3,3'-dicarbonic acid was prepared by oxidation of 1,10-phenanthroline with KMnO₄ under modifications of the literature procedure.¹² The methyl ester could be prepared when the anhydride of trifluoroacetic acid was used.¹³

1,1'-Trimethylene-2,2'-bipyridine-3,3'-dicarboxylic acid (2) and 1, 1'-tetramethylene-2,2'-bipyridine-3,3'-dicarboxylic acid (3) could not be prepared by conventional methods.¹¹ The carbonic acids and dibromoalkanes react only when DMF is added: 10.0 g of bipyridine(COOH)₂, 100 g of the dibromide, and 46 g of absolute DMF are stirred in a round-bottomed flask in an inert atmosphere and are slowly heated to 120 °C. The solution turns vellow. In order to dissolve all acid a short period of 135 °C is intermitted. After about 30 min precipitation is observed from the now brownish solution. The reaction may proceed for about 5-7 h. Longer reaction times increase the yield but even more the amount of byproducts. After cooling, precipitation is completed by addition of acetone, and the precipitate is filtered and washed with acetone, dried, and dissolved in ca. 150 mL of water. A small amount of 3 M NH₄PF₆ solution precipitates a dark material which is filtered off. The raw product of 2 or 3 is precipitated with about 700-800 mL of acetone and recrystallized twice from water/acetone. 2 precipitates in a few days as white crystals, and 3 as white needles or starlets. The NMR spectra were taken in D₂O. ¹³C NMR spectra indicate C_2 symmetry; there are only eight signals, and assignment was made using 2D-H,H-COSY. 2: ¹H NMR: $\delta = 2.56$ (m, 2 H, 8-H), 4.24 (m, 2 H, 7-H_a and 9-H_a); 4.73 (m, 2 H, 7-H_e and 9-He); 8.19 (dd, 2 H, 5,5'-H); 8.77 (d, 2 H, 6,6'-H), 8.97 (d, 2 H, 4,4'-H). ¹³C NMR: $\delta = 33.9$ (CH₂, 8-C); 60.1 (CH₂, 7-C and 9-C); 134.6 (CH, 5,5'-C); 145.1 (C, 2,2'-C); 148.4 (C, 3,3'-C); 150.3 (CH, 6,6'-C); 150.9 (CH, 4,4'-C); 170.4 (C, COO⁻). 3: ¹H NMR: $\delta = 1.86$ (m, 2 H, 8-H_a and 9-H_a); 2.24 (m, 2 H, 8-He and 9-He); 4.14 (m, 2 H, 7-Ha and 10-Ha); 4.77 (m, 2 H, 7-He and 10-He); 8.25 (dd, 2 H, 5,5'-H); 8.86 (d, 2 H, 6,6'-H); 9.17 (d, 2 H, 4,4'-H). ¹³C NMR: $\delta = 31.2$ (CH₂, 8-C and 9-C); 63.1 (CH₂, 7-C and 10-C); 135.7 (CH, 5,5'-C); 140.9 (C, 2,2'-C); 149.1 (C, 3,3'-C); 151.6 (CH, 6,6'-C); 152.3 (CH, 4,4'-C); 169.1 (C, COO⁻).

1,1'-Dimethylene-2,2'-bipyridine-3,3'-dicarboxylic acid (8) was synthesized the same way, however, with very low yield. The ¹H NMR spectrum in the aromatic region is comparable to those of 2 and 3; in the aliphatic region the expected AB quartet of diastereotropic methylene protons is observed ($\delta_A = 5.15$, $\delta_B = 5.40$, $J_{AB} = 11.0$ Hz).

2.2. Resolution of Racemates. $Ru(mvbpy)_3^{2+}$ (1) 120 mg of racemic [Ru(mvbpy)]_3Cl₂ was dissolved in 11 mL of 0.28 M aqueous NaCl and 1 mL MeOH. This solution was introduced into a Sephadex C-25 column (103 × 3.4 cm) and eluted with a solution of 0.15 mol/L of NaCl and 0.13 mol/L of L-(+)-potassium antimony tartrate in water. When the

leading Δ -(-)-enantiomer had made 75% of the distance the eluent was changed to 0.28 M NaCl. The effluent after 25-32 h carried the Δ -(-)-enantiomer and that after 35-41 h the Λ -(+)-enantiomer. CD monitoring showed baseline separation, $[\Theta]_{485} = + \text{ or } -54 \text{ 100} \pm 500 \text{ deg cm}^2 \text{ dmol}^{-1}$. (Ru(bpy)₃Cl₂ requires modifications for baseline separation.)

1,1'-Trimethylene-2,2'-bipyridine-3,3'-dicarboxylic acid (2) and 1,1'-Tetramethylene-2,2'-bipyridine-3,3'-dicarboxylic acid (3). Attempts to resolve these acids were only successful with specially conditioned columns of starch (95×3.0 cm): Native potato starch (550 g, Merck) was soaked and swollen in MeOH/ water 7:3 (650 mL) for 2 h under occasional shaking. The empty column obtained an extension of the same diameter, and the stopcock was opened. The vessel in which the starch was conditioned after settling of the mixture should show a clear head liquid of about one-half of the volume of the starch slurry. After vigorous shaking the slurry must be poured into the extension column quickly without interruption and the material allowed to settle. It is necessary to knock the column's flank gently with wood or cork under occasional rotation in a jerk in order to remove air bubbles. Fresh MeOH/water mixture 7:3 is put on top, the flow of liquid must not be interrupted. After about 4 days the solvent is gradually changed to pure water (2 days), and the starch swells. After the column is washed for 2 days with water the eluent is slowly adjusted to MeOH/water 6:5 (the filling shrinks) and then washed 2-3 weeks until no soluble starch remains in the effluent (UV scattering). After putting 1 cm of sand on top of the starch, the column can be used. (-)-2 appeared after 5.5-7.8 days and (+)-2 from 7.9 to 10.5 days; 3 was about 25% faster. In both cases, baseline separation was achieved. Spectroscopic data of 2 at pH 7 are $[\theta]_{283} = 21\ 000\ \text{deg}\ \text{cm}^2\ \text{dmol}^{-1}$ (maximum of the long wavelength CD band), $\Delta \epsilon / \epsilon = 8.06 \times 10^{-4}$, $\epsilon_{290} = 7900$ L $mol^{-1} cm^{-1}$ (maximum of the long wavelength UV band), of 3 $[\Theta]_{288} = 43\ 200\ \text{deg}\ \text{cm}^2\ \text{dmol}^{-1},\ \Delta\epsilon/\epsilon = 1.76\ \times\ 10^{-3},\ \epsilon_{284} =$ 7450 L mol⁻¹ cm⁻¹.

2.3. Quenching Experiments. Emission decay of 1 was observed with a laser flash equipment: a dye laser (coumarin 47, 467 nm, FL 2000 of Lambda Physik) pumped by an excimer laser (308 nm, EMG 101 MCS by Lambda Physik) excited the complex (typically 2×10^{-5} mol/L) in a thermostated square cell. The emission of 625 nm was selected by a monochromator (Oriel), detected with a photomultiplier (Hamatsu R 928), and fed into an oscilloscope (Tektronix 11302). The trace was digitized by means of a digitizing camera system (Tektronix 1001) and evaluated on an IBM PC with the DCS software of Tektronix.

The solutions were prepared by dissolving weighted (2, 3, $\pm 1 \times 10^{-5}$ g; 1, $\pm 1 \times 10^{-6}$ g) amounts of material in calibrated vessels. Diluting and mixing was done with calibrated pipets. The concentrations were checked by taking the absorption values. 1% accuracy was reached, and the relative accuracy of (+)- and (-) quencher was near 1‰. The solutions were placed in four-sighted cells with attached Young valves (Teflon stopcocks) and thoroughly deaerated by flushing them for 2.5 h with argon which was passed through an Oxysorb cartridge (Messer Griesheim) in order to remove traces of oxygen. After 30 min of thermostating the cells the measurements were taken. For a quenching experiment with racemic materials 5 cells with different quencher concentrations were used, for enantioselective quenching experiments 10 cells were used, two sets of 5 cells with Λ -1/(+)-3 and Λ -1/(-)-3 combinations of different quencher concentrations. They were interchanged at the deaerating stand and in the sequence of emission measurements in order to eliminate drifts in degassing and thermostating. Two



Figure 1. Absorption (–), emission (–-–) and CD (\times 5) (–) spectra of 1.



Figure 2. Absorption (---) and CD (---) spectra of 2, absorption (---) and CD (--) spectra of 3.

series of decay curves in different sequences of the cells were taken in 10 min intervals. One 10-cell experiment took 14 h.

UV spectra were taken by means of a HP diode spectrometer, emission spectra by means of a Perkin Elmer LS 50 instrument, and CD spectra by means of a Jasco 500 spectropolarimeter.

2.4. Electrochemistry. The redox potentials were determined by cyclovoltammetry, CV (impedance unit of Zahner-Elektrik, Kronach, Germany) or by differential pulse voltammetry, DPV (potentiostat Metrohm E506 and E626) by means of a three-electrode technique. References in aqueous solution were saturated calomel electrodes, SCE, in nonproton solvents, Ag/Ag^+ electrodes of two-diaphragm design, or silver rod pseudoreferences. Counter electrodes were Pt rods or sheets.

The glass cells (Metrohm) with five joints in the lid were flushed with solvent-saturated 4.8 argon which had passed an Oxisorb cartridge, and a 4 A molecular sieve, in order to remove traces of oxygen and water vapor.

3. Results

3.1. Spectra. Absorption, fluorescence, and CD spectra of 1 in aqueous solution are shown in Figure 1, and absorption and CD spectra of 2 and 3 in water are shown in Figure 2. The spectra of 1 are very similar to those of the parent Ru(bpy)₃²⁺: the long-wavelength absorption band is shifted to $\lambda_{max} = 467$ nm and the emission band to $\lambda_{max} = 625$ nm. The Stokes shift of 1 is identical with that of Ru(bpy)₃²⁺, so $E_{00} (=h\nu) = 2120$ mV.¹⁴ The emission lifetimes of 1 are $\tau_0 = 595 \pm 4$ ns at 10

 TABLE 1: Redox and Peak Potentials of First Reduction (2 to 8) and Oxidation (1) Step in Water^a

compd	potential (mV)	method	compd	potential (mV)	method
1	+1170 (r)	DPV (gc)	5	-540 r	CV (gc)
2	-685 (r)	DPV (gc)	6	-630 nr	DME ²³
3	-840 (nr)	DPV (gc)	7	-390 r	CV (gc, pH 7)
4	-365 (r)	CV (gc)	8	-380 r	CV (gc)

^a mV vs NHE; r (reversible): redox potential; nr (not reversible): peak potential; pH = 13; gc: glassy carbon; DME: polarography at dropping mercury electrode; DPV: differential pulse voltammetry; CV: cyclovoltammetry.



Figure 3. Differential pulse voltammetry of 3. Peak potentials of the first reductive wave (gc electrode, 0.1 M salt, pH (glass electrode) adjusted by NaOH or H_2SO_4 , pulse amplitude 20 mV, sweep 5 mV/s).



Figure 4. Stern–Volmer plots of emission quenching of Δ -1 by (+)-2.

°C, $\tau_0 = 570 \pm 3$ ns at 20 °C, $\tau_0 = 550 \pm 2$ ns at 30 °C, and $\tau_0 = 530 \pm 2$ ns at 40 °C. The larger twist angle in 3 compared to 2 causes a doubling of the maximum CD value near 285 nm.

3.2. Redox Potentials. The redox potentials are collected in Table 1. Those of 2, 3, and 8 show strong dependence on pH. In Figure 3 the peak potentials (not redox potentials) of 3 are plotted against pH.

3.3. Quenching of the Emission of $Ru(mvbpy)_3^{2+}$ by the Bipyridine Acceptor 2. Quenching of the emission of Δ -Ru-(mvbpy)_3²⁺ was determined in the dynamic mode. Stern-Volmer plots for the zwitterionic and protonated 2^+ ion quenchers in water were linear (Figure 4), and no kinetic salt effect became manifest.

For the combination of 1 and 2 at pH 7, the free enthalpy of the quenching reaction in water is $\Delta G^{\circ} = -26$ kJ mol⁻¹. The quenching constant at 293 K is $k_q = 1.18 \times 10^9 \pm 2\%$ L mol⁻¹ s⁻¹. This is to be compared to the diffusion-controlled rate constant k_{diff} . The latter may be calculated for neutral species in aqueous solution ($\epsilon_r = 78.5$, $\eta = 9 \times 10^{-4}$ N ms⁻²) according to Smoluchowski,¹⁵ for species carrying charges according to Debye¹⁶ and Eigen.¹⁷ With $r_D = 7.5 \times 10^{-10}$ m and $r_A = 4.0$

 TABLE 2:
 Stern-Volmer Results of Quenching of 1 by 3

 in Water and MeOH^a

	10 ⁻² mol/L HCl			10 ⁻² mol/L NaOH			methanol (pH ≈ 2.5)		
Τ	τ_0	K _{SV}	k _q	$ au_0$	Ksv	k _q	$ au_0$	K _{SV}	kq
10	595	210 ± 3	35.3	593	165 ± 1	28.9	1555	63.4 ± 1	4.08
20	567	244 ± 2	43.1	548	168 ± 4	30.7	1530	73.5 ± 3	4.80
30	546	276 ± 2	50.6	523	181 ± 4	34.3	1472	83.5 ± 4	5.67
40	524	298 ± 5	56.9	508	169 ± 1	33.3	1401	92.6 ± 6	6.61

^{*a*} T in °C; τ_0 in ns; K_{SV} in L/mol; k_q in $\times 10^7$ L/(mol s).



Figure 5. k_q values and ΔG^{\dagger}_{298} for the quenching of 1 by 3 in MeOH/ H₂O (pH ≈ 2.5): (•) 283 K, (Δ) 293 K, (•) 303 K, (□) 313 K, (O) ΔG^{\dagger}_{298} in kJ/mol.

× 10⁻¹⁰ m we arrive at $k_{\text{diff}} = 5 \times 10^9$ L mol⁻¹ s⁻¹. Thus the reaction of the zwitterionic species is nearly diffusion-controlled and thus it is no surprise that we could not find asymmetry in this quenching reaction. The linear Eyring plot gives the activation parameters $\Delta H^{\ddagger} = 15.3$ kJ mol⁻¹, $\Delta S^{\ddagger} = -19.6$ J K⁻¹ mol⁻¹, and $\Delta G^{\ddagger} = 21.0$ kJ mol⁻¹.

3.4. Quenching of the Emission of $\operatorname{Ru}(\operatorname{mvbpy})_3^{2+}$ by the Bipyridine Acceptor 3. The redox potential of 3 in water is about 140 mV (pH 7) more cathodic than that of 2 which means $\Delta G^\circ = -13$ kJ mol⁻¹ (pH 7). ΔG° in pure MeOH (pH 8.4) is close to zero as the difference of the redoxpotentials of 1 and 3 is 2105 mV and thus nearly equal to E_{00} . Table 2 provides the quenching data of 1 by the racemic acid (HCl) and zwitterionic (NaOH) forms of 3 in water and in methanol at pH 2.5 where the dissociation of carboxy groups of 3 is incomplete, and this increases quenching as compared to pH 8.4. In pure MeOH the quenching of the emission of 1 by 3 is near the limit of our equipment's sensitivity.

The quenching constants of **3** in aqueous solution are significantly smaller than those of **2**, as expected when ΔG° is less negative. Note the maximum in the k_q values of the quenching by the zwitterion. The emission lifetime of **1** in MeOH is about a factor of 3 longer than in water, and the quenching constant is about a factor of 10 smaller than in water. The dependence of the quenching constant on the composition of the solvent mixture water/methanol is shown in Figure 5. There is a steep decrease at the water-rich side which may be due to selective solvation.¹⁸

Three sets of quenching experiments with enantiomeric quenchers **3** were performed as 10-cell-experiments in MeOH/ water ($x_{MeOH} = 0.8$) at pH 1.8 and at pH 3.1 and in water at pH 6.8. The Stern–Volmer plots were linear in all cases.

In MeOH/water at pH 1.8 the carboxyl groups are protonated, and the donor and acceptor are carrying two charges of the same sign. At 293 K we find $k_q = 4.85 \times 10^7$ L/(mol s). Quenching is stronger at higher temperatures. High negative entropies of activation of $\Delta S^{+}_{298} \approx -66$ J/(mol K) are observed (Table 3),

TABLE 3: Activation Parameters for the Quenching of the Emission of A-1 by (+)- and (-)-3 in a MeOH/Water Mixture ($x_{MeOH} = 0.8$)

pН	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}_{298} \left(\text{J/(mol K)} \right)$	$\Delta G^{\#}_{298}$ (kJ/mol)
1.8			
$[\Lambda/(-)]$	9.4 ± 0.9	-65.4 ± 3.0	28.8 ± 1.8
[// (+)]	8.9 ± 0.6	-67.3 ± 2.0	28.9 ± 1.2
3.1			
$[\Lambda/(-)]$	4.5 ± 1.3	-90.5 ± 4.3	31.4 ± 2.6
[Λ/(+)]	6.1 ± 0.6	-85.4 ± 1.9	31.5 ± 1.2

 TABLE 4:
 Stern-Volmer Results of Quenching of 1 by

 (+)- and (-)-3 in Water^a

		$\frac{\Lambda - [Ru(vbpy)_3]^{2+*}}{(+)-SQQ}$		$\frac{\Lambda - [Ru(vbpy)_3]^{2+*}}{(-)-SQQ}$		
Τ	$ au_0$	K _{SV}	$k_q^{\Lambda+}$	K _{SV}	$k_q^{\Lambda-}$	$\kappa = k_{\rm q}^{\Lambda^-}/k_{\rm q}^{\kappa^+}$
10.7 20	588 562	189.2 ± 2.0 2037 + 14	3.218	198.8 ± 1.1 211.1 + 1.3	3.381	1.051
25 30 40	546 535.5 517.5	$207.1 \pm 2.1 \\ 204.7 \pm 1.1 \\ 195.9 \pm 0.5$	3.793 3.827 3.786	$215.1 \pm 1.3 \\ 215.0 \pm 0.4 \\ 207.0 \pm 0.9$	3.940 4.015 4.000	1.039 1.049 1.057

^{*a*} T in °C, τ_0 in ns; K_{SV} in L/mol; k_q in $\times 10^8$ L/(mol s).

which are identical within the limit of error for both enantiomers as are the ΔG^{\dagger}_{298} values of 29 kJ/mol. Asymmetry of quenching is not observed.

In MeOH/water at pH 3.1 the carboxyl groups are mainly dissociated, 3 is predominantly in its zwitterionic form. The constancy of the pH value has been controlled during the experiments. According to the change in the redox potential of 3 on deprotonation of the carboxylic groups (see Figure 3) the quenching reaction at pH 3.1 becomes less efficient than at pH 1.8, and this effect surpasses the opposite one due to the disappearance of repulsion between donor and acceptor. At 293 K we find $k_0 \approx 1.8 \times 10^7$ L/(mol s), about 3 times smaller than for the +2-charged quencher. Unfortunately, the errors are the same in absolute numbers. Again quenching is stronger at higher temperatures, and the activation entropy is very highly negative: $\Delta S^{\ddagger}_{298} \approx -88$ J/(mol K) (Table 3). Asymmetry seems to emerge; the κ values are 1.10 at 283.7 K, 1.03 at 293 K, 0.96 at 298 K, 1.02 at 202 K, and 1.04 at 313 K. But this is just about the error margin of the experiments in this solvent (see also Table 3).

In pure water **3** is present as a zwitterion (Figure 3). The results are presented in Table 4. The reproducibility of the decay times were better than in the solvent mixtures. The maximum deviation of the value of τ_0 was 4 ns in both series of experiments. The errors in k_q are those of the slopes in the Stern-Volmer plots. The quenching of 1 by the enantiomers of **3** is asymmetric, the effect is small but nonetheless significant, and the errors in κ are less than $\pm 2\%$ (see bars of maximum error in Figure 7).

Below 30 °C, quenching shows the normal positive temperature dependence but above 30 °C k_q becomes smaller again. The Eyring plots of the quenching reaction of the two enantiomers are shown in Figure 6. Above 25 °C ΔH^{\pm} becomes negative; however, the free enthalpy of activation ΔG^{\pm} remains positive, as, simultaneously, ΔS^{\pm} decreases strongly.

The temperature dependence of the asymmetry of the reaction indicates a minimum (Figure 7). This type of curves have been observed in some enantio- and diastereoselective photoreactions.¹⁹ But when the errors are taken into account, a monotonic behavior cannot be excluded. However, the same trend appears in the κ values determined in MeOH/H₂O at pH 3.1.



Figure 6. Eyring plot for the quenching of A-1 by (–)-3 and (+)-3 in H₂O (pH 6.8).



Figure 7. Asymmetry of emission quenching of 1 by 3.

SCHEME 1



4. Discussion

An asymmetric quenching reaction is composed of the independent parallel reactions of the two diastereomeric pairs D_R/A_R and D_R/A_S . Thus, one cannot expect asymmetry in diffusion-controlled reactions, where ET occurs at every encounter. In order to observe asymmetry in the quenching reaction, we searched for (slow) activation-controlled reactions.

Chiral recognition requires intimate contact of the partners. Weller²⁰ has given Scheme 1 for ET systems. Only the exciplex can transmit chiral information because it is characterized by intimate contact and orbital overlap of D and A with the consequences that (i) the exciplex CT state (D⁺A⁻) is stabilized (in the limiting case it is a contact ion pair), (ii) the transition of the system from the locally excited state (D^{*}A) to the CT state is fast due to strong electronic coupling, and (iii) the diastereomeric (Λ -D⁺A_R⁻) and (Λ -D⁺A_S⁻) exciplexes have slightly different energies of formation.

Indeed, Irie et al. attributed their finding of κ being as high as 7.9 in the binaphthyl/*N*-tert-butyl-*N*-(2-methylbutyl)aniline quenching system in hydrocarbon solution at low temperature to exciplex formation.⁵ However, as mentioned in section 1, we could not detect quenching asymmetry in the emitting exciplex system (+)- and (-)-hexahelicene/(S)-(+)-N-methyl-N-(2-methylbutyl)aniline.⁶ Thus, an exciplex does not induce asymmetry in all cases.

We followed two guidelines to optimize the system in terms of asymmetry of ET: On the one hand we increased chirality: in the donor $Ru(bpy)_3^{2+}$ by modifying the ligands by methyl and vinyl substituents, and on the viologen acceptor side by employing 2,2'-bipyridyls and making use of the atropisomerism by introducing longer N,N'-bridges. For the acceptor the success of this concept of modification of chirality is demonstrated by higher values of the circular dichroism (Figure 2).

On the other hand, we diminished the exergonicity (negative ΔG° value) of the quenching reaction according to

$$\Delta G^{\circ} = F[E(D^{+}/D) - E^{*}_{0,0} - E(A/A^{-})] + \frac{z_{\rm D} z_{\rm A} e_{0}^{2} N_{\rm A}}{4\pi\epsilon_{0}\epsilon d_{\rm AD}} \quad (2)$$

by changing the acceptor in the series 8, 2, and 3, the solvents and the pH values as reported in the section Results. In (2) F is the Faraday constant, $E^*_{0,0}$ is the excitation energy, $E(D^+/D)$ and $E(A/A^-)$ are the oxidation potential of the donor and the reduction potential of the acceptor, respectively, and d_{AD} is the donor-acceptor contact distance. We succeeded in observing asymmetry in ET quenching of the emission of 1 in water by the zwitterion of 3, an electroneutral species for which the exergonicity of ET is as small as $\Delta G^\circ = -13$ kJ/mol (Figures 6 and 7). Thus we have to infer the existence of a nonemitting exciplex in water.²¹ Such an exciplex is not observed in the system of 1 and the +2-charged carboxylic form of 3 at low pH values as both partners carry positive charges which disfavors the close contact necessary for chiral discrimination.

The quenching of 1 by 2 and 3 is characterized by large negative entropies of activation (Table 3). This supports the hypothesis of exciplex formation as negative entropies of activation of this order of magnitude indicate highly ordered structures. The existence of exciplexes has been established in MeOH^{6,22} and acetonitrile,²³ but to the best of our knowledge an exciplex has not been observed in water before. An exciplex also seems to exist in the zwitterionic system in the mixed solvent MeOH/water as here the system is of lower exergonicity (negative ΔG°), a smaller k_q ($\approx 5 \times 10^{-7}$ L/(mol s)) and probably exhibits asymmetry, too.

The most striking feature of the 1/3(zwitterion) system is the appearance of a nonlinear bell-shaped Eyring plot (Figure 6) concomitant with the appearance of asymmetry in ET. Such rare dependence of the quenching constant on temperature has been analyzed in detail by Tazuke and co-workers.²⁴ They assign the case with positive enthalpy of activation to a system with unidirectional ET step (caused by a large negative ΔG°) and the one with negative enthalpy of activation to a system in which the ET step is reversible, due to a small negative ΔG° . A bell-shaped Eyring plot indicates the transition between the two cases.²⁴ With this concept we realize that in the system 1/3(zwitterion) the exciplex has a chance to dissociate the excited donor from its thermally populated locally excited state, i.e., in Scheme 1 an arrow $(D^+A^-) \rightarrow (D^*A)$ should be introduced for the reverse electron transfer by population of the locally excited state of the exciplex and another arrow (D*A) \rightarrow (D* + A) for the separation of the components of the exciplex. Because of the different stabilities of the diastereomeric (Λ -D⁺A_R⁻) and (Λ -D⁺A_S⁻) exciplexes there are slight differences in the dissociation and thus asymmetry can be impressed on the quenching constants. However, all other reactions of the CT or contact ion pair state of the exciplex should also be enantiodiscriminative for the same reason, and therefore we cannot identify the most important enantioselective reaction. Unfortunately, there is no fast CD instrumentation available to determine the transient CD signal of the free ions. If this experiment were positive it would give information about the formation of exciplexes in more exergonic ET reactions.

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JP942742I