# Cyclotetraazocarbazole – A Multichromic Molecule

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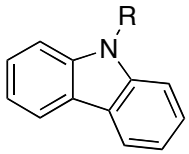
# Supporting Information

## Experimental

Synthesis 9-dodecyl-9*H*-carbazole:

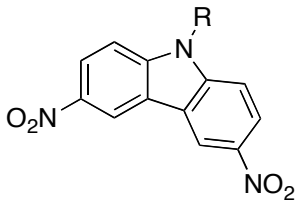



$R = C_{12}H_{25}$

In an oven dried flask, sodium hydride (0.468 g, 60% in mineral oil, 10.8 mmol, 1.80 eq.) was added carefully to a solution of carbazole (1.00 g, 5.98 mmol, 1.00 eq.) in 10 ml anhydrous DMF under nitrogen. The solution was stirred for 20 min after the addition. Then, 1-bromododecane (1.51 g, 6.04 mmol, 1.01 eq.) was added and the reaction mixture was stirred over night. Adding 20 ml water dropwise quenched the reaction mixture. Then, the mixture was extracted two times with 100 ml diethyl ether. The organic layers were combined and washed four times with 50 ml water, dried over $MgSO_4$ and concentrated under reduced pressure. The remaining bromide was removed by distillation (up to 135°C, 0.2 mbar) to obtain the product as brown oil (1.93 g, 5.75 mmol, 96%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.11 (d, $J$ = 7.7 Hz, 2H), 7.47 (ddd $J$ = 8.2, 6.9, 1.2 Hz, 2H), 7.41 (d, $J$ = 8.1 Hz, 2H), 7.23 (td, $J$ = 7.9, 7.0, 1.1 Hz, 2H), 4.30 (t, $J$ = 7.3 Hz, 2H), 1.87 (quin, $J$ = 7.3 Hz, 2H), 1.39 - 1.19 (m, 18H), 0.88 (t, $J$ = 6.9 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 140.8, 126.0, 123.2, 120.8, 119.1, 109.1, 43.5, 32.4, 30.04, 30.03, 30.01, 29.9, 29.8, 29.8, 29.40, 27.8, 23.1, 14.6; MS (EI, 70eV) *m/z* (%) = 335 (59) $[M]^+$, 180 (100); EA calc. for $C_{24}H_{33}N$: C 85.91%, H 9.91%, N 4.17%; found C 86.03, H 10.02, N 4.16. FT-IR ($\nu$ / $cm^{-1}$) 2919 (s), 1484 (w), 1462 (w), 1451 (w), 1346 (w), 1324 (w), 1151 (w), 746 (m), 719 (m).

Analytical data corresponds to literature. [1,2]

Synthesis of 3,6-dinitro-9-dodecyl-9*H*-carbazole (**2**)

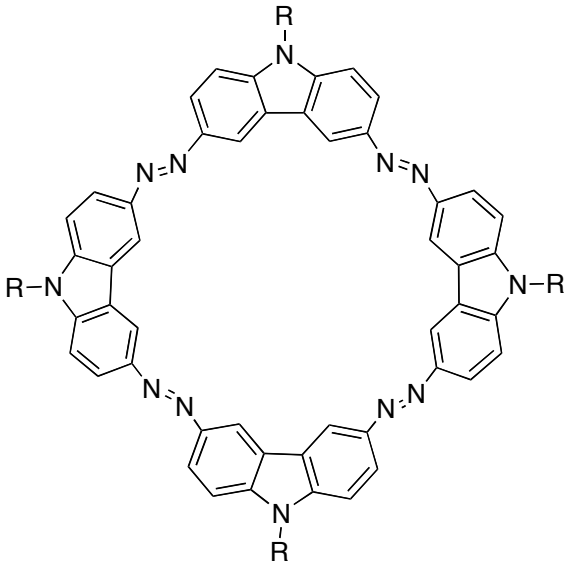



R = $C_{12}H_{25}$

Fuming nitric acid (21.4 g, 340 mmol, 3.00 eq.) was slowly added to acetic anhydride (81.0 g, 792 mmol, 7.00 eq.) at 0°C. This mixture was then added dropwise to a solution of 9-dodecyl-9*H*-carbazole (38.0 g, 113 mmol, 1.00 eq.) in 150 ml DCM. The reaction mixture was stirred at rt for 3 h (after 1 h light green crystals precipitated). The precipitate was filtrated, washed with water and dried under reduced pressure (0.1 mbar, 40°C) to obtain the product as yellow crystals (31.4 g, 73.9 mmol, 65%). $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.05 (d, $^{4}J$ = 2.2 Hz, 2H), 8.47 (dd, $J$ = 9.1 Hz, $^{4}J$ = 2.2 Hz, 2H), 7.53 (d, $J$ = 9.1 Hz, 2H), 4.41 (t, $J$ = 7.3 Hz, 2H), 1.93 (quin, $J$ = 7.3 Hz, 2H), 1.45 - 1.13 (m, 18H), 0.86 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 144.8, 142.0, 123.2, 122.7, 117.9, 109.7, 44.4, 32.0, 29.69 (2C), 29.62, 29.5, 29.44, 29.39, 29.0, 27.3, 22.8, 14.2; MS (EI, 70eV) m/z (%) = 425 (79) $[M]^+$, 270 (100); EA calc. for $C_{24}H_{31}N_3O_4$: C 67.74%, H 7.34%, N 9.88%; found C 67.57, H 7.22, N 9.82; FT-IR ($\nu$ / $cm^{-1}$) 2914 (w), 2849 (w), 1581 (w), 1513 (w), 1455 (w), 1331 (m), 1314 (m), 1312 (m), 1288 (m), 1269 (w), 1100 (w), 914 (w), 754 (w), 721 (w); m.p. 192°C.

Analytical data corresponds to literature. [1,2]

Synthesis of cyclic tetramer **3**:

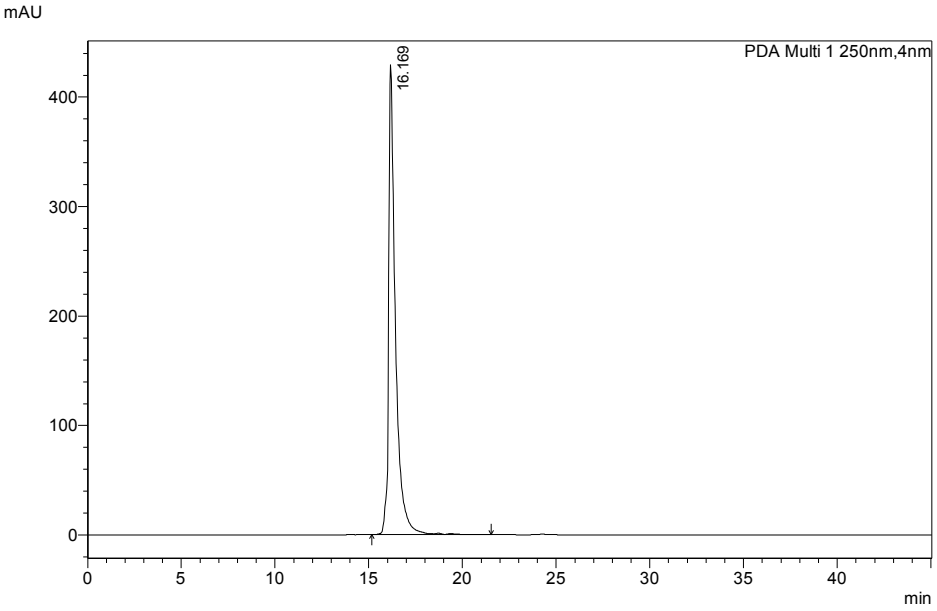


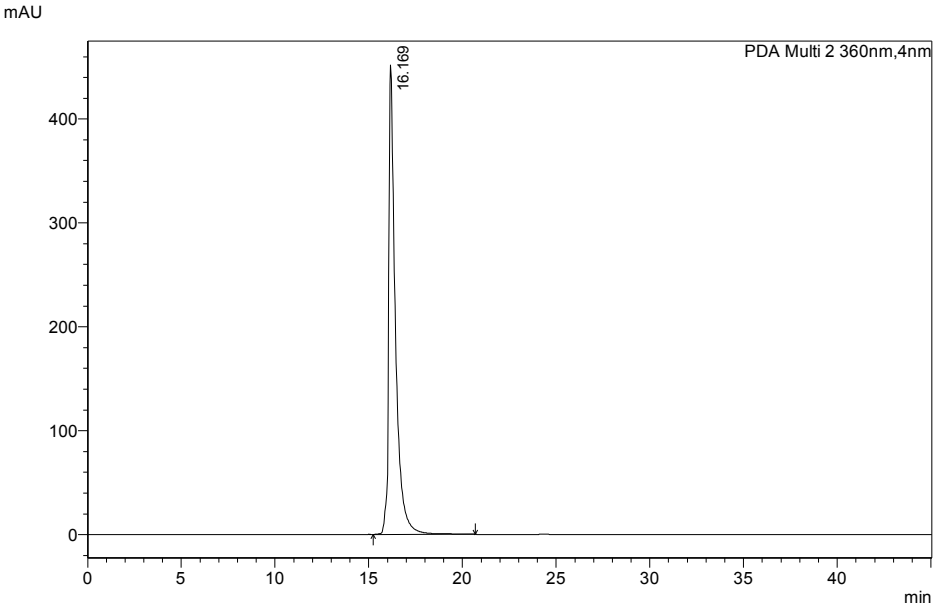
R = $C_{12}H_{25}$

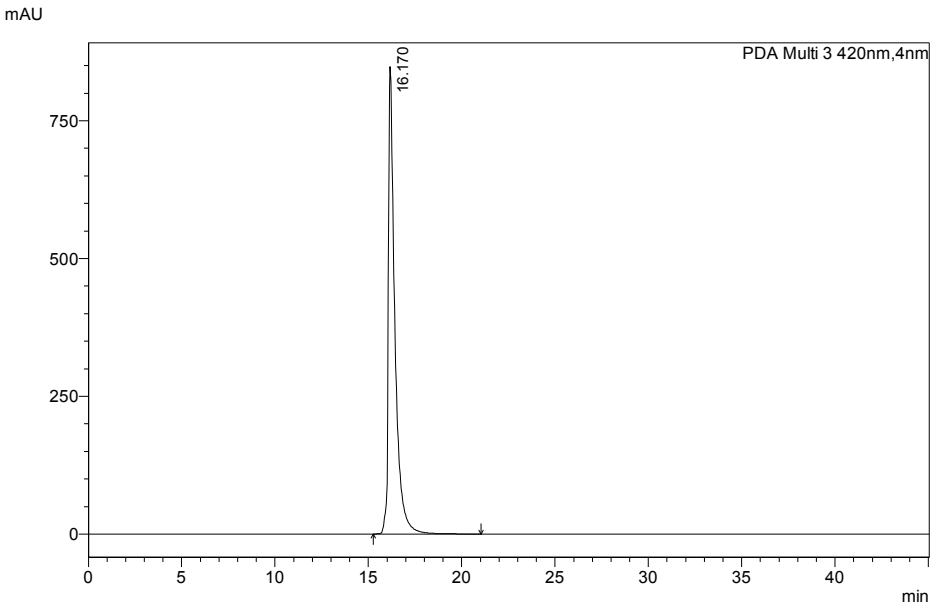
An oven dried flask was charged with a suspension of $LiAlH_4$ (2.68 g, 70.5 mmol, 6.00 eq.) in 250 ml anhydrous THF under nitrogen. Then, 3,6-dinitro-9-dodecylcarbazole (5.00 g, 11.8 mmol, 1.00 eq.) dissolved in 250 ml anhydrous THF was added slowly over a period of 1 h. The reaction mixture was stirred for 4 h at room temperature. Then, the mixture was cooled to 0°C. Afterwards, 3.0 ml water, 3.0 ml aq. KOH-solution (15%) and 9.0 ml water were added dropwise. The mixture was diluted with THF, filtrated and concentrated under reduced pressure (4.18 g). Then, the residue was purified by column chromatography ($SiO_2$, DCM / cyclo-hex 1:1) and GPC to obtain the product as an orange solid (9.10 mg, 6.29 µmol, 0.21%). $^1$H NMR (400 MHz, $CDCl_3$, ~14 mg/ml) $\delta$ 8.71 (d, $^4J$ = 1.8 Hz, 8H), 8.02 (dd, $J$ = 8.6 Hz, $^4J$ = 1.8 Hz, 8H), 7.27 (d, $J$ = 8.6 Hz, 8H), 4.16 (t, $J$ = 7.1 Hz, 8H), 1.91 (quin, $J$ = 7.3 Hz, 8H), 1.49 - 1.34 (m, 16H), 1.31-1.23 (m, 56H), 0.87 (t, $J$ = 6.8 Hz, 12H); $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 146.6, 142.5, 124.2, 121.8, 116.1, 108.8, 43.7, 32.1, 29.80, 29.78, 29.77, 29.73, 29.6, 29.5, 29.3, 27.5, 22.9, 14.3; FT-IR ($\nu$ / $cm^{-1}$) 2918 (s), 2849 (m), 1591 (m), 1479 (m), 1311 (m), 1261 (w), 1217 (w), 1193 (w), 1143 (w), 1118 (m), 1013 (w), 893 (m), 806 (m), 794 (w), 723 (w); m.p. 178°C; MS (MALDI): $m/z$ (%) = 1446 (100) $[M-H]^+$; HRMS-ESI: $m/z$ $[M + H]^+$ calc. for $C_{96}H_{124}N_{12}$: 1445.0072; found: 1445.0066; EA: (%) calc. for $C_{96}H_{124}N_{12}$•HCl: C, 77.77; H, 8.50; N, 11.34; found: C, 77.62; H, 8.18; N, 11.18.

**Analytical GPC of macrocycle 3:**

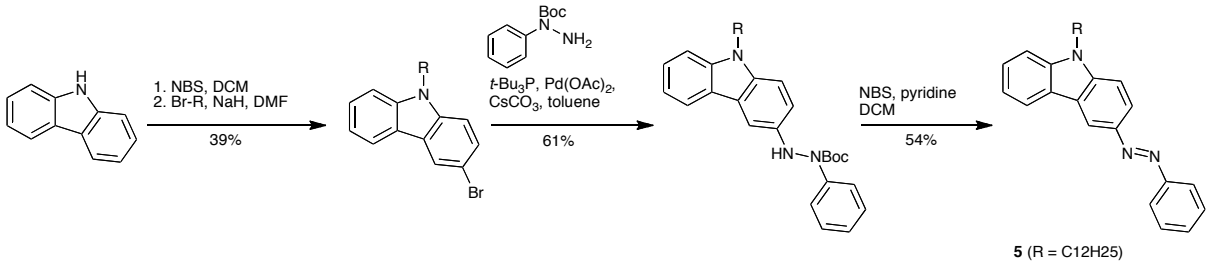
Column: Varian MesoPore, 300 x 7.5 mm (nominal particle size: 3 µm)
Detector: Shimadzu SPD-M20A
Pump: Shimadzu LC-20AD
Mobile Phase: chloroform
Injection volume: 20 µl
Flow rate: 0.5 ml/min



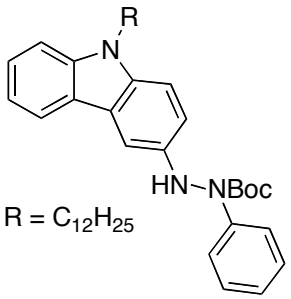





**Synthesis of azocarbazole 5 via a Pd catalyzed cross-coupling reaction.**

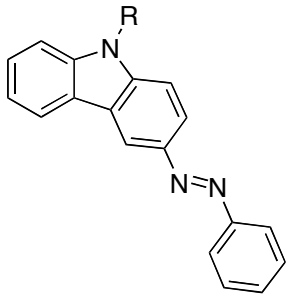



Synthesis of *N*-boc-phenylcarbazolehydrazine:




Under nitrogen an oven dried flask was charged with 3-bromo-9-dodecyl-9*H*-carbazole[3] (100 mg, 0.242 mmol, 1.00 eq.), *N*-boc benzohydrazine (60.5 mg, 0.290 mmol, 1.20 eq.), tri-*tert*-butylphosphine (2.5 mg, in toluene, 0.0121 mmol, 5.00 mol%), palladium(II) acetate (2.7 mg, 0.0121 mmol, 5.00 mol%), cesium carbonate (118 mg, 0.363 mmol, 1.50 eq.) and 2 ml anhydrous toluene. The solution was stirred for 30 min at room temperature before being heated to 110°C. After 1 h the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The dark brown residue was purified by column chromatography ($SiO_2$, cyclo-hex / DCM 1:3) to isolate the product as brown oil (79.3 mg, 0.146 mmol, 61%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.00 (d, $J$ = 7.7 Hz, 1H), 7.72 (d, $J$ = 7.8 Hz, 2H), 7.53 (d, $J$ = 2.2 Hz, 1H), 7.46 - 7.41 (m, 1H), 7.39 - 7.34 (m, 3H), 7.29 (d, $J$ = 8.7 Hz, 1H), 7.16 (m, 2H), 7.02 (dd, $J$ = 8.7, $^4J$ = 2.3 Hz, 1H), 6.51 (s, 1H), 4.25 (t, $J$ = 7.2 Hz, 2H), 1.85 (quin, $J$ = 7.3 Hz, 2H), 1.37 (s, 9H), 1.33 - 1.23 (m, 18H), 0.89 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 154.4, 143.3, 141.4, 141.0, 136.6, 129.1, 128.6, 125.7, 124.5, 123.3, 123.1, 122.6, 121.9, 120.6, 118.3, 113.5, 109.3, 108.8, 104.6, 43.3, 32.0, 29.74, 29.72, 29.71, 29.65, 29.56, 29.46, 29.2, 28.5, 28.3, 27.5, 22.8, 14.3; MS (EI, 70eV): $m/z$ (%) = 541 (100) $[M]^+$; HRMS (ESI) $m/z$ = 564.3560 ($[M+Na]^+$, $C_{35}H_{47}N_3O_2$ + $Na^+$ requires 564.3566); FT-IR ($\nu$ / $cm^{-1}$) 3335 (w), 2918 (m), 2852 (m), 1694 (m), 1467 (w), 1464 (w), 1453 (w), 1447 (w), 1367 (w), 1331 (m), 1315 (m), 1301 (m), 1285 (m), 1247 (w), 1230 (w), 1151 (s), 1123 (w), 1013 (m), 742 (m), 689 (w).

Synthesis of azocarbazole **5**

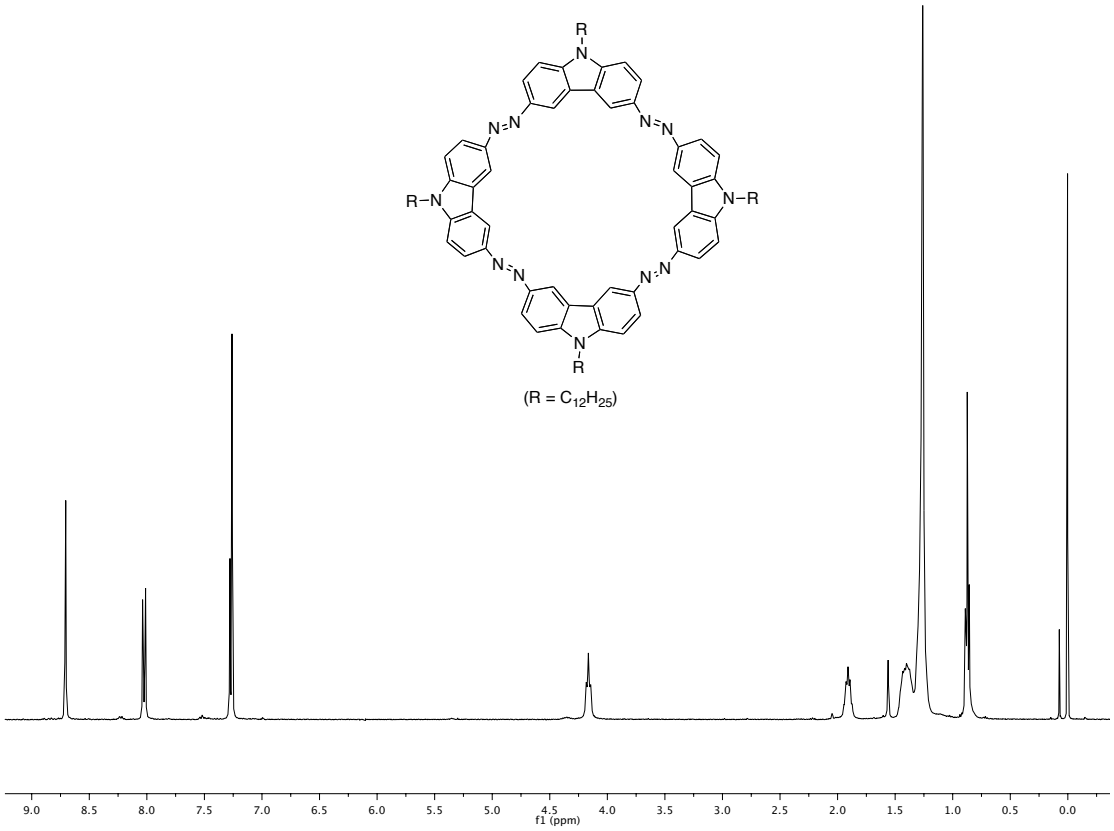



The *N*-boc-phenylcarbazolehydrazine (43.0 mg, 0.079 mmol, 1.00 eq.) was dissolved in 3 ml anhydrous DCM under nitrogen. Then, pyridine (7.54 mg, 0.095 mmol, 1.20 eq.) and *N*-bromosuccinimide (17.0 mg, 0.095 mmol, 1.20 eq.) were added. The reaction mixture was stirred for 2 h at room temperature and was then concentrated under reduced pressure. Finally, the residue was purified by preparative TLC ($SiO_2$, cyclo-hex / DCM 1:2) to isolate the product as red oil (19.0 mg, 0.0432 mmol, 54%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.73 (d, $J$ = 1.8 Hz, 1H), 8.20 (d, $J$ = 7.7 Hz, 1H), 8.16 (dd, $J$ = 8.8, 1.9 Hz, 1H), 8.00 - 7.95 (m, 2H), 7.57 - 7.51 (m, 3H), 7.50 - 7.43 (m, 3H), 7.34 - 7.28 (m, 1H), 4.33 (t, $J$ = 7.3 Hz, 2H), 1.91 (quin, $J$ = 7.3 Hz, 2H), 1.41 - 1.24 (m, 18H), 0.92 - 0.86 (m, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 153.0, 146.3, 142.5, 141.4, 130.2, 129.2 (2C), 126.4, 123.7, 123.4, 122.6 (2C), 121.2, 121.0, 119.8, 117.1, 109.4, 109.0, 43.6, 32.1, 29.742, 29.735, 29.70, 29.6, 29.53, 29.47, 29.2, 27.4, 22.8, 14.3; MS (EI, 70eV): $m/z$ (%) = 439 (100) $[M]^+$; HRMS (ESI) $m/z$ = 440.3060 ($[M+H]^+$, $C_{30}H_{37}N_3 + H^+$ requires 440.3060); FT-IR ($\nu$ / $cm^{-1}$) 2921 (m), 2850 (m), 1594 (m), 1468 (w), 1349 (m), 1325 (m)1233 (w), 1225 (w), 1118 (s), 1019 (w), 807 (m), 764 (m), 744 (s), 687 (m).

## NMR-spectra

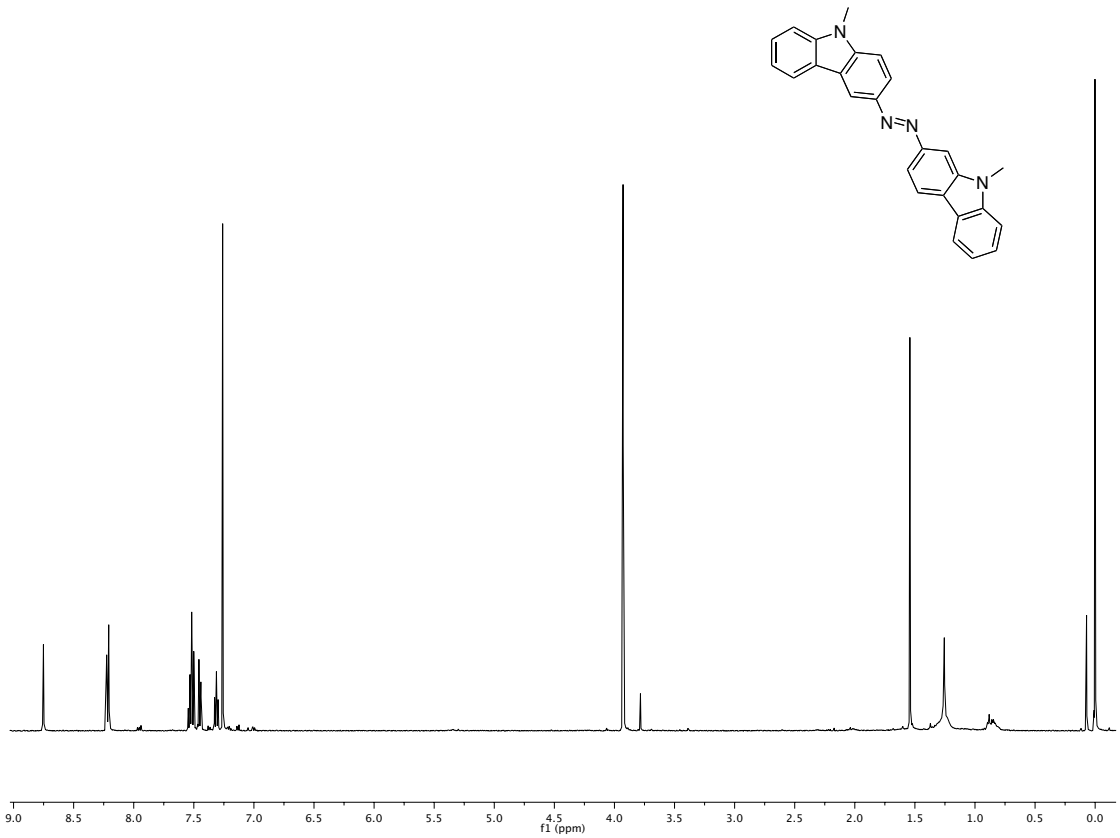
Macrocycle **3**

$^1$H-NMR spectrum in $CDCl_3$ (400MHz)



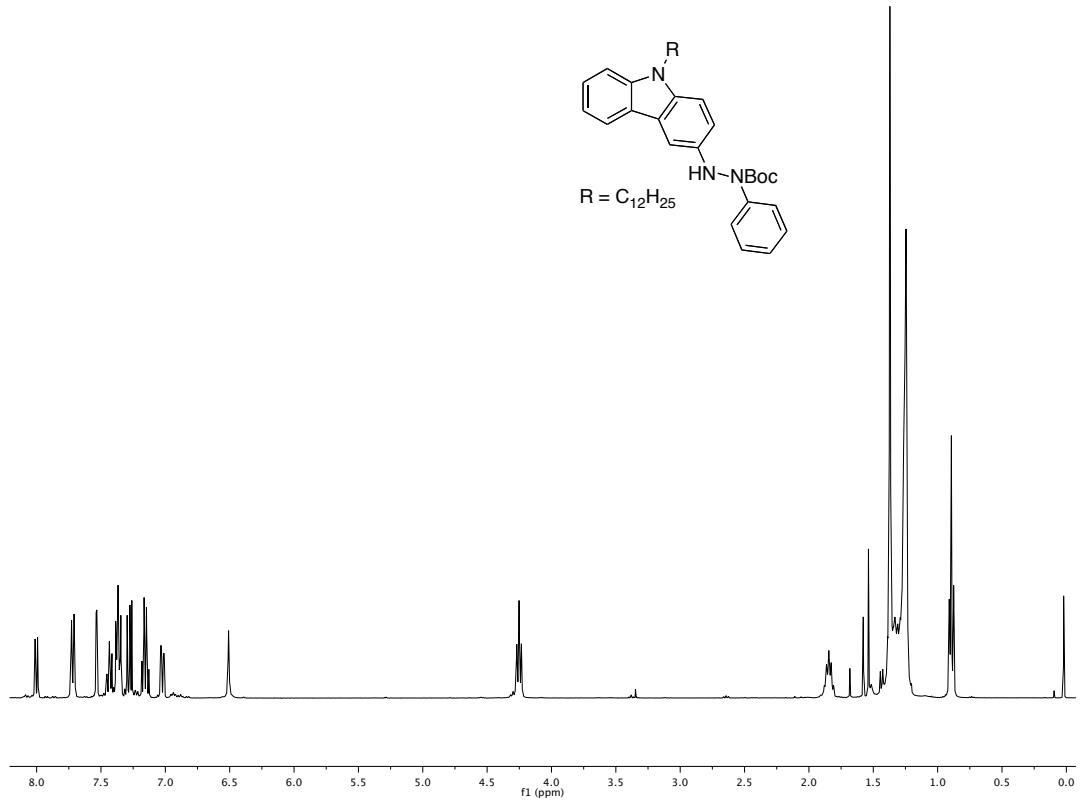
Dimer **4**

$^1$H-NMR spectrum in $CDCl_3$ (500 MHz)



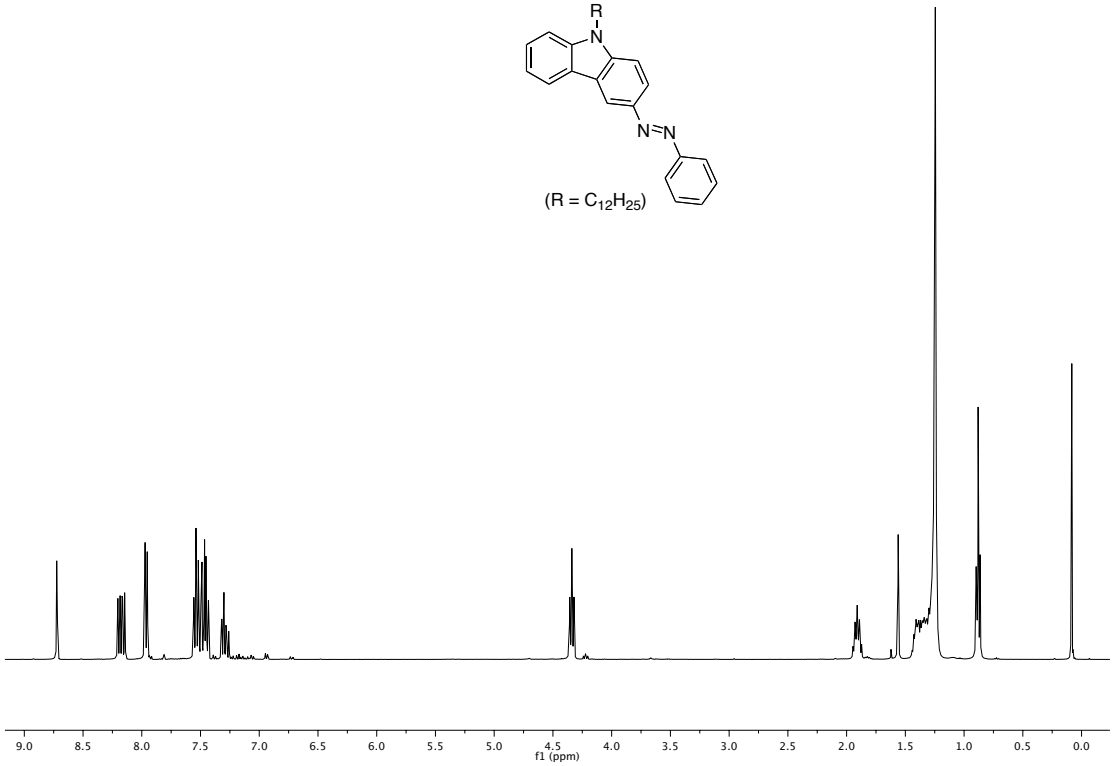

*N*-boc diaryl hydrazine:

$^1$H-NMR spectrum in $CDCl_3$ (400 MHz)

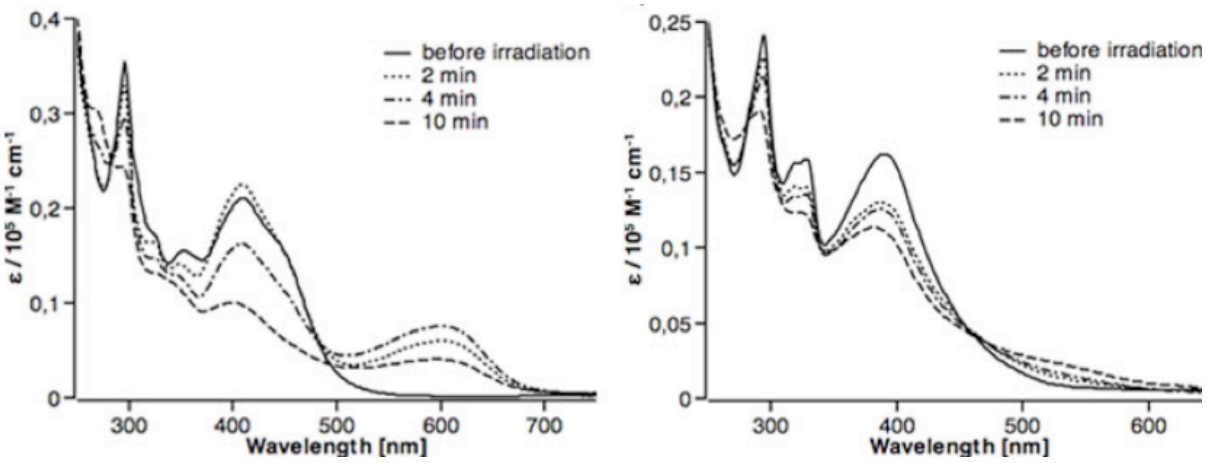


Azocarbazole **5**

$^1$H-NMR spectrum in $CDCl_3$ (400 MHz)



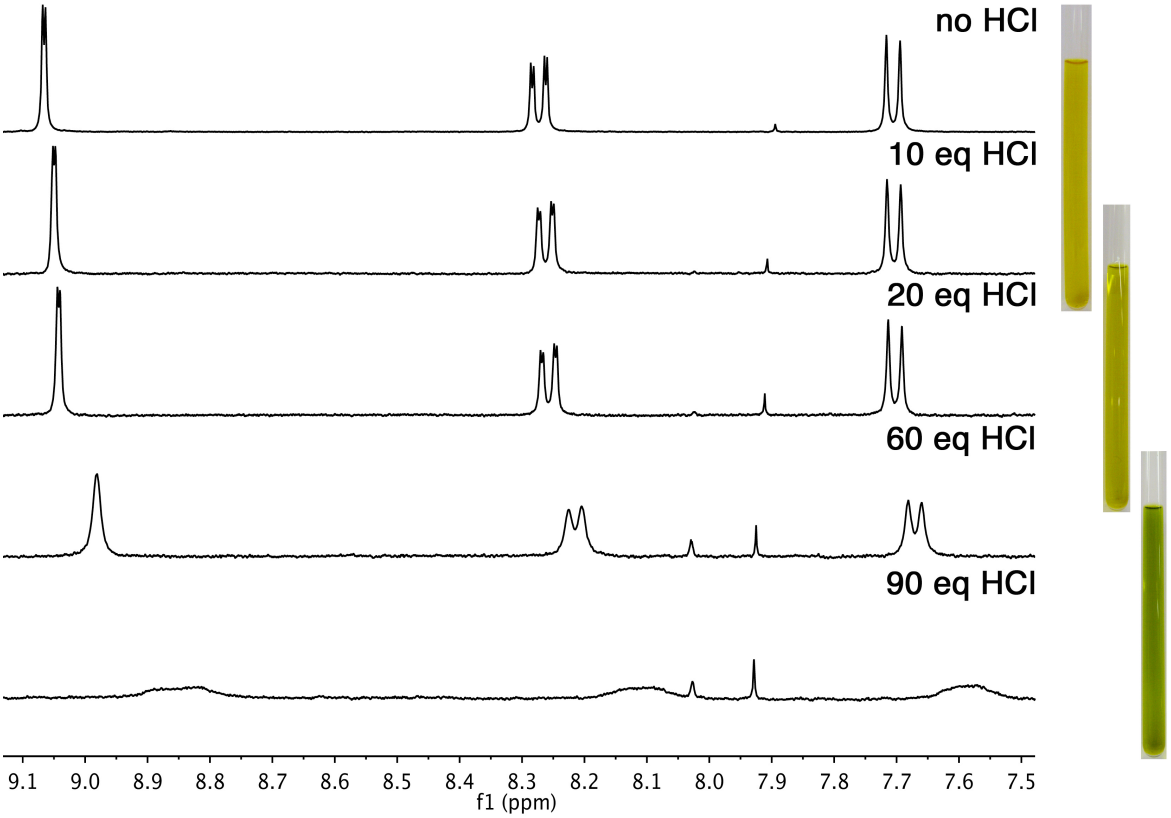
**Additional UV/VIS-spectra**



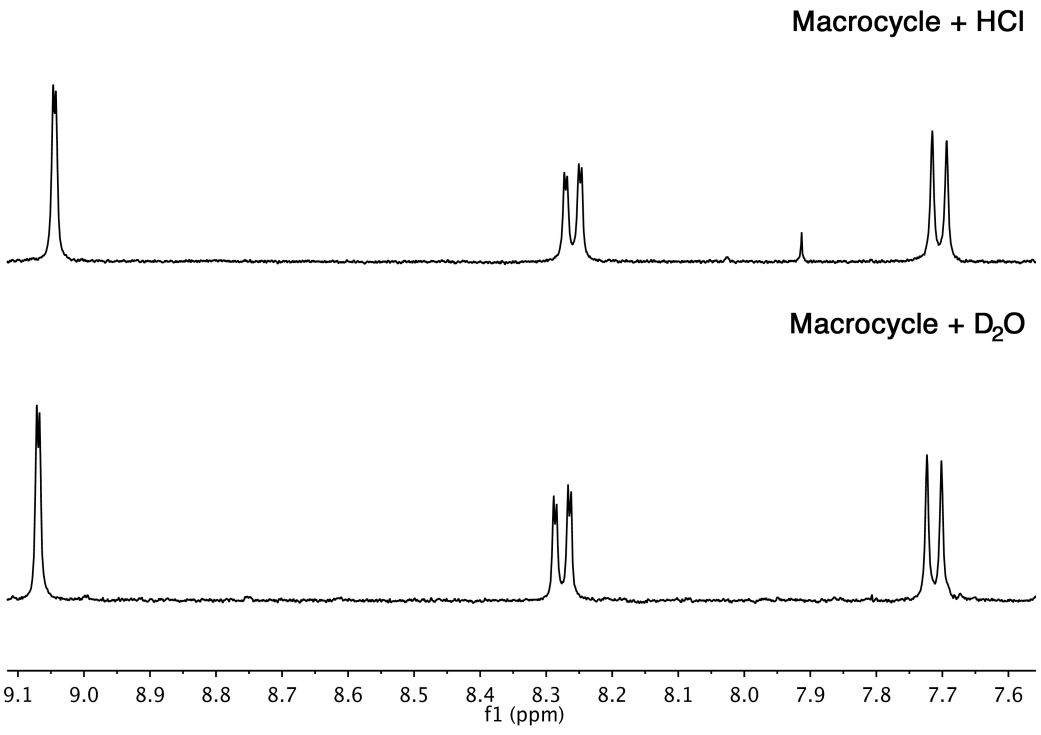

UV/VIS-spectra of dimer **4** (left) UV/VIS-spectra of azocarbazole **5** (right) (all in $CHCl_3$ after irradiation with 302 nm UV-light over different time periods).

**$^1$H NMR Titration experiments:**

Addition of HCl to Macrocycle **3** (in THF-d8).




$D_2O$ Exchange experiment (in THF-d8).



## References

1. İ. Kaya and S. Koyuncu, *J. Appl. Polym. Sci.*, 2009, **113**, 1975–1985.
2. S. Koyuncu, İ. Kaya, F. B. Koyuncu, and E. Ozdemir, *Synth Met*, 2009, **159**, 1034–1042.
3. H. Chen, X. R. Cai, Z. G. Xu, T. Zhang, B. Song, Y. Li, Q. Jiang, and M. G. Xie, *Polym. Bull.*, 2008, **60**, 581–590.