SUPPORTING INFORMATION

Phenyl-Annulated peri-Acenoacenes From

Anthanthrene Derivatives

Frédéric Lirette,^a Ali Darvish, ^a Zheng Zhou,^b Zheng Wei,^b Lukas Renn,^c Marina A. Petrukhina,^b R. Thomas Weitz,^c Jean-François Morin^a

 ^a Département de chimie and Centre de Recherche sur les Matériaux Avancés (CERMA), 1045 Ave de la Médecine, Université Laval, Québec, Canada GIV 0A6
 ^b Department of Chemistry, University at Albany, State University of New York, 1400 Washington Avenue, Albany, New York 12222-0100, USA
 ^c 1st Institute of Physics, Faculty of Physics, Georg-August-University, Göttingen, Germany and International Center for Advanced Studies of Energy Conversion (ICASEC), University of Göttingen, Göttingen, Germany

Corresponding author: jean-francois.morin@chm.ulaval.ca

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Apparatus

A Varian Inova AS400 spectrometer (Varian, Palo Alto, USA) at 400 MHz and an Agilent DD2 500 MHz were used to perform all NMR analyses. All peaks are reported on a ppm scale (δ), identified as m (multiplet), s (singlet), d (doublet), t (triplet) and dd (doublet of doublets). They are reported relatively to the residual solvent peak. The coupling constant (J) values are reported in hertz (Hz). HRMS (high-resolution mass spectroscopy) analyses were achieved on an Agilent 6210 TOF-LCMS instrument utilizing an APPI ion source (Agilent Technologies, Toronto, Canada). Absorption properties of the compounds were measured in a 1 cm path length quartz cells using a Cary 7000 spectrophotometer (varian diode-array apparatus). Fluorescence properties were measured in a 1 cm path length quartz cell using a Cary eclipse variant fluorometer. A Solartron 1287 potentiostat was used to perform cyclic voltammetry and differential pulse voltammetry. Platinum wires was use as electrodes at a scan rate of 50 mV s⁻¹. Ag/Ag⁺ (0.01 M AgNO₃ in dichloromethane) in an anhydrous nitrogen-purged solution of 0.1 and Μ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in dry dichloromethane was use as the reference electrode. All spectroelectrochemical measurements were performed with a honeycomb spectroelectrochemical cell kit from Pine Research. Gold electrodes were used with a Ag/AgNO₃ reference electrode. All measurements were performed in dichloromethane with *n*-Bu₄NPF₆ as the electrolyte.

For chemical reduction: All manipulations were carried out using break-and-seal and glove-box techniques under an atmosphere of argon.^[1] The UV–vis absorption spectra were recorded on a Thermo Scientific Evolution 201 UV–visible Spectrophotometer. The ¹H

NMR spectra were measured using Bruker Ascend-500 spectrometer (500 MHz for ¹H) and referenced to the resonances of THF- d_8 .

Chemicals

Chemical reagents were used as received and were ordered from Sigma–Aldrich Co. Canada and Oakwood Products Inc.

For chemical reduction: Tetrahydrofuran (THF) and hexanes (Sigma-Aldrich Co.) were dried over Na/benzophenone and distilled prior to use. Tetrahydrofuran- d_8 (\geq 99.5 atom %D, Sigma Aldrich) was dried over NaK2 alloy and vacuum-transferred. Cesium and 18-crown-6 ether were purchased from Sigma-Aldrich Co. and used as received.

Experimental section



Compound 1a: 4,10-dibromo-6,12-bis(triisopropylsilylethynyl)anthanthrene (2.26 g, 15.1 mmol) and lithium hydroxide monohydrate (660 mg, 15.7 mmol) were added to a screw-capped pressure vessel. 1,4-dioxane (30 mL) and water (5 mL) were added. The mixture was degassed with a flow of nitrogen for 15 min. Tris(dibenzylideneacetone) dipalladium(0) (173 mg, 0.19 mmol) and SPhos (310 mg, 0.75 mmol) were added. The mixture mixture was purged three times with nitrogen and heated at 80 °C for 16 h. The mixture

was diluted with chloroform, boiled and activated carbon was added. The organic layer was filtered through Celite and a short pad of silica. The solvent was removed under reduced pressure. The resulting solid was washed with diethyl ether to afford the desired compound as an orange solid (1,94 g, 61%). ¹H NMR (400 MHz, chloroform-*d*) δ 9.92 (d, J = 2.9 Hz, 2H), 9.19 (d, J = 8.1 Hz, 2H), 8.87 (s, 2H), 8.26 (d, J = 7.8 Hz, 2H), 8.19 (t, J = 7.9 Hz, 2H), 7.99 (d, J = 7.5 Hz, 2H), 7.88 – 7.81 (m, 2H), 7.78 – 7.68 (m, 4H), 1.33 – 1.16 (m, 42H). ¹³C NMR (126 MHz, chloroform-*d*) δ 191.77, 191.71, 143.83, 143.80, 137.56, 135.15, 135.13, 134.09, 134.05, 132.00, 131.88, 131.79, 131.74, 131.18, 129.11, 128.72, 127.50, 127.49, 127.18, 126.37, 124.97, 122.41, 121.54, 117.91, 105.54, 103.57, 18.87, 11.49. HRMS (APPI+): C₅₈H₆₀O₂Si₂ [M*]⁺ 844.4132; found, 844.4126.



Compound 1b: A screw-capped pressure vessel under nitrogen was charged with 4,10bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,12-bis(octyloxy)anthanthrene (1.50 g, 1.91 mmol), 2-bromobenzaldehyde (1.06)5.7 mmol), g, bis(triphenylphosphine)palladium(II) dichloride (134 0.19 mmol) mg, and triphenylphosphine (100 mg, 0.38 mmol). The mixture was purged and degassed with a flow of nitrogen for 30 min. Degassed toluene (22.5 mL) and a degassed aqueous solution of 2 M K₂CO₃ (12.5 mL) were added. The mixture was heated at 110 °C for 16 hours. Dichloromethane was added and the organic layer was washed with brine and filtered on a short pad of silica. The solvent was evaporated under reduced pressure and the crude product recrystallized from CHCl₃/EtOH to afford the desired compound as a yellow solid (1.18 g, 83%). ¹H NMR (500 MHz, chloroform-*d*) δ 9.97 (dd, *J* = 3.1, 0.8 Hz, 2H), 8.86 (ddd, *J* = 8.2, 1.9, 1.0 Hz, 2H), 8.49 (d, *J* = 0.9 Hz, 2H), 8.28 (dd, *J* = 8.0, 1.4 Hz, 2H), 8.12 (td, *J* = 7.9, 1.5 Hz, 2H), 7.90 – 7.84 (m, 4H), 7.78 – 7.72 (m, 4H), 4.41 (td, *J* = 6.6, 4.5 Hz, 4H), 2.13 (p, *J* = 6.8 Hz, 4H), 1.75 – 1.64 (m, 4H), 1.46 (dq, *J* = 9.0, 6.8 Hz, 4H), 1.41 – 1.24 (m, 12H), 0.91 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (126 MHz, chloroform-*d*) δ 192.10, 192.05, 150.13, 144.39, 144.35, 135.74, 135.32, 135.29, 134.23, 134.20, 132.52, 131.88, 131.84, 128.64, 127.51, 127.50, 126.22, 125.97, 124.49, 124.28, 123.79, 123.78, 121.42, 121.34, 119.98, 76.90, 76.88, 31.83, 30.74, 29.53, 29.32, 26.25, 22.69, 14.14. HRMS (APPI+): C₅₂H₅₃O₄ [M+H]⁺ 741.3944; found, 741.3938.

General procedure for compounds 2:

Dry THF (30 mL), 4 eq of triisopropylsilylacetylene and 4 eq of 1.6 M *n*-BuLi or 4 eq of 1 M 2-mesitylmagnesium bromide were added to a round-bottom flask under inert atmosphere in a dry ice/acetone bath. The mixture was stirred for 30 min at -78 °C. Compound **1a** or **1b** was directly added to the solution. The reaction was stirred for 3 h at room temperature. The mixture was extracted with dichloromethane and washed with HCl 2M and NH₄Cl sat., dried with MgSO₄, filtered and the solvent was removed under reduced pressure. The crude product was solubilized in dry dichloromethane (20 mL) in a round-bottom flask under inert atmosphere and a few drops of BF₃·OEt₂ were added. The mixture was stirred for an hour at room temperature before it was quenched and precipitated with MeOH. The product was washed and filtered with methanol. The crude mixture was solubilized in dry toluene (5 to 20 mL) and DDQ (2 eq) was added. The reaction was stirred

at room temperature for 2 hours, then quenched with methanol. The organic layer was collected and the solvent was evaporated under reduced pressure.



Compound 2a: 170 mg of starting material. After general procedure, the crude product was purified by column chromatography (silica gel, dichloromethane/hexanes 2:98 v/v) to afford the desired compound as a deep purple solid (32 mg, 14%). ¹H NMR 12.23 [mM] (500 MHz, chloroform-*d*) δ 10.26 (s, 2H), 9.15 (d, *J* = 8.3 Hz, 2H), 8.87 (d, *J* = 9.4 Hz, 2H), 8.80 (d, *J* = 9.5 Hz, 2H), 8.69 (d, *J* = 8.0 Hz, 2H), 7.91 – 7.83 (m, 2H), 7.80 (t, *J* = 7.4 Hz, 2H), 1.52 – 1.47 (m, 42H), 1.43 – 1.38 (m, 42H). ¹³C NMR (126 MHz, chloroform-*d*) δ 133.98, 132.59, 130.93, 129.10, 128.65, 128.44, 127.39, 127.23, 127.05, 126.91, 123.16, 121.97, 120.84, 120.17, 119.46, 117.34, 117.14, 104.83, 104.59, 104.48, 104.23, 19.20, 19.05, 11.85, 11.74. HRMS (APPI+): C₈₀H₉₉Si₄ [M+H]⁺ 1171.6824; found, 1171.6818.



Compound 2b: 400 mg of starting material. After general procedure, the crude compound was purified by column chromatography (silica gel, chloroform/hexanes 1:5 v/v) and washed with methanol and filtered to afford the desired compound as a dark red solid (94)

mg, 19%). ¹H NMR (500 MHz, chloroform-*d*) δ 10.82 (s, 2H), 9.55 (d, J = 8.3 Hz, 2H), 8.63 (d, J = 9.6 Hz, 2H), 7.97 – 7.86 (m, 2H), 7.80 – 7.69 (m, 4H), 7.64 (d, J = 9.6 Hz, 2H), 7.22 (s, 4H), 2.55 (s, 6H), 1.93 (s, 12H), 1.47 – 1.43 (m, 42H). ¹³C NMR (126 MHz, chloroform-*d*) δ 137.82, 137.54, 135.98, 134.69, 130.87, 129.68, 129.56, 128.54, 128.50, 127.95, 127.87, 127.72, 127.45, 126.95, 126.77, 123.80, 123.54, 122.14, 120.87, 120.63, 116.48, 104.30, 103.85, 21.38, 20.25, 19.15, 11.75. HRMS (APPI+): C₇₆H₇₉Si₂ [M+H]⁺ 1047.5720; found, 1047.5715.



Compound 2c: 148 mg of starting material. After general procedure, the crude product was purified by column chromatography (alumina, dichloromethane/hexanes 3:7 v/v) to afford the desired compound as a deep purple solid (43 mg, 20%). ¹H NMR 9.6 [mM] (500 MHz, chloroform-*d*) δ 9.79 (s, 2H), 9.06 (dd, *J* = 6.5, 3.1 Hz, 2H), 8.90 – 8.81 (m, 2H), 8.59 (d, *J* = 9.5 Hz, 2H), 8.33 (d, *J* = 9.5 Hz, 2H), 7.87 – 7.82 (m, 4H), 4.36 (t, *J* = 6.2 Hz, 4H), 2.31 – 2.18 (m, 4H), 1.89 (p, *J* = 7.5 Hz, 4H), 1.65 – 1.58 (m, 4H), 1.53 (t, *J* = 7.3 Hz, 4H), 1.49 – 1.38 (m, 50H), 1.12 – 0.88 (m, 6H)... ¹³C NMR (126 MHz, chloroform-*d*) δ 151.23, 139.76, 133.28, 131.33, 128.68, 127.47, 127.21, 127.12, 127.09, 126.47, 124.48, 123.89, 123.84, 123.12, 122.50, 121.63, 118.50, 115.48, 114.00, 104.83, 103.70, 32.02, 30.99, 29.81, 29.60, 29.34, 26.91, 22.82, 19.09, 14.21, 11.75. HRMS (APPI+): C₇₄H₉₁O₂Si₂ [M+H]⁺ 1067.6558; found, 1067.6552.



Compound 2d: 400 mg of starting material. After general procedure, the crude compound was purified by column chromatography (silica gel, chloroform/hexanes 1:5 v/v) and washed with methanol and triturated with 150 mL of a 1/1 DCM/hexanes solution and filtered to afford the desired compound as a red solid (161 mg, 32%). ¹H NMR (400 MHz, chloroform-*d*) δ 10.36 (s, 2H), 9.47 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 9.7 Hz, 2H), 7.99 – 7.88 (m, 2H), 7.83 – 7.67 (m, 4H), 7.48 (d, *J* = 9.7 Hz, 2H), 7.19 (s, 4H), 4.56 (t, *J* = 6.4 Hz, 4H), 2.53 (s, 6H), 2.30 (p, *J* = 6.4 Hz, 4H), 2.11 – 1.84 (m, 16H), 1.70 – 1.47 (m, 8H), 1.44 – 1.35 (m, 8H), 1.04 – 0.89 (m, 6H). ¹³C NMR (126 MHz, chloroform-*d*) δ 150.73, 137.82, 137.34, 134.87, 133.97, 130.99, 129.47, 128.46, 128.11, 127.71, 127.26, 126.78, 126.66, 126.38, 125.15, 124.83, 123.55, 123.02, 122.87, 122.69, 119.68, 113.94, 31.93, 31.07, 29.78, 29.70, 29.53, 26.88, 22.76, 21.32, 20.25, 14.14. HRMS (APPI+): C₇₀H₇₁O₂ [M+H]⁺ 943.5454; found, 943.5449.



Compound [{ $Cs^+(18\text{-crown-6})_2$ }₂($2a^{2^-}$)]: Hexanes (2.0 mL) was added to a customized glass system containing **2a** (5.0 mg, 0.0043 mmol) and excess Cs metal (5.0 mg, 0.038

mmol). The reaction mixture was stirred at 25 °C under argon for 24 hours in a closed system. The initial color was blue (neutral ligand), it changed to purple after 1 hour and deepened to dark brown after 4 hours. The resulting dark-brown suspension was filtered to afford a dark-brown precipitate (and an almost colorless filtrate). The solid was dissolved in THF (1.3 mL), the solution was filtered and layered with hexanes (1.5 mL) containing 18-crown-6 ether (5.0 mg, 0.019 mmol). The ampule was sealed and stored at 5 °C. Darkbrown needles were deposited after 14 days. Yield: 3.3 mg, 30%. ¹H NMR (500 MHz, THF-*d*₈, ppm): δ 7.92 (d, 2H), 7.53 (d, 6H), 7.15 (s, 2H), 6.23 (m, 2H), 4.75 (m, 2H), 1.54–1.55 (m, 12H), 1.00–1.02 (m, 72H). UV-vis (THF, nm): λ_{max} 451.

NMR Spectra

Compound 1a



Fig. S1: ¹H NMR spectrum of compound 1a in CDCl₃ at 400 MHz



Fig. S2: ¹³C NMR spectrum of compound 1a in CDCl₃ at 126 MHz

Compound 1b



Fig. S3: ¹H NMR spectrum of compound 1b in CDCl₃ at 500 MHz



Fig. S4: 13 C NMR spectrum of compound 1b in CDCl₃ at 126 MHz

Compound 2a



Fig. S5: ¹H NMR spectrum of compound 2a 12.23 [mM] in CDCl₃ at MHz



Fig. S6: ¹³C NMR spectrum of compound 2a 18.35 [mM] in CDCl₃ at 126 MHz

Compound 2b



Fig. S7: ¹H NMR spectrum of compound 2b in CDCl₃ at 500 MHz



Fig. S8: ¹³C NMR spectrum of compound 2b in CDCl₃ at 126 MHz

Compound 2c



Fig. S9: ¹H NMR spectrum of compound 2c 9.6 [mM] in CDCl₃ at MHz



Fig. S10: ¹³C NMR spectrum of compound 2c in CDCl₃ at 126 MHz

Compound 2d



Fig. S11: ¹H NMR spectrum of compound 2d in CDCl₃ at MHz



Fig. S12: ¹³C NMR spectrum of compound 2d in CDCl₃ at 126 MHz

Compound $[{Cs^+(18-crown-6)_2}_2(2a^{2-})]$

Sample preparation: THF- d_8 (0.6 mL) was added to an NMR tube containing 5 mg of crystals of [{Cs⁺(18-crown-6)₂}₂(**2a**²⁻)]. The tube was sealed under argon, and the ¹H NMR spectrum was collected at 25 °C.



Fig. S13: ¹H NMR spectrum of [$\{Cs^+(18 \text{-crown-6})_2\}_2(2a^{2-})$] in THF- d_8 at 25 °C.

Note: The crystalline product is only sparingly soluble in THF.

UV-visible absorption spectra



Figure S14: UV-vis spectrum in solution (CHCl₃, solid line) and in solid state (dashed line) of compound 2a



Figure S15: UV-vis spectrum in solution (CHCl₃, solid line) and in solid state (dashed line) of compound **2b**



Figure S16: UV-vis spectrum in solution (CHCl₃, solid line) and in solid state (dashed line) of compound 2d



Fig. S17: UV-vis spectrum of $[{Cs^+(18 \text{-crown-6})_2}_2(2a^{2-})]$ in THF at 25 °C

NMR aggregation studies



Compound 2a

 Table S1: Chemical shifts of aromatic protons at different concentrations in CDCl3 and association constants of compound 2a

| Conc [mM] | δНа | δHb | δНс | δHd | δНе | δHf | δHg |
|-----------|--------------|-------|-------|-------|-------|-------|-------|
| 39.85 | 10.044 | 8.87 | 8.789 | 9.009 | 7.841 | 7.738 | 8.566 |
| 18.35 | 10.181 | 8.869 | 8.794 | 9.097 | 7.865 | 7.777 | 8.645 |
| 12.23 | 10.261 | 8.87 | 8.799 | 9.147 | 7.877 | 7.805 | 8.692 |
| 9.17 | 10.304 | 8.872 | 8.802 | 9.173 | 7.887 | 7.822 | 8.718 |
| 7.34 | 10.329 | 8.873 | 8.804 | 9.188 | 7.892 | 7.828 | 8.733 |
| 3.67 | 10.439 | 8.876 | 8.812 | 9.257 | 7.913 | 7.867 | 8.799 |
| 1.83 | 10.541 | 8.88 | 8.82 | 9.321 | 7.933 | 7.901 | 8.861 |
| 1.22 | 10.588 | 8.881 | 8.823 | 9.351 | 7.943 | 7.917 | 8.889 |
| 0.92 | 10.617 | 8.882 | 8.826 | 9.369 | 7.947 | 7.929 | 8.908 |
| 0.61 | 10.644 | 8.884 | 8.828 | 9.388 | 7.955 | 7.936 | 8.924 |
| 0.46 | 10.659 | 8.884 | 8.829 | 9.396 | 7.958 | 7.941 | 8.933 |
| 0.37 | 10.667 | 8.884 | 8.83 | 9.401 | 7.961 | 7.943 | 8.938 |
| δm | 10.709 | 8.888 | 8.835 | 9.427 | 7.970 | 7.960 | 8.965 |
| ± | 0.007 | 0.002 | 0.001 | 0.005 | 0.001 | 0.002 | 0.004 |
| ба | 9.682 | 8.863 | 8.770 | 8.784 | 7.782 | 7.620 | 8.357 |
| ± | 0.03 | 0.002 | 0.001 | 0.02 | 0.003 | 0.008 | 0.01 |
| K (M-1) | 122 | 505 | 230 | 123 | 163 | 134 | 131 |
| ± | 11 | 240 | 21 | 12 | 11 | 11 | 11 |
| | 135 ± 17 | | | | | | |

*Values from H_b and H_c have not been considered in the average



Figure S18: Concentration vs. aromatic protons chemical shift of compound 2a

Table S2: Chemical shifts of aromatic protons at different concentrations in $CDCl_3$ andassociation constants of compound 2c

| Conc | δHa | δHb | δНс | δHd | δНе | ðΗf | δHg |
|---------|--------|-------|-------|------------|-------|-------|-------|
| [mM] | | | | | | | |
| 25.6 | 9.723 | 8.574 | 8.302 | 9.012 | 7.826 | 7.826 | 8.816 |
| 23 | 9.725 | 8.574 | 8.3 | 9.02 | 7.827 | 7.827 | 8.821 |
| 19.2 | 9.745 | 8.579 | 8.31 | 9.03 | 7.831 | 7.831 | 8.824 |
| 9.6 | 9.795 | 8.591 | 8.331 | 9.062 | 7.843 | 7.843 | 8.836 |
| 7.68 | 9.847 | 8.604 | 8.354 | 9.094 | 7.856 | 7.856 | 8.851 |
| 3.84 | 10.002 | 8.642 | 8.421 | 9.186 | 7.893 | 7.893 | 8.887 |
| 1.92 | 10.114 | 8.669 | 8.465 | 9.261 | 7.921 | 7.921 | 8.916 |
| 1.28 | 10.167 | 8.681 | 8.49 | 9.292 | 7.933 | 7.933 | 8.928 |
| 0.96 | 10.197 | 8.689 | 8.503 | 9.311 | 7.94 | 7.94 | 8.937 |
| 0.64 | 10.229 | 8.696 | 8.517 | 9.331 | 7.948 | 7.948 | 8.945 |
| 0.48 | 10.244 | 8.7 | 8.523 | 9.342 | 7.952 | 7.952 | 8.949 |
| 0.384 | 10.252 | 8.701 | 8.526 | 9.346 | 7.954 | 7.954 | 8.951 |
| δm | 10.35 | 8.72 | 8.57 | 9.41 | 7.98 | 7.98 | 8.97 |
| ± | 0.03 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.01 |
| ба | 9.39 | 8.49 | 8.16 | 8.81 | 7.75 | 7.75 | 8.74 |
| ± | 0.05 | 0.01 | 0.02 | 0.03 | 0.01 | 0.01 | 0.01 |
| K (M-1) | 253 | 244 | 255 | 258 | 257 | 257 | 259 |
| ± | 70 | 70 | 71 | 67 | 72 | 72 | 67 |
| | | | | 255 ± 70 | | | |



Figure S19: Concentration vs. aromatic protons' chemical shift of compound 2c

Electrochemistry

Platinum wires were use as electrodes with a scan rate of 50 mV s⁻¹. Ag/Ag⁺ (0.01 M AgNO₃ in dichloromethane) in an anhydrous and nitrogen-purged solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in dry dichloromethane was use as the reference electrode. The HOMO and LUMO energy levels were determined from the first maximum and first minimum of the differential pulse voltammetry experiment versus the redox coupling Fc/Fc⁺.



Fig. S20: Top: Cyclic voltammogram of 2a. Bottom: Differential pulse voltammogram of
2a. All potentials are corrected to the Fc/Fc⁺ redox couple in CH₂Cl₂ with Bu₄NPF₆ (0.1
M) as the electrolyte.



Fig. S21: Top: Cyclic voltammogram of 2b. Bottom: Differential pulse voltammogram of
2b. All potentials are corrected to the Fc/Fc⁺ redox couple in CH₂Cl₂ with Bu₄NPF₆ (0.1
M) as the electrolyte.



Fig. S22: Top: Cyclic voltammogram of 2c. Bottom: Differential pulse voltammogram of
2c. All potentials are corrected to the Fc/Fc⁺ redox couple in CH₂Cl₂ with Bu₄NPF₆ (0.1
M) as the electrolyte.



Fig. S23: Top: Cyclic voltammogram of 2d. Bottom: Differential pulse voltammogram of
2d. All potentials are corrected to the Fc/Fc⁺ redox couple in CH₂Cl₂ with Bu₄NPF₆ (0.1
M) as the electrolyte.

Spectroelectrochemistry

All spectroelectrochemical measurements were performed with a honeycomb spectroelectrochemical cell kit from Pine Research. Gold electrodes were used with a $Ag/AgNO_3$ reference electrode. All measurements were performed in dichloromethane with *n*-Bu₄NPF₆ as the electrolyte.



Fig. S24: Absorption spectrum of 2a in the neutral, oxidized and bis-oxidized states in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as the electrolyte.



Fig. S25: Absorption spectrum of 2a in the neutral and reduced states in CH₂Cl₂ with Bu₄NPF₆ (0.1 M) as the electrolyte.



Fig. S26: Absorption spectrum of 2b in in the neutral, oxidized and bis-oxidized states in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as the electrolyte.



Fig. S27: Absorption spectrum of 2b in the neutral and reduced states in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as the electrolyte.



Fig. S28: Absorption spectrum of 2c in the neutral, oxidized and bis-oxidized states in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as the electrolyte.



Fig. S29: Absorption spectrum of 2d in the neutral, oxidized and bis-oxidized states in CH_2Cl_2 with Bu_4NPF_6 (0.1 M) as the electrolyte.

Crystal Structure Details

Data collection of $[{Cs^+(18\text{-}crown-6)_2}_2(2a^{2^-})]$ ·THF was performed at 100(2) K on a Huber Kappa system with a DECTRIS PILATUS3 X 2M(CdTe) pixel array detector using ϕ scans (synchrotron radiation at $\lambda = 0.49594$ Å) located at the Advanced Photon Source. Argonne National Laboratory (NSF's ChemMatCARS. Sector 15. Beamline 15-ID-D). The dataset's reduction and integration were performed with the Bruker software package SAINT (version 8.38A).^[2] Data were corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).^[3] The structure was solved by SHELXT (version 2018/2)^[4] and refined by full-matrix least-squares procedures using the Bruker SHELXTL (version 2018/3)^[5] software package through the OLEX2 graphical interface.^[6] All non-hydrogen atoms. including those in the disordered parts. were refined anisotropically. Hydrogen atoms were included in idealized positions for structure factor calculations with $U_{iso}(H) = 1.2 U_{eq}(C)$ and $U_{iso}(H) = 1.5 U_{eq}(C)$ for methyl groups. In the structure model. two 18-crown-6 molecules and two trimethylsilyl groups were found to be disordered. The disordered molecules and groups were modeled with two orientations with their relative occupancies refined. The geometries of the disordered parts were restrained to be similar. They were also restrained to have the same U_{ij} components. with a standard uncertainty of 0.01 Å². In each unit cell. two THF solvent molecules were found to be severely disordered and removed by the Olex2's solvent mask subroutine.^[7] The total void volume was 333.0 Å³. equivalent to 4.91 % of the unit cell's total volume. Further crystal and data collection details are listed in Table S3.

| Compound | $[{Cs^+(18-crown-6)_2}_2(2^{2-})]$ ·THF |
|---|---|
| Empirical formula | $C_{132}H_{202}Cs_2O_{25}Si_4$ |
| Formula weight | 2567.10 |
| Temperature (K) | 100(2) |
| Wavelength (Å) | 0.49594 |
| Crystal system | Monoclinic |
| Space group | P2/c |
| <i>a</i> (Å) | 14.770(3) |
| <i>b</i> (Å) | 19.188(4) |
| <i>c</i> (Å) | 25.019(5) |
| α (°) | 90.00 |
| β (°) | 106.906(3) |
| $\gamma(^{\circ})$ | 90.00 |
| $V(Å^3)$ | 6784(2) |
| Ζ | 2 |
| $\rho_{\text{calcd}} \left(g \cdot \text{cm}^{-3} \right)$ | 1.257 |
| μ (mm ⁻¹) | 0.254 |
| <i>F</i> (000) | 2720 |
| Crystal size (mm) | 0.003×0.004×0.010 |
| θ range for data collection (°) | 0.949-17.254 |
| Reflections collected | 123258 |
| Independent reflections | 12080 |
| | $[R_{\rm int} = 0.1539]$ |
| Transmission factors (min/max) | 0.5385/0.6725 |
| Data/restraints/params. | 12080/2572/1185 |
| $R1.^{a} wR2^{b} (I > 2\sigma(I))$ | 0.1172. 0.3336 |
| $R1.^{a} wR2^{b}$ (all data) | 0.1778. 0.3795 |
| Quality-of-fit ^c | 1.278 |

 Table S3: Crystal data and structure refinement parameters.

 $R_{\rm int} = \overline{\Sigma |F_{\rm o}^2 - \langle F_{\rm o}^2 \rangle|} / \Sigma |F_{\rm o}^2|$

^a $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b $wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]$. ^cQuality-of-fit = $[\Sigma [w(F_o^2 - F_c^2)^2] / (N_{obs} - N_{params})]^{\frac{1}{2}}$. based on all data.



Fig. S30: ORTEP drawing of the asymmetric unit of $[{Cs^+(18\text{-}crown-6)_2}_2(2a^{2^-})]$ with thermal ellipsoids at 40% probability level. H-atoms are omitted for clarity. Both Cs⁺ ions sit in special positions and are half-occupied. The color scheme used: C grey. O red. Si gold. Cs dark-green.



Fig. S31: Crystal structure of $[{Cs^+(18\text{-}crown-6)_2}_2(2a^{2^-})]$ in a space-filling model.



Fig. S32: The $2a^{2-}$ core in ball-and-stick and space-filling models.

Thin film morphology



Fig. S33: Thin film morphology of the samples used for the charge transport measurements visualized by atomic force microscopy. a) Compound 2a was evaporated onto a Si/SiO₂ wafer which was passivated with an ODTS SAM.
b) Compound 2c was spincoated directly onto the Si/SiO₂ wafer. The AFM images reveal a mostly amorphous film for compound 2a, whereas compound 2c arranges in a polycrystalline thin film.

Charge transport measurements



Fig. S34: Charge transport measurements of compound 2c measured in a vacuum at room temperature. The measurements display very similar results as the measurements in compound 2a.
a) The output curve shows close to ideal p-type charge transport.
b) Linear-regime transfer curve and c) the corresponding charge carrier mobility.



Fig. S35: Temperature dependent charge transport measurements of compound 2a. Linear-regime transfer curves measured at different temperatures displayed as a a) linear and b) logarithmic plot. c) The corresponding mobilities show improved charge transport at higher temperatures with a maximum mobility of $\mu_{lin} \approx 2.6 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 400 K, which suggests a thermally activated hopping transport. At low temperatures a freeze-out of charge carriers can be observed and below 250 K it was not possible to measure any charge transport. d) Following an Arrhenius approach the activation energy was evaluated as $E_A = 220 \text{ meV}$.



Fig. S36: Temperature dependent charge transport measurements of compound 2c. Linear-regime transfer curves measured at different temperatures displayed as a a) linear and b) logarithmic plot. c) The corresponding mobilities show similar results compared to the temperature dependent measurements in compound 2a (Fig. S35) with an improved charge transport at higher temperatures. d) Following an Arrhenius approach the activation energy was evaluated as $E_A = 170$ meV.

DFT Calculations

DFT calculations for the geometry optimization as well as frequency optimization of compounds **2a-d** were carried out with Gaussian 09 suites^[8] at the B3LYP/6-31G(d,p) level of theory.

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