Supporting information for

Methano[10]annulene revisited: extended delocalization through conjugated polymers bearing larger Hückel aromatics

Patricia A. Peart and John D. Tovar*

Department of Chemistry
Johns Hopkins University
Baltimore, MD 21218 (USA)
Fax: (410) 516-7044
Email: tovar@jhu.edu

CONTENTS

Experimental details

Figure S1: UV-vis and fluorescence of ethynyl models: naphthalene **8** (top) and annulene **7** (bottom) taken at room temperature in $CHCl_3$.

Figure S2: Cyclic voltammetry of **3** (top, 2.5 mM) and **4** (bottom, 2.5 mM) leading to electropolymerization at a 2 mm^2 Pt button electrode in 0.1 M *n*-Bu_4PF_6 (CH_2Cl_2) measured at a scan rate of 100 mV/s.

Figures S3-S5: ^{1}H NMR spectra of **3**, **4** and **5** (400 MHz, $CDCl_3$).

Figure S6-S7: ^{13}C NMR spectra of **3** and **4** (100 MHz, $CDCl_3$).

Figure S8: UV-vis of the parent 1,6-methano[10]annulene and naphthalene hydrocarbons taken at room temperature in $CHCl_3$.

Experimental Section

General Considerations: Reactions were performed in oven and/or flame-dried glassware under an atmosphere of nitrogen. Dimethylformamide (DMF), diisopropylamine (DIPA) and copper iodide (CuI) were obtained from Aldrich, and the solvents were degassed by sparging with nitrogen. Tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$ was obtained from Strem Chemicals. Methanol (MeOH) and toluene were obtained from Fisher. 1,5-diiodonapthalene (**2**) was synthesized from 1,5-diaminonaphthalene (Acros) via the Sandmeyer reaction[1]. 2,7-dibromo-1,6-methano[10]annulene (**1**) was synthesized from 1,6-methano[10]annulene (prepared using the methods of Vogel *et al*[2]) by bromination with *N*-bromosuccinimide (Acros)[3]. 1,5-bis(phenylethynyl)naphthalene was synthesized by a Sonogashira coupling of phenylacetylene (Aldrich) with 1,5-diiodonaphthalene (**2**)[4]. 2,7-bis(phenylethynyl)-1,6-methano[10]annulene was synthesized by a Sonogashira coupling of phenylacetylene with 2,7-dibromo-1,6-methano[10]annulene (**1**)[5]. 5-tributylstannyl-2,2'-bithiophene was synthesized via stannylation of 2,2'-bithiophene (Aldrich)[6]. 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene was synthesized from hydroquinone via Williamson ether synthesis with 2-ethylhexyl bromide (Aldrich)[7] followed by iodination,[8] Sonogashira coupling with TMS-acetylene (GFS) and final deprotection of the silyl protecting groups.

^{1}H-NMR and ^{13}C-NMR were obtained in $CDCl_3$ at 400 MHz and 100 MHz respectively using a Bruker Avance 400 MHz FT-NMR spectrometer. Chemical shifts are reported in parts per million relative to residual protio solvent [$CHCl_3$, 7.24 (^{1}H) and 77.00 ppm (^{13}C)]. UV-vis absorption spectra were recorded using a Varian Cary 50 Bio UV-Visible Spectrophotometer. Fluorescence data was obtained using a Spex spectrometer. Electrochemical data was obtained using a PARSTAT 2273 potentiostat relative to a quasi-internal Ag wire reference electrode submersed in 0.01 M $AgNO_3$/0.1 M n-Bu_4NPF_6 in anhydrous acetonitrile. Cyclic voltammograms were recorded using a 2 mm^2 Pt button electrode as the working electrode and a platinum wire as the counter electrode and was performed in 0.1 M n-Bu_4PF_6 (in CH_2Cl_2) measured at a scan rate of 100 mV/s. Spectroelectrochemistry was performed under ambient laboratory conditions on polymer films electrodeposited onto ITO coated glass electrodes. The films were placed in an electrolyte-filled quartz cuvette in the path of the light source along with counter and reference electrodes as used above. GPC measurements were obtained on a Waters GPC system equipped with a 515 HPLC pump, 717+ AutoSampler, 410 RI detector, and 486 UV detector using three SDV columns (PSS), and reported values are relative to polystyrene standards.

2,7-bis(2',5-bithiophen-2-yl)-1,6-methano[10]annulene (3). A flame-dried 25 mL Schlenk tube was cooled under nitrogen and charged with **1** (101 mg, 0.337 mmol) and $Pd(PPh_3)_4$ (20 mg, 0.02 mmol) and placed under nitrogen, followed by the addition of DMF (5 mL). While stirring, 5-tributylstannyl-2,2'-bithiophene (390 mg, 0.86 mmol) was added dropwise. The reaction was heated to 80°C and left to stir for 12 h during which time an orange precipitate formed. The reaction was allowed to cool to room temperature and methanol (10 mL) was added while stirring vigorously. Vacuum filtration was carried out to obtain 132 mg of crude orange product. This material was dissolved in hot CH_2Cl_2, followed by the addition of hot MeOH. At which point that precipitates formed, hot CH_2Cl_2 was added to dissolve the soluble material, and the remaining insolubles were filtered off. Removal of the filtrate solvent yielded the title product in pure form (95 mg, 0.20 mmol, 61%) as an orange powder. mp 168-170°C (dec). ^{1}H-NMR (400

MHz, $CDCl_3$) δ: 7.91 (d, J = 8.8 Hz, 2H), 7.42 (m, 4H), 7.23 (m, 6H), 7.13 (t, J = 8.8 Hz, 2H), 7.04 (m, 2H), -0.01 (s, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 142.0, 138.5, 137.4, 134.7, 130.2, 128.2 (x2), 128.0, 127.3, 124.5 (x2), 123.7, 118.1, 35.9. HRMS (EI) calcd for $C_{27}H_{18}S_4$ [M^+]: 470.0291. Found: 470.0277.

1,5-bis(2',5-bithiophen-2-yl)naphthalene (4). A 25 mL Schlenk tube was charged with **2** (200 mg, 0.5 mmol) and $Pd(PPh_3)_4$ (30 mg, 0.03 mmol) and placed under nitrogen, followed by the addition DMF (5 mL). While stirring, 5-tributylstannyl-2,2'-bithiophene (508 mg, 1.12 mmol) was added dropwise. The reaction was heated to 80°C and left to stir for 12 h during which time a yellow precipitate formed. The reaction was allowed to cool to room temperature and MeOH (10 mL) was added with vigorous stirring. Vacuum filtration was carried out to obtain 276 mg of crude yellow product. The product was purified by recrystallization from $CHCl_3$ and MeOH to yield the product (160 mg, 0.35 mmol, 67%) as a yellow powder. mp 188-192°C. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 8.33 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 6.8 Hz, 2H), 7.53 (m, 2H), 7.20 (m, 6H), 7.16 (d, J = 3.6 Hz, 2H), 7.05 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 142.0, 138.1, 137.5, 132.64, 132.55, 128.61, 128.58, 128.1, 126.5, 126.0, 124.7, 124.2, 124.0. HRMS (EI) calcd for $C_{26}H_{16}S_4$ [M^+]: 456.0135. Found: 456.0129.

Polymer 5. To a 25 mL Schlenk tube **1** (173 mg, 0.577 mmol) and CuI (5 mg, 0.02 mmol) were added and the tube was placed under nitrogen. $Pd(PPh_3)_4$ (26 mg, 0.022 mmol) was added and the tube was again placed under N_2. Then a solution of 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (220 mg, 0.57 mmol) in toluene (4 mL) and DIPA (1.5 mL) was added. The reaction was heated to 85°C for 3 days. The reaction mixture was precipitated in MeOH (80 mL) while stirring vigorously. The polymer was collected as a yellow-brown solid on a Buchner funnel via vacuum filtration. This was redissolved in DCM and washed with NH_4Cl. The polymer was reprecipitated from MeOH, filtered and dried to collect the product (237 mg) as a yellow-brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.89 (m), 7.42 (m), 7.15 (m), 7.02 (s), 3.93 (bm), 1.84 (bm), 1.52 (bm), 1.23, (bm), 0.97 (bm), 0.85 (bm), -0.02 (s). GPC (THF): M_n 4700, M_w 14,000, PDI 2.97. Polymer repeat unit mass: 520.75.

Polymer 6. To a 25 mL Schlenk tube **2** (218 mg, 0.574 mmol) and CuI (5 mg, 0.02 mmol) were added and the tube placed under nitrogen. $Pd(PPh_3)_4$ (26 mg, 0.022 mmol) was added and the tube was again placed under N_2. Then a solution of 1,4-bis(2-ethylhexyloxy)-2,5-diethynylbenzene (220 mg, 0.57 mmol) in toluene (4 mL) and DIPA (1.5 mL) was added. The reaction was heated to 85°C and was left to stir for 3 days. The reaction mixture was precipitated in MeOH (80 mL) with vigorous stirring. The polymer was collected as an orange solid on a Buchner funnel via vacuum filtration. This was redissolved in DCM (did not fully dissolve) and washed with NH_4Cl. The solvent was dried, filtered and removed in vacuo to provide the product as an orange solid (105 mg). GPC (THF): M_n 4600, M_w 8600, PDI 1.86. Polymer repeat unit mass: 506.73.

References

1. Rodriguez, J. G.; Tejedor, J. L. *J. Org. Chem.* **2002**, *67*, 7631.
2. Vogel, E., Klug, W. and Breuer, A. *Org. Synth.* **1974**, *54*, 11.
3. Vogel, E., Böll, W.A., Biskup, M. *Tetrahedron Lett.* **1966**, 1569.
4. Bossenbroek, B., Shechter, H., *J. Am. Chem. Soc.* **1967**, *89*, 7111.

5. Bryant-Friedrich, A.C.; Neidlein, R. *Helv. Chim. Acta* **1997**, *80*, 1639.
6. Pinault, T., Chérioux, F., Therrien, B. Suss-Fink, G. *Heteroatom Chem.* **2004**, *15*, 121.
7. Kim, M.S., Yang, H.K., Kim R.H., Lee, K. *J. Non-linear Optical Phys. Mater.* **2004**, *13*, 467.
8. Weder, C., Wrighton, M.S., *Macromolecules* **1996**, *29*, 5157.

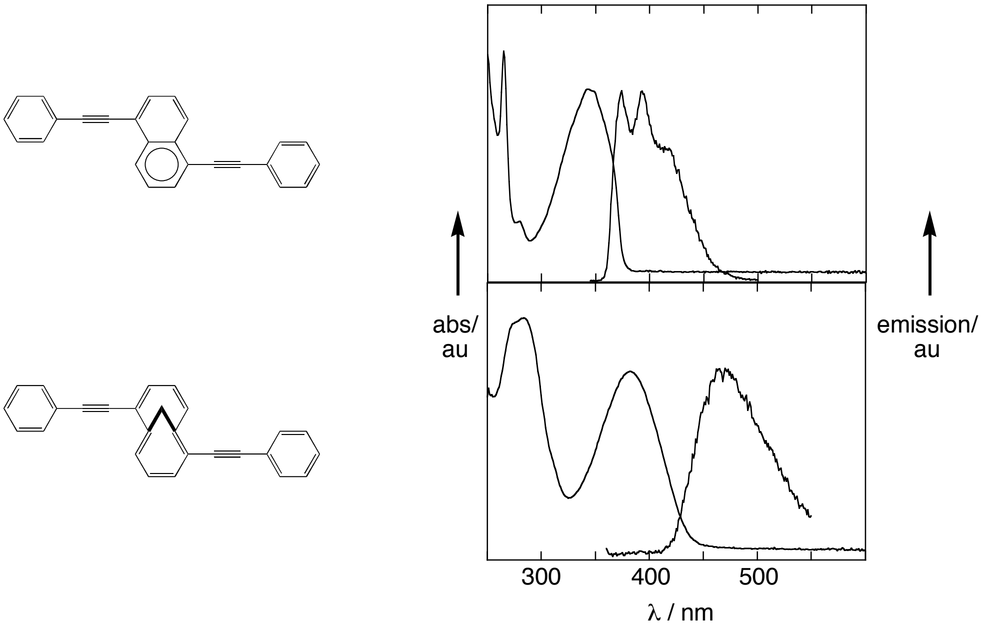


Figure S1: UV-vis and fluorescence of ethynyl models: naphthalene **8** (top) and annulene **7** (bottom) taken at room temperature in $CHCl_3$.

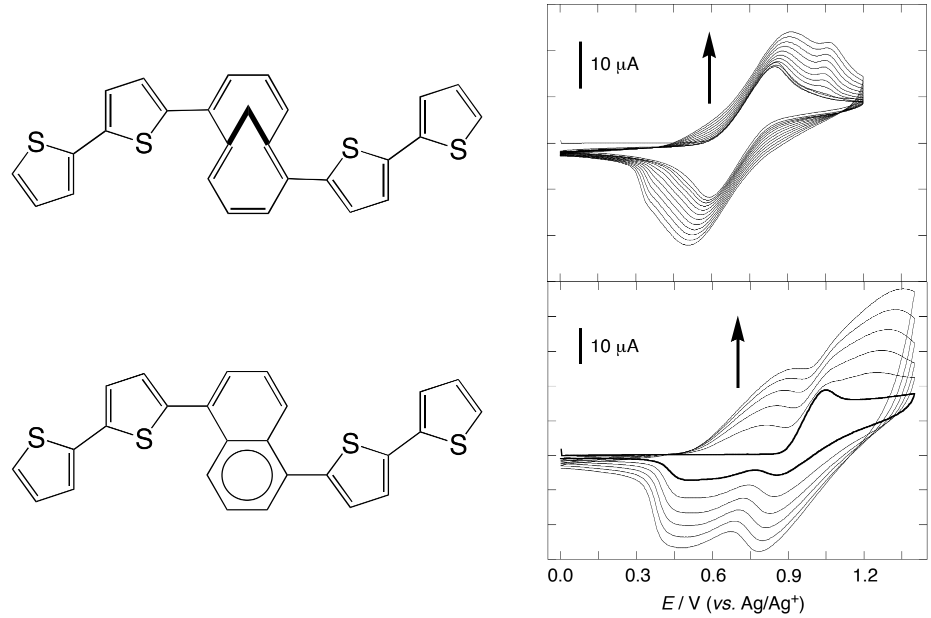
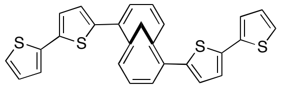


Figure S2: Cyclic voltammetry of **3** (top, 2.5 mM) and **4** (bottom, 2.5 mM) leading to electropolymerization at a 2 mm^2 Pt button electrode in 0.1 M *n*-Bu_4PF_6 (CH_2Cl_2) measured at a scan rate of 100 mV/s.



(Compound **3**)

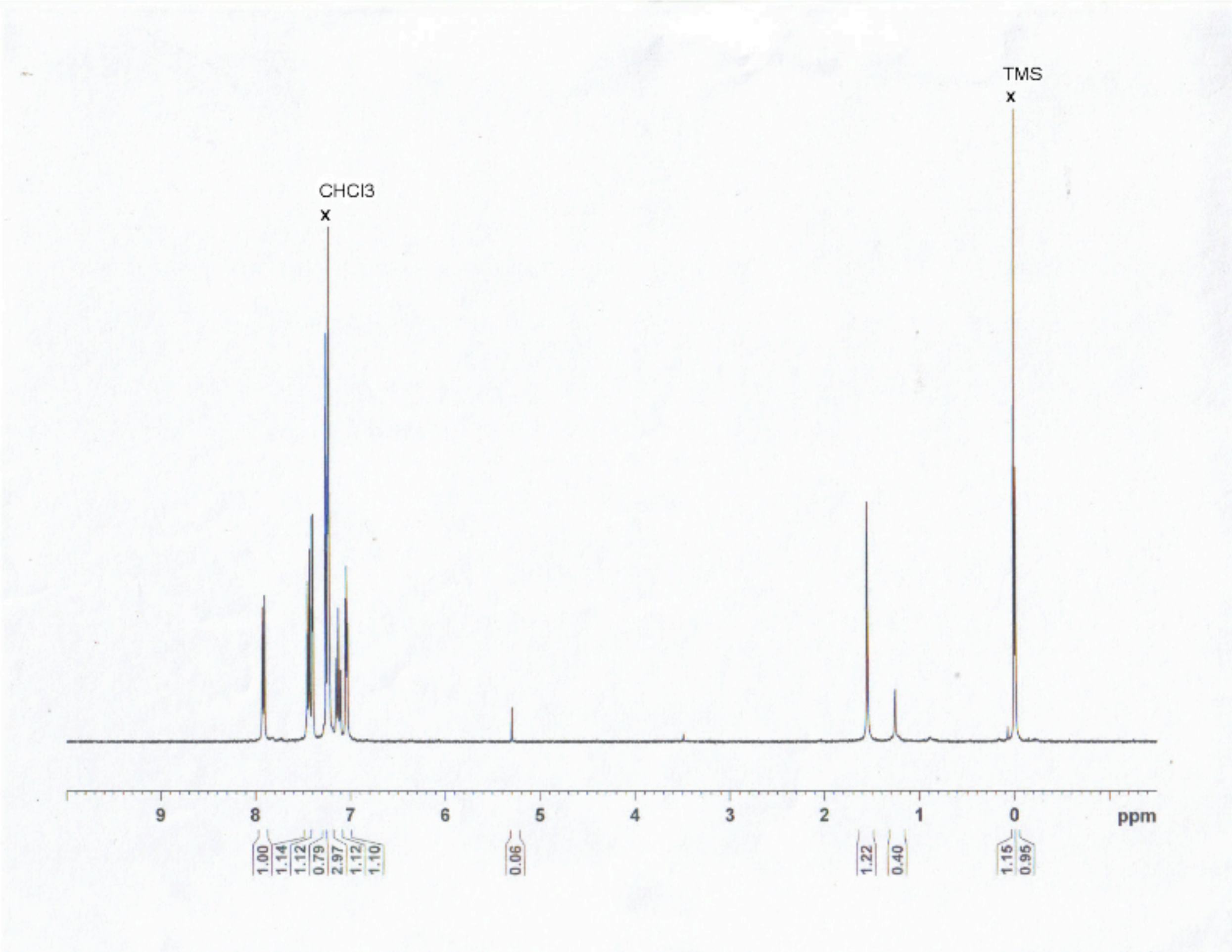
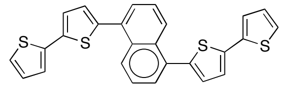


Figure S3: ^{1}H NMR spectra of **3** (400 MHz, CDCl$_3$).



(Compound **4**)

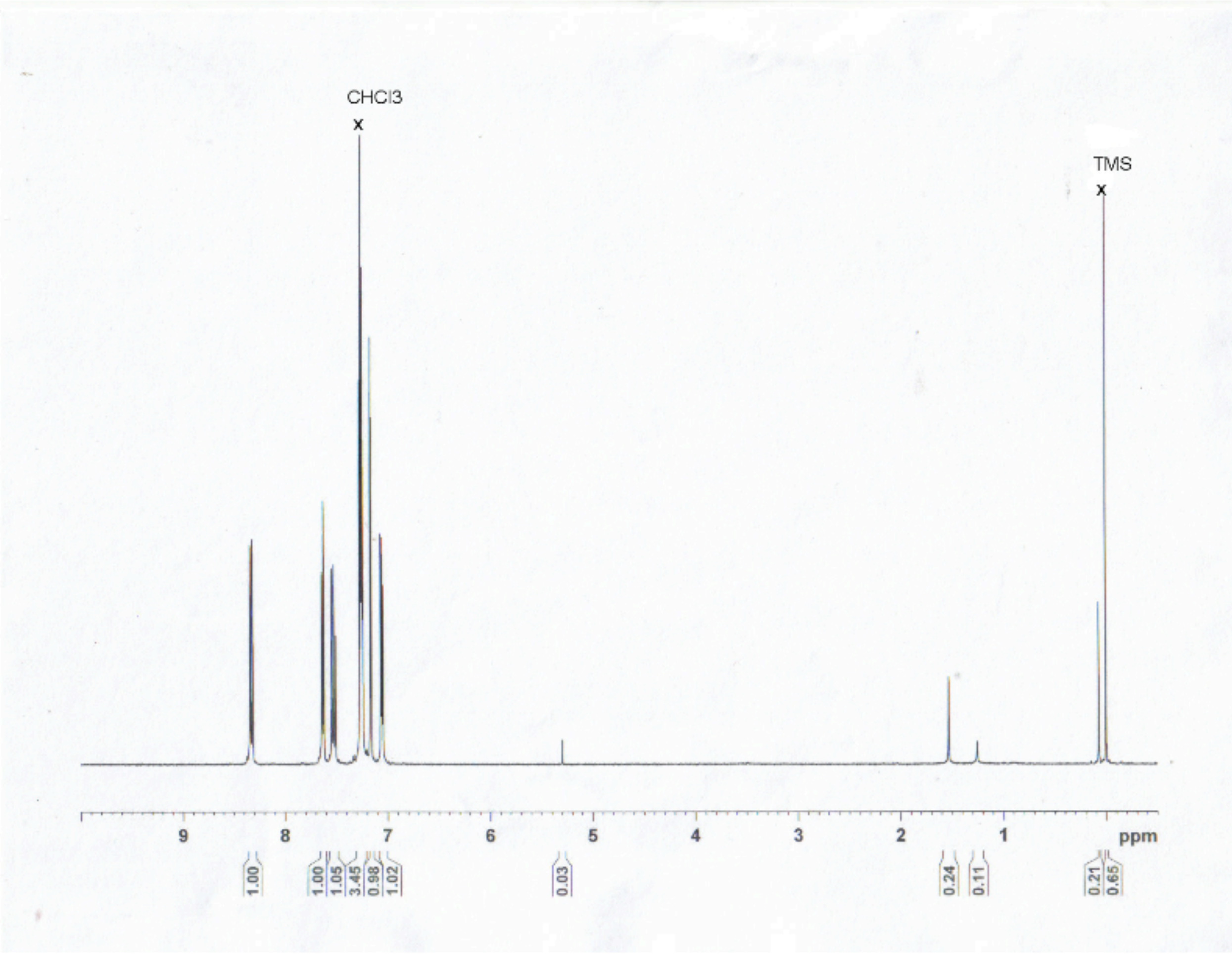
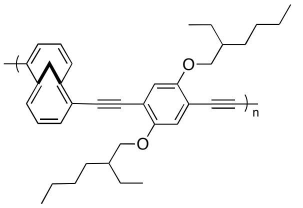


Figure S4: ^{1}H NMR spectra of **4** (400 MHz, $CDCl_3$).



(Compound **5**)

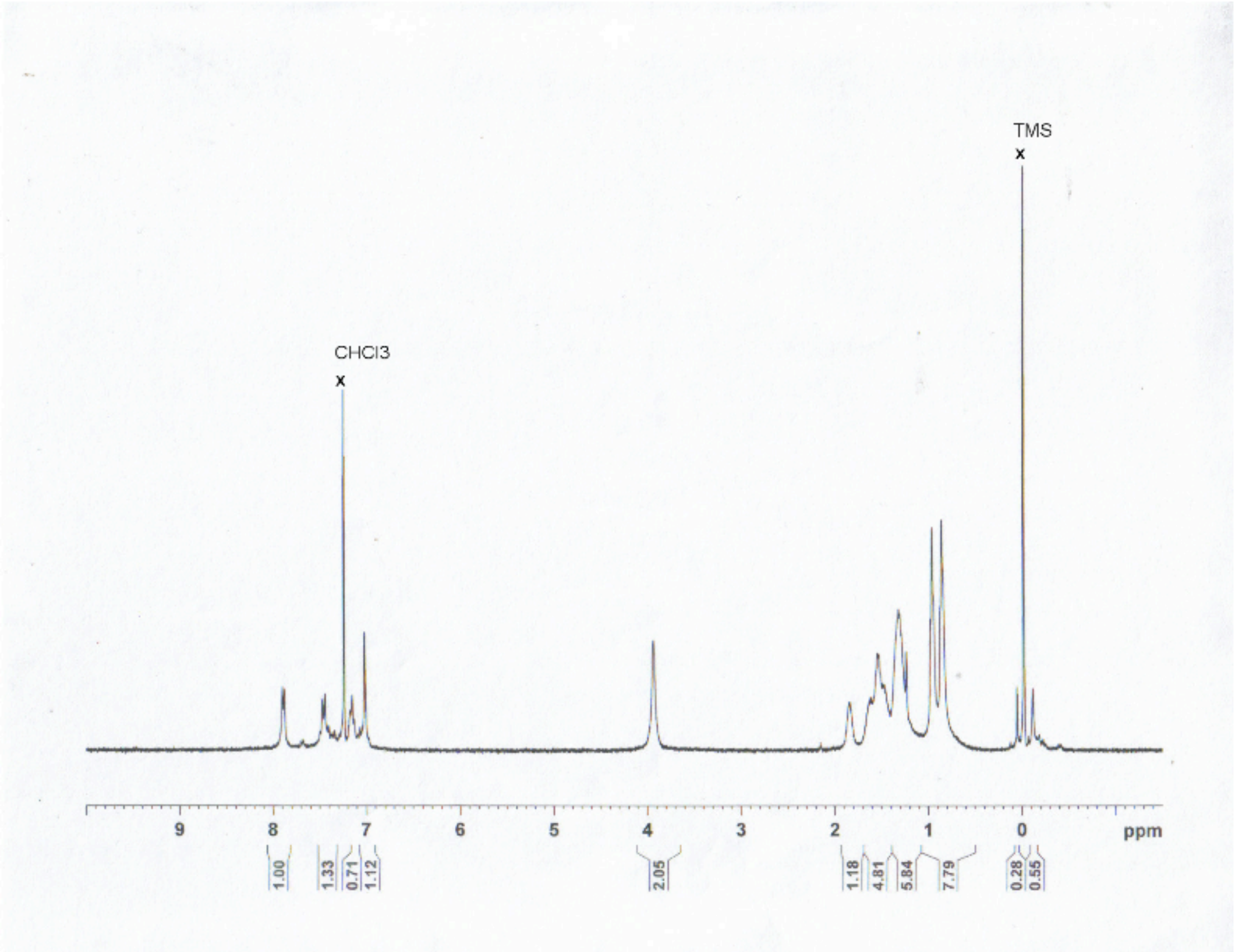
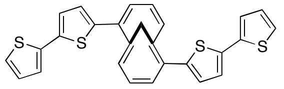


Figure S5: ^{1}H NMR spectra of **5** (400 MHz, $CDCl_3$).



(Compound **3**)

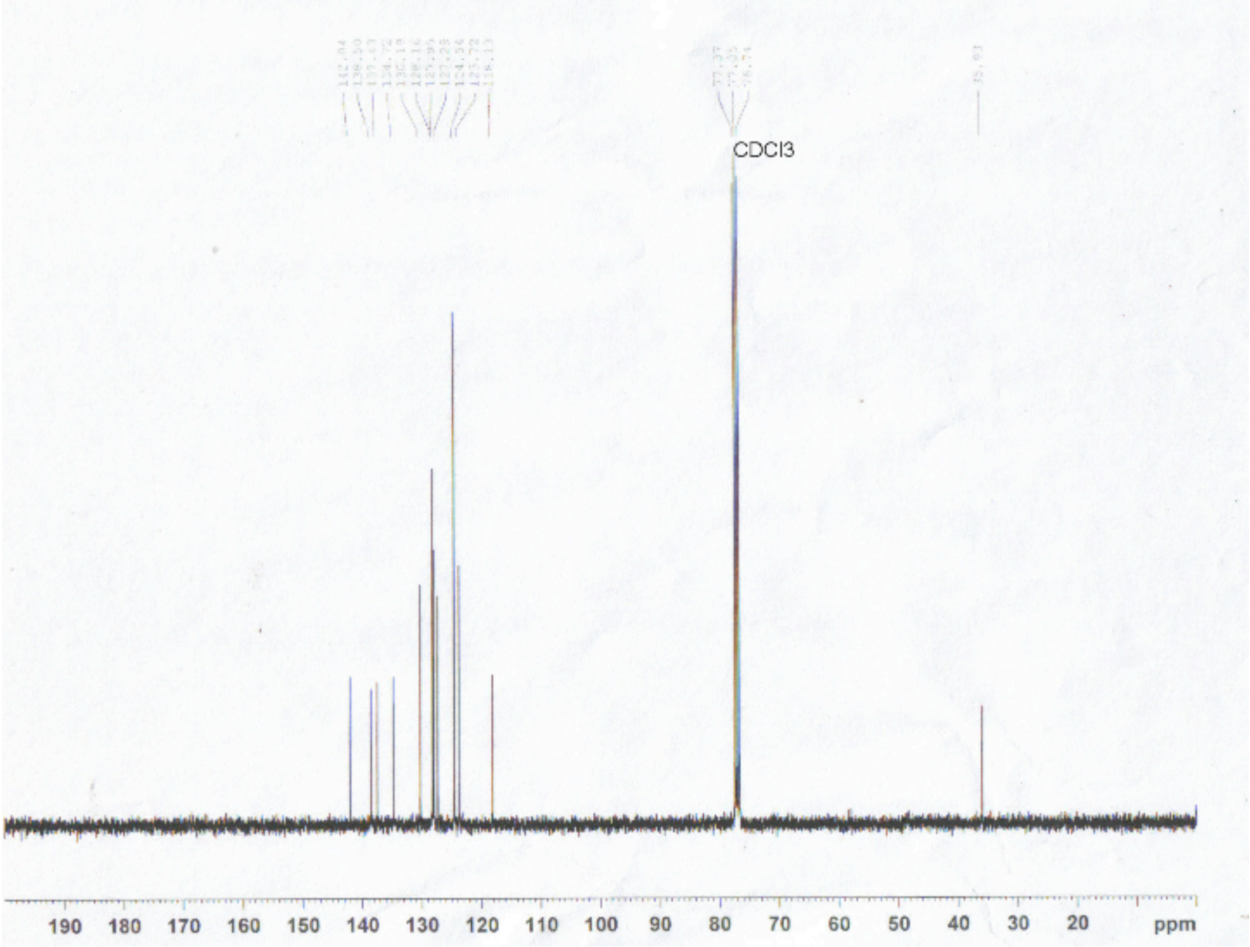
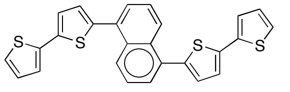


Figure S6: ^{13}C NMR spectra of **3** (100 MHz, $CDCl_3$).



(Compound **4**)

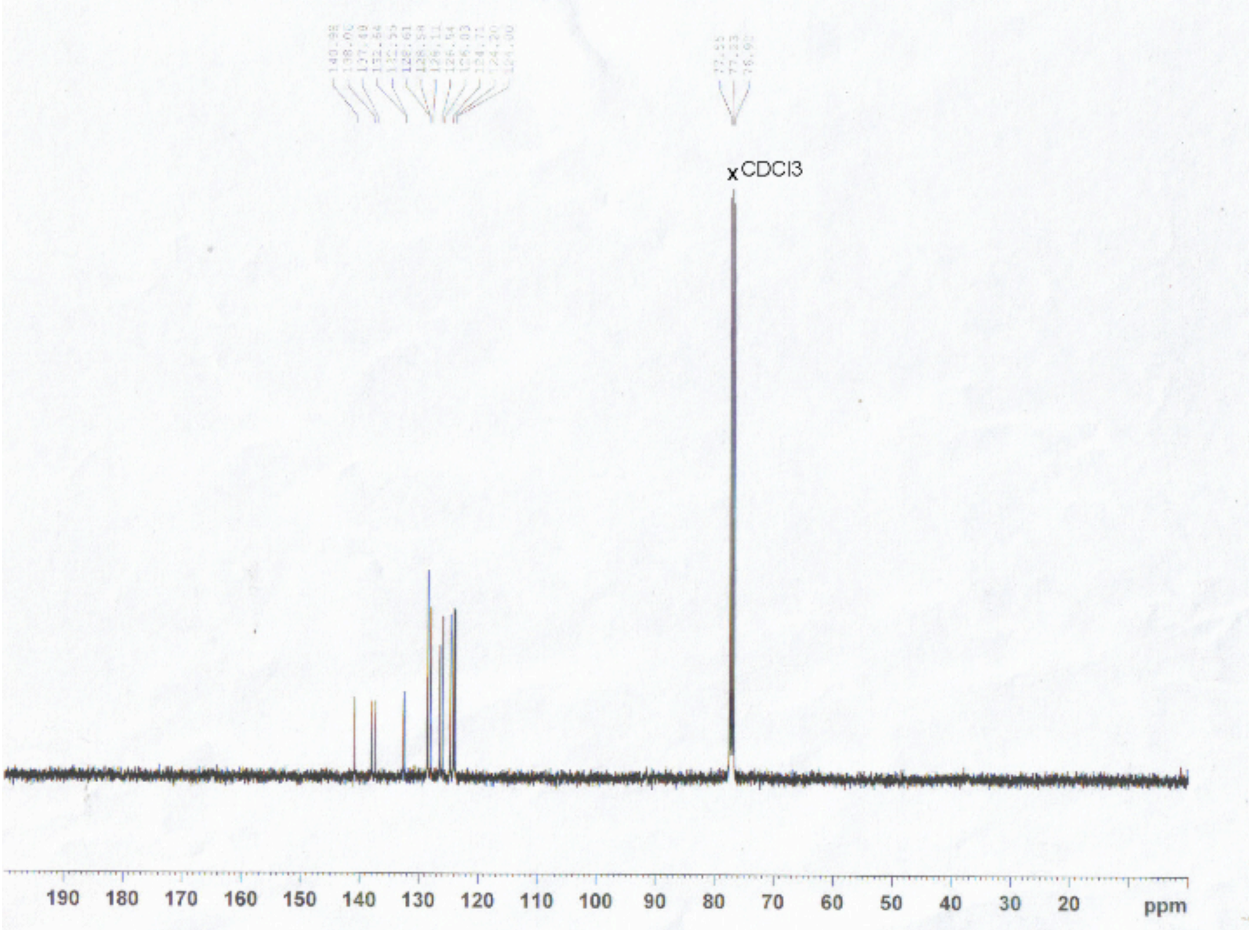


Figure S7: ^{13}C NMR spectra of **4** (100 MHz, $CDCl_3$).

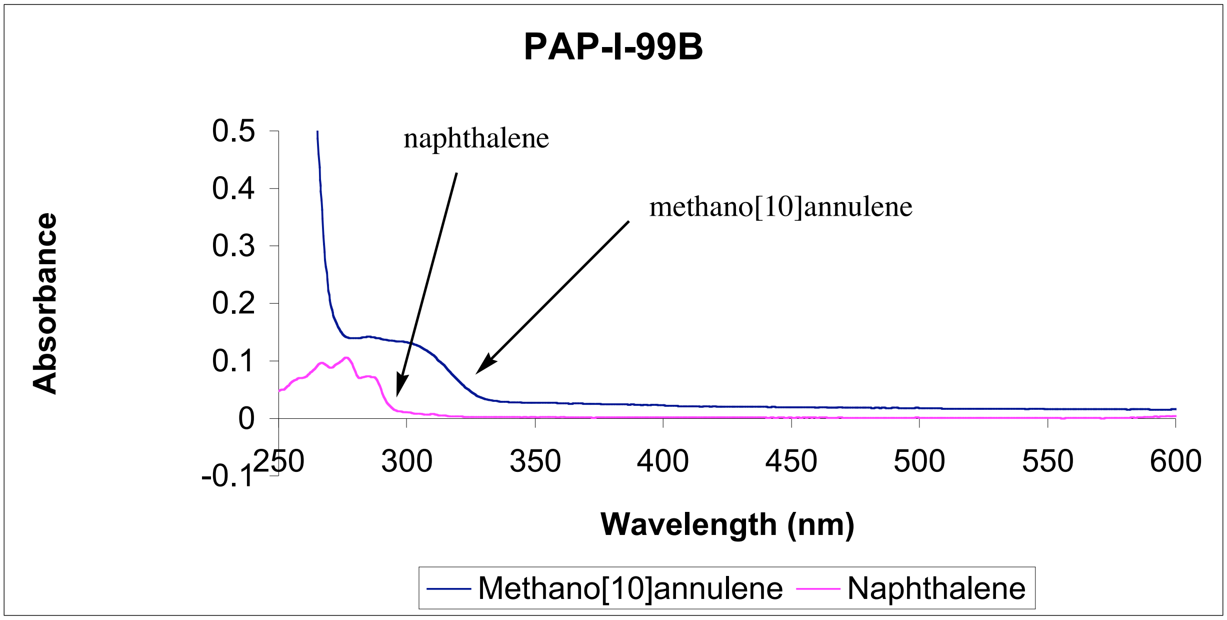


Figure S8: UV-vis of the parent 1,6-methano[10]annulene and naphthalene hydrocarbons taken at room temperature in $CHCl_3$.