10 mM ethylenediamine tetraacetate (EDTA), 1 mM 1,4-dithiothreitol (DTT), and 1 % bovine serum albumen (BSA) at 4 °C in a volume of 400 μL. After 30 minutes this exchange reaction was stopped by the addition of $MgCl_2$ to give a final concentration of 25 mM and the enzyme · substrate (E · S) complex purified on a PD10 column. The purified E · S complex was divided into separate aliquots of 150 μL, and rGTP was added to give a final concentration of 50 μM. The reactions were incubated at 30 °C for various times before mixing 7.5-μL samples with 7.5 μL of stop solution (100 μM rGTP, 100 μM rGDP, 250 mM EDTA, 0.5 % sodium dodecasulfate (SDS)). Conversion of GTP into GDP was monitored by chromatography on polyethyleneimine (0.3 M KH_2PO_4, 1 M $LiCl_2$, pH 3.5).

[24] For k_{cat} calculations based on monitoring the single-turnover experiment of the E · S complex in the presence of an excess of free unlabeled rGTP, the following relationship holds: $[P]/[E\cdot S]_0 = k_{cat}/(k_{cat}+k_{off})\exp[(-(k_{cat}+k_{off})t]$, where [P] is the concentration of the GDP product, t is time, and k_{off} the off-rate for GTP in the E · S complex. This relationship is based on the following assumptions: The E · S complex can break down only to product or to free enzyme and free substrate; the observed reaction is strictly single-turnover, because once the labeled substrate has dissociated from the enzyme it will not appreciably reassociate because of competition by excess unlabeled substrate; and the product off-rate is not limiting because the E · P complex is broken down in the stop reaction.

[25] Both WT and photocaged proteins were irradiated for up to five minutes with a frequency-tripled Spectra-Physics model GCR-150-10 laser (ca. 100 mJ at 355 nm, nominal pulse width of 7 ns). Longer photolysis times did not lead to greater conversion. Irradiation was performed in quartz cuvettes with stirring to ensure an even exposure. Reactions were chilled to 4 °C prior to irradiation to prevent overheating. The 500-μL reactions contained 10 nM WT or mutant ras protein in 50 mM Hepes (pH 7.5), 1 mM $MgCl_2$, 200 mM NaCl, 1 mM DTT, 0.1 % BSA, and 10 μM semicarbazide · HCl to scavange the nitrosobenzaldehyde by-product.

[26] The p120 – GAP assay was performed by isolation of the E · S complex as described in ref. [23], except that a greater than 100-fold excess of p120 – GAP over the ras protein was added after dividing the E · S complex into separate reactions. p120 – GAP was a gift from H. Chung and was prepared by overexpression from a derivative of pUC18 carrying the gene for bovine p120 – GAP behind the Trp promoter as described in M. S. Marshall, W. S. Hill, A. S. Ng, U. S. Vogel, M. D. Schaber, E. Scolnick, R. A. F. Dixon, I. S. Sigal, J. B. Gibbs, *EMBO J.* **1989**, *8*, 1105 – 1110.

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[28] Improved deprotection efficiencies have been reported when the *o*-nitrobenzyl group is substituted at the *α*-benzylic position because the photocleavage by-product of these compounds is the less reactive nitrosoketone. Attempts to improve the efficiency of the photocleavage reaction by using *β*-1-(3,4-methylenedioxy-6-nitrobenzyl)-ethyl aspartate resulted in lower yields of mutant protein.

[29] Under saturating conditions, p120 – GAP can catalyze the GTPase rate of ras by 10^5-fold;[30] however, catalysis in these experiments is limited by the ras protein, which is present in the reaction at a concentration of about 10 nM but has a k_d for p120 – GAP of about 17 μM.[31]

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One- and Two-Dimensional Electron Transfer Processes in Triarylamines with Multiple Redox Centers**

Christoph Lambert* and Gilbert Nöll

Intramolecular electron transfer (ET) processes have been studied extensively in inorganic binuclear transition metal complexes;[1] organic donor – acceptor systems that are bridged by σ frameworks have been investigated in order to mimic biological ET processes.[2] In contrast, much less is known about purely organic Robin/Day[3] class II compounds with bridging π-electron systems and the electron transfer processes involved: Nelsen et al.[4] studied a number of bis(hydrazine)phenylene radical cations and related species; Bonvoisin et al.[5] investigated *m*-phenylene-bridged triarylamine systems. These radical cations are characterized by intervalence charge-transfer (IV-CT) bands in the NIR spectra which are associated with a photoinduced intramolecular electron transfer between two redox centers. As the coupling of redox centers over π-conjugated bridges is of central interest for the design of new optoelectronic materials,[6] it was our aim to study basic intramolecular electron transfer processes in simple symmetrically substituted π systems. We chose π-bridged triarylamine derivatives since triarylamines in general are important hole carrier systems, which are widely used in organic optoelectronic devices.[7]

4,4′-Bis(*N*,*N*-di-*p*-methoxyphenylamino)tolane (**2**) was synthesized by two Hagihara cross-coupling steps, and the corresponding trimer hexakis[4-(*N*,*N*-di-*p*-methoxyphenylamino)phenyl]benzene (**3**) was formed from **2** by catalysis with $[Co_2(CO)_8]$ (Scheme 1).[8] These derivatives should exhibit an intramolecular degenerate electron transfer in the singly and triply oxidized forms, respectively. Both neutral compounds are yellow, and their UV/Vis spectra in CH_2Cl_2 contain a strong absorption band at 373 nm (**2**) and 308 nm (**3**, with a shoulder at 330 nm). The cyclic voltammogram (CV)[9] of **2** shows two waves at 200 and 340 mV (versus Fc/Fc^+) in CH_2Cl_2 (Figure 1) referring to two reversible oxidations. This corresponds to a comproportionation constant ($K_{co} = 10^{(\Delta E/0.059)}$, where ΔE is the difference of redox potentials for the two oxidative steps) of 236 and suggests **2** to be a class II derivative.[1, 3] In contrast, trimer **3** only shows one broad unresolved wave centered at 225 mV. This reversible oxidation process was calibrated by thin-layer coulometry with 2,5-bis(dicyanovinyl)furan as the reference, and it involves six electrons in total, leading to $\mathbf{3}^{6+}$.

UV/Vis/NIR spectroelectrochemical investigation[10] of **2** shows that besides a band at 734 nm, which is characteristic for triarylamine radical cations,[11] a second very intense band

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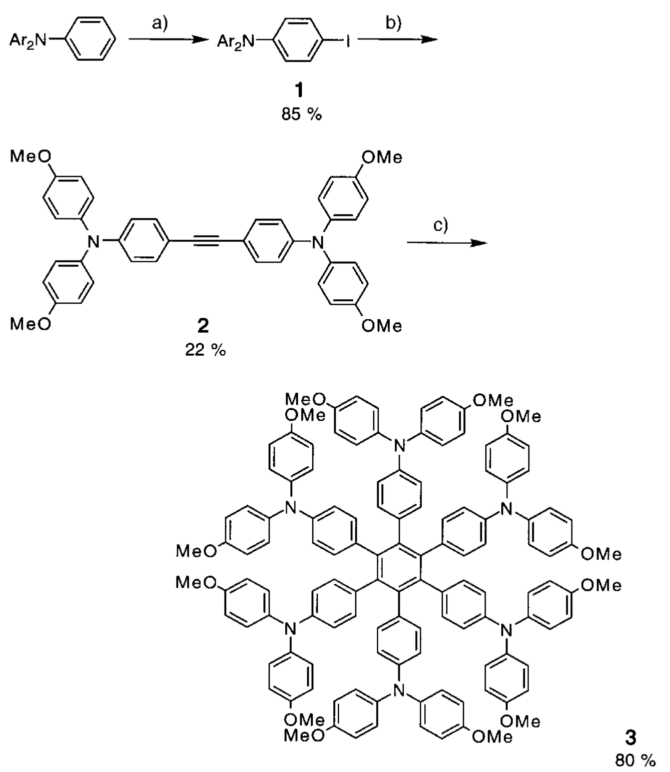


Scheme 1. Synthesis of **2** and **3**. Ar = 4-methoxyphenyl. a) $(CF_3CO_2)_2IPh/I_2$. b) 1. $HC{\equiv}CSiMe_3$, 5 mol% $[Pd(PPh_3)_2Cl_2]$, 2.5 mol% CuI/Et_2NH; 2. $K_2CO_3/MeOH$; 3. **1** + 5 mol% $[Pd(PPh_3)_2Cl_2]$, 2.5 mol% CuI/Et_2NH. c) $[Co_2(CO)_8]$/dioxane.

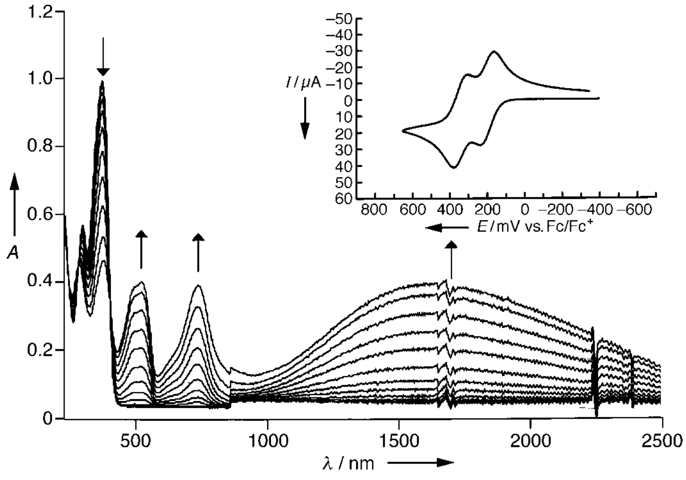


Figure 1. Spectroelectrochemistry of the oxidation of **2** to 2^+. Inset: cyclic voltammogram of **2**.

(ε_{max} = 22300 $M^{-1}cm^{-1}$) appears in the NIR spectrum at 1620 nm upon oxidation to the monocation 2^+ (6180 cm^{-1}, Figure 1). We attribute this band to a one-dimensional IV-CT. This band disappears when 2^+ is further oxidized to 2^{2+}, while the radical band at 734 nm rises continuously.[11] Figure 2 shows both the absorbance of the radical band and the IV-CT band versus the applied potential. The absorbance of the IV-CT band is maximal at a potential when the radical band shows half the absorbance of the fully oxidized 2^{2+}. This proves that the IV-CT band is solely associated with 2^+.

Spectroelectrochemistry of **3** also revealed, besides a radical band at 748 nm,[11] an IV-CT band of low intensity (in the order of 5000 M^{-1} cm^{-1}) at around 1390 nm (7200 cm^{-1}). A plot of the radical band and the IV-CT band against the potential again shows that the maximum of the IV-CT occurs at a potential when the radical band is at half the maximal intensity. Although 3^+ and 3^{5+} should exhibit IV-CT bands as well, we assign the observed band to be mainly due to the IV-CT in the trication 3^{3+} which should be the most intense. According to AM1-CI calculations[12] the ground state of 3^{3+} is a ^4A state. There are two doubly degenerate (E) IV-charge transfers at 1.556 and 1.584 eV connected to the ^4A ground state by very small oscillator strengths (f = 0.092 and 0.181, respectively). The two-dimensional IV-CT is drawn schematically in Scheme 2 and refers to a classical concerted electron transfer. There is a ^2E state only 0.0008 eV above the quartet ground state. This means that at ambient temperature both the ^4A and the ^2E state might be populated thermally. The ^2E state is connected to four excited ^2E and to four ^2A states lying between 1.556 and 1.586 eV. The oscillator strengths of these states amount in total to f = 0.24, which is comparable to the two excited ^4E states (f = 0.27). All these transitions may contribute to the observed IV-CT band of 3^{3+}.

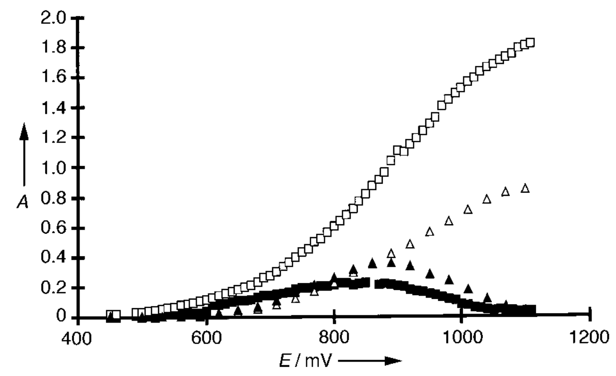
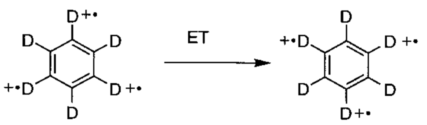


Figure 2. Plot of the absorbance of the radical band (**2**: △, **3**: □) and the IV-CT band (**2**: ▲, **3**: ■) during oxidation versus potential (relative to Ag/AgCl); absorbance of the IV-CT band of **3** × 10.



Scheme 2. Concerted two-dimensional ET of 3^{3+}. D = 4-[*N*,*N*-bis-(4-methoxyphenyl)amino]phenyl.

To apply Hush's adiabatic line shape analysis[1, 13, 14] to the observed IV-CT band of 2^+ we recorded UV/Vis/NIR spectra of chemically oxidized **2** (with $Cu(ClO_4)_2 \cdot 6H_2O$ in MeCN and $SbCl_5$ in all other solvents) in a number of different solvents at concentrations of about 10^{-4}–10^{-5} M (Table 1) since the spectral data from the spectroelectrochemical experiment are influenced to some extent by ion pairing due to high salt concentrations.[15]

According to Hush, the theoretical width at half-height of a Gaussian-shaped IV-CT band can be calculated from $\tilde{\nu}_{max}$ at the high-temperature limit (HTL) with Equation (1).[13] As

$$\tilde{\nu}_{1/2}(\mathrm{HTL}) = 47.94\sqrt{\tilde{\nu}_{max}} \quad (1)$$

expected for class II compounds, the experimentally observed $\tilde{\nu}_{1/2}$ in polar solvents is somewhat broader (about 17%) than

Table 1. Spectral data of **2**$^+$ in different solvents.[a]

	E_T^N	$\tilde{\nu}_{max}$ [cm^{-1}]	λ/λ_v [kcal mol^{-1}]	ε_{max} [M^{-1} cm^{-1}]	V [kcal mol^{-1}]	$\tilde{\nu}_{1/2}$ [cm^{-1}]	$\tilde{\nu}_{1/2}$(HTL) [cm^{-1}]	$g(\tilde{\nu}_v,T)$
2$^+$/CH_2Cl_2	0.309	5710	16.3/4.5	22300	3.1	3400	3620	0.94
2$^+$/PhCN	0.333	6490	18.5/4.5	–	–	4420	3860	1.15
2$^+$/EtCN	0.401	7370	21.1/4.5	–	–	5020	4120	1.22
2$^+$/DMF	0.404	7620	21.8/4.5	–	–	5140	4180	1.23
2$^+$/DMSO	0.444	7740	22.1/4.5	–	–	–	4220	–
2$^+$/MeCN	0.460	7990	22.8/4.5	14100	3.4	4640	4290	1.08
[Fc-CC-Fc]$^+$/MeCN[b]	0.460	7350	21.4/2.0	300–500	1.0	4000	4110	–

[a] E_T^N: normalized Dimroth–Reichardt solvent parameter. $\tilde{\nu}_{max}$: absorption maximum. λ/λ_v: total/inner reorganization energy. ε_{max}: molar absorptivity. V: coupling energy. $\tilde{\nu}_{1/2}$: observed band width at half-height. $\tilde{\nu}_{1/2}$(HTL): theoretical band width at half-height at the high-temperature limit. $g(\tilde{\nu}_v,T)$: ratio of $\tilde{\nu}_{1/2}/\tilde{\nu}_{1/2}$(HTL). [b] Diferrocenylethyne.[23]

the theoretical HTL width. However, $\tilde{\nu}_{1/2}$ decreases on going to less polar solvents until an even smaller value than $\tilde{\nu}_{1/2}$(HTL) is reached in CH_2Cl_2. The electronic coupling energy in CH_2Cl_2 and MeCN was calculated with Equation (2)[1, 13, 14] from the IV-CT energy $\tilde{\nu}_{max}$ (equivalent to the reorganization energy λ), from the observed width at half-height $\tilde{\nu}_{1/2}$, and from the molar absorptivity ε_{max}.[16] For the distance d between the two redox centers we used the AM1 calculated N–N distance of 12.48 Å.[17]

$$V = \frac{0.0206}{d}(\varepsilon_{max}\tilde{\nu}_{1/2}\tilde{\nu}_{max})^{1/2} \qquad (2)$$

The coupling energy V is 3.1 kcal mol^{-1} in CH_2Cl_2 and 3.4 kcal mol^{-1} in MeCN (Table 1), making the reaction strongly adiabatic. This is in reasonable agreement with the AM1-calculated[5a] splitting energy of the HOMO and HOMO − 1 ($E_{HOMO} - E_{HOMO-1} = 2\,V$; $V_{AM1} =$ 3.8 kcal mol^{-1}) of **2**, which refers in a first-order approximation to the coupling in **2**$^+$. The electronic mixing coefficient α is an estimate for the electron delocalization: $\alpha = V/\tilde{\nu}_{max}$.[18] Thus, with $\alpha = 0.19$ in CH_2Cl_2 and 0.15 in MeCN the delocalization in **2**$^+$ is much stronger than in diferrocenylethyne ($\alpha = 0.05$).[18] A very crude partitioning of the reorganization energy λ in an outer (solvent, λ_s) and an inner (vibronic, λ_v) contribution was carried out by correlating the IV-CT energies in different solvents (Table 1) with the normalized E_T^N parameters.[19] The intercept of a linear regression analysis is 1600 cm^{-1} (4.6 kcal mol^{-1}), which is in good agreement with the AM1 calculated[20] internal reorganization energy λ_v of 4.5 kcal mol^{-1}. For **3**$^{3+}$, a similar internal reorganization energy per positive charge (4.8 kcal mol^{-1}) was calculated as one third of the total inner reorganization energy.[20]

The rate constant for the adiabatic thermal ET process in MeCN was calculated with Equation (3).[21] The nuclear frequency factor $\tilde{\nu}_v$ was estimated from the ratio $g(\nu_v,T)$ [Eq. (4)] of the observed IV-CT band width at half-height and

$$k_{th} = \nu_v \exp(-\Delta G^*/RT) \qquad (3)$$

$$\tilde{\nu}_{1/2} = g(\nu_v,T)\tilde{\nu}_{1/2}(\mathrm{HTL}) \qquad (4)$$

the band width at the high-temperature limit (with the exception of the value for CH_2Cl_2 as solvent, we used an average of 1.17; Table 1).[22] A value of 450 cm^{-1} was obtained, which is similar to those observed for binuclear transition metal derivatives.[1]

Since the magnitude of V (3.4 kcal mol^{-1}) is comparable to that of $\lambda/4$ we used Sutin's[21] ΔG^* [= 2.8 kcal mol^{-1} for **2**$^+$ in MeCN; see Eq. (5)] for the evaluation.

$$\Delta G^* = (\lambda/4 - V + V^2/\lambda) \qquad (5)$$

This results in a very high rate constant $k_{th} = 1.2 \times 10^{11}$ s^{-1} in MeCN and an even higher value in CH_2Cl_2 compared to transition metal compounds.[1] Although the assumptions and the whole formalism employed are very approximate, our study suggests that the ET rate in **2**$^+$ is extremely high. This is due to the fact that electronic coupling V is high compared to than the reorganization energy λ. This strong coupling results in a high molar absorptivity of the IV-CT band [Eq. (2)] which is much larger than in other inorganic and organic compounds ($\varepsilon \approx 10^2$–10^3 M^{-1} cm^{-1}).[1] As there are neither spin nor symmetry constraints on the excitation, the reason for the high ε value must be a strong overlap of the ground and excited state wavefunction. This is reasonable, as **2**$^+$ has a rather low internal reorganization energy. For instance, in the case of diferrocenylethyne [Fc-CC-Fc]$^+$ $\tilde{\nu}_{max}$ in MeCN is similar (21.4 kcal mol^{-1}), but ε is very small (ca. 500 M^{-1} cm^{-1}) because of a relatively small V (ca. 1 kcal mol^{-1}).[23]

Since V is in a first-order approximation independent of the solvent polarity,[24] Equation (5) suggests that there is a limit ratio of λ/V at which ΔG^* becomes zero and the system transforms to a class III compound with delocalized centers. This is the case for $\lambda = 2\,V$ (= 6.8 kcal mol^{-1} in MeCN).[25] Because the internal reorganization energy λ_v (ca. 4–5 kcal mol^{-1}) is even lower than 2 V, **2**$^+$ should be more similar to a class III derivative in the gas phase or in nonpolar solvents when the total reorganization energy λ approaches λ_v. The fact that $\tilde{\nu}_{1/2}$ is smaller than $\tilde{\nu}_{1/2}$(HTL) in CH_2Cl_2 as well as the significantly higher ε values and electronic mixing coefficients α in CH_2Cl_2 ($\varepsilon = 22300$ M^{-1} cm^{-1}, $\alpha = 0.19$) than in MeCN ($\varepsilon = 14100$ M^{-1} cm^{-1}, $\alpha = 0.15$) support this assumption and places **2**$^+$ in CH_2Cl_2 at the borderline between class II and class III.[1, 26]

In conclusion, the symmetrically substituted aminotolane derivative **2**$^+$ is characterized by a very intense, solvent dependent IV-CT band in the NIR spectrum. Whereas in most binuclear transition metal class II systems the charge is mainly localized on one metal atom,[1] the charge in **2**$^+$ is partially delocalized in one triphenylamine moiety. Since the reorganization terms will increase in value with increased localization of the charge perturbation upon excitation, the partial delocalization leads to both a small λ_v and a small λ_s relative to V. This makes the ET extremely fast. A trimeric system **3**$^{3+}$ akin to **2**$^+$ has been investigated which shows a degenerate two-dimensional IV-CT.

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[9] Cyclic voltammetry has been performed with a conventional three-electrode set-up with a Pt-disk electrode and a Ag/AgCl pseudo-reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate/CH_2Cl_2. Internal standard: ferrocene (Fc/Fc$^+$); scan rate: 250 mV s^{-1}.

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Hexahelicenophanes and Their Racemization[**]

Herbert Meier,[*] Manfred Schwertel, and
Dieter Schollmeyer

*Dedicated to Professor Alan R. Katritzky
on the occasion of his 70th birthday*

Helicenes represent a fascinating class of compounds that exhibit exceptional properties.[1–4] Since the first synthesis of [6]helicene by Newman and Lednicer,[5] this area has developed rapidly, with the parent systems at the center of interest. The number of substituted [6]helicenes described in the literature remains relatively small, and bridged [6]helicenes are almost unknown.[3, 6–8] We have now synthesized [6]helicenes whose terminal benzene rings are linked by polymethylenedioxy chains so that the influence of the cyclophane structure on the racemization can be studied.

We first prepared the dialdehydes **3a–c** from salicylaldehyde (**1**) and α,ω-dibromoalkanes (**2a–c**) and then reduced them to the diols **4a–c** (Scheme 1). The transformation to the bisphosphonium salts **5a–c** and the subsequent twofold Wittig olefination, carried out in highly diluted solution with 2,7-naphthalenedicarbaldehyde (**6**), generated the macrocycles **7a–c**.[9] The compounds **7a–c** were obtained as mixtures of *E,E* and *E,Z* isomers; however, the configuration does not play a role in the subsequent oxidative photocyclization. (The *E,Z* ratio from the cyclization process **5** + **6** → **7** decreases with decreasing chain length from 33 % for **7a**, to 20 % for **7b**, and almost 0 % for **7c**). The twofold photocyclization in the presence of methyloxirane with iodine as an oxidating agent[10] yielded the bridged [6]helicenes **8a** and **8b**.[11] In **7c** the short polymethylenedioxy chain did not permit the formation of the corresponding helicene.

Even in high dilution photodimerization of **7c** dominated completely and a totally different type of cyclophane **9c** was formed (Scheme 2). To enable a better investigation of the latter reaction, we improved the solubility of the cyclophane by the introduction of two dodecyloxy groups and optimized the reaction conditions for the photodimerization. Cyclophane **9d**[12] was then obtained from **7d** in high yields. The dimerization reaction was also observed in competition to the photocyclization of **7b**, but to a smaller extent, while the dimerization of **7a** did not occur.

It was possible to enrich the enantiomers of **8a** and **8b** by chromatography on silica gel doped with the Newman reagent (*R*)-(−)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminoxy)propionic acid ((*R*)-(−)-TAPA).[13] The (*M*)-(−)-configuration forms weaker complexes with (*R*)-(−)-TAPA and was eluted first. The first-order kinetics for the racemization were determined by the measurement of the optical rotation $[\alpha]_D$ in 1,2,4-trichlorobenzene. Linear regression led to determination of the rate constant k_{rac} and the half-life $t_{1/2} = k_{rac}^{-1} \times$

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