is observed for equally labeled molecular beacons. Analogous to molecular beacons, preparatory denaturation or renaturation procedures were not required and the probes began to fluoresce almost immediately after addition of the target oligonucleotide. As illustrated in Figure 3 the fluorescence of PNA probe **11** reached a plateau five minutes thereafter.

It was shown that the combined use of orthogonal protecting-group techniques and chemoselective conjugations allows for the rapid solid-phase synthesis of doubly labeled PNA probes. The PNA conjugates were demonstrated to be only weakly fluorescing in the single-stranded state. Hybridization of the weakly fluorescing PNA probes to a complementary oligonucleotide conferred a vivid fluorescence enhancement providing a means for homogeneous DNA detection. It has to be emphasized that target-unrelated arm sequences were not required for maintaining the structural integrity of the probes. The observed fluorescence quenching, however, might depend on both the sequence and the site of labeling. Future studies will reveal whether the fluorescence increase can be generalized to any sequence. Applications such as real-time polymerase chain reaction monitoring and real-time RNA detection in living cells could be feasible and benefit from the increased biostability of the PNA-based hybridization probes.

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Redox Switches with Chiroptical Signal Expression Based on Binaphthyl Boron Dipyrromethene Conjugates[**]

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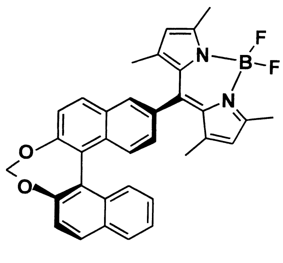
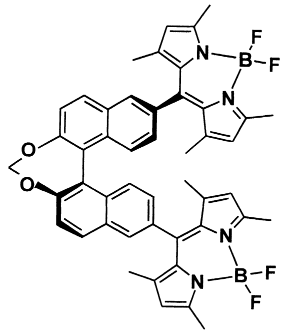
The interest in molecular building blocks with chiral and optoelectronic properties is driven on one hand by the higher specificity in molecular recognition and on the other by the polarization of electromagnetic radiation or light. Herein we report the synthesis and properties of optically active binaphthyl boron dipyrromethene (BDP) conjugates. Because of their favorable absorption and emission properties BDP dyes are frequently used as fluorescent probes for proton or metal ion detection,[1] in light-harvesting complexes within artificial photosynthetic arrays,[2] or as laser dyes.[3] It is also known that BDP dyes with appropriate functionalization can be reversibly oxidized and reduced.[1a, 4] Herein we present the optically active BDP derivatives (*R*)-**1** and (*R*)-**2** which were obtained by derivatization of a chiral 1,1′-



(*R*)-1



(*R*)-2

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binaphthyl system. The compounds were investigated with regard to their circular dichroism, their emission properties, their electrochemical behavior, and their potential use as chiroptic redox switches.

The compounds (*R*)-**1** and (*R*)-**2** were synthesized from enantiomerically pure 1,1′-binaphthyl carbaldehyde precursors and 2,4-dimethylpyrrole.[4b, 5]

The UV/Vis absorption spectra of (*R*)-**1** and (*R*)-**2** show the characteristic intense absorption bands of the BDP chromophore ((*R*)-**1**: $\lambda = 497$ nm, $\varepsilon = 65900\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$; (*R*)-**2**: $\lambda = 497$ nm, $\varepsilon = 132700\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$) in the long-wavelength region, whereas in the short-wavelength region transitions of the binaphthyl chromophore dominate. The emission spectra of (*R*)-**1** and (*R*)-**2** are characterized by BDP fluorescence with maxima at $\lambda = 507$ nm ($\Phi_f = 0.79$) and $\lambda = 509$ nm ($\Phi_f = 0.69$), respectively.[6] Investigation of the electrochemically generated luminescence (ECL)[7] of (*R*)-**2** shows a bathochromically shifted emission maximum at 546 nm. The circular dichroism (CD; Figure 1) for the long-wavelength absorption of the BDP chromophore in the monosubstituted-BDP compound (*R*)-**1** shows a positive CD effect ($\lambda = 495$ nm, $\Delta\varepsilon_{\max} = +10\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$) and in the disubstituted-BDP compound ((*R*)-**2**) a positive, strong asymmetric couplet ($\lambda = 501$ nm, $\Delta\varepsilon_{\max} = 53\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$; $\lambda = 485$ nm, $\Delta\varepsilon_{\max} = -5\,\text{L}\,\text{mol}^{-1}\text{cm}^{-1}$). The first excited states of (*R*)-**1**, (*R*)-**2**, and of several model systems were investigated by means of quantum-chemical calculations.[8] The first transitions of the di-BDP-substituted compound (*R*)-**2**, which correspond to the symmetrical and antisymmetrical combination of the long-wavelength transition of the BDP chromophore, are calculated at $\lambda = 420$ nm and $\lambda = 418$ nm (0.45 eV blue-shifted with respect to the experimental bands) with large rotatory strengths (*R*) of 976×10^{-40} and -886×10^{-40} cgs, respectively (Figure 2). This is in agreement with an exciton-coupled CD signal[9] which can be expected because the large electrical transition-dipole-moment of the BDP chromophore is polarized along the long molecular axis.[10] However, because of the large distance between the two BDP chromophores the two transitions of the couplet are only slightly split (0.014 eV); thus the rotatory strength of the two transitions cancel each other out to a large extent. The measurable Cotton effects are therefore relatively small and a weak, strongly asymmetric, rather atypical exciton couplet results.[11] In model system B the binaphthyl skeleton was removed from the structure of (*R*)-**2**, and the resulting free valences were saturated with H atoms at a standard distance (1.09 Å). For this model system approximately equal rotatory strengths were obtained for the first two transitions ($R = -966 \times 10^{-40}$, $R = 986 \times 10^{-40}$ cgs). Thus, the asymmetry of the long-wavelength couplet of (*R*)-**2** is predominantly caused by interactions with the binaphthyl skeleton. For the mono-BDP-substituted compound (*R*)-**1** the rotatory strength of the first transition, which is localized at the BDP chromophore, is calculated to be $+29 \times 10^{-40}$ cgs (Figure 3). To examine the origin of the Cotton effect of this transition, calculations were carried out for two model systems. In model system M^{I} the OCH_2O bridge and the naphthyl ring, which is not bound directly to the BDP chromophore (ring II), were removed from the calculated structure of (*R*)-**1**, while in model system M^{II} the OCH_2O bridge and the naphthyl ring bound directly to the BDP chromophore (ring I) were removed. The resulting free valences were saturated with H atoms at a standard distance (1.09 Å). For M^{I} a rotatory strength of only $R = 2 \times 10^{-40}$ cgs was obtained for the first transition, whereas for M^{II} a rotatory strength of 15×10^{-40} cgs was obtained. The Cotton effect of the first transition of (*R*)-**1** thus seems to be caused

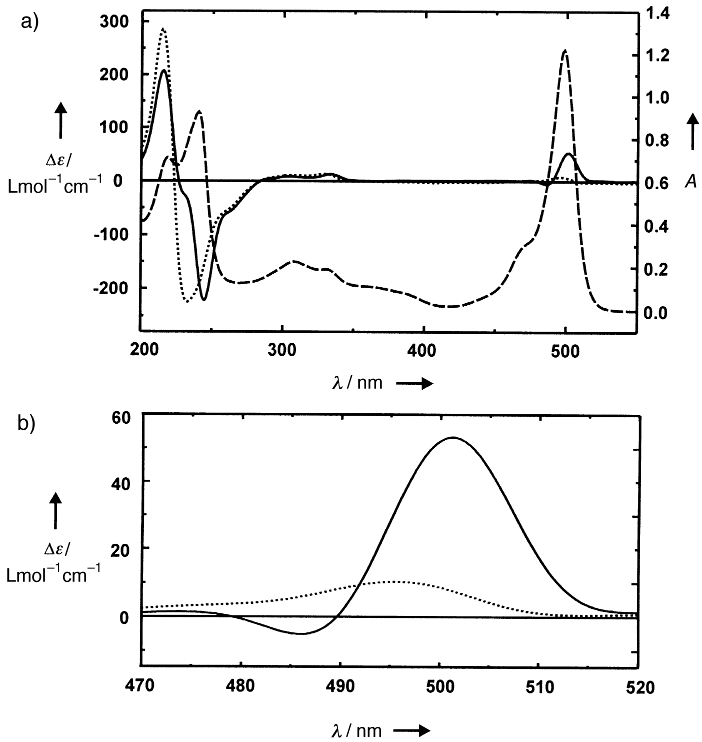

Figure 1. a) CD spectra of (*R*)-**1** (dotted line) and (*R*)-**2** (solid line), UV/Vis absorption spectrum of (*R*)-**2** (dashed line) in acetonitrile; b) the BDP absorption region of the CD spectra of (*R*)-**1** (dotted line) and (*R*)-**2** (solid line).

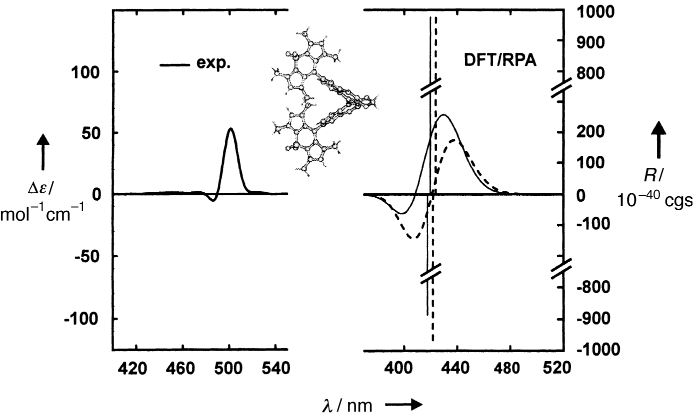

Figure 2. Comparison of the calculated absorption wavelengths, and the rotatory strengths *R* for the first transitions of (*R*)-**2** (solid line, right) with results for the model system B (dashed line) and the experimental bands (left). The simulated CD spectra were obtained by the addition of Gaussian curves with weighted calculated rotatory strengths and for which a half width of 0.25 eV was employed. In model B the two BDP chromophores are considered to be in the same arrangement as in (*R*)-**2** but without the binaphthyl skeleton.

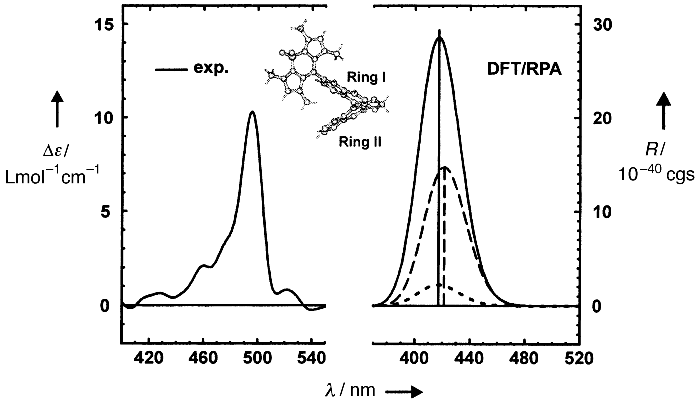

Figure 3. Comparison of the calculated absorption wavelengths and the rotatory strengths R for the first transition of (R)-**1** (solid line, right) with results for the model systems M^I (dotted line) and M^{II} (dashed line) and the experimental band (left). In the model systems M^I and M^{II} the BDP chromophore is, in each case, considered together with only one naphthyl ring of the binaphthyl skeleton (model M^I contains ring I, model M^{II} contains ring II).

by the interaction between the electric transition-dipole-moment of the long-wavelength transition of the BDP chromophore and electric dipole moment in ring II induced by this dipole. These results are also in agreement with a sector rule, which was derived from consideration of the interaction between the electric transition-dipole-moment of a chromophore with neighboring groups.[12] The intense long-wavelength transition allows the potential of the optically active BDP compounds as electrochemically controlled chiroptical switches to be tested. The redox behavior of (R)-**1** and (R)-**2** is most strongly influenced by the BDP chromophore, because the binaphthyl skeleton is electrochemically inactive. Oxidation of the monosubstituted compound (R)-**1** occurs at a half-wave potential of $E_{1/2} = 785$ mV (versus the ferrocenium ion/ferrocene couple) and is quasi-reversible. The reversible reduction cycle at $E_{1/2} = -1515$ mV is stable over several cycles in a thin-layer experiment. Analogous behavior is found for the disubstituted compound (R)-**2** with a quasi-reversible oxidation at $E_{1/2} = +795$ mV and a reversible reduction at $E_{1/2} = -1510$ mV. Thus, one electron is transferred per chromophore, which means overall two electrons are transferred to (R)-**2**. Through CD spectroelectrochemistry[13] and taking (R)-**2** as an example we have shown the application of these compounds as molecular "chiroelectro" switches[14]. UV/Vis-spectroelectrochemistry reveals that the absorption band at 495 nm disappears upon reduction of the neutral compound to the bisradical dianion and a weak radical absorption band with a maximum at 561 nm appears instead (Figure 4). In analogy to these results CD-spectroelectrochemical measurements show a decrease in the intensity of the Cotton effect at 501 nm with continuous increase of the reductive potential, and finally its total disappearance after the solution is completely electrolyzed (Figure 5). Detection of the radical-anion band in the CD spectrum is not possible. The shape of the initial CD spectrum is restored completely after reoxidation: thus the CD signal at 501 nm can be switched on and off electrochemically (Figure 5). In analogy to these results identical behavior can be

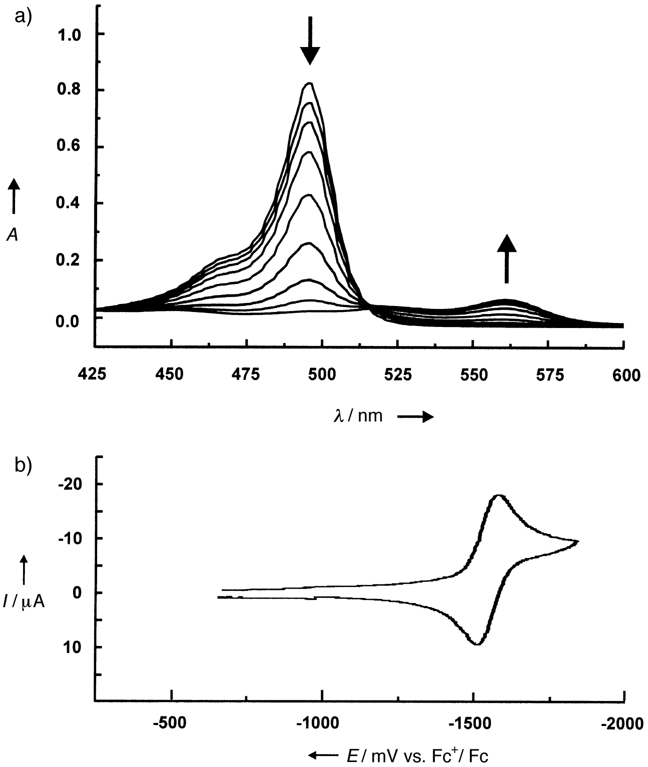

Figure 4. a) UV/Vis-spectroelectrochemical investigation of the reversible reduction (R)-**2** $\rightleftarrows$ (R)-$\mathbf{2}^{2-}$ in acetonitrile; b) cyclic voltammogram of the reduction.

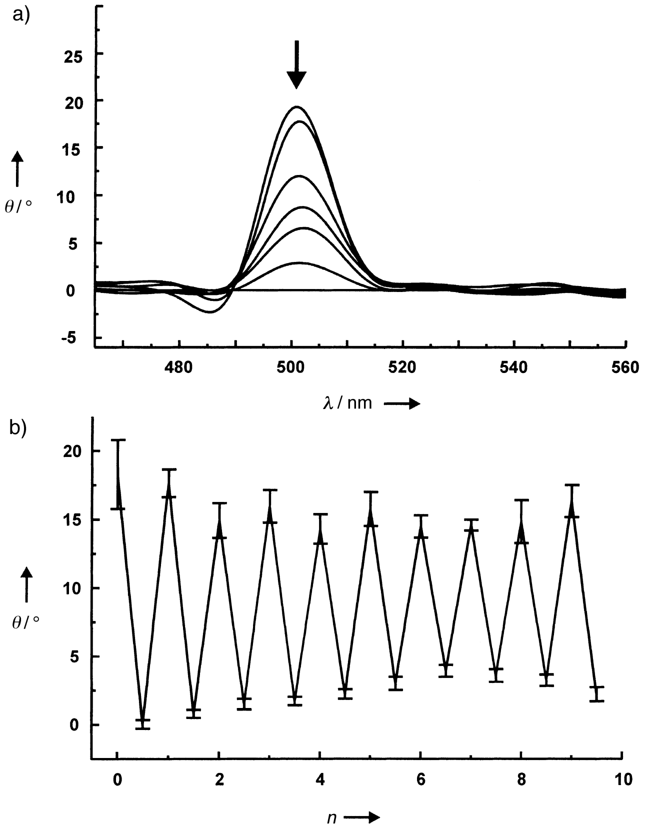

Figure 5. a) CD-spectroelectrochemical investigation of the reversible reduction (R)-**2** $\rightleftarrows$ (R)-$\mathbf{2}^{2-}$; b) variation of the CD signal intensity at $\lambda =$ 501 nm with repeated switching between the neutral compound and the reduced form over ten cycles (n = number of cycles).

observed for the monosubstituted compound (*R*)-**1**; however, in the CD spectrum the intensity of the signal is less than that of (*R*)-**2**. Thus, the presented compounds combine optoelectronical properties and chirality. These results are of relevance in several applications: a) chiral fluorophores within sensor systems,[15] b) circular-polarized photoluminescence[16] and also electrochemiluminescence, c) organic light-emitting diodes (OLED) with circular polarized luminescence,[17] and d) light-emitting diodes (LED) powered by spin-polarized carriers.[18]

Experimental Section

Cyclic voltammetry: solvent acetonitrile; potentials [mV] versus ferrocenium/ferrocene (Fc$^+$/Fc) as internal standard; reversible half wave potential $E_{1/2}$. Measurement conditions: room temperature, scan speed 250 mV s^{-1}, working electrode: platinum-disc electrode, quasi reference electrode: Ag/AgCl, counter electrode: platinum electrode, supporting electrolyte: 0.1 M tetrabutylammonium hexafluorophosphate.

UV/Vis and CD spectroelectrochemistry: solvent acetonitrile, transmission cell with minigrid gold working electrode.

Optical spectra: concentration 10^{-5} to 10^{-6} M in acetonitrile.

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Allosteric Regulation of Artificial Phosphoesterase Activity by Metal Ions**

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In enzyme catalysis allosteric regulation is the control of enzyme activity by noncovalent modifiers (molecules or ions) which bind to the enzyme at a site other than the active site but alter the conformation of the active site. Often, metal ions are involved in allosteric regulation in enzymes. In the active site of *E. coli* alkaline phosphatase a phosphate monoester substrate is hydrolyzed at a dizinc(II) site, while a "structure-stabilizing" Mg^{2+} ion located about 6 Å away from the zinc ions is a strong allosteric activator.[1] Replacement of Mg^{2+} by

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