Supplementary Information for

Connecting Molecule Oxidation to Single Crystal Structural and Charge Transport Properties in Rubrene Derivatives

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1) Synthesis

2) Electrochemical characterization

3) Crystal growth and XRD

4) AFM analysis

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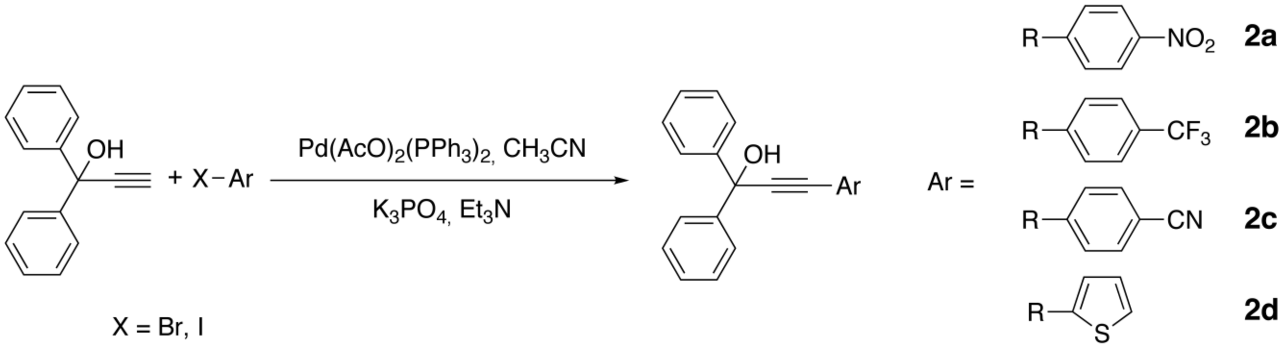
1) Synthesis

Solvents of analytical grade were used without further purification. Reagents were purchased from Sigma-Aldrich and used without further purification. UV spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. IR spectra were obtained with a Spectrum 100, FT-IR Spectrometer Perkin Elmer. NMR spectra were recorded in $CDCl_3$ on a Bruker 500 MHz Spectrometer. Molecular structures and purity were analyzed by GC-MS (GCD 1800C; Hewlett-Packard) with a 50-m DB-5MS column (J & W Scientific, Folsom, Calif.). Silica gel (230–400 Mesh) was used for column chromatography.

General procedure for the synthesis of 1,1-biphenyl-3-aryl-propargyl alcohol via Sonogashira coupling (1a-d):

In a sealable flask $Pd(AcO)_2$ (0.2 mmol) and triphenyl-phosphine (0.4 mmol) are dissolved in anhydrous CH_3CN (3 mL every 0.1 mmol of $Pd(AcO)_2$). The yellow suspension is sonicated at r.t. under N_2 atmosphere until the solution becomes dark red (usually in less than 2 h). This color change indicates that the formation of the catalyst is completed. Then, finely ground K_3PO_4 (8.0 mmol), triethylamine (20 mmol), 1,1-diphenylpropargyl alcohol (8.0 mmol) and the appropriate halogeno-arene (8.8 mmol) are added. The reaction can be carried out at r.t. or heated at reflux in the sealable flask, and is carried out until complete consumption of the propargyl alcohol. The reaction is monitored by TLC. At the end, the solvent is removed under reduced pressure and the crude is purified by column chromatography.



Scheme S1. Synthesis of propargyl alcohols (Sonogashira protocol)

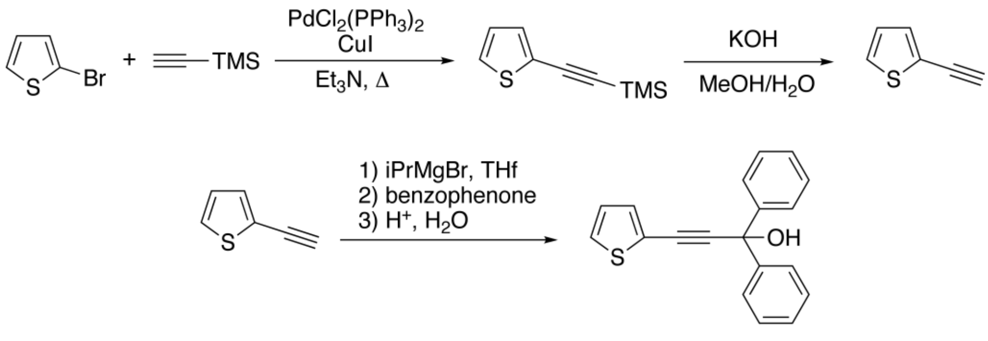
1,1-diphenyl-3-(4-nitrophenyl)prop-2-yn-1-ol (1a). The reaction was monitored by TLC (SiO_2, Hexane/AcOEt 9:1). 1,1-diphenylpropargyl alcohol is completely consumed after 20 h at r.t. or after 2 h at reflux. The crude was purified by column chromatography (SiO_2, Hexane/AcOEt 9:1) affording the desired product as a pale yellow solid (yield 75%). M.p. 127°C.
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, 8.9 Hz, 2H); 7.67 – 7.63 (m, 6H); 7.40 – 7.36 (t, 6.8 Hz, 4H); 7.34-7.31 (d, 7.2 Hz, 2 H,); 2.90 (s, 1H, OH).
IR (neat, cm^{-1}) 3466 (OH); 3105 (aromatic C-H); 1591 (aromatic C-C); 1502 – 1343 (N-O).
GC–MS; m/z (%): [M$^+$] 329 (retention time: 11.49 min).

1,1-diphenyl-3-(4-trifluoromethylphenyl)prop-2-yn-1-ol (1b). The reaction was monitored by TLC (SiO_2, Hexane/AcOEt 9:1). 1,1-diphenylpropargyl alcohol is completely consumed after 2 h 30' at reflux. The crude was purified by column chromatography (SiO_2, Hexane/AcOEt 9:1) affording the desired product as a dark yellow oil (yield 75%).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 – 7.65 (d, 8.1 Hz, 4H); 7.63 – 7.57 (q, J_1 = 8.6 Hz, J_2 = 5.1 Hz, 4H); 7.38 – 7.35 (t, 7.5 Hz, 4H); 7.32 – 7.29 (m, 2 H); 2.88 (s, 1H, OH).
IR (neat, cm^{-1}) 3566-3136 (broad, OH); 3068 (aromatic C-H); 1612 (aromatic C-C); 1317 (C-F).
MS-EI: m/z (%): 352 [M$^+$].

1,1-diphenyl-3-(4-benzonitryl)prop-2-yn-1-ol (1c).
The reaction was monitored by TLC (SiO_2, Hexane/AcOEt 9:1). 1,1-diphenylpropargyl alcohol is completely consumed after 10h at reflux. The crude was purified by column chromatography (SiO_2, Hexane/AcOEt 9:1) affording the desired product as yellow solid? (yield 75%).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 – 7.63 (d, 6.8 Hz, 4 H); 7.62 -7.60 (d, 8.4 Hz, 4H); 7.39 – 7.35 (t, 5.8 Hz, 4H); 7.33 – 7.29 (m, 2H); 2.92 (s, 1H, OH)
MS-EI: m/z (%): 309 [M$^+$].

1,1-diphenyl-3-(3-thienyl)prop-2-yn-1-ol (1d)
The reaction was monitored by TLC (Al_2O_3, Toluene/CH_2Cl_2 1:1). 1,1-diphenylpropargyl alcohol is completely consumed after 10h at reflux. The crude was purified by column chromatography (SiO_2, CH_2Cl_2/AcOEt 9:1) affording the desired product as yellow oil (yield 64%).
Analyses in accordance with data published in the literature.[1]

General Procedure for the synthesis of substituted triarylpropargyl alcohol, via Grignard Reagents.



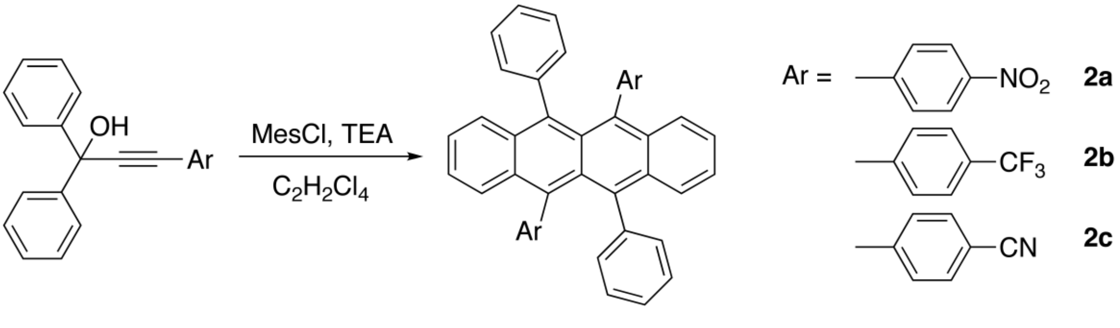
Scheme S2. Synthesis of substituted triarylpropargyl alcohol, via Grignard Reagents

a) Synthesis of 1-trimethylsilyl-2-(2-thienyl)-acetylene.
Under N_2 atmosphere, 2-bromothiophene (5.000 g, 30.07 mmol) and trimethylsilylacetylene (2.953 g, 30.07 mmol) are dissolved into 50 mL of anhydrous triethylamine. Then $PdCl_2(PPh_3)_2$ (421 mg, 0.6 mmol) and CuI are added (228.5 mg, 1.2 mmol). The viscous solution is heated under reflux and monitored by TLC (SiO_2, hexane). After 4 h, the solvent is evaporated under reduced pressure and the crude is purified by filtration through a silica bed (eluent: hexane), affording the pure product (4.9 g, 27.17 mmol, yield 90.0%). The nature of the product was confirmed by NMR.

b) Synthesis of 2-ethinylthiophene.
1-trimethylsilyl-2-(2-thienyl)-acetylene (4.900 g, 27.17 mmol) is dissolved in a mixture of 10 mL of MeOH and 5 mL of H_2O. KOH is added to the solution (1.680 g, 29.94 mmol) and the solution stirred at r.t. for 6h. Then, the solution is diluted with H_2O (200 mL) and extracted with CH_2Cl_2 (3x30 mL). Organic phase is dried over Na_2SO_4 and the solvent evaporated under reduced pressure, affording the desired product as colorless oil with quantitative yield. The nature of the product was confirmed by NMR.

c) Synthesis of 1,1-diphenyl-3-(3-thienyl)prop-2-yn-1-ol (1d)
2-ethinylthiophene (2.900 g, 27 mmol) is dissolved into anhydrous THF (100 mL) and a THF solution (2.9 M) of isopropyl magnesium bromide (10.3 mL, 30 mmol) is added under stirring, at 0°C. At the end, the solution is allowed to warm up until r.t. and then is kept under stirring at r.t. for 2h. Then benzophenone is added (4.9 g, 27 mmol) and the solution is heated a reflux for 4 h). The reaction was monitored by TLC (SiO_2, hexane/ AcOEt 9:1). At the end the reaction is quenched with H_2O and extracted with AcOEt (3x50 mL). Organic phase is dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The crude product was crystallized from Hexane affording the desired product (6.970 g, 24 mmol, yield 89%). Analyses in accordance with data published in the literature.[1]

General procedure for the synthesis of 5,11-biphenyl-6,12-biaryl-tetracenes (2a-c):
In a sealable vessel, 3 mmol of propargyl alcohol are dissolved in 3 mL of 1,1,2,2-tetrachloroethane, under N_2 atmosphere, then at 0°C Mesyl chloride (9 mmol) and triethylamine (0.2 mL) are added dropwise. The solution is stirred at r.t. until complete conversion of the alcohol into chloro allene. The reaction was monitored by TLC. After that, the solution is heated at reflux. At the end, the solvent is removed under reduced pressure and the solid purified by crystallization from MeOH or by column chromatography.



Scheme S3. Synthesis 5,6,11,12-tetraaryl-tetracenes from propargyl alcohols.

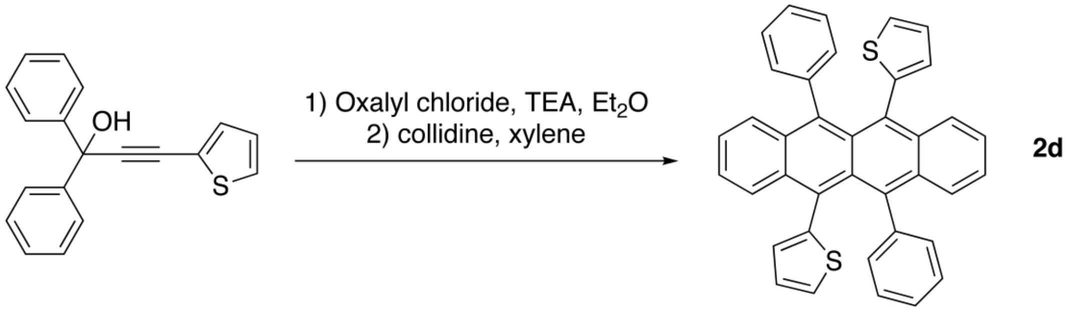
5,11-bis(4-nitrophenyl)-6,12-biphenyltetracene (2a). The reaction was monitored by TLC (SiO_2, Hexane/AcOEt 9:1). Propargyl alcohol is completely consumed after 20 h at r.t., then the corresponding chloroallene is heated at reflux in the sealed vessel for 4 h. At the end the

solvent is evaporated and the crude purified by crystallization from MeOH affording the desired product as red powder (yield 53%).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 – 7.93 (m, 4H); 7.39 – 7.37 (m, 2H); 7.23 – 7.16 (m, 8H); 7.10– 7.05 (m, 8H); 6.91– 6.89 (m, 4H).
MS: m/z (%): 622 [M+]; 500 [M- $C_6H_4NO_2$]

5,11-bis(4-trifluoromethylphenyl)-6,12-biphenyltetracene (2b). The reaction was monitored by TLC (SiO_2, Hexane/AcOEt 9:1). Propargyl alcohol is completely consumed after 20 h at r.t., then the corresponding chloroallene is heated at reflux in the sealed vessel for 15 h. At the end the solvent is evaporated and the crude purified by crystallization from MeOH affording the desired product as red powder (yield 41%).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.36 (m, 2H); 7.32 – 7.30 (m, 4H); 7.27 – 7.25 (m, 2H); 7.18– 7.12 (m, 6H); 7.09 – 7.06 (m, 4H); 7.01 – 6.99 (m, 4H) ; 6.85– 6.84 (m, 4H).
MS: m/z (%): 668 [M+]; 702 [M+O_2]; 591 [M- C_6H_5]

5,11-bis(4- benzonitryl)-6,12-biphenyltetracene (2c). The reaction was monitored by TLC (SiO_2, Hexane/AcOEt 9:1). Propargyl alcohol is completely consumed after 24 h at r.t., then the corresponding chloroallene is heated at reflux in the sealed vessel for 8 h. At the end the solvent is evaporated and the crude purified by crystallization from MeOH affording the desired product as red powder (yield 71%).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.36 (m, 6H); 7.23 – 7.21 (m, 2H); 7.18 – 7.11 (m, 10H); 7.07– 6.99 (m, 4H); 6.88– 6.86 (m, 4H).
MS: m/z (%): 582 [M+].

Synthesis of 5,11-bis(3-thienyl)-6,12-biphenyltetracene (2d).



Scheme S4. Synthesis of derivative **2d**

In a sealable vessel, 1,1-diphenyl-3-(3-thienyl)prop-2-yn-1-ol (7.760 g, 26.73 mmol, **1d**) is dissolved in 13 mL of anhydrous Et_2O and under N_2 atmosphere, triethylamine (4.5 mL) and oxalyl chloride (2.52 mL, 29.40 mmol, dissolved in 13 mL of anhydrous Et_2O) are added dropwise. The reaction is allowed to warm up at r.t. The reaction was monitored by TLC (SiO_2, Hexane/AcOEt 9:1). After 15' the solution is filtered on Büchner funnel with a sintered glass disc to remove the insoluble matter. The solvent is evaporated under reduced pressure, without heating, to avoid uncontrolled evolution of the chloro-allene. Then, the solid is taken up anhydrous xylene (10 mL), collidine is added (6.60 mL, 50 mmol) and the solution is refluxed for 1h. The solvent is removed under reduced pressure and the crude is purified by column chromatography (Hexane/AcOEt 9:1), affording the product as red solid (yield 42%). Analyses in accordance with data published in the literature.[1]
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 – 7.52 (m, 2H); 7.46 – 7.45 (m, 2H); 7.41 – 7.39 (m, 2H); 7.30– 7.29 (m, 2H); 7.21 – 7.13 (m, 14H); 6.73 (br, 2H); 6.45 (br, 2H).
MS: m/z (%): [M+]. 544 [M+], 461 (M+ – Thiophene)

2) Electrochemical characterization

For the electrochemical characterizations derivatives **2a-d** were dissolved (concentration about 10^{-4} M) in the supporting electrolyte that was a 0.1 M solution of tetrabutylammonium perchlorate (Fluka, electrochemical grade, ≥99.0%) in a mixture of anhydrous dichloromethane (Aldrich 99.9%) and anhydrous acetonitrile (Aldrich, 99.8%) 2:1. Differential pulsed voltammetry (DPV) and Cyclic Voltammetry (CV) were carried out at scan rate of 20 and 50 mV/s, respectively, using a PARSTA2273 potentiostat in a two compartments, three electrodes electrochemical cell in a glove box filled with Argon ([O2] ≤ 1 ppm). The working, counter, and the pseudo-reference electrodes were a glassy carbon pin, a Pt flag and a Ag/AgCl wire, respectively. The working electrodes discs were well polished with alumina 0.1 μm suspension, sonicated for 15 min in deionized water and washed with 2-propanol before use. The Ag/AgCl pseudo-reference electrode was calibrated, by adding ferrocene (10^{-4} M) to the test solution after each measurement.

3) Crystal growth and XRD

Good quality single crystals of derivatives **2a**, **2b**, **2c** and **2d**, suitable for X-rays analysis, were obtained by means of slow evaporation of a saturated solution of acetone; single crystals were also obtained by thermal gradient sublimation at low-pressure (6.0×10^{-4} mbar). Data collections were performed on a Rigaku R-Axis II diffractometer equipped with a SHINE monochromator (MoKα radiation λ= 0.71075 Å) and an image plate detector. The collected intensities were corrected for Lorentz-polarization factors and absorption using CrystalClear-SM Expert 2.0 suite of programs. The structures were solved by direct methods using SHELXS[2] and refined by full-matrix least-squares against F_o^2 using the ShelXle graphical user interface for SHELXL-2013.[3] ORTEP plots were produced with program Mercury CSD 3.0, that was also used to perform some of the structural parameters calculations on rubrene and the calculation of π – π stacking and centroid distances for all the tetraaryltetracenes.

During purification of compound **2d**, we isolated several single crystals with different colors and habits, obtained from slow evaporation of a hexane/ethyl acetate 9:1 solution. Single crystal X-ray diffraction data collection performed on these samples revealed, in addition to the formation of cyclobutene, the formation also of a number of unexpected additional side-products (Figures S1-5). The formation of these compounds can be rationalized within the frame of the reaction mechanism proposed by Rigaudy, which explain the formation of rubrene from the dimerization of 1,1,3-triphenyl-3-chloroallenes.[4] A new version of the reaction mechanism proposed by Rigaudy, accounting for the formation of compounds **E**, **H**, **I**, **L**, and **N** is presented in Scheme V.

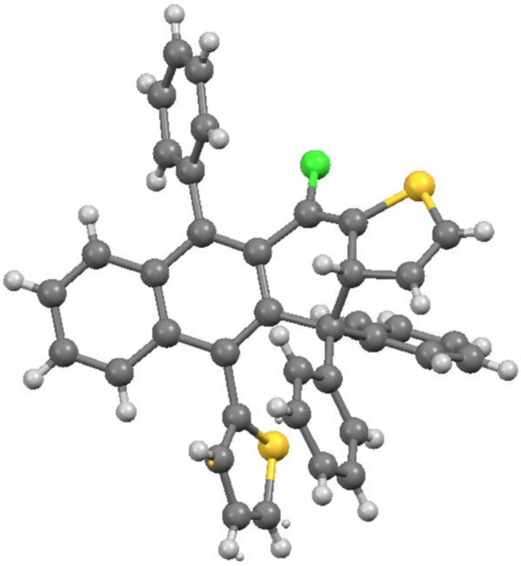


Figure S1: Ball and stick model of the crystal structure of compound **E**.

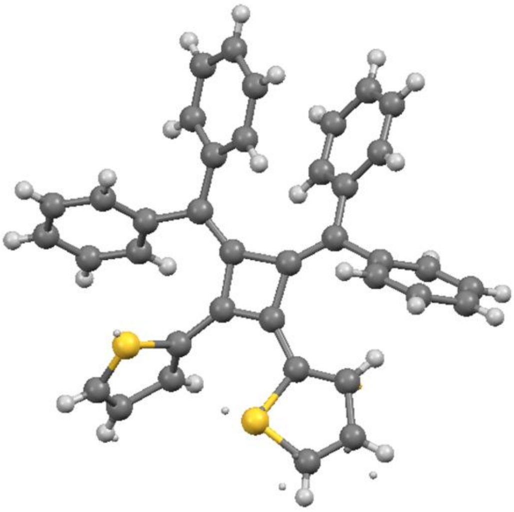


Figure S2: Ball and stick model of the crystal structure of compound **N**.

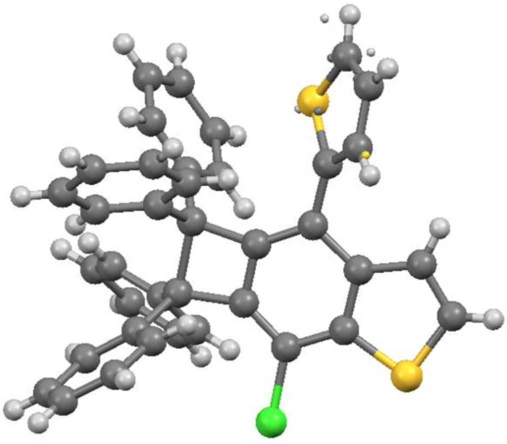


Figure S3: Ball and stick model of the crystal structure of compound **H**.

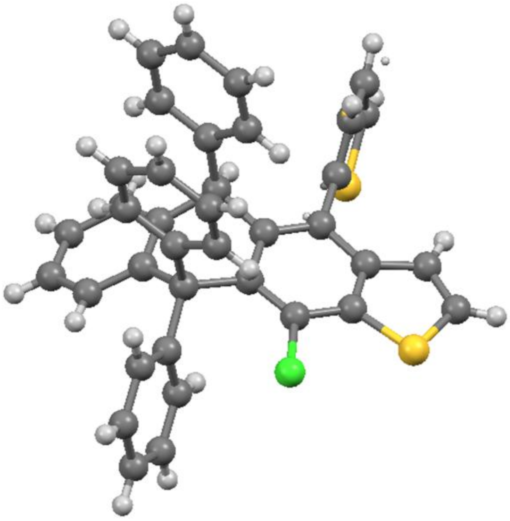


Figure S4: Ball and stick model of the crystal structure of compound **I**.

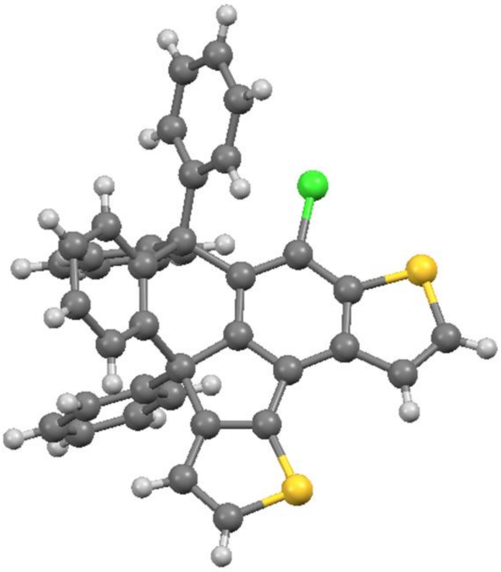
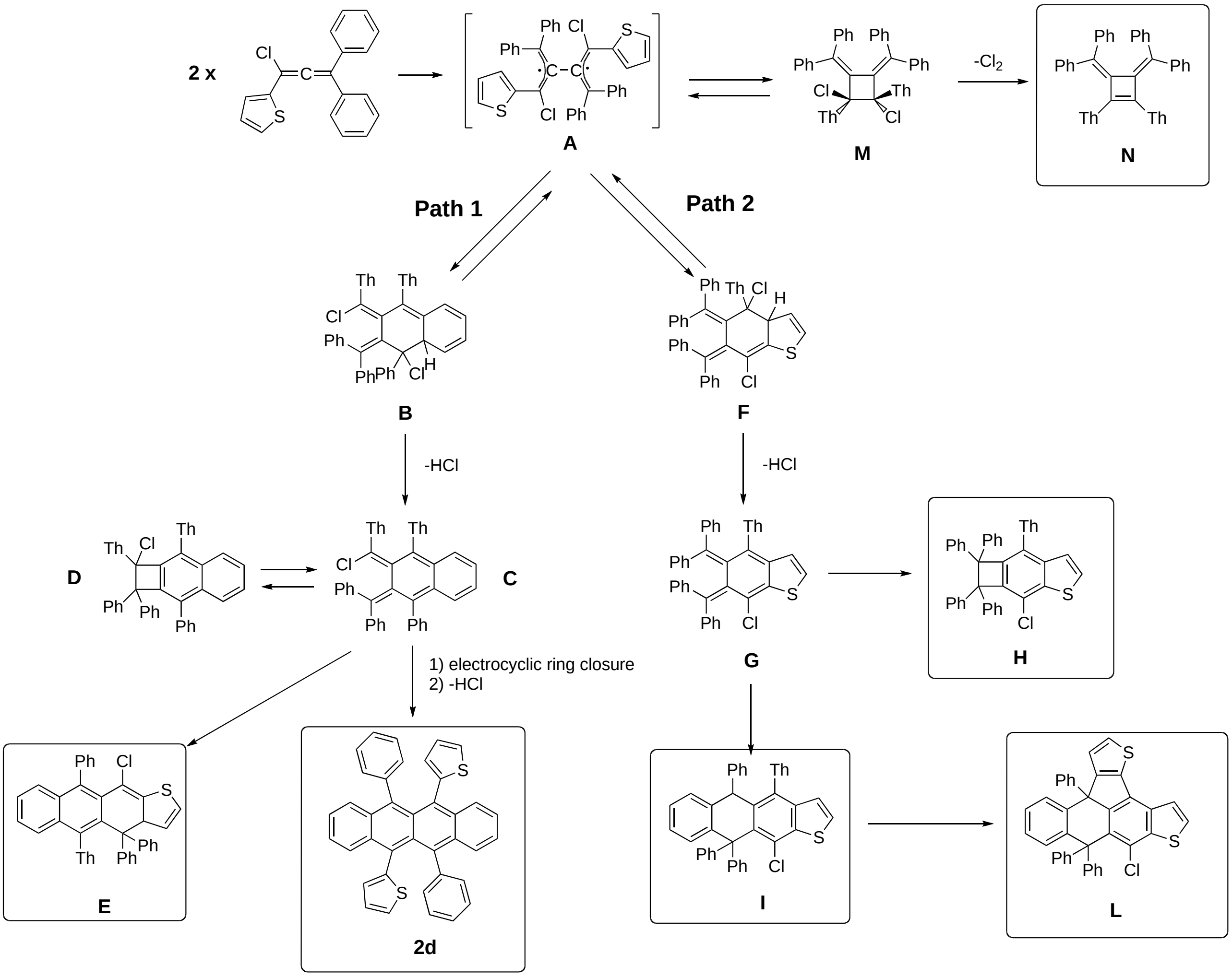


Figure S5: Ball and stick model of the crystal structure of compound **L**.



Scheme S5. Extended version of Rigaudy's mechanism accounting for the formation of compounds **E**, **H**, **I**, **L**, and **N.**[4]

4) c-AFM analysis

A Veeco Nanoscope Multimode V was used for c-AFM analysis. Transport properties were probed in a dark environment along the *b* lattice direction of the crystals, which corresponds both to the direction of maximum mobility for rubrene and to the direction in which the molecular packing is the same for all the crystals. The experimental set-up is sketched in Figure S6. For c-AFM measurement a Platinum tip (Rocky Mountain Nanotechnology) with a force constant of 0.3 N m^{-1}, a resonance frequency of 5 kHz and a tip curvature radius below 20 nm was used. The second electrode was prepared by depositing colloidal graphite paint (Agar Scientific) at the opposite sides of the crystals along the *b* lattice direction and letting it dry for one day.

I-V curves were collected in the −10÷10 V range from all the crystals. The tip was placed at a distance of ≈ 100 μm from the graphite electrode along the *b* lattice direction and the tip load was 50 nN for all the measurements (in order to have the same tip contact area for all the samples). The I-V curves have been collected sweeping the voltage between −10 V and 10 V (trace) and then sweeping it back (retrace), with a repetition rate of 0.5 Hz and measuring the current at each ≈ 0.02 V step.

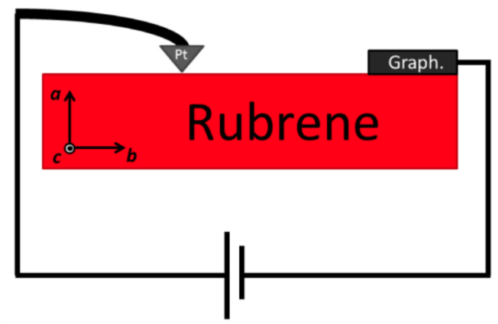


Figure S6. Scheme of the experimental setup used for the c-AFM measurements carried out on all the rubrene derivatives single crystals; during the measurements the Pt tip is grounded and bias is applied to the graphite electrode on the sample. The orientation of the crystalline axes is also indicated.

References

1. Braga, D.; Jaafari, A.; Miozzo, L.; Moret, M.; Rizzato, S.; Papagni, A.; Yassar, A., The Rubrenic Synthesis: The Delicate Equilibrium between Tetracene and Cyclobutene. *European Journal of Organic Chemistry* **2011,** 2011, 4160-4169.
2. Sheldrick, G., A short history of SHELX. *Acta Crystallographica Section A* **2008,** 64, 112-122.
3. Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B., ShelXle: a Qt graphical user interface for SHELXL. *Journal of Applied Crystallography* **2011,** 44, 1281-1284.
4. Rigaudy, J.; Capdevielle, P., Dimerisation des polyphenyl-allenes - I: Chloropolyphenyl-allenes: mecanisme de la reaction "Rubrenique". *Tetrahedron* **1977,** 33, 767-773.