Supporting Information for

A Controlled Approach to Well-Defined Oligothiophenes via Oxidatively Induced Reductive Elimination of Stable Pt(II) Oligothienyl Complexes

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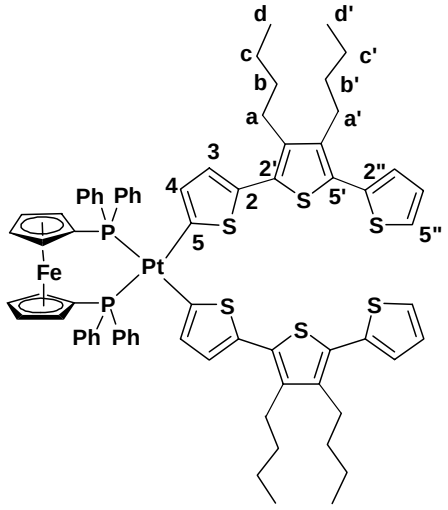
Contents

Synthetic procedures and analytical data

General. All reactions were conducted under dry argon atmosphere by using typical Schlenk techniques. Solvents and reagents were purified prior to use and dried by usual methods. The following compounds were prepared according to literature procedures: 3',4'-dibutyl-2,2':5'2"-terthiohpene (**1**),[1] dichloro[1,1'-(diphenylphosphino)ferrocene]platinum(II) (**2a**),[2] and dichloro[(1,3-bis(diphenylphosphino)propane]platinum (II) (**2b**).[3] Melting points were determined with an Electrothermal 9100 melting point apparatus and are uncorrected. HPLC analysis was accomplished with a Shimadzu SCL-10AVP controller, LC-10AT pump, SPD-M10A VP detector using a Macherey-Nagel nucleosil column NO_2 (4 mm×250 mm, corn diameter 5 μm), 1.3 mL/min flow rate. NMR spectra were recorded on a Bruker DMX 400 (400 MHz) and AMX 500 (500 MHz) spectrometer. EI and CI mass spectra were recorded on a Finnigan MAT SSQ-7000, FAB on a Finnigan MAT TSQ-7000 (matrix nitrobenzyl alcohol), ESI on a Waters-Micromass ZMD (sample sprays from THF-15% water-1% HCOOH solutions) and MALDI-TOF on a Bruker Daltonics Reflex III (matrix 1,8,9-trihydroxyanthracene). Elemental analyses were performed on an Elementar Vario EL (University of Ulm). Absorption spectra were recorded on a Perkin-Elmer Lambda 19 spectrometer. Electrochemical measurements were performed on a computer-controlled PGSTAT 30 potentiostat in a three-electrode single-compartment cell using a Pt-disk working electrode consisting of a platinum wire sealed in a soft glass tube with a surface of A = 0.785 mm^2, a Pt-wire-coil counter electrode and a Ag-wire reference electrode. The supporting electrolyte was 0.1 M $(n\text{-Bu})_4NPF_6$ and CH_2Cl_2 was used as the solvent. Ferrocene was used as an internal reference. CH_2Cl_2 as solvent was degassed and purged with argon before used.

[1,1'-Bis(diphenylphosphino)ferrocene]bis(3',4'-dibutyl-2,2':5',2"-terthien-5-yl)] platinum (II) [*dppf*Pt(3T)$_2$, 2a]. To a solution of 3',4'-dibutyl-2,2':5',2"-terthiohpene **1** (0.124 g, 0.344 mmol) in THF (10 ml) was added dropwise *n*-BuLi (1.6 M, 0.22 ml, 0.344 mmol) at -78 ^oC. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was cooled to -78°C and a suspen-

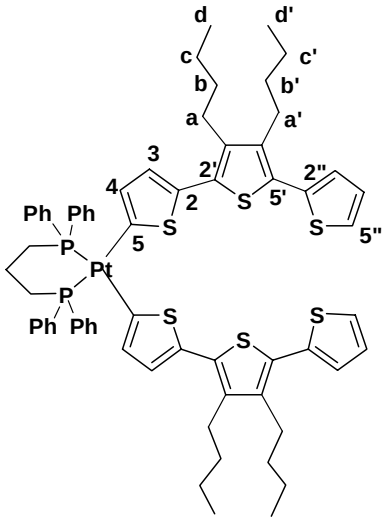
sion of *dppf*$PtCl_2$ (0.141 g, 0.172 mmol) in THF (15 ml) was added with a syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight. Several drops of methanol were added and the mixture stirred for several minutes. The solvent was removed under vacuum and the residue was washed with *n*-hexane (3×20 ml) and extracted into toluene (15 ml) and then filtered. The product was purified by recrystallization from toluene/*n*-hexane. Further purification was performed by diffusion of *n*-hexane into a saturated solution in THF to give 0.19 g (74 %) of **2a** as yellow crystals. M.p. 162°C (decomp.).



^{1}H NMR (400 MHz, THF-d_8): 0.84 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 6H, H-d), 0.89 (t, $^3J_{H\text{-}H}$ = 7.0 Hz, 6H, H-d'), 1.22 - 1.52 (m, 16H, H-b,b',c,c'), 2.49 (t, $^3J_{H\text{-}H}$ = 8.3 Hz, $^3J_{H\text{-}H}$ = 7.8 Hz, 4H, H-a), 2.61 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, $^3J_{H\text{-}H}$ = 8.1 Hz, 4H, H-a'), 4.33 (virtual triplet, $^3J_{H\text{-}H}$ = 1.5 Hz, 4H, Cp), 4.39 (virtual triplet, $^3J_{H\text{-}H}$ = 2.0 Hz, 4H, Cp), 6.03 (dd with Pt satellites, $^3J_{H\text{-}H}$ = 3.7Hz, $^4J_{P\text{-}H}$ = 2.3 Hz, $^3J_{Pt\text{-}H}$ = 39.1 Hz, 2H, H-4), 6.55 (d, $^3J_{H\text{-}H}$ = 3.3 Hz, 2H, H-3), 6.97 (dd, $^3J_{H\text{-}H}$ = 3.5 Hz, $^3J_{H\text{-}H}$ = 5.3 Hz, 2H, H-4"), 7.00 (dd, $^3J_{H\text{-}H}$ = 1.0 Hz, $^3J_{H\text{-}H}$ = 3.3 Hz, 2H, H-3"), 7.28 (dd, $^3J_{H\text{-}H}$ = 1.0 Hz, $^3J_{H\text{-}H}$ = 5.3 Hz, 2H, H-5"), 7.32-7.42 (m, 12H, Ph*H*-*o*,*p*), 7.67-7.72 (m, 8H, Ph*H*-*m*) ppm. ^{13}C NMR (100 MHz , THF-d_8): 14.2 (C-d or C-d'), 14.4 (C-d' or C-d), 23.8, 33.8, 33.9 (C-b,b',c,c'), 28.5 (C-a, a'), 73.8 (virtual triplet, *J* = 3.3 Hz, Cp), 75.8 (virtual triplet, *J* = 5.5 Hz, Cp), 76.5 (b, ipso-Cp), 125.2 (s, C-5"), 125.7 (s, C-3"), 126.9 (m, C-3), 127.7 (s, *Th*), 127.8 (C-4''), 128.6 (virtual triplet, *J* = 4.7 Hz, PPh), 129.8 (m, C-4), 131.0 (b, PPh), 134.0 (d, $^1J_{P\text{-}C}$ = 53.1 Hz, PPh*C*-*i*), 134.7 (s, *Th*), 135.5 (virtual triplet, *J* = 5.8 Hz, PPh*C*-*m*), 137.3 (s, *Th*),

137.4 (m, *Th*), 138.1 (s, *Th*), 140.1 (s, *Th*) ppm. $^{31}P\{^{1}H\}$NMR (161 MHz, THF-d_8): 14.33 (s, with Pt satellites, $^{1}J_{Pt\text{-}P}$= 2082 Hz). Anal. Calcd for $C_{74}H_{74}FeP_2PtS_6$ (1467.2587): C, 60.52; H, 5.08. Found: C, 60.52; H, 5.20. *m/z* Calcd for $[M+H]^+$ ($C_{74}H_{75}FeP_2PtS_6$: 1468.2666; Found: 1468.2668 (HRMS [ESI-FTICR]).

[1,3-Bis(diphenylphosphino)propane]-bis(3',4'-dibutyl-2,2':5',2"-terthien-5-yl)-platinum (II) [*dppp*Pt(3T)$_2$, 2b]. To a solution 3',4'-dibutyl-2,2':5',2"-terthiohpene **1** (0.157 g, 0.436 mmol) in THF (10 ml), was added dropwise *n*-BuLi (1.6 M, 0.30 ml, 0.480 mmol) at -78 ^{o}C. The reaction mixture was allowed to room temperature and stirred overnight. The reaction mixture was cooled -78°C and a suspension of *dppp*$PtCl_2$ (0.147 g, 0.217 mmol) in THF (15 ml) was added with a syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight. Several drops of methanol were added and the mixture stirred for several minutes. The solvent was removed under vacuum and the residue was washed with *n*-hexane (3×20 ml) and extracted into dichloromethane (15 ml), filtered and the solvent evaporated to give 0.16 g (56 %) of **2b** as yellow crystals. M.p. >101°C (decomp.).



^{1}H NMR (400 MHz, THF-d_8): 0.85 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 6H, H-d), 0.90 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 6H, H-d'), 1.25 - 1.51 (m, 16H, H-b,b',c,c'), 1.93 (b, 2H, $PCH_2CH_2CH_2P$), 2.51 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 6H, H-a), 2.63 (t, $^{3}J_{H\text{-}H}$ = 8.3 Hz, 6H, H-a'), 2.75 (b, 4H, $PCH_2CH_2CH_2P$), 6.12 (virtual triplet, with Pt satellites, $^{4}J_{P\text{-}H}$ = 2.5 Hz, $^{3}J_{Pt\text{-}H}$ *J* = 37.4

Hz, 2H, H-4), 6.56 (d, $^3J_{H\text{-}H}$ = 3.5 Hz, 2H, H-3), 6.97 (dd, $^3J_{H\text{-}H}$ = 5.0 Hz, $^3J_{H\text{-}H}$ = 5.6 Hz, 2H, H-4"), 7.01 (dd, $^3J_{H\text{-}H}$ = 1.3 Hz, $^3J_{H\text{-}H}$ = 4.6 Hz, 2H, H-3"), 7.28 (dd, $^3J_{H\text{-}H}$ = 1.5 Hz, $^3J_{H\text{-}H}$ = 5.3 Hz, 2H, H-5"), 7.28-7.36 (m, 12H, Ph*H-o,p*), 7.64-7.68 (m, 8H, Ph*H-m*) ppm. ^{13}C NMR (100 MHz , THF-d_8): 14.2 (C-d), 14.4 (C-d'), 23.8, 23.9, 33.8 (C-b,b',c,c'), 26.4 (PCH$_2$*C*H$_2$CH$_2$P), 26.9 (b, P*C*H$_2$CH$_2$*C*H$_2$P), 28.6 (C-a, a'), 125.2 (C-5"), 125.7 (C-3"), 126.9 (m, C-3), 127.7 (s, *Th*), 127.8 (C-4"), 128.8 (virtual triplet, *J* = 4.4 Hz, PPh), 129.6 (m, C-4), 130.9 (b, PPh), 132.0 (d, $^1J_{P\text{-}C}$ = 53.0 Hz, PPh*C-i*), 134.4 (virtual triplet, *J* = 5.5 Hz, PPh*C-m*), 134.8 (s, *Th*), 137.0 (m, *Th*), 137.3 (s, *Th*), 138.1 (s, *Th*), 140.0 (s, *Th*) ppm. ^{31}P{^{1}H}NMR (161 MHz, THF-d_8): -0.48 (s, with Pt satellites, $^1J_{Pt\text{-}P}$= 1951 Hz). Anal. Calcd for $C_{67}H_{72}P_2PtS_6$ (1325.3081): C, 60.67; H, 5.48. Found: C, 60.33; H, 5.78. *m/z* Calcd for $[M+H]^+$ ($C_{67}H_{73}P_2PtS_6$): 1326.3156; Found: 1326.3158 $[M+H]^+$ (HRMS [ESI-FTICR]).

3',4',3"",4""-Tetrabutyl-2,2':5',2":5",2"':5"',2"":5"",2""'-sexithiophene (3). We obtained identical analytical data as given in ref. 5.

X-Ray crystal structure analysis of Pt-complex 2a

Single crystals were obtained by slow diffusion of *n*-hexane into concentrated solution of **2a** in THF. Diffraction data were collected on a STOE-IPDS image plate diffractometer (Mo Kα radiation, graphite monochromator) in the φ rotation scan mode. The measured intensities were corrected for Lorentz and polarization effects. The structure determination was done with direct methods and refinements with full-matrix least-squares on F^2 with SHELXL-97.[6] Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. Both terminal thiophene groups are disordered over two orientations with respect to a 180^o rotation about the bond to the adjacent thiophene ring. For these two thiophene rings, the disorders were refined using split-atom model with bond lengths and angles constraints. One disordered butyl side chain was modeled by split-atom refinement with bond lengths and angles restraints. The final cycle of full-matrix least-squares refinement was based on 756 parameters and the observed data and converged with *R*1 =

0.0536 and *wR*2 = 0.1077. Experimental parameters and crystal data are listed in Table S-1, atomic coordinates and equivalent isotropic displacement parameters in Table S-2, bond lengths and angles in Table S3, anisotropic displacement parameters in Table S4 and hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters in Table S5.

Table S-1. Structure determination summary of complex **2a.**

	2a
formula	C_{74} H_{74} Fe P_2 Pt S_6
formula weight	1468.57
temperature [K]	190(2)
wavelength [Å]	0.71073
crystal system	triclinic
space group	*P*-1
a [Å]	13.8340 (17)
b [Å]	15.171(2)
c [Å]	18.296(3)
α [°]	108.040(16)
β [°]	101.599(16)
γ [°]	108.211(15)
V [$Å^3$]	3274.2(8)
Z	2
D_{calcd} [Mg m^{-3}]	1.490
Absorption Coefficient [mm^{-1}]	2.639
F(000)	1496
crystal size [mm]	0.2× 0.2 × 0.2
crystal color	orange
scan range (θ) [°]	2.09-25.82
index ranges	-16≤ h ≤16
	-18≤ k ≤18
	-22 ≤l ≤22
reflections collected / unique	25453 / 11748 [R(int) = 0.1005]
data / restraints / parameters	11748/ 0 / 756
goodness-of-fit on F^2	0.810
final R indices [I>2(I)]	*R1* = 0.0536
	wR^2 = 0.1077
R indices (all data)	*R1* = 0.1073

	$wR^2 = 0.1224$
largest diff. peak and hole [e Å^{-3}]	2.742/-2.353

Table S-2. Atomic coordinates (×10^5) and equivalent isotropic displacement parameters (Å^2 ×10^4) for complex **2a**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Pt(1)	10575(3)	-18541(3)	1982(2)	211(1)
Fe(1)	41575(11)	-20103(8)	6771(8)	288(3)
P(2)	16250(20)	-29428(15)	-6332(13)	246(6)
P(1)	27056(19)	-5825(15)	10729(13)	234(5)
S(1)	-1070(20)	-14964(15)	15495(13)	292(6)
S(4)	-11053(18)	-26822(15)	-13381(13)	276(5)
S(2)	-1710(20)	8072(16)	35073(14)	373(6)
S(5)	-44160(20)	-49368(17)	-23773(15)	430(7)
S(3)	-12120(40)	21670(30)	48870(20)	584(17)
S(3A)	-5070(60)	10730(50)	56240(40)	720(30)
S(6)	-68710(70)	-65740(60)	-43380(40)	1470(50)
C(56)	-21780(70)	-41830(60)	-11010(50)	330(20)
C(20)	35170(80)	24150(60)	7230(50)	340(20)
C(43)	-9360(80)	11520(70)	48080(50)	360(20)
C(59)	-33670(70)	-38050(60)	-29900(50)	330(20)
C(42)	-10320(70)	4310(60)	40040(50)	330(20)
C(34)	-1270(80)	-45000(60)	-19580(50)	330(20)
C(29)	6310(80)	-42400(60)	-12200(50)	330(20)
C(40)	-16610(80)	-9660(60)	27980(50)	360(20)
C(39)	-8090(70)	-3380(60)	26830(50)	270(20)
C(36)	3520(70)	-1070(60)	10340(50)	240(20)
S(6A)	-71970(50)	-52620(40)	-34710(40)	830(30)
C(32)	-10420(80)	-61840(60)	-20310(60)	430(30)
C(27)	21460(80)	-13780(70)	-20570(60)	460(30)
C(1)	39720(70)	-6930(60)	10820(50)	240(20)
C(46)	-24500(90)	-19910(80)	21280(70)	530(30)
C(54)	-4730(80)	-28290(60)	-4940(50)	280(20)
C(23)	19810(80)	-25630(60)	-14260(50)	290(20)
C(9)	43320(80)	-33510(60)	2770(70)	440(30)
C(62)	-62740(80)	-55320(80)	-36210(60)	570(40)
C(67)	-55120(100)	-27060(80)	-45470(70)	620(30)
C(24)	22250(100)	-31590(70)	-20370(60)	510(30)
C(18)	39460(80)	14450(60)	14620(50)	350(20)
C(26)	24290(100)	-19450(80)	-26400(60)	580(30)
C(30)	5400(80)	-49760(60)	-8960(50)	400(30)
C(37)	-920(70)	2100(60)	16420(50)	290(20)
C(50)	-26950(90)	-10300(80)	38270(60)	500(30)
C(57)	-22660(70)	-37610(60)	-16510(50)	300(20)
C(58)	-32180(80)	-40740(60)	-23340(50)	340(20)
C(28)	19190(70)	-16670(60)	-14420(50)	330(20)
C(17)	30120(70)	6140(60)	9510(50)	250(20)
C(61)	-51390(80)	-49050(70)	-32600(60)	450(30)
C(12)	26070(70)	5500(60)	25760(50)	340(20)
C(35)	4230(70)	-10200(60)	9040(50)	210(20)
C(10)	36220(80)	-32610(60)	-3680(60)	370(20)
C(60)	-44780(80)	-42620(60)	-34930(50)	360(20)

Table S-3. Bond lengths [Å] and angles [°] for complex **2a**.

Pt(1)-C(54)	2.020(9)	C(56)-C(55)	1.410(11)
Pt(1)-C(35)	2.045(8)	C(20)-C(21)	1.362(12)
Pt(1)-P(1)	2.313(2)	C(20)-C(19)	1.386(12)
Pt(1)-P(2)	2.322(2)	C(43)-C(42)	1.488(12)
Fe(1)-C(6)	2.007(9)	C(59)-C(58)	1.382(12)
Fe(1)-C(5)	2.010(8)	C(59)-C(60)	1.435(12)
Fe(1)-C(1)	2.022(8)	C(59)-C(69)	1.475(14)
Fe(1)-C(10)	2.027(9)	C(42)-C(41)	1.363(12)
Fe(1)-C(4)	2.039(10)	C(34)-C(29)	1.386(11)
Fe(1)-C(9)	2.046(9)	C(34)-C(33)	1.392(12)
Fe(1)-C(2)	2.047(8)	C(29)-C(30)	1.401(12)
Fe(1)-C(7)	2.047(9)	C(40)-C(39)	1.363(13)
Fe(1)-C(3)	2.052(9)	C(40)-C(41)	1.407(13)
Fe(1)-C(8)	2.054(9)	C(40)-C(46)	1.527(13)
P(2)-C(6)	1.812(9)	C(39)-C(38)	1.467(12)
P(2)-C(23)	1.819(9)	C(36)-C(35)	1.369(11)
P(2)-C(29)	1.822(9)	C(36)-C(37)	1.404(12)
P(1)-C(1)	1.809(9)	S(6A)-C(64)	1.45(3)
P(1)-C(11)	1.817(9)	S(6A)-C(62)	1.507(14)
P(1)-C(17)	1.826(8)	C(32)-C(31)	1.379(12)
S(1)-C(35)	1.732(8)	C(32)-C(33)	1.402(12)
S(1)-C(38)	1.734(8)	C(27)-C(26)	1.357(14)
S(4)-C(54)	1.729(8)	C(27)-C(28)	1.384(13)
S(4)-C(57)	1.729(9)	C(1)-C(5)	1.424(12)
S(2)-C(42)	1.703(10)	C(1)-C(2)	1.432(11)
S(2)-C(39)	1.719(8)	C(46)-C(47)	1.464(14)
S(5)-C(58)	1.731(10)	C(54)-C(55)	1.354(12)
S(5)-C(61)	1.744(9)	C(23)-C(24)	1.377(13)
S(3)-C(45)	1.627(12)	C(23)-C(28)	1.397(11)
S(3)-C(43)	1.670(10)	C(9)-C(8)	1.385(14)
S(3A)-C(44)	1.510(13)	C(9)-C(10)	1.447(13)
S(3A)-C(43)	1.549(11)	C(62)-C(61)	1.438(13)
S(6)-C(63)	1.51(3)	C(67)-C(66)	1.524(13)
S(6)-C(62)	1.538(12)	C(67)-C(68)	1.529(14)

S(6)-S(6A)	2.361(11)	C(24)-C(25)	1.395(14)
C(56)-C(57)	1.356(12)	C(18)-C(17)	1.378(11)
C(18)-C(19)	1.397(11)	C(48)-C(47)	1.596(15)
C(26)-C(25)	1.365(15)	C(51)-C(52)	1.514(17)
C(30)-C(31)	1.396(12)	C(45)-C(44)	1.345(16)
C(37)-C(38)	1.377(12)	C(7)-C(8)	1.418(13)
C(50)-C(41)	1.516(13)	C(52)-C(53)	1.446(15)
C(50)-C(51)	1.525(17)	C(14)-C(15)	1.358(13)
C(57)-C(58)	1.449(12)	C(3)-C(4)	1.400(13)
C(17)-C(22)	1.392(11)	C(5)-C(4)	1.417(12)
C(61)-C(60)	1.352(14)	C(64)-C(63)	1.26(4)
C(12)-C(13)	1.386(12)	C(72)-C(71B)	1.75(3)
C(12)-C(11)	1.388(11)	C(72)-C(71A)	1.76(3)
C(10)-C(6)	1.408(13)	C(15)-C(16)	1.389(13)
C(60)-C(65)	1.520(12)	C(11)-C(16)	1.414(12)
C(22)-C(21)	1.372(11)	C(13)-C(14)	1.357(13)
C(49)-C(48)	1.467(17)	C(6)-C(7)	1.447(12)
C(70)-C(71A)	1.20(2)	C(65)-C(66)	1.518(12)
C(70)-C(71B)	1.38(3)	C(70)-C(69)	1.535(16)
C(54)-Pt(1)-C(35)	87.3(3)	C(5)-Fe(1)-C(9)	139.5(4)
C(54)-Pt(1)-P(1)	171.9(2)	C(1)-Fe(1)-C(9)	179.2(4)
C(35)-Pt(1)-P(1)	84.8(2)	C(10)-Fe(1)-C(9)	41.6(4)
C(54)-Pt(1)-P(2)	87.8(2)	C(4)-Fe(1)-C(9)	111.5(4)
C(35)-Pt(1)-P(2)	174.3(2)	C(6)-Fe(1)-C(2)	142.5(4)
P(1)-Pt(1)-P(2)	100.23(8)	C(5)-Fe(1)-C(2)	68.5(3)
C(6)-Fe(1)-C(5)	107.1(3)	C(1)-Fe(1)-C(2)	41.2(3)
C(6)-Fe(1)-C(1)	110.2(3)	C(10)-Fe(1)-C(2)	175.8(4)
C(5)-Fe(1)-C(1)	41.4(3)	C(4)-Fe(1)-C(2)	67.8(4)
C(6)-Fe(1)-C(10)	40.9(4)	C(9)-Fe(1)-C(2)	138.6(4)
C(5)-Fe(1)-C(10)	108.8(4)	C(6)-Fe(1)-C(7)	41.8(3)
C(1)-Fe(1)-C(10)	138.7(3)	C(5)-Fe(1)-C(7)	136.8(4)
C(6)-Fe(1)-C(4)	134.1(4)	C(1)-Fe(1)-C(7)	111.1(4)
C(5)-Fe(1)-C(4)	41.0(3)	C(10)-Fe(1)-C(7)	68.9(4)
C(1)-Fe(1)-C(4)	69.3(4)	C(4)-Fe(1)-C(7)	175.9(4)
C(10)-Fe(1)-C(4)	108.0(4)	C(9)-Fe(1)-C(7)	68.2(4)
C(6)-Fe(1)-C(9)	69.5(4)	C(2)-Fe(1)-C(7)	115.3(4)
C(6)-Fe(1)-C(3)	174.1(4)	C(5)-Fe(1)-C(8)	176.2(4)

C(5)-Fe(1)-C(3)	68.0(4)	C(1)-Fe(1)-C(8)	139.7(4)
C(1)-Fe(1)-C(3)	68.5(4)	C(10)-Fe(1)-C(8)	68.1(4)
C(10)-Fe(1)-C(3)	136.5(4)	C(4)-Fe(1)-C(8)	141.6(4)
C(4)-Fe(1)-C(3)	40.0(4)	C(9)-Fe(1)-C(8)	39.5(4)
C(9)-Fe(1)-C(3)	111.8(4)	C(2)-Fe(1)-C(8)	114.7(4)
C(2)-Fe(1)-C(3)	39.8(4)	C(7)-Fe(1)-C(8)	40.5(4)
C(7)-Fe(1)-C(3)	144.1(4)	C(3)-Fe(1)-C(8)	115.8(4)
C(6)-Fe(1)-C(8)	69.1(4)	C(6)-P(2)-C(23)	106.4(4)
C(6)-P(2)-C(29)	102.0(4)	C(35)-S(1)-C(38)	94.2(4)
C(23)-P(2)-C(29)	102.0(4)	C(54)-S(4)-C(57)	94.7(4)
C(6)-P(2)-Pt(1)	115.7(3)	C(42)-S(2)-C(39)	92.1(4)
C(23)-P(2)-Pt(1)	113.2(3)	C(58)-S(5)-C(61)	92.5(5)
C(29)-P(2)-Pt(1)	115.9(3)	C(45)-S(3)-C(43)	93.8(6)
C(1)-P(1)-C(11)	103.1(4)	C(44)-S(3A)-C(43)	98.6(7)
C(1)-P(1)-C(17)	98.4(4)	C(63)-S(6)-C(62)	103.3(12)
C(11)-P(1)-C(17)	105.8(4)	C(63)-S(6)-S(6A)	65.4(11)
C(1)-P(1)-Pt(1)	122.8(3)	C(62)-S(6)-S(6A)	38.7(5)
C(11)-P(1)-Pt(1)	110.3(3)	C(57)-C(56)-C(55)	113.1(8)
C(17)-P(1)-Pt(1)	114.6(3)	C(21)-C(20)-C(19)	119.6(8)
C(42)-C(43)-S(3A)	123.7(8)	C(31)-C(32)-C(33)	119.6(8)
C(42)-C(43)-S(3)	120.8(7)	C(26)-C(27)-C(28)	121.3(9)
S(3A)-C(43)-S(3)	115.3(6)	C(5)-C(1)-C(2)	106.3(8)
C(58)-C(59)-C(60)	111.9(9)	C(5)-C(1)-P(1)	122.5(6)
C(58)-C(59)-C(69)	124.6(8)	C(2)-C(1)-P(1)	131.3(7)
C(60)-C(59)-C(69)	123.4(9)	C(5)-C(1)-Fe(1)	68.9(5)
C(41)-C(42)-C(43)	128.3(9)	C(2)-C(1)-Fe(1)	70.3(5)
C(41)-C(42)-S(2)	111.6(7)	P(1)-C(1)-Fe(1)	125.2(4)
C(43)-C(42)-S(2)	120.0(7)	C(47)-C(46)-C(40)	113.1(9)
C(29)-C(34)-C(33)	121.3(8)	C(55)-C(54)-S(4)	107.0(7)
C(34)-C(29)-C(30)	118.0(8)	C(55)-C(54)-Pt(1)	133.5(6)
C(34)-C(29)-P(2)	121.0(7)	S(4)-C(54)-Pt(1)	119.5(5)
C(30)-C(29)-P(2)	120.7(6)	C(24)-C(23)-C(28)	119.5(9)
C(39)-C(40)-C(41)	113.2(8)	C(24)-C(23)-P(2)	122.5(7)
C(39)-C(40)-C(46)	122.2(8)	C(28)-C(23)-P(2)	117.8(7)
C(41)-C(40)-C(46)	124.3(9)	C(8)-C(9)-Fe(1)	70.5(6)
C(40)-C(39)-C(38)	131.6(7)	C(10)-C(9)-Fe(1)	68.5(5)
C(40)-C(39)-S(2)	110.6(7)	C(61)-C(62)-S(6A)	128.1(10)
C(38)-C(39)-S(2)	117.7(7)	C(61)-C(62)-S(6)	129.7(11)

C(35)-C(36)-C(37)	114.9(8)	S(6A)-C(62)-S(6)	101.7(7)
C(64)-S(6A)-C(62)	109.1(13)	C(66)-C(67)-C(68)	111.9(10)
C(64)-S(6A)-S(6)	70.8(13)	C(23)-C(24)-C(25)	119.5(9)
C(17)-C(18)-C(19)	120.5(8)	C(27)-C(26)-C(25)	119.8(10)
C(31)-C(30)-C(29)	121.3(9)	C(7)-C(6)-P(2)	122.6(7)
C(38)-C(37)-C(36)	113.9(8)	C(10)-C(6)-Fe(1)	70.3(5)
C(41)-C(50)-C(51)	113.7(9)	C(7)-C(6)-Fe(1)	70.6(5)
C(56)-C(57)-C(58)	126.3(8)	P(2)-C(6)-Fe(1)	124.6(4)
C(56)-C(57)-S(4)	108.7(6)	C(66)-C(65)-C(60)	111.9(7)
C(58)-C(57)-S(4)	124.6(7)	C(3)-C(2)-C(1)	108.3(8)
C(59)-C(58)-C(57)	131.5(9)	C(3)-C(2)-Fe(1)	70.3(5)
C(59)-C(58)-S(5)	110.8(7)	C(1)-C(2)-Fe(1)	68.5(4)
C(57)-C(58)-S(5)	117.7(7)	C(32)-C(31)-C(30)	119.9(9)
C(27)-C(28)-C(23)	119.1(9)	C(49)-C(48)-C(47)	111.8(10)
C(18)-C(17)-C(22)	118.4(8)	C(52)-C(51)-C(50)	116.9(13)
C(18)-C(17)-P(1)	120.3(6)	C(44)-C(45)-S(3)	113.7(9)
C(22)-C(17)-P(1)	121.2(6)	C(20)-C(19)-C(18)	119.8(8)
C(60)-C(61)-C(62)	130.9(9)	C(34)-C(33)-C(32)	119.9(8)
C(60)-C(61)-S(5)	110.3(7)	C(8)-C(7)-C(6)	107.0(9)
C(62)-C(61)-S(5)	118.8(8)	C(8)-C(7)-Fe(1)	70.0(5)
C(13)-C(12)-C(11)	120.2(9)	C(6)-C(7)-Fe(1)	67.6(5)
C(36)-C(35)-S(1)	108.4(6)	C(45)-C(44)-S(3A)	118.3(9)
C(36)-C(35)-Pt(1)	135.2(7)	C(53)-C(52)-C(51)	115.3(14)
S(1)-C(35)-Pt(1)	116.3(4)	C(13)-C(14)-C(15)	121.1(9)
C(6)-C(10)-C(9)	108.1(9)	C(9)-C(8)-C(7)	109.8(9)
C(6)-C(10)-Fe(1)	68.8(5)	C(9)-C(8)-Fe(1)	70.0(5)
C(9)-C(10)-Fe(1)	69.9(5)	C(7)-C(8)-Fe(1)	69.5(5)
C(61)-C(60)-C(59)	114.3(8)	C(2)-C(3)-C(4)	109.2(8)
C(61)-C(60)-C(65)	122.0(9)	C(2)-C(3)-Fe(1)	69.9(5)
C(59)-C(60)-C(65)	123.5(9)	C(4)-C(3)-Fe(1)	69.5(5)
C(21)-C(22)-C(17)	120.8(8)	C(4)-C(5)-C(1)	108.7(8)
C(71A)-C(70)-C(71B)	88.5(16)	C(4)-C(5)-Fe(1)	70.6(5)
C(71A)-C(70)-C(69)	122.6(17)	C(1)-C(5)-Fe(1)	69.8(5)
C(71B)-C(70)-C(69)	131.5(18)	C(3)-C(4)-C(5)	107.4(9)
C(42)-C(41)-C(40)	112.4(8)	C(3)-C(4)-Fe(1)	70.5(5)
C(42)-C(41)-C(50)	122.6(8)	C(5)-C(4)-Fe(1)	68.4(5)
C(40)-C(41)-C(50)	124.9(8)	C(63)-C(64)-S(6A)	109(2)
C(12)-C(11)-C(16)	117.9(8)	C(59)-C(69)-C(70)	111.7(10)

C(12)-C(11)-P(1)	122.1(7)	C(65)-C(66)-C(67)	113.7(8)
C(16)-C(11)-P(1)	119.6(6)	C(71B)-C(72)-C(71A)	61.9(14)
C(37)-C(38)-C(39)	127.9(7)	C(14)-C(15)-C(16)	119.6(9)
C(37)-C(38)-S(1)	108.5(7)	C(20)-C(21)-C(22)	120.8(8)
C(39)-C(38)-S(1)	123.3(6)	C(70)-C(71B)-C(72)	96.1(17)
C(14)-C(13)-C(12)	120.7(9)	C(15)-C(16)-C(11)	120.5(9)
C(54)-C(55)-C(56)	116.4(8)	C(46)-C(47)-C(48)	110.1(10)
C(10)-C(6)-C(7)	107.6(8)	C(26)-C(25)-C(24)	120.6(10)
C(10)-C(6)-P(2)	129.8(7)	C(70)-C(71A)-C(72)	103.5(17)
C(64)-C(63)-S(6)	114.3(18)		

Symmetry transformations used to generate equivalent atoms:

Table S-4. Anisotropic displacement parameters ($Å^2 \times 10^4$) for complex **2a**. The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2a^{*2}U11+\ldots+2hka^*b^*U12]$

	U11	U22	U33	U23	U13	U12
Pt(1)	235(2)	211(2)	194(2)	53(1)	57(1)	134(1)
Fe(1)	270(8)	255(6)	398(8)	144(6)	104(6)	169(6)
P(2)	309(15)	227(11)	249(12)	69(9)	121(11)	176(10)
P(1)	258(14)	242(11)	231(12)	84(9)	80(10)	150(10)
S(1)	379(15)	263(11)	301(12)	105(10)	161(11)	191(11)
S(4)	285(14)	244(11)	262(12)	82(9)	40(10)	110(10)
S(2)	464(17)	320(12)	345(13)	76(10)	212(12)	177(11)
S(5)	371(16)	362(13)	426(15)	184(11)	-44(12)	67(12)
S(3)	760(30)	600(30)	460(20)	107(18)	200(20)	470(20)
S(3A)	820(60)	720(50)	520(40)	160(30)	280(40)	230(40)
S(6)	1200(80)	1270(70)	720(50)	-140(40)	360(40)	-540(50)
C(56)	210(50)	300(50)	360(50)	110(40)	20(40)	10(40)
C(20)	490(70)	310(50)	390(60)	160(40)	210(50)	290(50)
C(43)	350(60)	510(60)	290(50)	120(40)	200(40)	240(50)
C(59)	260(60)	260(50)	380(50)	20(40)	-10(40)	160(40)
C(42)	280(60)	320(50)	460(60)	120(40)	220(50)	170(40)
C(34)	450(70)	220(40)	300(50)	50(40)	70(50)	200(40)
C(29)	360(60)	350(50)	330(50)	110(40)	60(40)	270(40)
C(40)	350(60)	270(50)	330(50)	90(40)	50(50)	40(40)
C(39)	300(60)	270(50)	250(50)	30(40)	60(40)	200(40)
C(36)	230(50)	340(50)	200(40)	100(40)	80(40)	160(40)

S(6A)	390(40)	710(40)	1290(60)	260(40)	270(40)	240(30)
C(32)	430(70)	230(50)	440(60)	10(40)	10(50)	90(40)
C(27)	510(70)	370(60)	500(70)	220(50)	140(60)	160(50)
C(1)	230(50)	240(40)	280(50)	110(40)	110(40)	120(40)
C(46)	540(80)	690(70)	640(70)	430(60)	380(60)	310(60)
C(54)	430(60)	260(50)	180(40)	40(40)	70(40)	220(40)
C(23)	380(60)	220(40)	290(50)	110(40)	120(40)	140(40)
C(9)	340(70)	310(50)	710(80)	220(50)	120(60)	190(50)
C(62)	290(60)	570(70)	570(70)	390(60)	-210(60)	-120(50)
C(67)	670(90)	540(70)	710(80)	300(60)	90(70)	350(60)
C(24)	870(100)	440(60)	430(60)	180(50)	340(60)	440(60)
C(18)	440(60)	260(50)	280(50)	50(40)	40(50)	150(40)
C(26)	820(100)	680(80)	440(70)	320(60)	340(60)	370(70)
C(30)	480(70)	300(50)	310(50)	60(40)	20(50)	150(50)
C(37)	260(60)	250(40)	330(50)	100(40)	70(40)	130(40)
C(50)	510(80)	570(60)	380(60)	210(50)	200(50)	110(60)
C(57)	280(60)	260(40)	280(50)	60(40)	-10(40)	100(40)
C(58)	450(70)	240(40)	290(50)	50(40)	60(50)	200(40)
C(28)	380(60)	310(50)	270(50)	30(40)	50(40)	210(40)
C(17)	320(60)	260(40)	200(40)	60(40)	90(40)	170(40)
C(61)	370(70)	390(60)	430(60)	140(50)	-100(50)	110(50)
C(12)	330(60)	380(50)	250(50)	70(40)	70(40)	160(40)
C(35)	150(50)	310(50)	170(40)	50(40)	130(40)	110(40)
C(10)	410(70)	300(50)	440(60)	130(40)	190(50)	190(50)
C(60)	350(60)	320(50)	380(50)	110(40)	30(50)	180(50)
C(22)	230(50)	280(50)	300(50)	90(40)	90(40)	170(40)
C(49)	1060(130)	370(70)	840(100)	50(70)	200(90)	40(70)
C(70)	1000(120)	2090(170)	580(90)	760(110)	580(90)	1280(120)
C(41)	480(70)	470(60)	310(50)	250(50)	240(50)	230(50)
C(11)	210(50)	280(50)	270(50)	30(40)	20(40)	110(40)
C(68)	790(100)	560(70)	1140(110)	420(70)	390(80)	500(70)
C(38)	250(50)	230(40)	340(50)	60(40)	110(40)	140(40)
C(13)	440(70)	460(60)	260(50)	40(40)	130(50)	130(50)
C(55)	370(60)	310(50)	300(50)	80(40)	-40(40)	110(40)
C(6)	320(60)	320(50)	360(50)	140(40)	230(40)	250(40)
C(65)	450(70)	310(50)	260(50)	80(40)	30(40)	180(40)
C(2)	370(60)	230(40)	300(50)	110(40)	40(40)	120(40)
C(31)	530(70)	280(50)	460(60)	160(50)	10(50)	90(50)

C(48)	1020(120)	390(70)	880(100)	290(70)	400(90)	120(70)
C(51)	540(90)	2300(190)	1040(110)	1120(120)	660(90)	800(110)
C(45)	730(100)	630(70)	510(70)	40(60)	250(70)	330(70)
C(19)	370(60)	210(50)	490(60)	100(40)	200(50)	30(40)
C(33)	430(60)	390(50)	170(40)	90(40)	20(40)	200(50)
C(7)	320(60)	270(50)	460(60)	130(40)	160(50)	120(40)
C(44)	500(80)	880(90)	290(60)	130(60)	270(50)	210(70)
C(52)	610(100)	1030(110)	920(110)	250(90)	260(80)	230(80)
C(14)	520(70)	500(60)	280(50)	110(50)	190(50)	160(50)
C(53)	950(120)	740(90)	730(90)	200(80)	90(80)	190(80)
C(8)	340(60)	370(50)	540(60)	270(50)	60(50)	180(50)
C(3)	130(50)	410(50)	590(70)	180(50)	120(50)	160(40)
C(5)	190(50)	280(50)	450(60)	200(40)	170(40)	140(40)
C(4)	340(60)	390(50)	620(70)	230(50)	280(50)	220(50)
C(64)	540(130)	2000(300)	4200(500)	2400(300)	500(200)	600(190)
C(69)	420(70)	640(70)	450(60)	270(50)	40(50)	150(60)
C(66)	350(60)	430(60)	450(60)	160(50)	20(50)	190(50)
C(15)	420(70)	590(70)	310(60)	230(50)	60(50)	150(50)
C(21)	340(60)	330(50)	400(50)	120(40)	130(50)	240(50)
C(16)	400(60)	310(50)	320(50)	140(40)	60(50)	120(40)
C(47)	960(110)	680(80)	480(70)	260(60)	260(70)	440(70)
C(25)	990(110)	780(80)	400(70)	210(60)	430(70)	490(80)
C(63)	1300(200)	1800(200)	700(110)	970(130)	-660(120)	-1020(160)

Table S-5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($A^2 \times 10^3$) for complex **2a**.

	x	Y	z	U(eq)
H(56A)	-2719	-4761	-1140	40
H(20A)	3677	3020	654	41
H(34A)	-73	-4027	-2188	39
H(36A)	579	275	742	29
H(32A)	-1594	-6828	-2304	52
H(27A)	2105	-783	-2070	55
H(46A)	-3177	-2083	2125	64
H(46B)	-2407	-1991	1605	64
H(9A)	4973	-3428	278	53

H(67A)	-6185	-3239	-4943	74
H(67B)	-4985	-2602	-4825	74
H(24A)	2219	-3780	-2053	61
H(18A)	4406	1403	1884	42
H(26A)	2586	-1735	-3045	70
H(30A)	1042	-4817	-403	48
H(37A)	-169	822	1794	34
H(50A)	-2403	-910	4394	60
H(50B)	-3001	-1756	3512	60
H(28A)	1728	-1271	-1046	40
H(12A)	2551	1020	2362	40
H(10A)	3718	-3285	-861	44
H(22A)	1691	154	-13	31
H(49A)	-3564	-4623	316	134
H(49B)	-2316	-4002	729	134
H(49C)	-3076	-3442	604	134
H(68A)	-5910	-1539	-4645	111
H(68B)	-5014	-1200	-3817	111
H(68C)	-6220	-1837	-3950	111
H(13A)	2440	1252	3646	51
H(55A)	-1016	-3867	-46	44
H(65A)	-4384	-3872	-4465	43
H(65B)	-5567	-4543	-4571	43
H(2A)	4771	-633	2222	37
H(31A)	-338	-6420	-1076	56
H(48A)	-3047	-4445	1647	94
H(48B)	-3837	-3916	1510	94
H(51A)	-3279	75	4059	126
H(51B)	-3858	-748	3170	126
H(45A)	-992	3152	6181	78
H(19A)	4839	2908	1695	46
H(33A)	-1480	-5610	-2849	41
H(7A)	2452	-3129	981	42
H(44A)	-473	2116	6740	69
H(52A)	-4278	-1123	4507	110
H(52B)	-4959	-715	4016	110
H(14A)	2595	127	4195	53
H(53A)	-5834	-2403	3622	135

H(53B)	-4867	-2580	3376	135
H(53C)	-5561	-2172	2892	135
H(8A)	4178	-3346	1378	47
H(3A)	6222	-847	1676	44
H(5A)	3976	-815	-95	33
H(4A)	5755	-959	254	48
H(69A)	-2021	-2570	-2699	62
H(69B)	-2797	-2958	-3590	62
H(66A)	-4469	-2489	-3473	51
H(66B)	-5665	-3162	-3615	51
H(15A)	2815	-1281	3478	54
H(21A)	2159	1620	-225	40
H(16A)	2913	-1563	2180	43
H(47A)	-2265	-2839	2755	80
H(47B)	-1528	-2774	2206	80
H(25A)	2689	-3207	-3025	79

Uv-vis spectra of compounds 1, 2a, 2b and 3

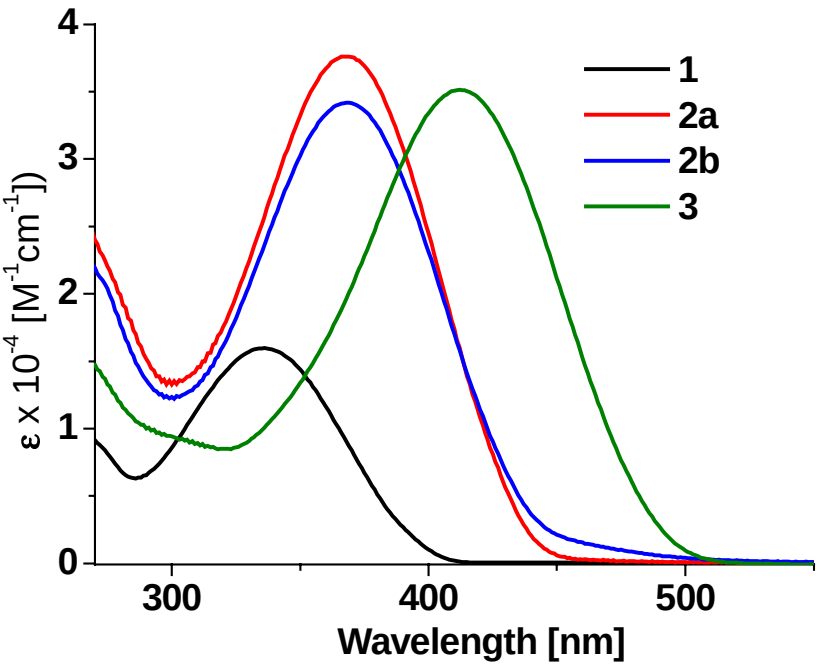


Figure S1. Absorption spectra of **1**, **2a**, **2b** and **3** in dichloromethane.

Potentiostatic electrolysis of Pt-complexes 2a,b

Electrochemical-activated reductive eliminations of complexes **2a** and **2b** were performed with an EG&G PAR 363 potentiostat/galvanostat in a three-electrode single-compartment cell using a platinum foil (10 mm × 10 mm) as working electrode, a Pt-wire-coil counter electrode and an Ag-wire reference electrode. The supporting electrolyte was 0.1 M $(n\text{-Bu})_4NPF_6$, and dichloromethane was used as the solvent. A solution of complex **2a** (4.09×10^{-3} M) and **2b** (5.10×10^{-3} M) was electrolyzed with a constant cell potential (E = 0.67 V vs. Ag/AgCl) for 3 hours at room temperature. After work-up and filtration through a short silica column, a product mixture was obtained, which mainly contained sexithiophene **3** (*ca.* 80%) and higher oligomers (*ca.* 20%). After purification by column chromatography, sexithiophene **3** was isolated in 67% yield from complex **2a** and in 63% from **2b**.

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