# Synthesis, Electronic Properties and On-Surface Switching Behaviour of Triazatruxene Di- and Tetramers

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### Materials and Methods

#### NMR spectroscopy

NMR spectra were recorded on a Bruker Avance III 400 (<sup>1</sup>H-NMR: 400 MHz, <sup>13</sup>C-NMR: 101 MHz), a Bruker Avance Neo 800 (<sup>1</sup>H-NMR: 800 MHz, <sup>13</sup>C-NMR: 202 MHz), a Bruker Avance III 600 (<sup>1</sup>H-NMR: 600 MHz, <sup>13</sup>C-NMR: 152 MHz), or a Jeol JNM-ECZR (<sup>1</sup>H-NMR: 500 MHz, <sup>13</sup>C-NMR: 121 MHz) spectrometer. The spectra were measured in deuterated solvents using the resonance of the residual protonated solvents for internal referencing of the <sup>1</sup>H-NMR spectra and the <sup>13</sup>C-Signal for <sup>13</sup>C-NMR spectra.

#### Size exclusion chromatography

Size exclusion chromatography was measured in CHCl<sub>3</sub> at 35 °C on a PSS SECcurity<sup>2</sup> instrument, equipped with PSS SDV linear M columns (2 × 30 cm, additional guard column), two UV detectors (PSS SECcurity<sup>2</sup> UV) and a refractive index detector (PSS SECcurity<sup>2</sup> RI). A flow rate of 1 mL/min was used. The results were interpreted versus polystyrene standards using the software PSS WinGPC, version 8.32.

#### **Electrochemical investigations**

Cyclic voltammograms were measured in an argon flushed cell in 0.04 M solution of  $CH_2CI_2/NBu_4^+[BAr^{F_{24}}]^- ([BAr^{F_{24}}]^- = [B\{C_6H_3(CF_3)_2-3,5\}_4]^-)$ , or in 0.06 M solution of  $CH_2CI_2/NBu_4^+$  PF<sub>6</sub><sup>-</sup> as the electrolyte. The Na<sup>+</sup> salt of the  $[BAr^{F_{24}}]^-$  ion was prepared from 3,5-bis(trifluoromethyl)bromobenzene,<sup>1</sup> and then converted to the NBu\_4<sup>+</sup> salt by cation exchange.<sup>2</sup> Voltammetric studies were performed using a computer-controlled *BASi* potentiostat. A custom-made cylindrical, vacuum-tight, single-compartment cell equipped with a platinum working electrode from *BASi*, a coiled platinum wire as the counter electrode, and a coiled silver wire as the (pseudo)reference electrode was used in these measurements. All electrodes were sealed into glass capillaries and fixed to the cell ports using Quickfit screws. The working electrode was polished prior to the measurements using diamond pastes with 1.0 µm and 0.25 µm grain size. For internal referencing, either decamethylferrocene (Cp\*<sub>2</sub>Fe, *E*<sub>1/2</sub> = -550 mV vs FcH<sup>0/+</sup>) or cobaltocenium hexafluorophosphate ([Cp<sub>2</sub>Co]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup>, *E*<sub>1/2</sub> = -1330 mV vs FcH<sup>0/+</sup> in CH<sub>2</sub>Cl<sub>2</sub>/NBu<sub>4</sub><sup>+</sup> [BAr<sup>F<sub>24</sub></sup>]<sup>-</sup>) were used as internal calibrant. Potentials are provided relative to the ferrocene/ferrocenium (FcH/FcH<sup>+</sup>) redox standard.

Redox titrations were performed as follows: 5 mg of compound **1** were dissolved in 2 mL of  $CH_2CI_2$ . As oxidant, a stock solution of 5 mg of the bis(acetonitrile) solvate Ag<sup>+</sup> [SbF<sub>6</sub>]<sup>-</sup> ×(CH<sub>3</sub>CN)<sub>2</sub> in 2.50 mL of  $CH_2CI_2$  was used. **1**<sup>+</sup> was obtained by mixing 0.35 mL of the solution containing the compound with 0.20 mL of the oxidant solution, and **1**<sup>2+</sup> by mixing 0.35 mL of the solution of **1** with 0.60 mL of the oxidant solution. The resulting solutions were diluted with  $CH_2CI_2$  to a total volume of 1 mL. IR spectra were directly recorded from these solutions. For measuring UV/vis/NIR and EPR spectra, the solutions of **1**<sup>+</sup> and **1**<sup>2+</sup> were diluted to 1/5 of the initial concentration.

6 mg of compound **2** were dissolved in 3 mL of  $1,2-C_2H_4CI_2$ . As oxidant, a stock solution of 10 mg of Ag<sup>+</sup> [SbF<sub>6</sub>]<sup>-</sup>×(CH<sub>3</sub>CN)<sub>2</sub> in 10 mL of  $1,2-C_2H_4CI_2$  was used. In order to obtain similar concentrations of the cationic compounds, the different samples were diluted to a total volume of 1.75 mL using  $1,2-C_2H_4CI_2$ . **2**<sup>n+</sup> (n = 1-4) were obtained by mixing 0.5 mL of the solution containing **2** and n × 0.25 mL of the stock solution of the oxidant. IR spectra were directly recorded on the thus obtained solutions of **2**<sup>n+</sup>. UV/vis/NIR- and EPR spectra were recorded on solutions that were diluted with CH<sub>2</sub>Cl<sub>2</sub> to 12-times the initial volume. All background solutions were measured with the respective solvent mixtures.

# IR and UV/vis/NIR Spectroscopy and Spectroelectrochemistry

IR/NIR spectra were recorded on a *Bruker* Tensor III instrument, and UV/vis/NIR spectra were obtained on a *TIDAS* fiberoptic diode array spectrometer with MCS UV/Vis and PGS NIR instruments from *J&M*. Extinction coefficients were determined from measurements in Hellma quartz cuvettes of 1 mm thickness. Spectroelectrochemical (SEC) studies were conducted employing a custom-made optically transparent thin-layer electrolysis (OTTLE) cell built according to the design of HARTL and coworkers.<sup>3</sup> The cell is made of CaF<sub>2</sub> windows, Pt-mesh working and counter electrodes, and of a Ag/AgCl thin-layer pseudoreference electrode. All SEC measurements employed dry, degassed 0.14 M solutions of the NBu<sub>4</sub><sup>+</sup> [BAr<sup>F<sub>24</sub>]<sup>-</sup> electrolyte in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>. Potentials were applied with a *Wenking Pos 2* potenstiostat of *Intelligent Controls GmbH*.</sup>

### **DFT calculations**

Quantum chemical calculations on  $1^{n+}$  (n = 0, 1, 2) and  $2^{n+}$  (n = 0-4) were performed using the GAUSSIAN 16 program package.<sup>4</sup> Electronic transitions are based on the time-dependent DFT approach (TD-DFT). For C,H and N atoms, triple- $\zeta$  basis sets (6-31G(d))<sup>5</sup> were used. All calculations employed the PBE1PBE functional.<sup>6</sup> Solvent effects were modelled with the polarizable conductor continuum model (PCCM).<sup>7</sup> Molecular orbitals are pictured in blue and white for positive and negative signs of their wavefunctions. The isovalues for all molecular orbitals were set to 0.02 and to 0.001 for spin orbitals.

# Scanning Tunneling Microscopy Experiments

All experiments were performed in a two-chamber ultrahigh vacuum (UHV) system (base pressure  $5 \cdot 10^{-11}$  mbar), equipped with an *Omicron* Cryogenic-STM. The Ag(111) crystal (Surface Preparation Laboratory B. V.) was cleaned by repeated cycles of Ar<sup>+</sup> sputtering (2 kV) and subsequent annealing to 600°C. Compounds **1** and **2** were deposited *in situ* via electrospray deposition (ESD),<sup>8</sup> from freshly prepared solutions in a mixture of dichloromethane and methanol (ratio: 4:1). The sample was kept at room temperature during the deposition and then transferred into the STM without any further treatment. STM measurements were carried out at 3-6 K in the constant current mode. For all measurements, grinded and polished PtIr tips (*Nanoscore GmbH*) were used. Bias voltages refer to the sample potential with respect to the tip.

### **Experimental Section**

All syntheses were carried out under inert atmosphere using common Schlenk techniques. Solvents were used after drying with the appropriate drying agent and deoxygenation by purging with dinitrogen or three consecutive freeze-pump-thaw cycles. Degassed solvents were stored under a dinitrogen atmosphere. All starting materials were purchased from commercial vendors and used without further purification, or prepared from procedures in the literature according to the indicated references. **2-Br<sub>3</sub>-EtTAT**<sup>9</sup> and **2-A<sub>1</sub>-EtTAT**<sup>10</sup> were prepared according to the provided literature procedures.

Bis(2-(*N*,*N*',*N*''-triethyltriazatruxene))-buta-1,3-diyne (1)

70 mg (0.15 mmol, 1 eq.) of **2-A<sub>1</sub>-<sup>Et</sup>TAT** and 23 mg (0.12 mmol, 0.80 eq.) of copper(II)acetate monohydrate were suspended in 7.5 mL of  $CH_2Cl_2$  and 7.6 mL of piperidine under air. The reaction mixture was stirred for 24 hours. Then, 30 mL of  $H_2O$  were added and the mixture was extracted with  $CH_2Cl_2$  (3 x 100 mL). The combined organic phases were washed with  $H_2O$  (3 × 50 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvents were removed under reduced pressure. The crude product was redissolved in 3 mL of  $CH_2Cl_2$  and precipitated by

addition of 40 mL of <sup>*n*</sup> pentane. The precipitate was washed with further portions of <sup>*n*</sup> pentane  $(3 \times 10 \text{ mL})$ . The product was isolated in a yield of 67 % (47 mg, 0.05 mmol) as a yellow solid.



<sup>1</sup>**H NMR** (800 MHz, CDCl<sub>3</sub>): δ [ppm] = 8.32 (d,  ${}^{3}J_{HH}$  = 8.1 Hz, 4H, H-4<sub>b,c</sub>), 8.26 (d,  ${}^{3}J_{HH}$  = 8.4 Hz, 2H, H-4<sub>a</sub>), 7.86 (s, 2H, H-7<sub>a</sub>), 7.66 (d,  ${}^{3}J_{HH}$  = 8.4 Hz, 4H, H-7<sub>b,c</sub>), 7.53 (d,  ${}^{3}J_{HH}$  = 8.4 Hz, 2H, H-5<sub>a</sub>), 7.46 (vt,  ${}^{3}J_{HH}$  = 7.6 Hz, 4H, H-6<sub>b,c</sub>), 7.35 (vt,  ${}^{3}J_{HH}$  = 7.6 Hz, 4H, H-5<sub>b,c</sub>), 5.07 – 4.97 (m, 12H, H-9<sub>a,b,c</sub>), 1.67 – 1.54 (m, 18H, H-10<sub>a,b,c</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR (202 MHz, CDCl<sub>3</sub>):  $\delta$  [ppm] = 140.9 (s, C-8<sub>b,c</sub>), 140.3 (s, C-8<sub>a</sub>), 139.3 (s, C-1<sub>b,c</sub>), 138.5 (s, C-1<sub>a</sub>), 124.3 (s, C-3<sub>a</sub> and C-5<sub>a</sub>), 123.5 (s, C-3<sub>b,c</sub>), 123.2 (s, C-6<sub>b,c</sub>), 121.7 (s, C-4<sub>b,c</sub>), 121.4 (s, C-4<sub>a</sub>), 120.2 (s, C-6<sub>b,c</sub>), 115.5 (s, C-6<sub>a</sub>), 114.5 (s, C-7<sub>a</sub>), 110.6 (s, C-7<sub>b,c</sub>), 103.7 (s, C-2<sub>b,c</sub>), 103.2 (s, C-2<sub>a</sub>), 83.5 (s, C-11<sub>a</sub>), 74.0 (s, C-12<sub>a</sub>), 41.9 (s, C-9<sub>a,b,c</sub>), 15.7 (s, C-10<sub>a,b,c</sub>).

2,2',2"-Tris-(N,N',N"-triethyltriazatruxene-2-ethynyl)-N,N',N"-triethyltriazatruxene (2)

150 mg (0.33 mmol, 5 eq.) of 2-A1-EtTAT were dissolved in 15 mL of dry THF in a Schlenk tube and cooled to -78 °C. Subsequently, 0.15 mL of a 2.5 M solution of "BuLi in hexane (0.36 mmol, 5.5 eq.) were added to the reaction mixture. After allowing to stir for 2 h, a solution of 109 mg (0.43 mmol, 6.5 eq.) of ZnCl<sub>2</sub>(TMEDA) in 6 mL of dry THF was added. The reaction mixture was stirred for 15 minutes and then allowed to warm to r. t. while stirring for further 90 min. Subsequently, 44 mg (0.06 mmol, 1 eq.) of 2- Br<sub>3</sub>-EtTAT in 2 mL of dry THF and  $Pd(PPh_3)_4$  (8 mg, 12 mol%) were added to the reaction mixture, which was then stirred for 7 days at 70 °C. After cooling to r. t., the red reaction mixture was filtered through Celite545, and the solvents were removed under reduced pressure. The crude product was purified via column chromatography using a mixture of CH<sub>2</sub>Cl<sub>2</sub>/petroleum benzene/ethyl acetate (4/4/1) as the eluent. Tetramer 2 was obtained as red-brownish solid in a yield of 18 % (20 mg, 0.003 mmol). A second impure fraction containing substantial amounts of the product was obtained from the column using CH<sub>2</sub>Cl<sub>2</sub>/ethyl acetate (1/1) as the eluent. Further purification of the second fraction was performed by a second chromatography step using the ternary solvent mixture as described above. The combined yield after three column cycles was 45% (50 mg, 0.008).



<sup>1</sup>**H-NMR** (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K) δ [ppm] = 8.41 – 8.33 (m, 12H, H-4<sub>a-c</sub> and H-16<sub>a-c</sub>), 8.01 – 7.95 (m, 6H, H-7<sub>a-c</sub> and H-19<sub>a</sub>), 7.74 – 7.68 (m, 6H, H-18<sub>b,c</sub>), 7.67 – 7.63 (m, 6H, H-5<sub>a-c</sub> and H-17<sub>a</sub>), 7.52 – 7.46 (m, 6H, H-19<sub>b,c</sub>), 7.42 – 7.36 (m, 6H, H-17<sub>b,c</sub>), 5.13 – 5.05 (m, 12H, H9 and

H-21<sub>a-c</sub>), 5.07 – 4.94 (m, 12H, H-21<sub>b,c</sub>), 1.78 – 1.63 (m, 18H, H-10<sub>a-c</sub> and H-22<sub>a</sub>), 1.63 - 1.48 (m, 18H, H-22<sub>b,c</sub>).

<sup>13</sup>C{<sup>1</sup>H} -NMR (152 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K) δ [ppm] = 140.8 (s, C-20<sub>b,c</sub>), 140.5 (s, C-8 and C-20<sub>a</sub>), 139.3 (m, C-1 and C-13<sub>a</sub>), 138.9 (s, C-13<sub>b or c</sub>), 138.3 (s, C-23<sub>b or c</sub>), 123.6 (s, C-3 and C-15<sub>a</sub>), 123.4 (m, C-5 and C-17<sub>a</sub>), 123.3 (s, C-18<sub>b,c</sub>), 123.1 (s, C-17<sub>b,c</sub>), 121.5 (m, C-4 and C-16<sub>a-c</sub>), 120.0 (m, C-19<sub>b,c</sub>), 117.8 (s, C-6 or C-18<sub>a</sub>), 117.4 (s, C-6 or C-18<sub>a</sub>), 113.4 (m, C-7 and C-19<sub>a</sub>), 110.5 (s, C-15<sub>b,c</sub>), 103.4 (m, C-2 and C-14<sub>a</sub>), 103.2 (s, C-14<sub>b or c</sub>), 103.1 (s, C14<sub>b or c</sub>), 90.4 (m, C-11 or C-12), 90.1 (m, C-11 or C-12), 41.8 (s, C-9, C-21<sub>a-c</sub>), 15.4 (m, C-10 and C-22<sub>a</sub>), 15.2 (s, C-22<sub>b,c</sub>).

#### NMR Spectra and size exclusion chromatography



Figure S1. <sup>1</sup>H-NMR spectrum of 1 (CD<sub>2</sub>Cl<sub>2</sub>, 800 MHz, T = 300 K).



Figure S2.  ${}^{13}C{}^{1}H$ -NMR spectrum of 1 (CD<sub>2</sub>Cl<sub>2</sub>, 202 MHz, T = 300 K).



Figure S3. <sup>1</sup>H-NMR spectrum of 2 (CD<sub>2</sub>Cl<sub>2</sub>, 600 MHz, T = 300 K).



Figure S5. DOSY measurement of 1; D =  $6.47 \cdot 10^{-6}$  cm<sup>2</sup>/s; estimated MW = 969 g/mol.<sup>11-16</sup>



Figure S6. DOSY measurement of 2;  $D = 3.82 \cdot 10^{-6} \text{ cm}^2/\text{s}$ ; estimated MW = 3462 g/mol.<sup>11–16</sup>



Sample :	Vial 2: GMLV-07 - 1		
Integration from:	Friday 08.11.24 14:36:04		15,940 ml
Integration to :	Friday 08.11.24 14:42:27		22.328 ml
Calibration File :	D:\GPC\Kalibrierung\2024-04 CHCl3 Ea	siVialsElu/aenstaeule Lars.0	CAlhloroform
MHK - A (Cal.):	0.000E+0	MHK - K (Cal.):	1.000E+0 ml/g
Int.standcal.:	50.000 ml	Int.standsam.:	ml
Pump :	PSS SECcurity	Flowrate :	1.000 ml/min
Concentration :	1.000 g/l	Inject volume :	20.000 ul
Column 1 :	PSS SDV Vorsäule	Temperature :	35.000 °C
Column 2 :	PSS SDV Linear M 5µm	Temperature :	35.000 °C
Column 3 :	PSS SDV Linear M 5µm	Temperature :	35.000 °C
Detector 1 :	PSS SECcurity <sup>2</sup> UV	Delay volume :	0.000 ml
Detector 2 :	PSS SECcurity <sup>2</sup> UV	Delay volume :	0.000 ml
Detector 3 :	PSS SECcurity <sup>2</sup> RI	Delay volume :	0.135 ml
Detector 4 :	11: IsoPump 1, Pressure	Delay volume :	0.000 ml
Operator :	Gast	Acquisition interv	/al1.000 sec

#### PSS SECcurity<sup>2</sup> UPSS SECcurity<sup>2</sup> UPSS SECcurity<sup>2</sup> RI

Mn:	2.0394e3	1.9932e3	2.0086e3	g/mol
Mw:	2.9597e3	2.9041e3	2.9477e3	g/mol
Mz:	4.1768e3	4.1327e3	4.2600e3	g/mol
Mv:	0.000000	0.000000	0.000000	g/mol
D :	1.4513e0	1.4570e0	1.4676e0	
[n]:	0.000000	0.000000	0.000000	ml/g
Vp:	1.9337e1	1.9354e1	1.9352e1	ml
Mp:	1.9637e3	1.9391e3	1.9415e3	g/mol
A :	3.0707e3	2.9203e3	1.4728e1	ml*V
< 188	0.00	0.00	0.00	
w%:	100.00	100.00	100.00	
> 24692	0.00	0.00	0.00	

Figure S7. Size exclusion chromatography of 2 in CHCl<sub>3</sub> at 35 °C. Experimentally determined molecular mass: MW(UV1) = 1964 g/mol; MW(UV2) = 1939 g/mol, MW(RI) = 1941 g/mol.

# Voltammetric measurements



Figure S8. Cyclic voltammogram of <sup>Et</sup>TAT (v = 100 mV/s, CH<sub>2</sub>Cl<sub>2</sub>, 0.06 M NBu<sub>4</sub><sup>+</sup> PF<sub>6</sub><sup>-</sup>, r. t.).



Figure S9. Cyclic voltammogram of  $2-A_1$ -<sup>Et</sup>TAT (v = 100 mV/s, CH<sub>2</sub>Cl<sub>2</sub>, 0.06 M NBu<sub>4</sub>+ PF<sub>6</sub><sup>-</sup>, r. t.).



**Figure S10.** Left panel: Square wave voltammogram of 1 (frequency = 15 Hz, potential step = 4 mV, square wave amplitude = 25 mV,  $CH_2Cl_2$ , 0.04 M  $NBu_4^+$  [BAr<sup>F24</sup>], r. t.); right panel: deconvolution of the square wave voltammogram into two separate peaks for the  $1^{0/+}$  and  $1^{+/2+}$  redox steps.



Figure S11. Cyclic voltammogram of 1 (v = 100 mV/s, CH<sub>2</sub>Cl<sub>2</sub>, 0.06 M NBu<sub>4</sub><sup>+</sup> PF<sub>6</sub><sup>-</sup>, r. t.).



**Figure S12.** Left panel: Oxidative (top) and reductive (bottom) square wave voltammogram of **1** (frequency = 15 Hz, potential step = 4 mV, square wave amplitude = 25 mV,  $CH_2Cl_2$ , 0.06 M NBu<sub>4</sub><sup>+</sup> PF<sub>6</sub><sup>-</sup>, r. t.). The peak positions are: Oxidative: 441, 535, and 1084 mV; reductive: 1029 and 512 mV; Potentials are given vs.  $Cp_2Fe^{0/+}$ . Right panel: Baseline-corrected inset of the first oxidation process taken from the oxidative square wave voltammogram of **1** (black; frequency = 15 Hz, potential step = 4 mV, square wave amplitude = 25 mV,  $CH_2Cl_2$ , 0.06 M NBu<sub>4</sub>PF<sub>6</sub>, r. t.) and second derivative for peak positions (light blue; maxima at 441 and 535 mV). The positions are marked in light purple; potentials are given vs.  $Cp_2Fe^{0/+}$ .



**Figure S13.** Square wave voltammogram of **2** (frequency = 15 Hz, potential step = 4 mV, square wave amplitude = 25 mV, CH<sub>2</sub>Cl<sub>2</sub>, 0.04 M NBu<sub>4</sub><sup>+</sup> [BAr<sup>F<sub>24</sub>]<sup>-</sup>, r. t.).</sup>



**Figure S14.** Deconvolution (superposition as red; dashed line) of the square wave voltammogram (black) of **2** using individual gaussian peaks. The curve corresponding to the oxidations of the TAT to TAT<sup>+</sup> entities is depicted in violet (Peak 1). The curve corresponding to the oxidations of TAT<sup>+</sup> to TAT<sup>2+</sup> entities is depicted in blue (Peak 3). Two additional peaks were used to fit the experiment. Data corresponding to the different peaks and the deconvolution is listed above.

#### UV/vis/NIR and IR experiments



**Figure S15.** IR spectra of **2-A**<sub>1</sub>-**ETAT** in region of the alkynyl  $\equiv$ C-H and C $\equiv$ C stretching modes in the neutral state (left, purple line), and after oxidation to the radical cation with Ag<sup>+</sup> [SbF<sub>6</sub>]<sup>-</sup> (right, blive line) in CH<sub>2</sub>Cl<sub>2</sub> at r. t.



**Figure S16.** Changes in the IR/NIR spectra of **1** (0.14  $\bowtie$  NBu<sub>4</sub><sup>+</sup> [BAr<sup>F<sub>24</sub>]<sup>-</sup> in 1,2-C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) during gradual oxidation to radical cation **1**<sup>+</sup> (left; purple to blue), and during further oxidation of **1**<sup>+</sup> to **1**<sup>2+</sup> (right; blue to green) as obtained by SEC inside an optically transparent thin-layer electrolysis cell.</sup>



**Figure S17.** Stepwise chemical oxidation of 1 by using  $Ag^+[SbF_6]^-$  as oxidant and corresponding UV/vis/NIR spectra in  $CH_2Cl_2$  at r. t. at identical concentrations. The vis/NIR region is given as inset (top right). The full spectra were measured after dilution to obtain a maximal absorption coefficient of 0.7 - 1.0.



**Figure S18.** IR spectra in  $CH_2Cl_2$  at r. t. recorded on neutral **1** (purple line) and after oxidation of **1** to **1**<sup>+</sup> (blue line) or **1**<sup>2+</sup> (green line) using Ag<sup>+</sup> [SbF<sub>6</sub>]<sup>-</sup> as the oxidant. The spectra were measured using identical concentrations. The inset shows the region of the ethynyl C=C stretching vibrations.



**Figure S19.** (a) Normalized UV/vis/NIR spectra and (b) non-normalized vis/NIR spectra of chemically generated samples of **1**<sup>+</sup> in different solvents at identical concentration. For oxidation, 4 mg of Ag<sup>+</sup> [BAr<sup>F24</sup>]<sup>-</sup> in 3 mL of CH<sub>2</sub>Cl<sub>2</sub> were added to 4 mg of **1** in 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. Four 1 mL portions each of this solution were separated for different samples. After removal of CH<sub>2</sub>Cl<sub>2</sub>, 3 mL of the indicated solvent were added and the spectra recorded. Gutmann donor numbers (DN) of the solvents are: DN(toluene) = 0.1; DN(CH<sub>2</sub>Cl<sub>2</sub>) = 1.0; DN(THF) = 20.0.



**Figure S20.** UV/vis/NIR spectra recorded on neutral and chemically oxidized samples of tetramer **2** (CH<sub>2</sub>Cl<sub>2</sub>, r. t.), using  $Ag^+[SbF_6]^-$  as the oxidant. The number of the added equivalents of the oxidant is provided in the legend.



**Figure S21.** IR/NIR spectra recorded on neutral and chemically oxidized samples of tetramer **2** (CH<sub>2</sub>Cl<sub>2</sub>, r. t.), using Ag<sup>+</sup> [SbF<sub>6</sub>]<sup>-</sup> as the oxidant. The number of the added equivalents of the oxidant is given in the legend. The inset shows the alkynyl C=C stretching vibrations. The spectra were measured using identical concentrations.



**Figure S22.** Comparison of IR spectra of **2** in the neutral state (purple) and after oxidation with five equivalents of  $Ag^+[SbF_6]^-$  (blue) in  $CH_2CI_2$  at r. t., showing the absence and presence of the ethynyl C=C stretching mode.

#### **EPR Spectroscopy**



**Figure S23.** EPR spectra of  $1^{n+}$  in CH<sub>2</sub>Cl<sub>2</sub> at r. t. The samples were generated by adding the indicated number of equivalents of Ag<sup>+</sup>[SbF<sub>6</sub>]<sup>-</sup> as the oxidant. The samples are identical to those used for measuring the IR/NIR spectra of Figure S16.



**Figure S24.** EPR spectra of chemically generated, oxidized  $2^{n+}$  in CH<sub>2</sub>Cl<sub>2</sub> at r. t.. Samples of oxidized 2 were generated by using the indicated number of equivalents of Ag<sup>+</sup> [SbF<sub>6</sub>]<sup>-</sup> as oxidant. The samples are identical to those used for measuring the IR/NIR spectra of Figure S19.

# **Quantum Chemistry**

Table S1. DFT-calculated energies of oxidized  $1^{n+}$  (n = 1,2) and  $2^{n+}$  (n = 1-4) in their different possible spin states. Energies are given in kJ/mol and referenced to the state with the lowest multiplicity for every redox state.

2+		3+		4+					
	Singlet	Open shell singlet	triplet	Doublet	Quartet	Singlet	Open shell singlet	Triplet	Quintet
1	0	21.8	-21.9	-	-	-	-	-	-
2	0	25.4	-25.4	0	-28.6	0	0.04	-69.5	-53.9

Charge (bold) and localization	Compound 1	Charge (bold) and localization	Compound 2
1+		1+	
TAT1	0.478	Central TAT	0.348
TAT2	0.476	TAT2	0.542
Bridge	0.046	TAT3	0.027
	1.000	TAT4	0.031
		Bridge	0.051
			1.000
2+ (S=3)		2+ (S=3)	
TAT1	1.041	Central TAT	0.336
TAT2	0.918	TAT2	0.026
Bridge	0.032	TAT3	0.765
	1.991	TAT4	0.770
		Bridge	0.103
			2.000
		3+ (S=4)	
		Central TAT	0.387
		TAT2	0.821
		TAT3	0.820
		TAT4	0.820
	-	Bridge	0.153
			3.000
		4+ (S=5)	
		Central TAT	0.899
		TAT2	0.914
		TAT3	0.922
		TAT4	1.100
		Bridge	0.164
	-		4.000

Table S2. DFT-calculated NBO charges on individual fragments for  $1^{n+}$  (n = 1, 2) and  $2^{n+}$  (n = 1-4).

Charge (bold) and localization	Compound 1	Charge (bold) and localization	Compound 2
1+		1+	
TAT1	0.448	Central TAT	0.366
TAT2	0.446	TAT2	0.543
Bridge	0.106	TAT3	0.009
	1.00	TAT4	0.012
		Bridge	0.070
			1.000
2+ (S=3)		2+ (S=3)	
TAT1	1.044	Central TAT	0.320
TAT2	0.895	TAT2	0.08
Bridge	0.061	TAT3	0.775
	2.000	TAT4	0.780
		Bridge	0.117
			2.000
		3+ (S=4)	
		Central TAT	0.349
		TAT2	0.831
	-	TAT3	0.830
		TAT4	0.830
		Bridge	0.160
			3.000
		4+ (S=5)	
		Central TAT	0.899
		TAT2	0.821
		TAT3	0.922
	-	TAT4	1.100
		Bridge	0.164
			4.000

Table S3. DFT-calculated Mulliken spin densities of  $1^{n+}$  (n = 1,2) and  $2^{n+}$  (n = 1-4).



Figure S25. Calculated spin density plots of  $1^+$  (left) and  $1^{2+}$  (right; S=3).



**Figure S26.** Calculated IR spectra of **1** with the angles between the TAT planes fixed at  $0^{\circ}$ ,  $30^{\circ}$ ,  $60^{\circ}$ , and  $90^{\circ}$ , as given in the legend. The figure on the right shows the enlarged section of computed ethynyl C=C stretches.



**Figure S27.** Calculated UV/vis/NIR spectra of **1** with the angles between the TAT planes fixed at 0°, 30°, 60°, and 90°, as given in the legend.



**Figure S28.** Calculated spin densities of **1**<sup>+</sup> with the angles between the TAT planes fixed at 0°, 30°, 60°, and 90°, as given in the legend.



**Figure S29.** TD-DFT calculated UV/vis/NIR spectrum of **1** with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.



**Figure S30.** TD-DFT calculated UV/vis/NIR spectrum of one electron-oxidized 1<sup>+</sup> with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.



**Figure S31.** TD-DFT calculated UV/vis/NIR spectrum of two electron-oxidized 1<sup>2+</sup> (triplet state) with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.



**Figure S32.** TD-DFT calculated UV/vis/NIR spectrum of **2** with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.



**Figure S33.** TD-DFT calculated UV/vis/NIR spectrum of one electron-oxidized **2**<sup>+</sup> with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.



**Figure S34.** TD-DFT calculated UV/vis/NIR spectrum of two electron-oxidized **2**<sup>2+</sup> (triplet state) with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.



**Figure S35.** TD-DFT calculated UV/vis/NIR spectrum of three electron-oxidized **2**<sup>3+</sup> (quartet state) with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.



Figure S36. DFT-calculated UV/vis/NIR spectrum of 2<sup>4+</sup> in the quintet (S=5 in purple), and in the triplet state (S=3 in blue).



**Figure S37.** TD-DFT calculated UV/vis/NIR spectrum of four electron-oxidized **2**<sup>4+</sup> (quintet state) with electron density difference maps (blue: electron density loss; red: electron density gain) for the individual transitions. Contributing MOs and band assignments are also provided.

#### **STM Measurements**



**Figure S38.** A series of STM images representing all observed spatial orientations for different configurations of molecules of compound **1** on Ag(111) found within this study (5 x 5 nm<sup>2</sup>, U = 10 mV, I = 100 pA). Adsorption geometries include following combinations of configurations of the TAT moieties: *1R-2R*, *1S-2S*, *1R-2S*, *2R-1S*, *2R*, *1S-1S*, *2S-2S*, *1S-1R*, *2S-2R*. For the *1R-2R* and the *1S-2S* combinations, the adsorption configurations i-iii were the most abundant ones. For the *1R-2S/2R-1S* combinations, all shown adsorption configurations were equally abundant. The overall abundances of *2R-2R*, *1S-1S*, *2S-2S*, *1S-2R*, *2S-2R* were much lower compared to *1R-2R*, *1S-2S*, *1R-2S/2R-1S*.



**Figure S39.** STM image of a  $1S^{\alpha}-2R^{\alpha}$  configuration of a compound **1** molecule (4.75 × 4.75 nm<sup>2</sup>, I = 100 pA, U = 10 mV) together with the  $\Delta z(t)$ -trace of low-bias switching including the dwell time histogram. Parameters for the  $\Delta z(t)$ -trace measurement are: U = 50 mV; I = 500 pA. The tip position for the time trace measurement is marked by the encircled green cross in the STM image.

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