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Unidirectional Redox-Stimulated Movement around a C–C Single Bond

Christina Tepper and Gebhard Haberhauer*[a]

Dedicated to Professor Rolf Gleiter on the occasion of his 75th birthday

Abstract: A remarkable challenge for the design of molecular machines is the realization of a synchronized and unidirectional movement caused by an external stimulus. Such a movement can be achieved by a unidirectionally controlled change of the conformation or the configuration. Biphenol derivatives are one possibility to realize a redox-driven unidirectional molecular switch. For this reason, a 4,4′-biphenol derivative was fixed to a chiral cyclopeptidic scaffold and stimulated by chemical oxidants and reduction agents. The conformation of the switch was determined by DFT calculations by using B3LYP and the 6-31G* basis set. The switching process was observed by UV and circular dichroism (CD) spectroscopic measurements. Several oxidation agents and various conditions were tested, among which (diacetoxy)iodobenzene (DAIB) in methanol proved to be the best. In this way it was possible to synthesize a redox-stimulated molecular switch with a movement that is part of a rotation around a biaryl binding axis.

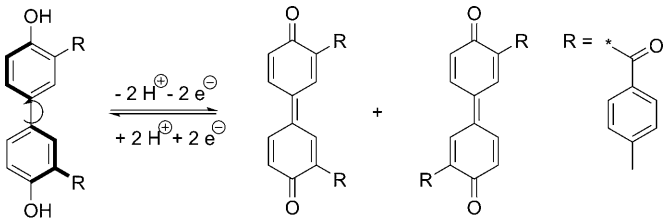
Keywords: circular dichroism · chirality · molecular devices · redox chemistry · unidirectional movement

Introduction

In recent years, the development of molecular motors and switches has become more and more important.[1,2] Such machines are able to carry out movements powered by external stimuli. Until now, numerous examples of switches,[3] rotors,[4] or shuttles[5] have been described that can be controlled chemically, electrochemically, thermally, or by light. A special challenge is the realization of a directed movement that represents a rotation around a binding axis. Indeed, there are only few systems in which the rotation occurs directedly—that is, unidirectionally—around a binding axis.[4,6] Chiral systems that are switched between conformation or configuration isomers[4–8] are one possibility to realize such a concept. Up to now, a system with a unidirectional rotation in which the propulsive stimulus is a redox reaction has not been described. So far, the published redox switches are almost exclusively metal complexes,[9] catenanes,[10] rotaxanes,[11] or other chiroptical systems,[12] which show, however, either no unidirectional processes or the movement of which describes no rotation around a binding axis.

Biphenols could be suitable redox-active systems that perform a directed rotation. Although oxidation to the quinone has been known for a long time, to our knowledge it has never been examined for its quality as a molecular switch.[13]

However, the switching of the biphenol derivative brings with it two problems. On the one hand, the movement occurs bidirectionally because of the free rotatability around the binding axis, and on the other hand, oxidation generates two isomers *cis*-**2** and *trans*-**2** (Scheme 1). It should, however, be possible to annul the free rotatability and to allow a unidirectional movement by fixing the switch panel to a chiral discriminating clamp and thus stabilizing one conformer. Moreover, such a redox switch should permit the formation of only one oxidation product (Scheme 2). Although this kind of switch cannot perform a full rotation of 360°, it is possible to create a system with a smaller amplitude.



Scheme 1. Principle of the switching mechanism of the biphenol derivative **1**.

[a] C. Tepper, Prof. Dr. G. Haberhauer
Institut für Organische Chemie
Fakultät für Chemie, Universität Duisburg-Essen
Universitätsstrasse 7, 45117 Essen (Germany)
Fax (+49) 201-1834252
E-mail: gebhard.haberhauer@uni-due.de

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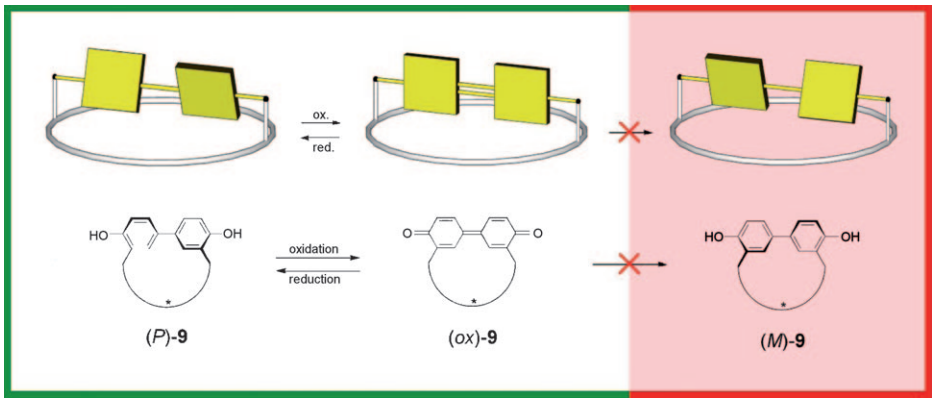
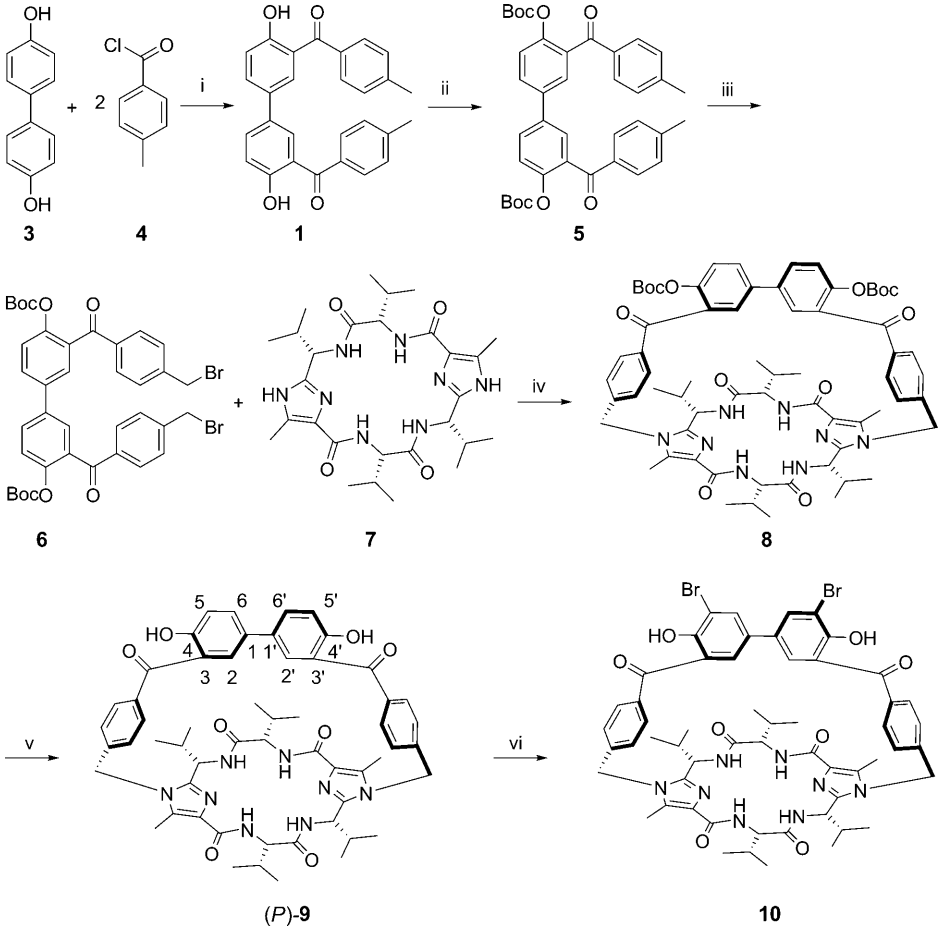


Scheme 2. Principle of the redox switch **9**: The combination of a biphenol derivative with a chiral clamp allows the rotation to take place in only one direction (green area) when the system is reduced.

Results and Discussions

Synthesis: We were already able to produce unidirectional switchable bipyridine and azobenzene derivatives. In these systems the switching unit was strained over a C_2-symmetric cyclopeptidic imidazole clamp **7**,[14] which allowed a unidirectional movement. For this reason we decided to fix the biphenol derivative **1**, too, over the clamp **7** and to examine the properties of the resulting redox switch.

The biphenol derivative is prepared by coupling 4,4′-biphenol (**3**) with two equivalents of *p*-toluoyl chloride (**4**) under aluminum chloride catalysis in a Fries rearrangement. To link it to the clamp **7**, it is necessary to protect the hydroxyl function. *t*-Butyloxycarbonyl (Boc) protection proved to be particularly suitable. Subsequently, compound **5** can be brominated according to Wohl–Ziegler. The coupling of the biphenol derivative **6** to the clamp **7** is carried out in acetonitrile with cesium carbonate as base. Yields up to 64% were achieved. Subsequent hydrolysis of **8** succeeds with HCl in ethyl acetate quantitatively and yields the redox switch (*P*)-**9**. The introduction of bromine at the 5- and 5′-positions—which offers the possibility of introducing larger arms into the switch—can be carried out by simple bromination in dichloromethane at room temperature (Scheme 3).



Scheme 3. Synthesis of the biphenol derivative **1** and of the switch **9**, reaction conditions: i) 1,2-dichlorobenzene, $AlCl_3$, 0–190 °C, 75%; ii) CH_2Cl_2, Boc_2O, 4-dimethylaminopyridine (DMAP), Et_3N, RT, 92%; iii) CCl_4, *N*-bromosuccinimide (NBS), azobisisobutyronitrile (AIBN), 85 °C, 71%; iv) CH_3CN, Cs_2CO_3, 90 °C, 64%; v) HCl/AcOEt, RT, 100%; and vi) Br_2, CH_2Cl_2, RT, 100%.

Proof of the switching process: At first, the switching process was optimized with the biphenol derivative **1** as reference. For this purpose, several oxidation agents and various conditions were tested, among which (diacetoxy)iodobenzene (DAIB) proved to be the most appropriate. The solvent plays an important role in this case. Thus, the oxidation in methanol is completed after just five minutes, whereas in dichloromethane it lasts more than 30 h (Table 1).

The switching process can be observed by NMR spectroscopy. The signals of the methyl group of **1** show a highfield shift of about $\delta = 0.07$ and 0.04 ppm in the oxidized form. This allows one to calculate the starting material/product

Table 1. Selected oxidation agents and conditions.

Oxidation agents	Reaction conditions	Ratio of product/ starting material
$Cu(OAc)_2$	H_2O/AcOH, 4 h, reflux	0:100
$Cu(OAc)_2$	H_2O/AcOH, 10 h, reflux	0:100
H_2O_2	AcOH, 5 h, reflux	0:100
DDQ	CH_2Cl_2, 6 h, reflux	0:100
DDQ	toluene, 6 h, 120 °C	0:100
DDQ	toluene, NaH, 7 h, 120 °C	0:100
DAIB	MeOH, 14 h, RT	86:14
DAIB	MeOH, 5 min, RT	86:14
DAIB	CH_2Cl_2, 32 h, RT	86:14

and the *cis*/*trans* ratio based on the integrals of the methyl group. After oxidation using DAIB in MeOH, we found a starting material/product ratio of 14:86 and a *cis*/*trans* ratio of 50:50. After reduction of the oxidized form, the spectrum shows the same peaks und integrals as the initial state. The oxidation of the redox switch (*P*)-**9** with DAIB in dichloromethane can also be observed by NMR spectroscopy. The spectra of the initial state and the oxidized form are shown in Figure 1. In the latter spectrum, the (*P*)-**9**/(*ox*)-**9** ratio was determined to be 3:7.

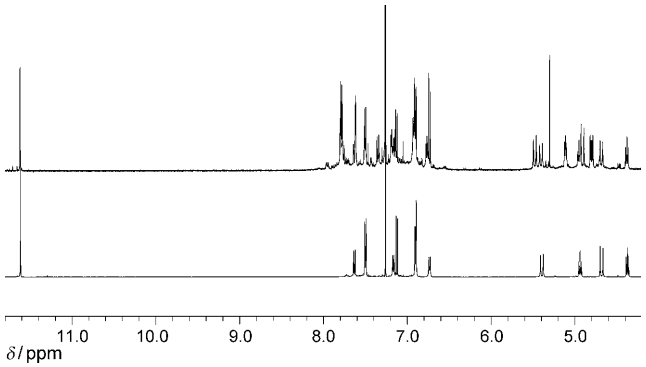


Figure 1. ^{1}H NMR ($CDCl_3$, 500 MHz) spectra of switch (*P*)-**9** (bottom) and (*ox*)-**9** (top).

Another method that allows one to investigate the redox-switching process is UV spectroscopy. The chromophoric unit of the switch is changed during the redox reaction, which should be observable in the corresponding UV spectra. In Figure 2, the UV spectra of the biphenol derivative **1** and the switch (*P*)-**9** are shown in the reduced initial state and after oxidation (**2** and (*ox*)-**9**). Based on the oxidation of **1** with (diacetoxy)iodobenzene, a bathochromic shift of the characteristic band occurs from 360 to 417 nm. A similarly strong change of the absorption maximum to a longer wavelength after addition of the oxidant was also observed with the redox switch (*P*)-**9**. Here, the shift takes place from 360 to 414 nm. After addition of the reduction agent, the new maxima of both systems disappear. This is a concrete evidence for the successful back-switch. In contrast to the biphenol derivative **1**, the reductive back-switch of (*ox*)-**9** is not complete.

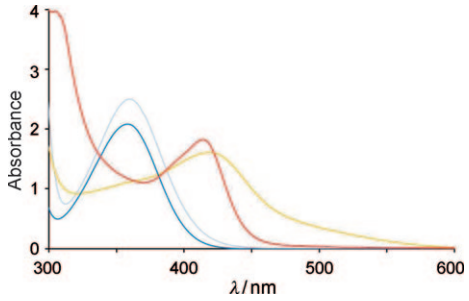


Figure 2. UV spectra of **1** (light blue), *cis*-(**2**) and *trans*-(**2**) (orange), (*P*)-**9** (dark blue), and (*ox*)-**9** (red) ($c = 4 \times 10^{-4}$ M in CH_2Cl_2).

Proof of the unidirectionality of the switching process: For the verification of the unidirectionality, the existence of **9** in only one conformation (here: the *P* conformation) is of crucial importance. For the authentication of the present conformation, ab initio calculations were carried out. Therefore, the energy profiles of the biphenol derivatives **1** and **9** in relation to the dihedral angles $\theta_{C2\text{-}C1\text{-}C1'\text{-}C2'}$ was calculated by using B3LYP and the 6-31G* basis set (Figure 3).[15] In the

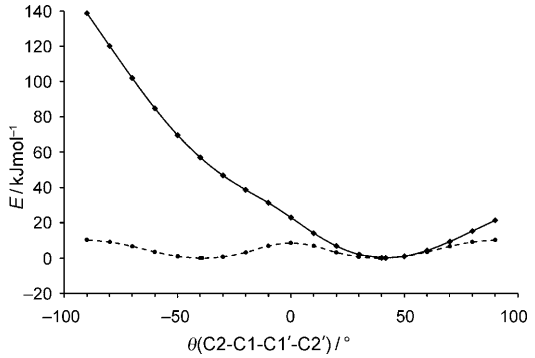


Figure 3. Calculated energy profiles of the biphenol derivative **1** (dashed line) and **9** (solid line) in relation to the dihedral angles $\theta_{C2\text{-}C1\text{-}C1'\text{-}C2'}$ by use of B3LYP/6-31G*.

case of the biphenol derivative **1**, the dihedral angle between the C atoms of the biphenol binding axis (C2-C1-C1′-C2′) of the *P* isomer was calculated to be 40°. The transition state between the *M* and the *P* isomers exhibits a dihedral angle $\theta_{C2\text{-}C1\text{-}C1'\text{-}C2'}$ of 0° and its energy is by 8.5 kJ mol^{-1} higher than that of the enantiomers. A completely different situation is found in the switch (*P*)-**9**. The chiral peptidic clamp energetically destabilizes the *M* conformation so much that only the *P* isomer was calculated to be a minimum on the potential energy surface. The dihedral angle between the C atoms of the biphenol binding axis (C2-C1-C1′-C2′) was calculated to be 42° for the *P* isomer. This means an amplitude of about 42° when oxidation of the biphenol unit takes place. Since the corresponding *M* isomer is not a minimum, the calculated state with a fixed dihedral angle $\theta_{C2\text{-}C1\text{-}C1'\text{-}C2'}$ of −40° was defined as *M* isomer for the further discussions (Figure 4). The energy difference between the *M*

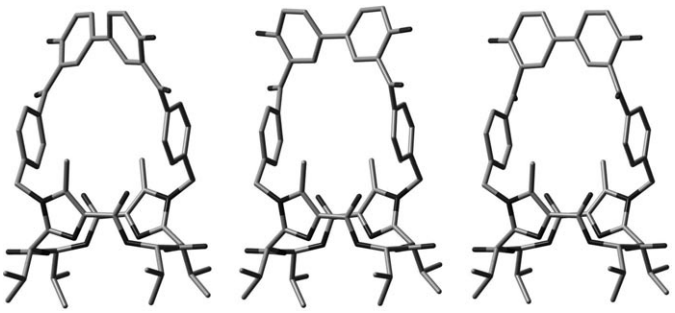


Figure 4. Structures of (*P*)-**9**, (*M*)-**9**, and (*ox*)-**9** calculated with B3LYP/6-31G*. All hydrogen atoms were omitted for clarity.

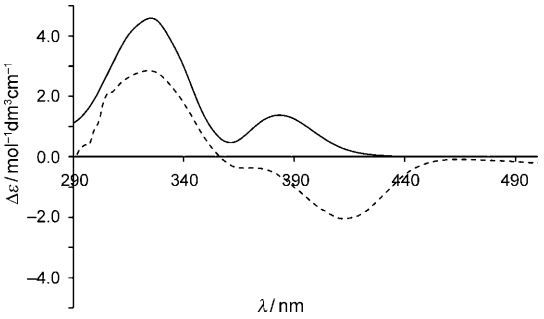


Figure 6. CD spectra of (*P*)-**9** (solid line) and (*ox*)-**9** (dashed line) ($c = 10^{-4}$ M in CH_2Cl_2).

and the *P* isomers of the switch (*P*)-**9** amounts to 58.9 kJ mol^{-1}. This means that even if the *M* isomer were a minimum, the ratio of *M* to *P* calculated by the Boltzmann distribution at room temperature (25 °C) would be 1 to 2.7×10^{10}. This in turn means that only the *P* conformation of **9** is present in solution.

An explanation for the strong preference of the *P* conformation of **9** can be found in its structure (Figure 4). In the stable *P* conformer, the carbonyl functions of the bridging unit are located in one plane with the phenyl rings of the biphenol unit. This leads to the formation of hydrogen bonds and thus to a stabilization of this conformation. In the *M* conformer, however, a planarity between the carbonyl groups and the hydroxyl groups is not given. This lowers the ability of forming hydrogen bonds and thus results in an increase of energy.

Another piece of evidence for the existence of switch **9** in the *P* conformation can be provided by CD spectroscopy. For this purpose, the CD spectra of (*P*)-**9** and (*ox*)-**9** in dichloromethane as solvent were recorded. Additionally, the CD spectra of (*P*)-**9** and (*M*)-**9** were simulated with the time-dependent density functional theory (TD-DFT) with B3LYP as functional and by employing the 6-31G* basis set (Figure 5 and Figure 6). TD-DFT calculations were performed at the optimized ground-state geometry for (*P*)-**9** and at the state with a fixed dihedral angle of −40° for (*M*)-**9**, calculating the energy, oscillator strength, and rotatory strength for each of the 100 lowest singlet excitations. The CD spectrum was simulated by overlapping Gaussian functions for each transition in which the width of the band at 1/*e* height was fixed at 0.3 eV and the resulting intensity of the combined spectrum was scaled to the experimental values.

The measured and the calculated spectra of the redox switch **9** are shown in Figure 5. The comparison of the spectra shows a very good consistency of the experimental spectrum with the calculated one of the *P* isomer. Although there is a positive Cotton effect for the experimentally measured spectrum of **9** and the calculated one of the *P* isomer at 390 nm, the *M* isomer shows a negative Cotton effect at this wavelength. This allows the conclusion that the *P* isomer is present in solution.

Also, the switching of (*P*)-**9** can be clearly detected by CD spectroscopy. The bands at 325 and 380 nm are connected with the axial chirality of the biphenol unit. The band at 325 nm is retained even after oxidation. Instead of the positive band at 382 nm, a negative Cotton effect appears at 411 nm after oxidation. The changes in the CD spectrum confirm that oxidation has succeeded and hence a conformational change has taken place. After reduction of the oxidized state, the negative Cotton effect at 411 nm disappears again and the corresponding positive Cotton reappears.

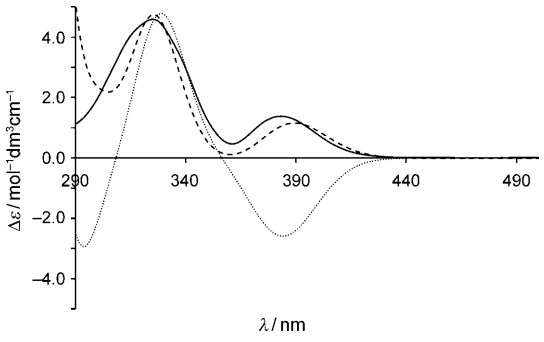


Figure 5. Comparison of the TD-DFT-B3LYP/6-31G*-calculated CD spectra of (*P*)-**9** (dashed line) and (*M*)-**9** (dotted line) with the experimentally determined spectrum of **9** (solid line; $c = 10^{-4}$ M in CH_2Cl_2).

Conclusion

In summary, we can state that we were able to fix the biphenol derivative **1** onto a C_2-symmetric cyclopeptidic scaffold. This resulted in a stabilization of the resulting (*P*)-**9** conformer compared to the (*M*)-**9** conformer and enabled a unidirectional rotation around a C–C single bond by a redox process. This concept is a first step towards an electrochemically driven molecular motor.

Experimental Section

General remarks: All chemicals were reagent grade and were used as purchased. Reactions were monitored by TLC analysis with silica gel 60 F254 thin-layer plates. Flash chromatography was carried out on silica gel 60 (230–400 mesh). ^{1}H and ^{13}C NMR spectra were measured using

Bruker Avance DMX 300 and Avance DRX 500 spectrometers. All chemical shifts (δ) are given in ppm relative to TMS. The spectra were referenced to deuterated solvents indicated in brackets in the analytical data. HRMS spectra were recorded using a Bruker BioTOF III instrument. IR spectra were measured using a Varian 3100 FTIR Excalibur Series spectrometer. UV/Vis absorption spectra were obtained using Jasco J-815 and V-550 spectrophotometers. CD absorption spectra were recorded using a Jasco J-815 spectrophotometer.

Redox switch 9: Compound **8** (27 mg, 0.02 mmol) was dissolved in ethyl acetate (1 mL). HCl in ethyl acetate (5 mL) was added. The mixture was stirred for four days at room temperature. The solution was poured into an ethyl acetate/water mixture. The organic phase was separated, dried over magnesium sulphate and the solvent was removed in vacuo. The residue was purified by column chromatography over silica gel (CH_2Cl_2/AcOEt: 75:25). The product was obtained as a yellow solid (20 mg, 100%). M.p. > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 11.62 (s, 2H; *H*O-Ph), 7.64 (d, ^4J(H,H) = 2.3 Hz, 1H; H_{ar}), 7.62 (d, ^4J(H,H) = 2.3 Hz, 2H; H_{ar}), 7.50 (d, ^3J(H,H) = 8.3 Hz, 4H; H_{ar}), 7.14–7.11 (m, 4H, H_{ar}; N*H*), 6.92–6.88 (m, 6H; H_{ar}), 6.86 (d, ^3J(H,H) = 8.1 Hz, 2H; N*H*), 5.41 (d, ^2J(H,H) = 16.1 Hz, 2H; CH_2-Ph), 5.00–4.94 (m, 2H; NH-C*H*-CO), 4.69 (d, ^2J(H,H) = 16.2 Hz, 2H; CH_2-Ph), 4.41–4.36 (m, 2H; NH-C*H*-CH(CH$_3$)$_2$), 2.17–2.14 (m, 4H; C*H*(CH$_3$)$_2$), 2.03 (s, 6H; imidazole-C*H*$_3$), 1.17 (d, ^3J(H,H) = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$), 1.12 (d, ^3J(H,H) = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 0.93 ppm (d, ^3J(H,H) = 6.7 Hz, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 201.9 (*C*=O), 171.7 (*C*=O), 163.1 (*C*=O), 162.2 (C_{ar}), 147.8 ($C_{imidazole}$), 137.9 (C_{ar}), 137.7 (C_{ar}), 134.7 (C_{ar}), 132.6 (C_{ar}), 131.8 (C_{ar}), 131.4 ($C_{imidazole}$), 130.3 ($C_{imidazole}$), 129.3 (C_{ar}), 127.4 (C_{ar}), 120.2 (C_{ar}), 118.9 (C_{ar}), 60.6 (*C*H-CH(CH$_3$)$_2$), 51.1 (*C*H-CH(CH$_3$)$_2$), 47.7 (*C*H$_2$-Ph), 35.0 (*C*H(CH$_3$)$_2$), 30.2 (*C*H(CH$_3$)$_2$), 20.0 (C(*C*H$_3$)$_3$), 19.44 (CH(*C*H$_3$)$_2$), 19.41 (CH(*C*H$_3$)$_2$), 19.1 (CH(*C*H$_3$)$_2$), 10.2 ppm (imidazole-*C*H$_3$); IR (ATR): $\tilde{\nu}$ = 3386, 2961, 2923, 2853, 1668, 1591, 1470, 1257 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 250 (4.54), 359 nm (3.60); CD (CH_2Cl_2): λ ($\Delta\varepsilon$) = 226 (+0.6), 239 (+14.6), 256 (−32.2), 282 (+2.3), 327 (+3.0), 387 nm (−0.9 mol^{-1} m^3 cm^{-1}); HRMS (ESI): *m*/*z* calcd for $C_{56}H_{62}N_8O_8$ [*M*+H]$^+$: 975.4763; found 975.4806; [*M*+Na]$^+$: 997.4583; found 997.4597.

Redox switch 10: Redox switch **9** (18 mg, 18.5 μmol) was dissolved in dichloromethane (3 mL). A mixture of bromine (3.5 μL, 65.6 μmol) in dichloromethane (2 mL) was added dropwise. The mixture was stirred for 18 h at room temperature. Afterwards, the reaction solution was poured into a saturated sodium sulfite solution. The organic phase was separated, dried over magnesium sulfate, and the solvent was removed in vacuo. The product was obtained as a yellow solid (21 mg, 100%). M.p. > 250 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 12.22 (s, 2H; O*H*-Ph), 7.88 (d, ^4J(H,H) = 2.2 Hz, 2H; H_{ar}), 7.50 (d, ^3J(H,H) = 8.3 Hz, 4H; H_{ar}), 7.16 (d, ^3J(H,H) = 8.3 Hz, 2H; N*H*), 6.90 (d, ^3J(H,H) = 8.2 Hz, 4H; H_{ar},), 6.84 (d, ^4J(H,H) = 2.2 Hz, 2H; H_{ar}), 6.78 (d, ^3J(H,H) = 8.0 Hz, 2H; N*H*), 5.40 (d, ^2J(H,H) = 16.2 Hz, 2H; CH_2-Ph), 4.96–4.93 (m, 2H; NH-C*H*-CO), 4.70 (d, ^2J(H,H) = 16.3 Hz, 2H; CH_2-Ph), 4.39–4.36 (m, 2H; NH-C*H*-CH(CH$_3$)$_2$), 2.36–2.24 (m, 4H; C*H*(CH$_3$)$_2$), 2.01 (s, 6H; imidazole-C*H*$_3$), 1.16 (d, ^3J(H,H) = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$), 1.11 (d, ^3J(H,H) = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 0.92 ppm (d, ^3J(H,H) = 6.7 Hz, 6H; CH(C*H*$_3$)$_2$); ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 201.3 (*C*=O), 171.7 (*C*=O), 163.2 (*C*=O), 158.9 (C_{ar}), 147.8 ($C_{imidazole}$), 138.5 (C_{ar}), 137.6 (C_{ar}), 137.0 (C_{ar}), 132.3 (C_{ar}), 131.1 (C_{ar}), 131.0 ($C_{imidazole}$), 130.4 ($C_{imidazole}$), 129.4 (C_{ar}), 127.5 (C_{ar}), 120.9 (C_{ar}), 112.9 (C_{ar}), 60.5 (*C*H-CH(CH$_3$)$_2$), 51.1 (*C*H-CH(CH$_3$)$_2$), 47.6 (*C*H$_2$-Ph), 34.9 (*C*H(CH$_3$)$_2$), 30.2 (*C*H(CH$_3$)$_2$), 19.9 (C(*C*H$_3$)$_3$), 19.4 (CH(*C*H$_3$)$_2$), 19.1 (CH(*C*H$_3$)$_2$), 10.1 ppm (imidazole-*C*H$_3$); IR (ATR): $\tilde{\nu}$ = 3396, 3058, 2963, 2932, 2873, 1668, 1593, 1498, 1434, 1338, 1239 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 252 (5.19), 360 nm (4.33); HRMS (ESI): *m*/*z* calcd for $C_{56}H_{60}Br_2N_8O_8$ [*M*+H]$^+$: 1133.2961; found 1133.3005.

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