Supporting Information for:

Redox, Transmetalation, and Stacking Properties of Tetrathiafulvalene-2,3,6,7-tetrathiolate Bridged Tin, Nickel, and Palladium Compounds

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General Methods

All manipulations were performed under an inert atmosphere of dry N2 using a Schlenk line or MBraun UNIlab glovebox unless otherwise noted. Elemental analyses (C, H, N) were performed by Midwest Microlabs. Acetone was sparged with N2 and stored in the glovebox over 4 Å molecular sieves. MeOH was dried with NaOH overnight, distilled, transferred into the glovebox and stored over 4 Å molecular sieves. All other solvents used in molecular synthesis were initially dried and purged with N2 on a solvent purification system from Pure Process Technology. THF was further stirred with liquid NaK alloy and then filtered through activated alumina and stored over 4 Å molecular sieves. Other solvents were passed through activated alumina and stored over 4 Å molecular sieves. Unless noted, all other chemicals were purchased from commercial sources and used as received. TTFtPG (PG=C2H4CN),1 dppeNiCl22 and [Fe][BARF4]3 were prepared as previously described. [FeAcO][BARF4] and [FeBzO][BARF4] were prepared using the same synthetic method as [Fe][BARF4] but stirred at room temperature instead of boiling DCM during [BARF4]⁻ anion exchange to avoid decomposition of FeAcO or FeBzO cations. Nuclear Magnetic Resonance (NMR) spectra for 1H, 13C, 31P, 119Sn were recorded on either Bruker DRX-400 or AVANCE-500 spectrometers. Tetramethyltin in CD2Cl2 and 85% phosphoric acid were used as reference for 119Sn and 31P NMR spectra, respectively. Note that 119Sn NMR shifts can be affected by concentration, so caution must be used in interpreting any reported shifts.4 All experiments were performed at room temperature. Residual solvent peaks were referenced and labelled as the deuterated solvents. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker Elexsys E500 spectrometer with an Oxford ESR 900 X-band cryostat and a Bruker Cold-Edge Stinger. Spin quantitation was performed by double integration of derivative spectra and compared to a standard CuII solution. Electrochemical experiments were performed using cyclic voltammetry (CV) on a BASi Epsilon potentiostat/galvanostat. A glassy carbon working electrode, platinum wire counter electrode, and silver wire pseudoreference electrode were used for all measurements. FeCp2+/FeCp2 was used as an internal reference. Infrared spectra were recorded on a Bruker Tensor II FTIR spectrometer with MCT detector operated at 77 K. Data were processed and background corrected with OPUS software (version 7.5). An additional manual correction for scattering was also applied. Samples were prepared under N2 by grinding solid 1-10 with Nujol, placed between two KBr crystal plates, and measured in air under ambient conditions. UV-visible-NIR absorption spectra were recorded on a Shimadzu UV-3600 Plus spectrophotometer. All solutions were prepared in an N2-filled glovebox and transferred into a 1×1 cm quartz cuvette for room-temperature measurements in sequence. The spectrum of pure DCM in the same cuvette was used for background calibration. A Hellma Analytics Excalibur Immersion Probe with a 10 mm path length (artikel no. 661-202-10-S-46) was used for variable-temperature UV-vis-NIR spectroscopic measurements and the solution of 5 in DCM was transferred to a custom-made, airtight apparatus equipped with 14/20 ground glass joint, #2 size ground glass plug and #25 size threaded Teflon plug for the immersion probe to go through which was sealed with a Teflon coated O-ring. The entire apparatus was sealed inside the glovebox before connecting to the spectrophotometer. The temperature was adjusted by adding dry ice into an isopropanol bath and each temperature point was the average of reads before and after a spectroscopic scan. Solid-state magnetic measurements were carried out with a MPMS-XL Quantum Design SQUID operating at temperatures between 1.8 and 400 K and dc magnetic fields ranging from -2 to 2 T. Measurements were performed on powder samples of 5 in sealed plastic heat-shrink tubing, whose diamagnetic contribution was corrected after experiment. All measured samples were diamagnetic in the solid state. Evans method on a CDCl3 solution of 5 at room temperature was used for solution phase magnetic
measurements. The diffraction data were measured at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Mo-target micro-focus X-ray tube ($\lambda = 0.71073$ Å). Data reduction and integration were performed with the Bruker APEX3 software package (Bruker AXS, version 2015.5-2, 2015). Alternatively, data were also collected at the Advanced Photon Source of Argonne National Laboratory (beamline 15-ID-B,C,D) using X-ray radiation with a wavelength of $\lambda = 0.41328$ Å at 110 K. Data were scaled and corrected for absorption effects using the multi-scan procedure as implemented in SADABS (Bruker AXS, version 2014/5, 2015, part of Bruker APEX3 software package). The structure was solved by the dual method implemented in SHELXT$^5$ and refined by a full-matrix least-squares procedure using OLEX2$^{36}$ software package (XL refinement program version 2014/7$^7$). Suitable crystals were mounted on a cryo-loop and transferred into the cold nitrogen stream of the Bruker D8 VENTURE diffractometer. Most of the hydrogen atoms were generated by geometrical considerations and constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Disorder was modeled with common constraints or restraints.
Synthetic Procedures

Since compounds, 3, 5, 6, 8, and 10 can be prepared via multiple approaches, the primary bulk procedure is described in detail below while other alternative ways are reported with product formation verified by NMR spectroscopic monitoring of the reactions.

Safety note: organotin compounds are toxic. Appropriate PPE, labeling, and disposal techniques must be employed.

TTFtt(SnBu2)2 (1)
TTFtt(C2H4CN)4 (11 mmol, 5.9 g) and NaOMe (86.4 mmol, 4.75 g) were added into a 500 mL Schlenk flask with dry MeOH (27 mL) in a N2-filled glovebox. The resulting suspension was stirred at room temperature overnight until all solids disappeared and a homogeneous dark red solution was observed. This solution was transferred into a sealed Schlenk flask and brought outside the glovebox. Volatiles were then removed under vacuum. Note that the higher vacuum from a Schlenk line is required to remove the volatile byproducts of the deprotection. When the solution was dried, the Schlenk flask was sealed and transferred back into the glovebox. The remaining solid was re-dissolved in MeOH (144 mL) and treated with Bu2SnCl2 (43.2 mmol, 13.1 g) in MeOH (36 mL). After the mixture was stirred over an additional night at room temperature, MeOH was removed again under Schlenk line vacuum. The remaining solid was extracted with DCM and filtered sequentially through Celite and silica. After flash silica chromatography with DCM or THF, all of the filtrate was collected and dried under vacuum to provide red solid. The crude solid was washed with 10 mL of cold acetone and dried under vacuum to yield 1 as a pink powder (3.5 g, yield: 41 %). Crystals were prepared by either recrystallization from boiling MeCN followed by cooling to −35 °C or DCM/Et2O vapor diffusion overnight at −35 °C. Crystals suitable for single crystal XRD were selected from the MeCN recrystallization. 1H NMR (400 MHz, CDCl3, 298 K): δ 0.94 (3H, t, J = 0.94 Hz), 1.38 (2H, q, J = 1.38 Hz), 1.76 (4H, m, J = 1.75 Hz) ppm. 119Sn{1H} NMR (149 MHz, CDCl3, 298 K): δ 220.89 ppm. 13C{1H} NMR (126 MHz, CD2Cl2, 298 K) δ 13.61, 24.89, 26.77, 28.14, 111.59, 117.89 ppm. UV-vis-NIR (DCM, nm): 328.5, 515.6. IR (Nujol, KBr plates, cm−1): 2724(m), 2668(m), 1304(m), 1288(m), 1242(w), 1173(m), 1146(m), 1075(m), 1016(w), 979(m), 966(w), 936(w), 885(s), 866(m), 846(w), 773(s), 722(s), 666(m). Anal. calc. for 1, C22H36S8Sn2: C 33.26%, H 4.57%, N 0%; found: purification via DCM/Et2O vapor diffusion: C 33.24%, H 4.52%, N none; purification via MeCN recrystallization: C 32.89%, H 4.66%, N none.

[TTFtt(SnBu2)2][BArF4] (2)
1 (0.03 mmol, 24 mg) was treated with [Fc][BArF4] (0.027 mmol, 28 mg) in Et2O (1 mL). After stirring for 10 mins, the solution was filtered through Celite and concentrated to about 0.5 mL volume. Petroleum-ether (4 mL) was added dropwise leading to the formation of a brown precipitate. The yellow petroleum-ether supernatant was decanted gently. The solid was washed with fresh petroleum-ether and dried under vacuum to provide 2 as a brown solid (35 mg, 78 %). Suitable crystals for single crystal XRD were obtained by Et2O/petroleum-ether layered diffusion at −35 °C for 3 days. UV-vis-NIR (DCM, nm): 384.1, 428.6, 465.4, 490.8, 591.0, 1053.7. IR (Nujol, KBr plates, cm−1): 3174(m), 2728(m), 1650(m), 1608(w), 1309(s), 1276(s), 1110(bs), 1003(w), 966(w), 887(m), 848(m), 838(m), 818(w), 769(w), 741(m), 720(s), 680(m), 668(m). EPR (THF, 15K, 9.63 GHz, 6 μW): g eff = 2.008. Anal. calc. for 2, C54H48BF24S8Sn2: C 39.13%, H 2.92%, N 0%; found: C 38.85%, H 3.03%, N 0%.
Compound 1 (0.03 mmol, 24 mg) was treated with [Fc\(^{\text{BzO}}\)][BAr\(^{\text{F}_4}\)] (0.066 mmol, 76 mg) in THF (1 mL). After stirring for 5 mins, the dark green solution was filtered through Celite and concentrated to about 0.5 mL volume. Petroleum-ether (4 mL) was added dropwise leading to the formation of a dark green oil-like precipitate and the orange supernatant was decanted gently. The precipitate was washed with fresh petroleum-ether (2 mL) for 3 times, redissolved in THF (1 mL), and reprecipitated by adding petroleum-ether (4 mL). The petroleum-ether supernatant was removed and the solid was washed with fresh petroleum-ether 3 times and dried under vacuum. The green solid was then collected and recrystallized from THF/petroleum-ether layered diffusion at \(-35\,^\circ\text{C}\) for 2 days to obtain 3 as dark green-brown crystals (56 mg, 74\%). The resulting crystals are suitable for single crystal XRD. \(^1\text{H}\) NMR (400 MHz, CDCl\(_3\), 298 K): \(\delta 0.94\) (3H, bt), 1.42 (2H, bs), 1.77 (4H, bs), 1.98 (s, THF adduct), 3.87 (s, THF adduct), 7.52 (s, [BAr\(^{\text{F}_4}\)]\(^-\)), 7.72 (s, [BAr\(^{\text{F}_4}\)]\(^-\)) ppm. \(^{119}\text{Sn}\{^{1}\text{H}\}\) NMR (149 MHz, CDCl\(_3\), 298 K): \(\delta -192.70\) ppm. \(^{13}\text{C}\{^{1}\text{H}\}\) NMR (126 MHz, CD\(_2\)Cl\(_2\), 298 K): \(\delta 13.52\), 26.83, 28.07, 117.95 (m, [BAr\(^{\text{F}_4}\)]\(^-\)), 125.04 (q, [BAr\(^{\text{F}_4}\)]\(^-\)), 129.36 (q, [BAr\(^{\text{F}_4}\)]\(^-\)), 162.21 (q, [BAr\(^{\text{F}_4}\)]\(^-\)) ppm. UV-vis-NIR (DCM, nm): 469.5, 940.5. IR (Nujol, KBr plates, cm\(^{-1}\)): 2723(w), 2666(w), 1651(s), 1608(m), 1352(s), 1278(s), 1237(w), 1119(bs), 886(m), 839(m), 742(m), 721(m), 682(m), 670(m). Anal. calc. for \(\text{3}\cdot\text{2THF}\): C 42.36\%, H 2.87\%, N 0\%; found: C 41.91\%, H 3.05\%, N none. Note that the \(^1\text{H}\) NMR spectrum of crystalline 3 in CDCl\(_3\) shows broad peaks and uneven splitting patterns which suggests a small amount of radical may be present (Fig. S2). Similarly, the TTF peaks in the \(^{13}\text{C}\) NMR are not visible, again likely due to exchange with some small amount of a radical species.

If the same reaction is finished in Et\(_2\)O instead of THF, then the product is dark purple throughout the workup and \(\text{3}\cdot\text{2Fc}\(^{\text{BzO}}\) is obtained as dark purple crystals from a Et\(_2\)O/petroleum ether layered diffusion at \(-35\,^\circ\text{C}\) for 3 days (Figure S53). Transmetalation of \(\text{3}\cdot\text{2Fc}\(^{\text{BzO}}\) is also facile as judged by \(^1\text{H}\) NMR.

Alternative method: Compound 3 can also be generated by oxidation of 2 with 1.1 equivalents of [Fc\(^{\text{BzO}}\)][BAr\(^{\text{F}_4}\)] in THF and purified as described above.

(dppeNi)_2TTFtt (4)

(dppeNiCl\(_2\) (0.2 mmol, 105 mg) was suspended in DCM (3 mL) and mixed with 1 (0.1 mmol, 80 mg) in DCM (3 mL) and then stirred for 15 mins. The yellow-orange precipitate was separated by centrifugation (additional THF can help the separation). The solid was washed with THF (3 mL) 3 times and dried under vacuum. 4 was obtained as an orange powder (115 mg, 93\%). IR (Nujol, KBr plates, cm\(^{-1}\)): 2724(w), 2671(w), 1305(m), 1185(w), 1159(w), 1101(m), 1073(w), 1025 (w), 996(w), 971(w), 907(m), 873(w), 820(w), 764(w), 744(m), 690(s), 649(m). Anal. calc. for 4, C\(_{58}\)H\(_{48}\)Ni\(_2\)P\(_4\)S\(_8\): C 56.05\%, H 3.89\%, N 0\%; found: C 55.79\%, H 4.11\%, N none.

[(dppeNi)_2TTFtt][BAr\(^{\text{F}_4}\)] (5)

Compound 4 (0.03 mmol, 37.2 mg) was treated with [Fc][BAr\(^{\text{F}_4}\)] (0.027 mmol, 29 mg) in DCM (3 mL) and stirred for 10 mins. After filtration through Celite, the filtrate was concentrated to about 0.5 mL and slow addition of petroleum-ether (4 mL) caused a brown precipitate to form. The petroleum-ether supernatant was removed and the precipitate was washed with fresh petroleum-ether 3 times and dried under vacuum to provide 5 as a brown solid (50 mg, 88\%). Brown crystals were obtained via PhCl/petroleum-ether vapor diffusion at room temperature for one day (32 mg, S8
1H NMR (400 MHz, CDCl3, 298 K): δ 2.44 (bs, dppe), 7.51 (s, [BArF4]4−), 7.61 (bs, dppe), 7.63 (bs, dppe), 7.71 (s, [BArF4]4−), 8.00 (bs, dppe) ppm. UV-vis-NIR (DCM, nm): 429.9, 457.4, 491.1, 570.3, 1268.4. IR (Nujol, KBr plates, cm−1): 2721(w), 2664(w), 1274(s), 1118(bs), 1098(m), 1028(w), 998(w), 968(w), 932(w), 878(m), 838(m), 817(w), 772(w), 743(m), 680(m). Evans method (CDCl3, room temperature): μeff = 1.19 B.M. EPR (THF, 15K, 9.63 GHz, 0.2 μW): geff = 2.013, 2.007, 2.003. Anal. calc. for C90H60BF24Ni2P4S8: C 51.33%, H 2.87%, N 0%; found: C 51.64%, H 2.98%, N none.

Alternative method: Complex 5 was also prepared through the metalation of 2 with 2 equivalents of dppeNiCl2 in DCM as indicated by 1H NMR spectra (Figures S13 and S14).

[(dppeNi)2TTFtt][BArF4]2 (6)
To simplify the synthesis, 3 was generated in situ and used directly for the preparation of 6. Compound 1 (0.01 mmol, 8 mg) was treated with [Fc BzO][BArF4] (0.022 mmol, 25 mg) in Et2O (0.5 mL). The resulting dark purple solution was added to dppeNiCl2 (0.02 mmol, 11 mg) which over 3 mins resulted in the dissolution of the yellow dppeNiCl2. The solution was then filtered through Celite and concentrated to about 0.5 mL volume. Petroleum-ether (4 mL) was added to the resulting dark purple solution to precipitate the product. After gently removing the orange supernatant and washing with fresh petroleum-ether several times, the purple-red powder was dried under vacuum. Compound 6 can then be obtained as purple-red crystals by PhCl/petroleum-ether vapor diffusion at room temperature for 2 days (24 mg, 81 %). 1H NMR (400 MHz, CDCl3, 298 K): δ 2.47 (d, dppe), 7.48 (s, [BArF4]4−), 7.50-7.60(m, dppe), 7.61-7.70 (m, dppe), 7.70 (s, [BArF4]4−) ppm. 31P{1H} NMR (162 MHz, CDCl3, 298 K): δ 62.95 ppm. 13C{1H} NMR (126 MHz, CD2Cl2, 298 K) δ 27.00 (t, dppe), 117.95 (m, [BArF4]4−), 125.04 (q, [BArF4]4−), 126.79 (t, dppe), 129.36 (q, [BArF4]4−), 130.10(t, dppe), 133.53 (s, dppe), 133.71 (t, dppe) 156.09 (s, TTFtt), 162.21 (q, [BArF4]4−), 173.46 (s,TTFtt) ppm. UV-vis-NIR (DCM, nm):515.6, 1039.5. IR (Nujol, KBr plates, cm−1): 2723(w), 2670(w), 1305(m), 1185(w), 1159(w), 1101(m), 1073(w), 1025 (w), 996(w), 971(w), 894(m), 876(m), 843(w), 822(w), 766(w), 743(m), 690(s), 649(m). Anal. calc. for C122H72B2F48Ni2P4S8: C 49.35%, H 2.44%, N 0%; found: C 49.02%, H 2.69%, N none.

Alternative method 1: Complex 6 can be obtained by direct metalation of isolated 3 or 3•2FcBzO with 2 equivalents of dppeNiCl2. The products were verified by 1H NMR spectra (Figures S15-S19).

Alternative method 2: 6 was also prepared by oxidation of 4 with 2 equivalents [FcAcO][BArF4] or 5 with 1 equivalent [FcAcO][BArF4] in Et2O and the purification is the same as above (Figure S20).

(dppePd)2TTFtt (7)
dppePdCl2 (0.06 mmol, 35 mg) was partially dissolved in DCM (2 mL) and mixed with 1 (0.029 mmol, 23 mg) in DCM (2 mL) and then stirred for 15 mins. The shiny pink precipitate was separated by centrifugation. The solid was washed with DCM (3 mL) 3 times and dried under vacuum. 7 was obtained as a pink powder (38 mg, 99 %). IR (Nujol, KBr plates, cm−1): 2724(w), 2671(w), 1305(m), 1185(w), 1159(w), 1101(m), 1073(w), 1025 (w), 996(w), 971(w), 894(m), 876(m), 843(w), 822(w), 766(w), 747(m), 690(s), 649(m). Anal. calc. for C58.5H49ClPd2P4S8: C 50.89%, H 3.58%, N 0 %; found: C 50.70%, H 3.68%, N none. Note that the combustion analysis was calculated for a half of DCM solvate since the collected product was precipitate directly from DCM and washed with DCM.
Compound 1 (0.025 mmol, 20 mg) was treated with [Fc][BAR₄] (0.025 mmol, 27 mg) in Et₂O (5 mL). The resulting dark brown solution was added to dppePdCl₂ (0.05 mmol, 29 mg) which over 5 mins resulted in the dissolution of the pale yellow dppePdCl₂. After filtration through Celite, the filtrate was concentrated to about 0.5 mL and slow addition of petroleum-ether (4 mL) caused a brown precipitate to form. The petroleum-ether supernatant was removed. After being washed with fresh petroleum-ether 3 times and dried under vacuum, brown crystals were obtained via PhCl/petroleum-ether vapor diffusion at room temperature for one day (28 mg, 51%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 2.72 (bs, dppe), 7.50 (s, [BAR₄]), 7.58 (bs, dppe), 7.66 (bs, dppe), 7.71 (s, [BAR₄]), 8.00 (bs, dppe) ppm. UV-vis-NIR (DCM, nm): 429.9, 457.4, 491.1, 570.3, 1078.1, 1271.4. IR (Nujol, KBr plates, cm⁻¹): 2721(w), 2664(w), 1274(s), 1165(w), 1118(bs), 1098(m), 1028(w), 998(w), 968(w), 932(w), 887.4(w), 878(w), 838(m), 772(w), 743(m), 684(m). EPR (THF, 10K, 9.63 GHz, 1 μW): gₑff = 2.013, 2.008, 2.002. Anal. calc. for 8, C₉₀H₆₀BF₂₄Pd₂P₄S₈: C 49.10%, H 2.75%, N 0%; found: C 48.88%, H 2.77%, N none.

Alternative method: Compound 7 (0.006 mmol, 10 mg) was treated with [Fc][BAR₄] (0.057 mmol, 6 mg) in Et₂O (2 mL) and stirred for 10 mins. Complex 8 was then purified with the same procedure as outlined above. (Figure S21).

(dppePd)₂TTFtt (9)
dppePdCl₂ (0.06 mmol, 44 mg) was dissolved in DCM (3 mL) and mixed with 1 (0.03 mmol, 24 mg) in DCM (2 mL) and then stirred for 15 mins. The orange precipitate was separated by centrifugation. The solid was washed with DCM (3 mL) 3 times and dried under vacuum. 9 was obtained as an orange powder (46 mg, 94%). IR (Nujol, KBr plates, cm⁻¹): 2724(w), 2671(w), 1667(m), 1301(m), 1185(w), 1165(m), 1101(m), 1087(s), 1028 (m), 996(w), 971(w), 901(m), 873(w), 820(w), 746(m), 690(s), 632(m). Anal. calc. for 9·DCM, C₇₅H₅₈Cl₂Pd₂P₄S₈: C 51.92%, H 3.37%, N 0%; found: C 51.32%, H 3.37%, N non. Note that the combustion analysis was calculated for a DCM solvate since the collected product was precipitate directly from DCM and washed with DCM.

[(dppePd)₂TTFtt][BAR₄] (10)
Compound 1 (0.009 mmol, 7.2 mg) was treated with [Fc][BAR₄] (0.009 mmol, 9.5 mg) in Et₂O (2 mL). The resulting dark brown solution was added to dppePdCl₂ (0.02 mmol, 15 mg) which over 5 mins resulted in the dissolution of the red dppePdCl₂. After filtration through Celite, the filtrate was concentrated to about 0.5 mL and slow addition of petroleum-ether (4 mL) caused a brown precipitate to form. The petroleum-ether supernatant was removed. After being washed with fresh petroleum-ether 3 times and dried under vacuum, brown crystals were obtained via PhCl/petroleum-ether vapor diffusion at room temperature for one day (18 mg, 80%). ¹H NMR (400 MHz, CDCl₃, 298 K): δ 4.25 (bs, dppe), 4.55 (bs, dppe), 7.28-7.35 (m, dppe), 7.52 (s, [BAR₄]), 7.71 (s, [BAR₄]) ppm. UV-vis-NIR (DCM, nm): 429.9, 457.4, 491.1, 570.3, 1342.3. IR (Nujol, KBr plates, cm⁻¹): 2721(w), 2664(w), 1667(m), 1353(s), 1274(s), 1157(m), 1118(bs), 1089(m), 1035(w), 1028(w), 998(w), 968(w), 924(w), 885(m), 838(m), 821(m), 743(m), 711(m), 692(m), 680(m), 668(m), 628(m). EPR (THF, 10K, 9.63 GHz, 0.4 μW): gₑff = 2.014, 2.008, 2.001. Anal. calc. for 10, C₁₀₆H₆₈BF₂₄Fe₂Pd₂P₄S₈: C 50.66%, H 2.73%, N 0%; found: C 50.78%, H 2.86%, N none.
Alternative method: Compound 9 (0.005 mmol, 8 mg) was treated with [Fc][BARF₄] (0.045 mmol, 4.5 mg) in Et₂O (2 mL) and stirred for 10 mins. Complex 10 was then purified with the same procedure as outlined above. However, the product collected via the direct oxidation is typically associated with an impurity, likely 9, although pure crystals can be grown (Figure S22).
NMR Spectra
1. $^1$H NMR Spectra

Figure S1. $^1$H NMR spectrum of 1 in CDCl$_3$.

Figure S2. $^1$H NMR spectrum of 3•2THF in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of 5 in CDCl$_3$.

Figure S4. $^1$H NMR spectrum of 6 in CDCl$_3$. 
Figure S5. $^1$H NMR spectrum of 8 in CDCl$_3$. 
Figure S6. $^1$H NMR spectrum of 10 in CDCl$_3$. 
2. $^{13}$C NMR Spectra

Figure S7. $^{13}$C$\{^1$H$\}$ NMR spectrum of 1 in 0.5 mL THF + 0.1 mL CD$_2$Cl$_2$. 
Figure S8. $^{13}$C$\{^1$H$\}$ NMR spectrum of 3 in CD$_2$Cl$_2$. Due to a possible exchange with a small amount of radicals, the peaks of TTF and the first carbon of butyl groups connecting to the Sn atoms are not visible.
Figure S9. $^{13}$C$\{^1\text{H}\}$ NMR spectrum of 6 in CD$_2$Cl$_2$. The spectrum from 118-136 ppm is expanded and shown in the inset graph.
3. $^{31}$P NMR Spectra

![31P NMR spectrum of 6 in CDCl3.]

Figure S10. $^{31}$P{$^1$H} NMR spectrum of 6 in CDCl3.

4. $^{119}$Sn NMR Spectra

![119Sn NMR spectrum of 1 in CDCl3.]

Figure S11. $^{119}$Sn{$^1$H} NMR spectrum of 1 in CDCl3.
Figure S12. $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of 3 in CDCl$_3$.  

**Alternative synthesis methods monitored by $^1\text{H}$ NMR experiments**

1. Synthesis of 5 by metatation of 2

Figure S13. $^1\text{H}$ NMR spectrum in CDCl$_3$ of metatation products of 2. Note the residual dppeNiCl$_2$ was due to an excess of this reagent added to the reaction.

S20
Figure S14. $^1$H NMR spectra in CDCl$_3$ monitoring the metalation process of 2.

2. Synthesis of 6 by metalation of 3•2THF

Figure S15. $^1$H NMR spectrum in CDCl$_3$ of metalation products of 3•2THF.
Figure S16. $^1$H NMR spectra in CDCl$_3$ monitoring the metalation process of 3•2THF.

3. Synthesis of 6 by metalation of 3•2Fe$^{BzO}$

Figure S17. $^1$H NMR spectrum in CDCl$_3$ of metation products of 3•2Fe$^{BzO}$ after petroleum-ether extraction.
Figure S18. $^1$H NMR spectrum in CDCl$_3$ of metalation products of $3\cdot2$Fe$^{BzO}$ in extracted petroleum-ether portion.

Figure S19. $^1$H NMR spectra in CDCl$_3$ monitoring the metalation process of $3\cdot2$Fe$^{BzO}$. 

S23
4. Synthesis of 6 by oxidation of 4.

Figure S20. $^1$H NMR spectrum in CDCl$_3$ of oxidation products of 4.
5. Synthesis of 8 by oxidation of 7.

Figure S21. $^1$H NMR spectrum in CDCl$_3$ of 8 via oxidation of 7.
6. Synthesis of 10 by oxidation of 9.

Figure S22. $^1$H NMR spectrum in CDCl$_3$ of 10 via oxidation of 9. Two additional peaks at 4.18 and 4.40 ppm are assigned as probably mixed 9.
Air stability test of 6 monitored by $^1$H and $^{31}$P NMR spectra

**Figure S23.** $^1$H NMR spectrum of 6 in CDCl$_3$ before and after air exposure for 35 mins and sealed placement overnight.
Figure S24. $^{31}$P{${}^1$H} NMR spectrum of 6 in CDCl$_3$ after air exposure for 35 mins and sealed placement overnight.

**EPR Spectra**

Figure S25. X-band EPR spectrum of 2 collected on a 3 mM solution in THF at 15 K.
Microwave frequency: 9.63 GHz, microwave power: 6 μW, and $g_{\text{eff}} = 2.008$.

Figure S26. X-band EPR spectrum of 5 collected on a 1 mM solution in THF at 15 K. Microwave frequency: 9.63 GHz, microwave power: 0.2 μW, and $g_{\text{eff}} = 2.013, 2.007, 2.003$. 

S29
Figure S27. X-band EPR spectrum of \textbf{8} collected on a 1 mM solution in THF at 10 K. Microwave frequency: 9.63 GHz, microwave power: 1 μW, and $g_{\text{eff}} = 2.013, 2.008, 2.002$.

Figure S28. X-band EPR spectrum of \textbf{10} collected on a 1 mM solution in THF at 10 K. Microwave frequency: 9.63 GHz, microwave power: 0.4 μW, and $g_{\text{eff}} = 2.014, 2.008, 2.001$. 
Infrared Spectra

Figure S29. Infrared transmittance spectrum of 1 as a Nujol mull. Note CO$_2$ signals at 2350 cm$^{-1}$.

Figure S30. Infrared transmittance spectrum of 2 as a Nujol mull.
Figure S31. Infrared transmittance spectrum of 3 as a Nujol mull.

Figure S32. Infrared transmittance spectrum of 4 as a Nujol mull. Note CO₂ signals at 2350 cm⁻¹.
Figure S33. Infrared transmittance spectrum of 5 as a Nujol mull. Note CO$_2$ signals at 2350 cm$^{-1}$.

Figure S34. Infrared transmittance spectrum of 6 as a Nujol mull.
Figure S35. Infrared transmittance spectrum of 7 as a Nujol mull.
Figure S36. Infrared transmittance spectrum of 8 as a Nujol mull.
Figure S37. Infrared transmittance spectrum of 9 as a Nujol mull.
Figure S38. Infrared transmittance spectrum of 10 as a Nujol mull.

Electrochemical Measurements
Figure S39. Cyclic voltammogram of 1 in 0.01 M [Na][BArF$_4$] in DCM and Et$_2$O (10:1). Arrow denotes scan direction. Scan rate: 0.1V/s.

Figure S40. Cyclic voltammogram of 8 in 0.1 M [TBA][PF$_6$] in DCM. Arrow denotes scan direction. Scan rate: 0.1V/s.
Figure S41. Cyclic voltammogram of 10 in 0.1 M [TBA][PF$_6$] in DCM. Arrow denotes scan direction. Scan rate: 0.1V/s.

Optical Spectroscopy

Figure S42. UV-vis-NIR absorption spectra of 2 and 5 in DCM. Concentration: 50 μM.
Figure S43. UV-vis-NIR absorption spectra of 3 and 6 in DCM. Concentration: 50 μM.
**Figure S44.** UV-vis-NIR absorption spectra of 5, 6, 8 and 10 in DCM. Concentration: about 50 μM. Besides the same absorption at 1271.4 nm as 5, 8 has a shoulder absorption peak at 1078.1 nm. Since the energy of this band is obviously lower than the same feature in dicationic 6 (1039.5 nm) and no TTF-dication UV-vis peak is observed, this shoulder peak likely arises from some other speciation due to π-dimers or oligomers.
Figure S45. Variable-temperature UV-vis-NIR absorption spectra of 5 in DCM. Concentration: about 30 μM. Due to the strong background absorptions of the instrument setup and DCM, the peaks in the NIR region are somewhat convoluted. However, a clear continuous increase of NIR feature with cooling suggests the equilibrium shifts to more π-dimers when the temperature decreases.

X-ray Crystallography

1. Crystallographic Data

Table S1. Crystallographic data for complexes 1, 2 and 3.

|                  | 1•2MeCN       | 2•0.5THF•0.5MeCN | 3•2THF      |
|------------------|---------------|------------------|-------------|
| Empirical formula| C_{26}H_{42}N_{2}S_{8}Sn_{2} | C_{57}H_{53.5}BF_{24}N_{0.5}O_{0.5}S_{8}Sn_{2} | C_{102}H_{92}B_{2}F_{48}O_{4}S_{8}Sn_{2} |
| Formula weight   | 876.47        | 1714.17          | 2809.23     |
| Temperature/K    | 100(2)        | 100(2)           | 100(2)      |
| Crystal system   | triclinic     | monoclinic       | triclinic   |
| Space group      | P-1           | P2_1/c           | P-1         |
| a/Å              | 7.7711(3)     | 9.5804(15)       | 12.9111(17) |
| b/Å              | 10.3961(4)    | 23.505(4)        | 15.863(2)   |
| c/Å              | 12.6341(5)    | 30.294(5)        | 16.368(2)   |
| α/°              | 113.062(2)    | 90               | 88.537(3)   |
| Parameter               | Value 1  | Value 2  | Value 3  |
|-------------------------|----------|----------|----------|
| β/°                     | 96.284(2)| 97.920(4)| 88.979(3)|
| γ/°                     | 98.114(2)| 90       | 69.195(3)|
| Volume/Å³               | 914.39(6)| 6756.8(18)| 3132.5(7)|
| Z                       | 1        | 4        | 1        |
| ρcalc g/cm³             | 1.592    | 1.685    | 1.489    |
| μ/mm⁻¹                  | 1.842    | 1.091    | 0.649    |
| F(000)                  | 440.0    | 3408.0   | 1406.0   |
| Crystal size/mm³        | 0.32 × 0.18 × 0.07 | 0.24 × 0.04 × 0.04 | 0.29 × 0.24 × 0.04 |
| Radiation               | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.384 to 52.974 | 4.402 to 44.196 | 4.358 to 50.398 |
| Index ranges            | -9 ≤ h ≤ 9, -12 ≤ k ≤ 13, -9 ≤ h ≤ 10, -24 ≤ k ≤ 24, -15 ≤ h ≤ 15, -18 ≤ k ≤ 18, 15 ≤ l ≤ 15 31 ≤ l ≤ 31, -19 ≤ l ≤ 19 |
| Reflections collected   | 26492    | 103447   | 32479    |
| Independent reflections | 3767 [Rint = 0.0370, Rsigma = 0.0253] | 8304 [Rint = 0.1444, Rsigma = 0.0648] | 11153 [Rint = 0.1152, Rsigma = 0.1068] |
| Data/restraints/parameters | 3767/0/175 | 8304/1098/850 | 11153/487/815 |
| Goodness-of-fit on F²   | 1.081    | 1.065    | 1.087    |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0271, wR₂ = 0.0569 | R₁ = 0.0820, wR₂ = 0.1755 | R₁ = 0.0977, wR₂ = 0.2003 |
| Final R indexes [all data] | R₁ = 0.0343, wR₂ = 0.0590 | R₁ = 0.1244, wR₂ = 0.1992 | R₁ = 0.1437, wR₂ = 0.2241 |
| Largest diff. peak/hole / e Å⁻³ | 1.59/-0.33 | 0.96/-0.94 | 1.40/-0.98 |

**Table S2.** Crystallographic data of complex 3•2FeBzO.

| Parameter               | Value |
|-------------------------|-------|
| Empirical formula       | C₁₂₀H₈₈B₂F₄₈Fe₂O₈S₈Sn₂ |
| Formula weight          | 3101.08 |
| Temperature/K           | 100(2)  |
| Crystal system          | monoclinic |
| Space group             | P2₁/c   |
| a/Å                     | 12.734(2) |
| b/Å                     | 31.568(5) |
| c/Å                     | 18.543(3) |
| α/°                     | 90      |
| β/°                     | 107.358(3) |
| γ/°                     | 90      |
| Volume/Å³               | 7114(2) |
| Z                       | 2       |
Table S3. Crystallographic data of complexes 5 and 6.

|     | 5                                           | 6                                           |
|-----|---------------------------------------------|---------------------------------------------|
|     | C_{122}H_{72}B_{2}F_{48}Ni_{2}P_{4}S_{8}    | C_{90}H_{60}BF_{24}Ni_{2}P_{4}S_{8}         |
| Empirical formula | 2969.19                                     | 2105.97                                     |
| Formula weight     | 100(2)                                      | 100(2)                                      |
| Temperature/K      | monoclinic                                  | triclinic                                   |
| Crystal system     | C2/c                                        | P-1                                         |
| Space group        | 40.752(3)                                   | 14.1624(15)                                 |
| a/Å                 | 18.9850(12)                                 | 18.3974(19)                                 |
| b/Å                 | 17.7197(11)                                 | 20.189(2)                                   |
| c/Å                 | 90                                          | 94.073(2)                                   |
| α/°                 | 107.903(2)                                  | 103.397(2)                                  |
| β/°                 | 90                                          | 106.515(2)                                  |
| γ/°                 |                                             |                                             |
| Volume/Å³           | 13045.5(14)                                 | 4852.8(9)                                   |
| Z                    | 2                                           | 2                                           |
| ρ_{calc}/g/cm³      | 1.512                                       | 1.441                                       |
| μ/mm⁻¹              | 0.582                                       | 0.169                                       |
| F(000)              | 5960.0                                      | 2130.0                                      |
| Crystal size/mm³    | 0.25 × 0.23 × 0.02                          | 0.002 × 0.002 × 0.001                       |
| Radiation           | MoKα (λ = 0.71073)                          | synchrotron (λ = 0.41328)                   |
| 2Θ range for data collection/° | 4.202 to 51.594                           | 1.686 to 31.652                             |
| Index ranges        | -49 ≤ h ≤ 49, -23 ≤ k ≤ 23, -21 ≤ l ≤ -18 ≤ h ≤ 18, -24 ≤ k ≤ 24, -26 ≤ l ≤ 21 | 26                                          |
| Reflections collected | 166738                                     | 141909                                      |
| Independent reflections | 12520 [R_{int} = 0.0661, R_{sigma} = 0.0320] | 22441 [R_{int} = 0.0384, R_{sigma} = 0.0261] |
Table S4. Crystallographic data of complexes 8 and 10.

| 8                  | 10                  |
|--------------------|---------------------|
| **Empirical formula** | C_{540}H_{360}B_{6}F_{144}P_{24}Pd_{12}S_{48} | C_{106}H_{68}BF_{24}Fe_{2}P_{4}Pd_{2}S_{8} |
| **Formula weight**  | 13208.08            | 2513.27              |
| **Temperature/K**  | 100(2)              | 100(2)               |
| **Crystal system**  | triclinic           | triclinic            |
| **Space group**     | P-1                 | P-1                  |
| **a/Å**             | 29.421(4)           | 13.503(3)            |
| **b/Å**             | 31.324(5)           | 19.054(4)            |
| **c/Å**             | 35.123(5)           | 28.239(6)            |
| **α/°**             | 92.011(3)           | 105.082(5)           |
| **β/°**             | 91.984(3)           | 91.975(4)            |
| **γ/°**             | 99.304(3)           | 90.730(5)            |
| **Volume/Å^3**      | 31896(8)            | 7009(3)              |
| **Z**               | 2                   | 2                    |
| **ρ_{calc}/g/cm^3** | 1.375               | 1.191                |
| **μ/mm^-1**         | 0.637               | 0.688                |
| **F(000)**          | 13212.0             | 2514.0               |
| **Crystal size/mm^3** | 0.22 × 0.01 × 0.01 | 0.28 × 0.24 × 0.02   |
| **Radiation**       | MoKα (λ = 0.71073)  | MoKα (λ = 0.71073)   |
| **2Θ range for data collection/°** | 1.162 to 42.074 | 4.29 to 44.728 |
| **Index ranges**    | -29 ≤ h ≤ 29, -31 ≤ k ≤ 31, -35 ≤ l ≤ -14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -30 ≤ l ≤ 35 | -14 ≤ h ≤ 14, -20 ≤ k ≤ 20, -30 ≤ l ≤ 30 |
| **Reflections collected** | 362133        | 59637               |
| **Independent reflections** | 68469 [R_{int} = 0.1554, R_{sigma} = 0.1701] | 17875 [R_{int} = 0.1086, R_{sigma} = 0.1360] |
| **Data/restraints/parameters** | 68469/1269/2177 | 17875/754/1458 |
| **Goodness-of-fit on F^2** | 1.204      | 1.070               |
| **Final R indexes [I>=2σ(I)]** | R_1 = 0.1770, wR_2 = 0.3523 | R_1 = 0.0914, wR_2 = 0.1827 |
| **Final R indexes [all data]** | R_1 = 0.2699, wR_2 = 0.3959 | R_1 = 0.1467, wR_2 = 0.2038 |
| **Largest diff. peak/hole / e Å^-3** | 3.25/-3.71 | 1.25/-1.04 |
2. Molecular planarity diagram for complexes 1, 2, 3, 5 and 6.

Figure S46. Molecular planarity diagram for 1, 2 and 3. [BArF₄] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Sn, grey; S, yellow; O, red; N, blue; C, white.). Disorder is shown.
**Figure S47.** Molecular planarity diagram for 5 and 6. [BARF₄] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Ni, light blue; S, yellow; P, purple; C, white.)

**3. The extended structures of 1, 2, 3, 5, and 6.**

**Figure S48.** Supermolecular structure of 1: 1D chain. The red dash lines represent the intermolecular S-S interactions. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Sn, grey; S, yellow; N, blue; C, white.)
**Figure S49.** The extended structure of 2: dimer unit (a) and 1D chain of dimers (b). The red dash lines represent the intermolecular S-S interactions. [BAr$_4^-$] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Sn, grey; S, yellow; O, red; N, blue; C, white.). Disorder is shown.
**Figure S50.** The molecular structure of 3: the diactionic 3 encompassed by two bulk [BArF₄] anions. H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Sn, grey; S, yellow; F, vivid green; B, light blue; O, red; C, white.). Disorder is shown.

**Figure S51.** The extended structure of 5: ladder-shaped 1D chain. The red dash lines represent the intermolecular S-S interactions. Phenyl groups of dppe, [BArF₄] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Ni, light blue; S, yellow; P, purple; C, white.)
Figure S52. The extended structure of 6: twisted 1D chain. The red dashed lines represent the intermolecular S-S interactions. Phenyl groups of dppe, [BAR̈F4] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Ni, light blue; S, yellow; P, purple; C, white.)
3. Single-crystal X-ray Diffraction Structures of complex 3•2FeBzO, 8 and 10.

Figure S53. Single-crystal X-ray diffraction structures of complex 3•2FeBzO. [BArF$_4$] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Sn, grey; Fe, orange; S, yellow; O, red; C, white.). Disorder is shown.
Figure S54. Single-crystal X-ray diffraction structures of complex 8: a pentamer in 1D chain (a), a perpendicular dimer (b), and a parallel dimer (c). Phenyl groups of dppe, [BArF$_4$] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Pd, light grey; S, yellow; P, purple; C, white.).

Figure S55. Single-crystal X-ray diffraction structure of complex 10 in a dimer unit. The red dashed lines represent the intermolecular S-S interactions. [BArF$_4$] anions and H atoms are omitted for clarity. Ellipsoids are shown at 50% probability. (Pd, light grey; Fe, orange; S, yellow; P, purple; C, white.).

4. Crystallographic Characterization of a Polymorph of 5.
During attempts to obtain crystals of 5, an alternative polymorph was found with an unusual packing interaction. The crystals of this polymorph are extremely unstable and quickly decompose and lose crystallinity. Many attempts failed to provide a better-quality data set. Attempts to collect data at a synchrotron only revealed a different polymorphic form. The polymorph crystallizes in a large unit cell of over 50000 Å$^3$ with many co-crystallized solvent molecules. Dichloromethane is
the only solvent which provides this polymorph out of many variations that have been investigated. Both amorphous solvent regions and heavy disorder of several independent [BArF₄] anionic units led to diffraction only up to ~1.2 Å. Some atoms of the [BArF₄] anions could not be located in the difference Fourier map due to heavy disorder. These [BArF₄] anions were modeled by adding bis(trifluoromethyl)benzene moieties to boron in approximate tetrahedral geometry and utilizing the visible residual electron density of benzene rings for initial placement. After that, these moieties were allowed to freely move as a whole unit with a fixed internal geometry. All atoms of the cationic TTFtt portion were located in the difference Fourier map. This has allowed for accurate assignment of the charge, general 3D packing, and connectivity of the TTFtt units from this data. The coordinates of the TTFtt packing from this solution were then used for further calculations. In the figures below, Ni is blue, P is purple, S is yellow, F is green, B is pink, H is white, and C is grey.

### Table S5. Crystal data and structure refinement for the polymorph of 5.

| Property                  | Value                  |
|---------------------------|------------------------|
| Empirical formula         | C₂₂₅H₁₅₀B₂₅F₆₀Ni₁₅P₁₀S₂₀ |
| Formula weight            | 5264.92                |
| Temperature/K             | 100(2)                 |
| Crystal system            | monoclinic             |
| Space group               | C2/c                   |
| a/Å                       | 53.053(5)              |
| b/Å                       | 21.9471(19)            |
| c/Å                       | 51.656(5)              |
| α/°                       | 90                     |
| β/°                       | 118.338(2)             |
| γ/°                       | 90                     |
| Volume/Å³                 | 52938(8)               |
| Z                         | 8                      |
| ρcalc/g/cm³               | 1.321                  |
| μ/mm⁻¹                    | 0.656                  |
| F(000)                    | 21300.0                |
| Radiation                 | MoKα (λ = 0.71073)     |
| 2Θ range for data collection/° | 4.238 to 35          |
| Index ranges              | -44 ≤ h ≤ 44, -18 ≤ k ≤ 18, -43 ≤ l ≤ 43  |
| Reflections collected     | 187662                 |
| Independent reflections   | 16783 [Rint = 0.1277, Rsigma = 0.0503] |
| Data/restraints/parameters| 16783/1154/761         |
| Final R indexes [I>=2σ (I)] | R₁ = 0.2814, wR₂ = 0.6230 |
| Final R indexes [all data]| R₁ = 0.3436, wR₂ = 0.6770 |
Figure S56. Symmetry-grown unit showing 3 Ni complexes along with 3 [BAR$_4$]$^-$ counterions.

Figure S57. Part of 3D packing showing the growth of a cationic chain.
Figure S58. Diagram showing the orthogonal dimeric stacking of two TTFtt units in the polymorphic version of 5. Note that Ni is green in this figure.

Table S6. Fractional Atomic Coordinates for the polymorph of 5 ($\times 10^4$).

| Atom | x     | y     | z     |
|------|-------|-------|-------|
| Ni1  | 5985.5(9) | -263(2) | 5716.9(10) |
| Ni2  | 3770.8(9) | 2607(2)  | 4764.1(10)  |
| S1   | 5615(2)  | -315(4)  | 5787(2)     |
| S2   | 5765(2)  | 275(4)   | 5312(2)     |
| S3   | 5180(2)  | 855(4)   | 5036(2)     |
| S4   | 5049(2)  | 331(4)   | 5477(2)     |
| S5   | 4496(2)  | 1143(4)  | 5266(2)     |
| S6   | 4556(2)  | 1574(4)  | 4767(2)     |
| S7   | 4063(2)  | 2458(4)  | 4589(2)     |
| S8   | 3983(2)  | 1955(4)  | 5117(2)     |
| P1   | 6226(2)  | -801(5)  | 6106(2)     |
| P2   | 6371(2)  | -287(5)  | 5693(2)     |
| P3   | 3554(2)  | 3302(4)  | 4437(2)     |
| P4   | 3440(2)  | 2739(5)  | 4877(2)     |
| C3   | 6469(11) | 652(16)  | 6744(11)    |
| C4   | 6735(10) | 486(19)  | 6972(8)     |
| C5   | 6848(8)  | -90(20)  | 6972(8)     |
| C6   | 6695(11) | -491(16) | 6743(10)    |
| C1   | 6430(11) | -320(20) | 6515(7)     |
| C2   | 6317(8)  | 250(20)  | 6515(8)     |
| C7   | 5987(9)  | -1440(20)| 6211(12)    |
| C8   | 5921(10) | -1347(16) | 6438(10) |
| C9   | 5737(10) | -1740(20) | 6476(9) |
| C10  | 5619(8)  | -2240(20) | 6287(12) |
| C11  | 5685(9)  | -2332(17) | 6060(10) |
| C12  | 5869(10) | -1940(20) | 6022(9) |
|     |    |    |    |
|-----|----|----|----|
| C13 | 6473(7) | -1283(17) | 6056(5) |
| C14 | 6493(7) | -1099(18) | 5787(5) |
| C15 | 6409(12) | -30(20) | 5316(8) |
| C20 | 6601(9) | 380(20) | 5302(7) |
| C19 | 6581(10) | 531(18) | 5031(10) |
| C18 | 6369(11) | 270(20) | 4775(7) |
| C17 | 6177(9) | -140(20) | 4789(8) |
| C16 | 6197(10) | -295(19) | 5059(12) |
| C22 | 6611(7) | 820(30) | 6072(9) |
| C23 | 6809(11) | 1210(16) | 6282(11) |
| C24 | 7091(9) | 1020(20) | 6453(8) |
| C25 | 7175(7) | 450(20) | 6413(9) |
| C26 | 6977(11) | 56(16) | 6203(10) |
| C21 | 6695(9) | 240(20) | 6033(8) |
| C27 | 3741(9) | 4174(12) | 4452(12) |
| C32 | 3780(9) | 4561(17) | 4261(8) |
| C31 | 3945(10) | 5084(15) | 4368(11) |
| C30 | 4071(8) | 5220(15) | 4666(12) |
| C29 | 4032(10) | 4830(20) | 4858(8) |
| C28 | 3867(11) | 4310(20) | 4750(11) |
| C33 | 3422(12) | 3010(20) | 3996(5) |
| C38 | 3644(9) | 3050(20) | 3925(9) |
| C37 | 3596(10) | 2890(20) | 3645(11) |
| C36 | 3327(12) | 2690(20) | 3436(6) |
| C35 | 3106(9) | 2650(20) | 3506(7) |
| C34 | 3153(10) | 2810(20) | 3786(9) |
| C39 | 3228(4) | 3579(13) | 4461(6) |
| C40 | 3110(5) | 3050(13) | 4552(6) |
| C41 | 3530(12) | 3362(18) | 5228(8) |
| C46 | 3326(9) | 3760(20) | 5225(8) |
| C45 | 3398(10) | 4171(18) | 5455(11) |
| C44 | 3675(12) | 4179(17) | 5689(8) |
| C43 | 3880(8) | 3780(20) | 5692(8) |
| C42 | 3807(11) | 3371(18) | 5462(11) |
| C48 | 3219(10) | 1490(20) | 4812(9) |
| C47 | 3293(10) | 1962(16) | 5015(12) |
| C52 | 3275(9) | 1880(16) | 5272(10) |
| C51 | 3182(10) | 1330(20) | 5327(9) |
| C50 | 3108(10) | 854(13) | 5124(12) |
| C49 | 3126(10) | 936(19) | 4867(10) |
| C53 | 4265(7) | 1722(16) | 5054(8) |
| C54 | 4303(7) | 1895(17) | 4845(8) |
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C55 | 4702(7) | 1111(16) | 5100(8) |
| C56 | 4939(8) | 784(16) | 5184(8) |
| C57 | 5364(7) | 169(16) | 5509(8) |
| C58 | 5449(7) | 396(16) | 5322(8) |
| Ni3 | 4856.3(11) | 2310(3) | 6199.1(13) |
| Ni4 | 4651.3(14) | 4069(3) | 3877.1(16) |
| S9 | 5031(2) | 1992(5) | 5929(2) |
| S10 | 4623(3) | 3042(7) | 5917(3) |
| S11 | 4565(2) | 3432(6) | 5321(3) |
| S12 | 4982(2) | 2522(5) | 5368(2) |
| S13 | 4898(3) | 2943(5) | 4738(3) |
| S14 | 4876(3) | 3309(6) | 4162(3) |
| S15 | 4433(2) | 4374(5) | 4118(3) |
| S16 | 4489(2) | 3884(5) | 4693(2) |
| P5 | 4609(3) | 2301(7) | 6435(3) |
| P6 | 5125.6(12) | 1629(3) | 6556.3(10) |
| P7 | 4428.9(13) | 4747(3) | 3538.6(11) |
| P8 | 4930.4(14) | 3962(3) | 3695.1(12) |
| C63 | 4094(8) | 3900(20) | 6474(10) |
| C64 | 4154(9) | 3301(16) | 6434(9) |
| C59 | 4424(11) | 3148(14) | 6473(10) |
| C60 | 4634(8) | 3590(30) | 6552(10) |
| C61 | 4574(10) | 4190(20) | 6592(9) |
| C62 | 4304(12) | 4345(12) | 6553(10) |
| C65 | 4304(8) | 1566(16) | 6279(11) |
| C66 | 4171(11) | 1610(18) | 5975(12) |
| C67 | 3925(10) | 1270(20) | 5804(8) |
| C68 | 3812(7) | 890(20) | 5938(10) |
| C69 | 3945(9) | 849(18) | 6243(11) |
| C70 | 4191(9) | 1185(19) | 6414(8) |
| C71 | 4854(9) | 2037(14) | 6805(5) |
| C72 | 4992(5) | 1442(15) | 6813(5) |
| C78 | 5498(3) | 510(6) | 6516.2(14) |
| C73 | 5233(3) | 765(5) | 6444.6(15) |
| C74 | 4983(3) | 441(6) | 6273(2) |
| C75 | 4998(3) | -138(6) | 6172(2) |
| C76 | 5263(3) | -393(6) | 6244(2) |
| C77 | 5513(3) | -70(6) | 6415.8(18) |
| C81 | 5946.4(13) | 1875(4) | 7213.4(13) |
| C80 | 5670.5(12) | 1651(3) | 7044.7(10) |
| C79 | 5487.9(12) | 1924(3) | 6777.6(10) |
| C84 | 5581.1(15) | 2421(4) | 6679.3(16) |
|   |      |      |      |
|---|------|------|------|
| C83 | 5856.9(17) | 2646(4) | 6848(2) |
| C82 | 6039.5(14) | 2372(5) | 7115.0(18) |
| C85 | 4715(10) | 2940(20) | 5637(10) |
| C86 | 4897(9) | 2530(20) | 5655(9) |
| C87 | 4735(9) | 3150(20) | 5165(10) |
| C88 | 4728(9) | 3205(19) | 4932(10) |
| C89 | 4575(9) | 3830(20) | 4417(9) |
| C90 | 4772(10) | 3420(20) | 4449(10) |
| C92 | 4086(4) | 5696(5) | 3650.0(14) |
| C91 | 4367(4) | 5591(5) | 3710.1(16) |
| C96 | 4579(4) | 6017(6) | 3869(2) |
| C95 | 4509(4) | 6548(6) | 3968(2) |
| C94 | 4228(4) | 6653(6) | 3908(2) |
| C93 | 4017(4) | 6227(6) | 3748.8(19) |
| C97 | 4053.2(14) | 4235(5) | 3257.0(18) |
| C98 | 3911(3) | 3702(6) | 3254(5) |
| C99 | 3657(3) | 3547(10) | 3005(6) |
| C100 | 3546(2) | 3926(18) | 2760(3) |
| C101 | 3689(2) | 4459(18) | 2764(3) |
| C102 | 3942(2) | 4614(10) | 3012(4) |
| C103 | 4659(5) | 4978(15) | 3384(5) |
| C104 | 4826(8) | 4443(12) | 3372(5) |
| C110 | 4727.3(16) | 2732(6) | 3342.9(15) |
| C105 | 4944.7(16) | 3027(6) | 3583.2(14) |
| C106 | 5192.7(17) | 2713(7) | 3770.2(18) |
| C107 | 5223(2) | 2104(7) | 3717(2) |
| C108 | 5006(2) | 1809(6) | 3477(2) |
| C109 | 4758(2) | 2123(6) | 3289.7(19) |
| C112 | 5552(4) | 4288(4) | 3921(2) |
| C111 | 5326(4) | 4416(4) | 3977(2) |
| C116 | 5365(4) | 4813(6) | 4202(3) |
| C115 | 5631(4) | 5083(6) | 4372(3) |
| C114 | 5857(4) | 4955(6) | 4316(3) |
| C113 | 5817(4) | 4557(5) | 4090(2) |
| F25 | 6429(7) | 4884(13) | 4959(6) |
| F26 | 6676(8) | 4878(13) | 5406(5) |
| F27 | 6364(5) | 4229(15) | 5180(7) |
| F28 | 6916(6) | 2183(10) | 5279(7) |
| F29 | 7293(6) | 2663(17) | 5575(5) |
| F30 | 7256(5) | 2515(16) | 5208(6) |
| C181 | 7470(2) | 6535(4) | 5226(2) |
| F37 | 7794(4) | 5774(7) | 5930.8(18) |
|   |  |   |   |
|---|---|---|---|
| F38 | 7379(4) | 6204(7) | 5784(3) |
| F39 | 7741(4) | 6746(6) | 5831(3) |
| F40 | 7568(4) | 7079(5) | 4702(3) |
| F41 | 7231(3) | 7420(4) | 4790(3) |
| F42 | 7131(4) | 6756(5) | 4440(3) |
| C178 | 7434.9(15) | 5324(4) | 5041.9(16) |
| C179 | 7370.1(19) | 5797(4) | 4839.5(18) |
| C180 | 7387(2) | 6401(4) | 4932(2) |
| C182 | 7535(2) | 6057(5) | 5427(2) |
| C183 | 7518(2) | 5453(4) | 5336.4(16) |
| C184 | 7328(3) | 6913(4) | 4717(3) |
| C185 | 7614(3) | 6196(6) | 5743(2) |
| C190 | 7114(4) | 3289(6) | 5204(4) |
| C191 | 7278(5) | 3639(9) | 5114(7) |
| C186 | 7214(7) | 4252(10) | 5048(8) |
| C187 | 6987(6) | 4515(7) | 5070(7) |
| C188 | 6824(4) | 4165(10) | 5160(6) |
| C189 | 6887(4) | 3552(10) | 5226(5) |
| C192 | 6586(3) | 4503(10) | 5176(4) |
| C193 | 7073(4) | 2674(7) | 5305(4) |
| C197 | 7003(2) | 4786(5) | 3961.4(18) |
| F43 | 7468(4) | 5741(8) | 3970(3) |
| F44 | 7745(3) | 4947(9) | 4139(3) |
| F45 | 7363(3) | 4909(8) | 3710(3) |
| F46 | 6406(2) | 4763(8) | 3656(2) |
| F47 | 6491(3) | 3851(8) | 3844(2) |
| F48 | 6375.8(16) | 4576(9) | 4056(3) |
| C194 | 7262.6(16) | 4677(3) | 4573.8(18) |
| C195 | 6971.1(16) | 4554(4) | 4404.1(19) |
| C196 | 6841.2(19) | 4609(5) | 4098.4(18) |
| C198 | 7294(2) | 4908(5) | 4133(2) |
| C199 | 7425.1(18) | 4855(4) | 4440(2) |
| C200 | 6529(2) | 4453(7) | 3914(2) |
| C201 | 7467(3) | 5123(7) | 3988(3) |
| C205 | 8214.0(19) | 3514(5) | 5350(2) |
| F31 | 7844(3) | 2746(6) | 4650(3) |
| F32 | 7902(3) | 2258(4) | 5041(4) |
| F33 | 8274(3) | 2594(6) | 5011(4) |
| F34 | 8611(2) | 3806(8) | 5927(2) |
| F35 | 8615.5(18) | 4648(7) | 5706(3) |
| F36 | 8361(3) | 4589(8) | 5934(2) |
| C202 | 7711.1(16) | 4207(4) | 5087.3(15) |

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| C203  | 7731.4(19) | 3670(4) | 4954.3(18) |
|-------|------------|---------|------------|
| C204  | 7983(2)    | 3325(4) | 5085(2)    |
| C206  | 8191.0(18) | 4051(5) | 5482.6(19) |
| C207  | 7940.4(17) | 4399(4) | 5352.1(17) |
| C208  | 8001(3)    | 2734(5) | 4947(3)    |
| C209  | 8444(2)    | 4271(7) | 5763(2)    |
| B2    | 7415.0(17) | 4612(4) | 4933.8(18) |
| F7    | 8717(6)    | 5200(17)| 7364(5)    |
| F8    | 8873(5)    | 5234(17)| 7833(5)    |
| F9    | 8473(6)    | 5696(11)| 7539(6)    |
| F10   | 8870(4)    | 3064(17)| 7888(6)    |
| F11   | 8557(7)    | 2496(10)| 7622(6)    |
| F12   | 8579(6)    | 2932(17)| 8028(5)    |
| F13   | 7766(4)    | 3259(15)| 8042(8)    |
| F14   | 7430(6)    | 3952(10)| 7973(7)    |
| F15   | 7394(7)    | 2935(10)| 7985(7)    |
| F16   | 6706(5)    | 2352(15)| 7033(6)    |
| F17   | 6754(8)    | 2754(15)| 6642(4)    |
| F18   | 6971(7)    | 2047(10)| 6889(7)    |
| F19   | 7659(5)    | 1800(14)| 6612(5)    |
| F20   | 8077(4)    | 2035(17)| 6657(6)    |
| F21   | 7700(6)    | 2067(17)| 6227(4)    |
| F22   | 7396(3)    | 4408(13)| 5876(6)    |
| F23   | 7799(5)    | 4801(8) | 6131(7)    |
| F24   | 7757(4)    | 4011(12)| 5885(4)    |
| C149  | 7140(3)    | 5635(6) | 6961(3)    |
| F1    | 6665(4)    | 4751(9) | 6326(4)    |
| F2    | 6826(5)    | 5612(10)| 6252(3)    |
| F3    | 6583(3)    | 5596(10)| 6495(4)    |
| F4    | 7373(4)    | 6574(7) | 7370(4)    |
| F5    | 7391(4)    | 5833(11)| 7658(3)    |
| F6    | 7772(4)    | 6078(10)| 7625(4)    |
| C146  | 7496(5)    | 4642(9) | 7024(5)    |
| C147  | 7236(4)    | 4709(8) | 6767(4)    |
| C148  | 7058(3)    | 5204(6) | 6737(3)    |
| C150  | 7400(3)    | 5564(7) | 7218(3)    |
| C151  | 7579(4)    | 5070(9) | 7250(4)    |
| C152  | 7485(4)    | 6014(8) | 7467(3)    |
| C153  | 6783(4)    | 5290(8) | 6454(3)    |
| C157  | 7200(3)    | 3003(10)| 7399(3)    |
| C158  | 7433(4)    | 3354(11)| 7587(3)    |
| C159  | 7594(5)    | 3660(13)| 7479(5)    |
| Atom | Coordinates |
|------|-------------|
| C154 | 7520(6)     |
| C155 | 7286(6)     |
| C156 | 7126(4)     |
| C160 | 6867(4)     |
| C161 | 7491(4)     |
| C166 | 8456(4)     |
| C167 | 8166(4)     |
| C162 | 8022(4)     |
| C163 | 8168(6)     |
| C164 | 8458(6)     |
| C165 | 8602(3)     |
| C168 | 8639(4)     |
| C169 | 8588(4)     |
| C172 | 7696(5)     |
| C171 | 7687(7)     |
| C170 | 7712(9)     |
| C175 | 7746(8)     |
| C174 | 7756(6)     |
| C173 | 7731(6)     |
| C176 | 7798(4)     |
| C177 | 7666(3)     |
| B1   | 7678(3)     |
| Ni5  | 5834.4(12)  |
| S17  | 5649(3)     |
| S18  | 5623(3)     |
| S19  | 5197(3)     |
| S20  | 5250(3)     |
| P9   | 6131.7(16)  |
| P10  | 5947.0(14)  |
| C120 | 5128(9)     |
| C119 | 5406(11)    |
| C118 | 5634(7)     |
| C117 | 5583(8)     |
| C122 | 5305(11)    |
| C121 | 5078(6)     |
| C124 | 6007.0(15)  |
| C125 | 6063.2(19)  |
| C126 | 6177(3)     |
| C127 | 6234(5)     |
| C128 | 6178(5)     |
| C123 | 6064(2)     |
| C129 | 6264(9)     |
| Ni5  | 5834.4(12)  |
| S17  | 5649(3)     |
| S18  | 5623(3)     |
| S19  | 5197(3)     |
| S20  | 5250(3)     |
| P9   | 6131.7(16)  |
| P10  | 5947.0(14)  |
| C120 | 5128(9)     |
| C119 | 5406(11)    |
| C118 | 5634(7)     |
| C117 | 5583(8)     |
| C122 | 5305(11)    |
| C121 | 5078(6)     |
| C124 | 6007.0(15)  |
| C125 | 6063.2(19)  |
| C126 | 6177(3)     |
| C127 | 6234(5)     |
| C128 | 6178(5)     |
| C123 | 6064(2)     |
| C129 | 6264(9)     |
|    |        |        |        |
|----|--------|--------|--------|
| C130 | 6239(9) | 1716(18) | 5368(8) |
| C136 | 6779.9(19) | 2602(8) | 5862.6(12) |
| C135 | 7029(2) | 2932(11) | 6029.7(18) |
| C134 | 7012(4) | 3540(10) | 6095(3) |
| C133 | 6746(4) | 3817(8) | 5994(4) |
| C132 | 6497(3) | 3486(6) | 5827(3) |
| C131 | 6514(2) | 2879(6) | 5761.4(16) |
| C141 | 5681(7) | 1519(17) | 5934(7) |
| C140 | 5858(7) | 1625(17) | 6232(6) |
| C139 | 6111(7) | 1953(16) | 6323(4) |
| C138 | 6185(7) | 2175(18) | 6117(3) |
| C137 | 6007(6) | 2069(16) | 5819(4) |
| C142 | 5755(5) | 1741(14) | 5728(5) |
| C143 | 5447(7) | 3952(15) | 4988(8) |
| C144 | 5440(8) | 3874(17) | 5189(9) |
| C145 | 5110(6) | 4746(12) | 5017(3) |
| F49  | 4236(9) | 634(18) | 2555(8) |
| F50  | 4469(8) | -89(19) | 2900(8) |
| F51  | 4359(8) | 758(18) | 2976(8) |
| F52  | 5486(7) | 26(9) | 3538(6) |
| F53  | 5573(7) | 930(11) | 3651(5) |
| F54  | 5723(4) | 525(14) | 3390(6) |
| F57A | 5808(10) | 2771(11) | 2301(7) |
| F58A | 6091(4) | 3380(20) | 2637(10) |
| F59A | 5651(9) | 3695(13) | 2258(7) |
| C213 | 4952(4) | 536(13) | 3092(5) |
| C214 | 5219(3) | 776(15) | 3159(5) |
| C215 | 5241(5) | 1240(15) | 2988(7) |
| C210 | 4996(7) | 1466(14) | 2749(7) |
| C211 | 4729(5) | 1226(16) | 2682(6) |
| C212 | 4707(3) | 762(15) | 2853(6) |
| C216 | 5488(3) | 563(9) | 3420(4) |
| C217 | 4436(5) | 480(20) | 2820(11) |
| C221 | 5720(3) | 3317(6) | 2895(3) |
| F1G  | 5464(5) | 3875(9) | 3299(4) |
| F55  | 5613(5) | 3005(10) | 3522(4) |
| F56  | 5914(4) | 3625(9) | 3483(3) |
| F57  | 5645(5) | 3217(12) | 2164(3) |
| F58  | 6048(4) | 2924(12) | 2532(4) |
| F59  | 5896(5) | 3852(10) | 2518(4) |
| C218 | 5311(5) | 2388(10) | 2662(5) |
| C219 | 5376(4) | 2644(9) | 2934(4) |
Computational Methodology

Variational two-electron reduced density matrix (V2RDM) calculations were performed using the Maple Quantum Chemistry Package (QCP).\(^8\) Natural orbital density plots were obtained using the DensityPlot3D procedure in QCP. As with wave-function-based complete active-space self-consistent-field (CASSCF) techniques, active-space V2RDM variationally solves the Schrödinger equation for an active set of orbitals, known as an active space, followed by orbital rotations between the active and inactive orbitals to lower the energy until self-consistency is achieved.\(^9\) V2RDM has been successfully used to account for most of the strong correlation in a variety of large transition-metal molecules.\(^10\) The major advantage of V2RDM over traditional wave-function-based methods is its favorable polynomial scaling of \(O(r^6)\), compared to the \(O(r^N)\) exponential scaling of conventional wave-function-based methods (where \(r\) is the number of basis functions and \(N\) is the number of active electrons). This scaling is the result of the fact that in V2RDM calculations the 2-RDM is computed directly, avoiding the explicit calculation of the entire wave function.

As fermionic interactions are pairwise the energy of any system can be expressed as a linear functional of the 2-RDM: 
\[
E = \text{Tr}[^2\mathcal{K}^2\mathcal{D}],
\]
where \(^2\mathcal{K}\) is the 2-electron reduced Hamiltonian, and \(^2\mathcal{D}\) is the 2-RDM. The energy is variationally minimized using a semidefinite program,\(^11\) which minimizes the energy as a functional of the 2-RDM subject to several \(N\)-representability constraints:\(^12\)

\[
\begin{align*}
^2\mathcal{D} &\succeq 0 & (1) \\
^2\mathcal{Q} &\succeq 0 & (2) \\
^2\mathcal{G} &\succeq 0 & (3)
\end{align*}
\]

These conditions are termed the DQG conditions, where \(^2\mathcal{D}\) is the two-particle matrix, \(^2\mathcal{Q}\) is the two-hole matrix, \(^2\mathcal{G}\) the particle-hole matrix, and \(\succeq 0\) indicates that matrix \(M\) is positive semidefinite, meaning its eigenvalues are nonnegative. As the 2-RDM is calculated directly, without the wave function, the DQG conditions are necessary to ensure that the 2-RDM remains \(N\)-representable, meaning there must be a corresponding \(N\)-electron wave function. The minimized energy from a V2RDM calculation represents a lower bound to the true ground state energy. Calculations using [19,20] active spaces as carried out in this in study remain outside the scope of traditional wave-function-based CASSCF methods.
Figure S59. Orbital density plots for the computationally treated dimers and trimers viewed along the stacking interaction.

Table S7. Energies, NO occupations and Mulliken charges for the two different dimerization geometries. V2RDM calculations with a [19,20] active space and 3-21G basis set.

|        | Parallel          | Orthogonal        |
|--------|-------------------|-------------------|
| E(a.u.)| -16430.761095     | -16430.712292     |
| λ382   | 1.88571           | 1.912486          |
| λ383   | 1.49923           | 1.224860          |
| λ384   | 0.51331           | 0.771141          |
| λ385   | 0.08481           | 0.073175          |
| q1     | 0.40607           | 0.37830           |
| q2     | 0.56836           | 0.43482           |
| q3     | 0.57037           | 0.45403           |
| q4     | 0.40265           | 0.43870           |

Table S8. Energies, NO occupations and Ni atom Mulliken charges for the trimer unit. V2RDM calculations were performed with a [17,20] active space and 3-21G basis set.
Cited References

1 Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. The Chemistry of TTFTT; 1: New Efficient Synthesis and Reactions of Tetraphthalvalene-2,3,6,7-Tetrathiolate (TTFTT): An Important Building Block in TTF-Syntheses. Synthesis. 1994, 809–812.

2 (a) Van Hecke, G. R.; Horrocks, W. D. Ditertiary Phosphine Complexes of Nickel. Spectral, Magnetic, and Proton Resonance Studies. A Planar-Tetrahedral Equilibrium. Inorg. Chem. 1966, 5 (11), 1968–1974. (b) Angulo, I. M.; Bouwman, E.; van Gorkum, R.; Lok, S. M.; Lutz, M.; Spek, A. L. New Nickel-Containing Homogeneous Hydrogenation Catalysts. J. Mol. Catal. A Chem. 2003, 202 (1–2), 97–106.

3 Chávez, I.; Alvarez-Carena, A.; Molins*, E.; Roig, A.; Maniukiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manuel Manriquez*, J. Selective Oxidants for Organometallic Compounds Containing a Stabilising Anion of Highly Reactive Cations: (3,5(CF₃)₂C₆H₃)₄B⁻)Cp₂Fe⁺ and (3,5(CF₃)₂C₆H₃)₄B⁻)Cp*₂Fe⁺. J. Organomet. Chem. 2000, 601 (1), 126–132.

4 Hunter, B. K.; Reeves, L. W. Chemical Shifts for Compounds of the Group IV Elements Silicon and Tin Can. J. Chem. 1968, 46, 1399-1414.

5 Sheldrick, G. M. SHELXT- Integrated space-group and crystal-structure determination. Acta Cryst. 2015, A71, 3-9.

6 Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, A. K.; and Puschmann, H., Olex2, a complete structure solution, refinement, and analysis program. J. Appl. Cryst. 2009, 42, 339.

7 (a) Sheldrick, G. M. A Short History of SHELX. Acta Cryst. 2008, A64, 112-122; (b) Sheldrick, G. M. Crystal structure refinement with SHELXL. Acta Cryst. 2015, C71, 3-8.

8 Maple Quantum Chemistry Toolbox (2019). Maplesoft, a division of Waterloo Maple Inc., Waterloo, Ontario.

9 (a) Mazziotti, D. A. Two-Electron Reduced Density Matrix as the Basic Variable in Many-Electron Quantum Chemistry and Physics. Chem. Rev. 2012, 112, 244–262. (b) Mazziotti, D. A., Ed. Variational Two-Electron Reduced-Density Matrix Theory. In Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules; John Wiley and Sons, Inc.: Hoboken, NJ, 2007; pp 19–59. (c) Nakata, M.; Nakatsuji, H.; Ehara, M.; Fukuda, M.; Nakata, K.; Fujisawa, K. Variational Calculations of Fermion Second-Order Reduced Density Matrices by Semidefinite Programming Algorithm. J. Chem. Phys. 2001, 114, 8282–8292. (d) Mazziotti, D. Realization of Quantum Chemistry without Wave Functions through First-Order Semidefinite
Programming. *Phys. Rev. Lett.* **2004**, 93, 213001. (e) Gidofalvi, G. and Mazziotti, D. A. Active-Space Two-Electron Reduced-Density-Matrix Method: Complete Active-Space Calculations without Diagonalization of the N-electron Hamiltonian. *J. Chem. Phys.* **2008**, 129, 134108. (f) Shenvi, N.; Izmaylov, A. F. Active-Space N-Representability Constraints for Variational Two-Particle Reduced Density Matrix Calculations. *Phys. Rev. Lett.* **2010**, 105, 213003. (g) Verstichel, B.; van Aggelen, H.; Poelmans, W.; Van Neck, D. Variational Two-Particle Density Matrix Calculation for the Hubbard Model Below Half Filling Using Spin-Adapted Lifting Conditions. *Phys. Rev. Lett.* **2012**, 108, 213001. (h) Fosso-Tande, J.; Nguyen, T.-S.; Gidofalvi, G.; DePrince, A. E., III Large-Scale Variational Two-Electron Reduced-Density-Matrix Driven Complete Active Space Self-Consistent Field Methods. *J. Chem. Theory Comput.* **2016**, 12, 2260–2271. (i) Mazziotti, D. A. Enhanced Constraints for Accurate Lower Bounds on Many-Electron Quantum Energies from Variational Two Electron Reduced Density Matrix Theory. *Phys. Rev. Lett.* **2016**, 117, 153001.

10 (a) Schlimgen, A. W.; Heaps, C. W.; Mazziotti, D. A. Entangled Electrons Foil Synthesis of Elusive Low-Valent Vanadium Oxo Complex. *J. Phys. Chem. Lett* **2016**, 7, 627–631. (b) Schlimgen, A. W.; Mazziotti, D. A. Static and Dynamic Electron Correlation in the Ligand Noninnocent Oxidation of Nickel Dithiolates. *J. Phys. Chem. A* **2017**, 121, 9377–9384. (c) Montgomery, J. M.; Mazziotti, D. A. Strong Electron Correlation in Nitrogenase Cofactor, FeMoco. *J. Phys. Chem. A* **2018**, 122, 4988–4996. (d) McIsaac, A. R.; Mazziotti, D. A. Ligand Non-innocence and Strong Correlation in Manganese Superoxide Dismutase Mimics. Phys. Chem. Chem. Phys. **2017**, 19, 4656–4660.

11 (a) Mazziotti, D. A. First-order Semidefinite Programming for the Two-electron Treatment of Many-Electron Atoms and Molecules. *ESAIM: Math. Modell. Numer. Anal.* **2007**, 41, 249–259. (b) Mazziotti, D. A. Large-Scale Semidefinite Programming for Many-Electron Quantum Mechanics. *Phys. Rev. Lett.* **2011**, 106, 083001.

12 (a) Mazziotti, D. A. Variational reduced-density-matrix method using three-particle N-representability conditions with application to many-electron molecules. *Phys. Rev. A: At., Mol., Opt. Phys.* **2006**, 74, 032501. (b) Garrod C. and Percus, J. Reduction of the N-Particle Variational Problem. *J. Math. Phys. (N.Y.)* **1964**, 5, 1756.