

Synthesis and Characterization of a Semiconducting and Solution-processable Ruthenium-based Polymetallayne

Supporting Information

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Table of Contents

General	1
Synthesis – <i>trans</i> -Ru(dppe) ₂ Cl ₂ and <i>cis</i> -Ru(dppe) ₂ Cl ₂	3
Tris(triphenylphosphine)ruthenium(II) dichloride (2)	3
<i>Trans</i> -Ru(dppe) ₂ Cl ₂	3
[RuCl(dppe) ₂]OTf (3)	3
<i>Cis</i> -Ru(dppe) ₂ Cl ₂	3
2-Bromo-5-trimethylsilylethynylthiophene (5).....	4
2-Bromo-5-ethynylthiophene (6)	4
<i>Trans</i> -[Ru(dppe) ₂ (TBr) ₂]	4
Synthesis – Organic ligands	5
3,3'-Bis(dodecyl)bithiophene (8).....	5
3,3'-Bis(dodecyl)-5,5'-dibromo-bithiophene (9)	5
3,3'-Bis(dodecyl)-5,5'-bis(trimethylsilylethynyl)bithiophene (10)	5
(3,3'-Didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (L1)	6
((3,3'-Didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(ethyne-1,2-diyl))bis(trimethylstannane) (L2)	6
3,3'-Didodecyl-5,5'-diethynyl-2,2'-bithiophene (DDBT)	6
Synthesis – P[Ru(dppe) ₂ -DDBT]-L.....	7
P[Ru(dppe) ₂ -DDBT]-L	7
NMR studies.....	8
<i>Trans</i> -[Ru(dppe) ₂ (TBr) ₂]	8
P[Ru(dppe) ₂ -DDBT]-L	9
Assigned endgroup signals.....	9
Calculation of substituent ¹³ C chemical shift increments	10
Calculation of ¹³ C chemical shifts of P[Ru(dppe) ₂ -DDBT].....	11
GPC – monitoring	14
FTIR studies	15
X-ray crystallography of <i>trans</i> -[Ru(dppe) ₂ (TBr) ₂].....	16
MALDI-TOF-MS study	18
Calibration.....	18
Sample plate cleaning procedure	18
Sample preparation	19
Cyclic voltammetry and UV-vis absorption studies.....	21
Cyclic voltammetric studies	21
UV-vis absorption of P[Ru(dppe) ₂ -DDBT]	23
AFM images.....	24
OTS surface treatment procedures	24

Spin-coating.....	24
Thickness and roughness results	24
TGA and DSC	26
References	28

General

All chemicals were purchased from commercial sources and used without further purification unless stated otherwise. All solvents were of reagent grade unless otherwise stated.

NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^1H , 125.77 MHz for ^{13}C , 470.59 MHz for ^{19}F and 202.46 MHz for ^{31}P using the standard pulse sequences included in the TOPSPIN 3.2 software package. The ^1H and ^{13}C NMR spectra were referenced on the solvent signal (CDCl_3 : $\delta(^1\text{H}) = 7.26$ ppm, $\delta(^{13}\text{C}) = 77.0$ ppm; CD_2Cl_2 : $\delta(^1\text{H}) = 5.31$ ppm, $\delta(^{13}\text{C}) = 53.7$ ppm). The ^{19}F NMR spectrum was referenced on external C_6F_6 ($\delta(^{19}\text{F}) = -163.0$ ppm). All chemical shifts are reported in ppm.

GPC measurements were carried out on an Agilent 1100 Series (Agilent, USA) normal temperature size exclusion chromatograph equipped with a refractive index detector and a PL Gel MIXED-B column (Polymer Laboratories, UK). Chloroform was used as eluent and the flow rate was 1 ml min^{-1} . The measurements were carried out at 40°C . Number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

FTIR spectra were obtained on a FTIR spectrometer Vertex80v with Golden Gate Diamant ATR Unit (SPECAC) and MCT detector. The detection range is from $4000\text{--}600 \text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . For each spectrum, 100 scans were accumulated.

X-ray single-crystal data were collected at $160(1) \text{ K}$ on a XtaLAB Synergy Dualflex (Pilatus 200K detector) diffractometer¹ with an Oxford liquid-nitrogen Cryostream cooler. A single wavelength X-ray source from a micro-focus sealed X-ray tube was used with the Cu K_α radiation ($\lambda = 1.54184 \text{ \AA}$). The selected single crystal was mounted using polybutene oil on a loop fixed on a goniometer head and transferred to the diffractometer. Pre-experiment, data collection, data reduction and analytical absorption correction² were performed with the program suite *CrysAlisPro*³ Using *Olex2*,⁴ the structure was solved with the SHELXT⁵ small molecule structure solution program and refined with the SHELXL2018/3 program package⁶ by full-matrix least-squares minimization on F^2 . The thermal ellipsoid plot was created using *Mercury 4.0*.⁷ The crystal data collection and structure refinement parameters are summarized in Table S3. CCDC 1942075 contains the supplementary crystallographic data and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

MALDI-TOF mass spectra were measured with a Bruker autoflex speed MALDI-TOF/TOF using linear mode. The laser of the instrument is a smartbeam-II with a wavelength of 355 nm .⁸ The software for measuring and evaluating the spectra is flexControl 3.4 and flexAnalysis 3.4. All measurements were carried out using a standard set of parameters, given in Table S4. All spectra depicted in the ESI are a combination of 20 spectra à 500 shots, resulting in a total shot number of 10000 per spectrum. All 20 measurements per spectrum were measured on different spots of the dried droplet spot and were chosen randomly by the operator. When a spectrum exhibited a good quality (e.g. high S/N-ratio, etc.) it was added to the final combination. The best measurements were obtained from the edges of the dried droplet spot.

The cyclic voltammetric (CV) measurements of the polymer samples were performed in a glove box under inert (nitrogen) atmosphere using a three-electrode system with a platinum wire as working electrode, a silver chloride-coated silver wire as pseudo-reference electrode, and a platinum sheet as counter electrode. $0.1 \text{ M } n\text{-Bu}_4\text{NPF}_6$ (for electrochemical analysis, $\geq 99.0\%$, Sigma-Aldrich) in dichloromethane (anhydrous, $\geq 99.8\%$, Sigma-Aldrich) or acetonitrile (anhydrous, 99.8% , Sigma-Aldrich) was used as supporting electrolyte. The potentials are given versus ferrocene/ferrocenium (Fc/Fc^+). The cyclovoltammogram of the polymer in solution was recorded using dichloromethane. To measure cyclic voltammetry of thin films, the polymer was deposited on the electrode surface by dip coating: The electrode was dipped into the dichloromethane solution, which contains the polymer.

After then it was gently removed from the solution and dried. Finally, the electrode with the polymer film was immersed in an acetonitrile solution and the cyclic voltammogram was measured.

Electrochemical experiments of the low-molecular weight organometallic compounds were carried out with a potentiostat/galvanostat PARSTAT4000 using the VersaStudio software 2.52.3 (Princeton Applied Research).

The UV/Vis measurements were carried out on a Perkin Elmer "Lambda800" instrument. The solution sample was prepared from a 0.01 mg/ml polymer solution in chloroform and the thin-film sample was prepared by spin-coating 10 mg/ml polymer solution on glass substrate.

Bottom-contact, top-gate thin-film transistors ($L = 20 \mu\text{m}$; $W = 1 \text{ mm}$) were fabricated on glass substrates with photolithographically defined contacts (Cr/Au 5 nm/ 25 nm). After oxygen plasma treatment, the contacts were immersed in a solution of pentafluorobenzene thiol (PFBT) in isopropanol (1 $\mu\text{l/ml}$) for 30 min.⁹ After rinsing with isopropanol and drying with a stream of nitrogen, the polymer was spin-coated from 1,2-dichlorobenzene (5 mg/ml) in a nitrogen filled glovebox. Afterwards, the samples were annealed for 1h at 100°C in N_2 and then the cytop gate dielectric (Asahi Glass) was spin-coated (500 nm) and annealed at 80 °C for 2 min. Finally, 30 nm aluminum gate electrodes were deposited by thermal evaporation in vacuum through a shadow. Transfer and output characteristics were measured with an Agilent 4155B Semiconductor Parameter Analyser in a nitrogen glovebox.

AFM measurements were carried out on a Dimension FastScan (Bruker-Nano, USA). The measurements were done in the peak force tapping mode using FastScan-C cantilevers (Bruker-Nano, USA).

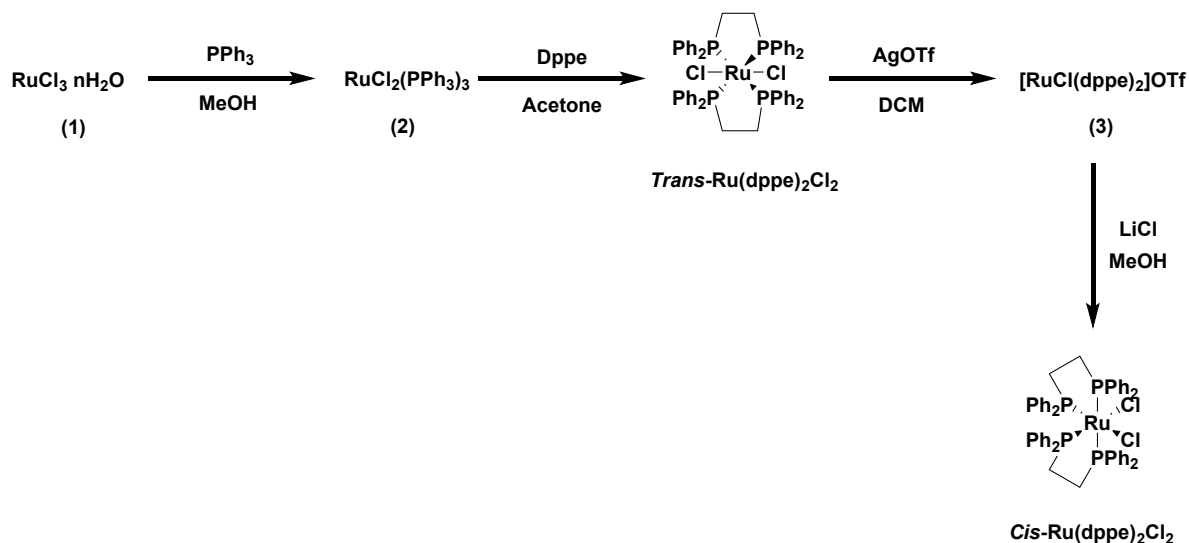
Elemental analysis was carried out on EuroEA Elemental Analyser. The combustion process was carried out at 1000 °C with 15 ml of oxygen. Calibration type was selected as single-point (K-Factor) regression.

The TGA analysis was recorded on TGA Q5000 V3.17 Build 265, and DSC analysis on a DSC 2500.

Further details are given in the respective ESI chapters.

Synthesis – *trans*-Ru(dppe)₂Cl₂ and *cis*-Ru(dppe)₂Cl₂

The described synthesis was carried out in a modification of literature reports.¹⁰



Tris(triphenylphosphine)ruthenium(II) dichloride (2) In a 250 ml one-necked-round-bottom flask, triphenylphosphine (12 g, 45.8 mmol) was added into 100 ml of analytic grade methanol. The addition of ruthenium trichloride hydrate (1) (2.0 g, 7.7 mmol) resulted in a deeply brown colored solution. The reaction was heated to reflux for 4 hours, then the mixture was filtered, washed with diethyl ether and dried in air. Tris(triphenylphosphine)ruthenium(II) chloride (2) was obtained (6.4 g, 6.7 mmol, 87%). ³¹P NMR (202 MHz, CDCl₃) δ: 40.9 (br s). Splitting in two broad signals at 75.2 ppm (1P) and 24.8 ppm (2P) was observed in CDCl₃ at -50°C.¹¹

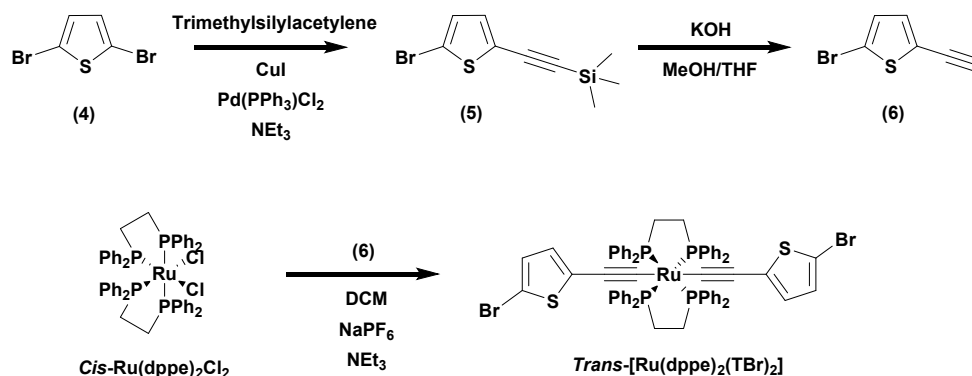
Trans-Ru(dppe)₂Cl₂ Tris(triphenylphosphine)ruthenium(II) dichloride (2) (6.4 g, 6.7 mmol) was dissolved in 70 ml of acetone, giving a deeply brown colored solution. 1,2-Bis(diphenylphosphino)ethane (dppe, 5.6 g, 14.1 mmol) was then added, leading to the formation of a yellow colored precipitate after 1 hour of stirring at room temperature. The mixture was filtered, and the obtained yellow solid washed with acetone and dried in air. The powder was recrystallized in chloroform to afford *trans*-Ru(dppe)₂Cl₂ as yellow crystals. (4.9 g, 5.1 mmol, 76%). ¹H NMR (500 MHz, CDCl₃) δ: 7.27 (m, 16H; H_{Ar}), 7.20 (t, J = 7.5 Hz, 8H; H_{Ar}), 7.00 (t, J = 7.5 Hz, 16H; H_{Ar}), 2.74 (m, 8H; CH₂). ³¹P NMR (202 MHz, CDCl₃) δ: 45.0 (s).

[RuCl(dppe)₂]OTf (3) *Trans*-Ru(dppe)₂Cl₂ (4.9 g, 5.1 mmol) was dissolved in 75 ml of dichloromethane, followed by the addition of silver trifluoromethane sulfonate (1.3 g 5.1 mmol), giving a deep red solution. The mixture was stirred at room temperature for 1 hour and then filtered over a pack of celite. The filtrate was collected, diluted with hexane and concentrated at the rotary evaporator. The product (3) was obtained as a dark red powder (4.7 g, 4.3 mmol, 85%). ³¹P NMR (202 MHz, CDCl₃) δ: 84.1 (t, J = 12.0 Hz, 2P), 55.9 (t, J = 12.0 Hz, 2P). ¹⁹F NMR (470 MHz, CDCl₃) δ: -79.0 (s).

Cis-Ru(dppe)₂Cl₂ [RuCl(dppe)₂]OTf (3) (4.7 g, 4.3 mmol) was dissolved in 600 ml of methanol. Lithium chloride (2.2 g, 52 mmol, 12.0 eq.) was added into the solution, leading immediately to the precipitation of a yellow powder. The mixture was stirred at room temperature for 10 minutes, then the obtained powder was collected by filtration and washed with methanol, giving yellow *cis*-Ru(dppe)₂Cl₂, which was air dried (3.8 g, 3.9 mmol, 92%). Overall yield based on ruthenium trichloride is 52%. ¹H NMR (500 MHz, CDCl₃) δ: 8.23 (m, 4H; H_{Ar}), 7.55 (m, 4H; H_{Ar}), 7.28 (6H; H_{Ar}), 7.01 (m, 4H; H_{Ar}), 6.93 (m, 2H; H_{Ar}), 6.9-6.7 (20H; H_{Ar}), 3.2-2.8 (6H; CH₂), 2.56 (m, 2H;

CH₂). ³¹P NMR (202 MHz, CDCl₃) δ: 52.6 (t, J = 19.5 Hz, 2P), 37.9 (t, J = 19.5 Hz, 2P).

Synthesis – *Trans*-[Ru(dppe)₂(TBr)₂]



2-Bromo-5-trimethylsilylethynylthiophene (5) 100 ml of trimethylamine was degassed over molecular sieve for 30 min. 2,5-Dibromothiophene (4) (3.9 g, 16 mmol), and subsequently CuI (0.07 g, 0.4 mmol, 0.024 eq.), and *bis*(triphenylphosphine)-palladium chloride (0.3 g, 0.4 mmol, 0.024 eq.) were added into the solution. Finally, trimethylsilylacetylene (1.5 g, 14.9 mmol, 0.98 eq.) was added into the mixture and the reaction was allowed to stir at room temperature overnight. Upon the addition of trimethylsilylacetylene, the color of the reaction mixture changed from yellow to greenish yellow. The mixture was dried by rotary evaporation and purified by flash column chromatography with *n*-hexane as the eluent. The title compound (5) was obtained as a pale yellow oil (1.6 g, 6.3 mmol, yield = 42%). ¹H NMR (500 MHz, CDCl₃) δ: 6.96 (d, J = 3.9 Hz, 1H; thienyl-H), 6.90 (d, J = 3.9 Hz, 1H; thienyl-H), 0.24 (s, 9H; CH₃).

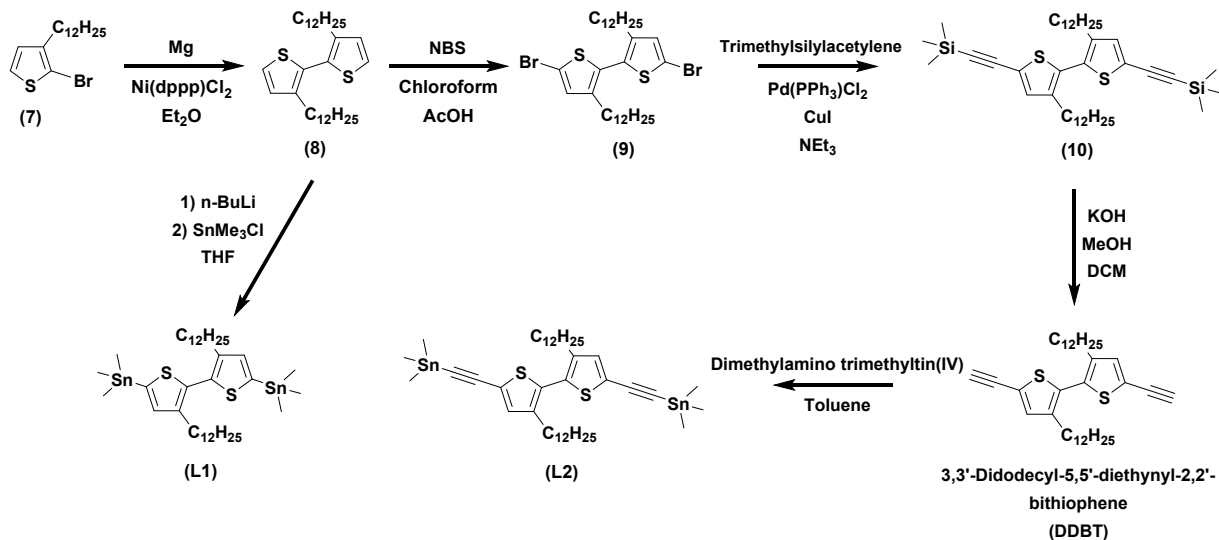
2-Bromo-5-ethynylthiophene (6) 2-Bromo-5-trimethylsilylethynylthiophene (5) (1.3 g, 5.0 mmol) was dissolved in a THF/MeOH 1:1 mixture (20 ml), to which KOH aqueous solution (5M, 1 ml) was added. The reaction mixture was allowed to stir for 1 hour, washed with brine and extracted with ethyl acetate three times. The organic layers were combined and dried using anhydrous MgSO₄. The organic solvent was removed by rotary evaporator and a 90% yield was assumed. The product was directly transferred to the next reaction without purification.

***Trans*-[Ru(dppe)₂(TBr)₂]** *Cis*-Ru(dppe)₂Cl₂ (0.3 g, 0.3 mmol) was stirred in a 100 ml round-bottom flask with dichloromethane (50 ml). Sodium hexafluorophosphate (0.2 g, 1.0 mmol, 3.1 eq.) was added, immediately causing the color of the solution to change from bright yellow to deep red. A large excess of 2-bromo-5-ethynylthiophene (6) (0.5 g, 2.67 mmol) and trimethylamine (0.2 g, 1.9 mmol, 6.2 eq.) was added without causing an obvious color change. Stirring overnight led to the formation of a yellow precipitate, which was filtered through PTFE filter paper and washed with ACN and DCM. The title compound *trans*-[Ru(dppe)₂(TBr)₂] was collected as a powder and dried by air (0.3 g, 0.23 mmol, 74%).

NMR data and spectra are given on page S8. ESI MS *m/z*: 1269.9859 g mol⁻¹. FTIR *v*: 2041 cm⁻¹ (*v*_{C≡C}).

Synthesis – Organic ligands

The described synthesis was carried out in a modification of literature reports.^{12,13}



3,3'-Bis(dodecyl)bithiophene (8) Magnesium (0.1 g, 4.1 mmol) was added into a three-necked round-bottom flask and dried under vacuum. Dry diethyl ether (30 ml), and then 2-bromo-3-dodecylthiophene (7) (1 g, 2.9 mmol) were subsequently added. Few drops of 1,2-dibromoethane were used to initiate the reaction. The reaction mixture was heated at reflux for 1 hour under N₂ flow (giving “solution A”). Ni(dppp)Cl₂ (90 mg, 0.16 mmol) was added into another two-necked round-bottom flask and dried under vacuum. 30 ml of diethyl ether and 2-bromo-3-dodecylthiophene (7) (1 g, 2.92 mmol) were added (giving “solution B”). Solution A was filtered and transferred to solution B at room temperature. The resulting mixture was heated at 40°C overnight. The product was extracted with diethyl ether. The organic phase was combined and dried with MgSO₄, and the organic solvent removed. A column chromatography carried out with *n*-hexane as eluent afforded the product (8) as a pale yellow oil (0.78 g, 1.6 mmol, 51%). ¹H NMR (500 MHz, CDCl₃) δ: 7.28 (d, J = 5.3 Hz, 2H; thienyl-H), 6.96 (d, J = 5.3 Hz, 2H; thienyl-H), 2.50 (t, J = 7.5 Hz, 4H; CH₂), 1.54 (m, 4H; CH₂), 1.35-1.20 (36H; CH₂), 0.88 (t, J = 6.7 Hz, 6H; CH₃).

3,3'-Bis(dodecyl)-5,5'-dibromo-bithiophene (9) In a 25 ml one-necked round-bottom flask, acetic acid (5 ml) and chloroform (5 ml) were added to 3,3'-bis(dodecyl)bithiophene (8) (0.2 g, 0.4 mmol), and the solution cooled down to 0°C with an ice bath. *N*-Bromosuccinimide (0.15 g, 0.83 mmol, 2.1 eq.) was added at 0°C in one portion. The reaction mixture was stirred at room temperature overnight, and then quenched by addition of water. After extraction with diethyl ether, all organic phases were combined and sequentially washed with water, 10 ml of 10 wt% KOH (aq) and brine. The organic phase was combined and dried with MgSO₄. The obtained brown oil was purified by column chromatography with *n*-hexane as eluent, and the product (9) was obtained as a pale yellow oil (0.25 g, 0.37 mmol, 94%). ¹H NMR (500 MHz, CDCl₃) δ: 6.91 (s, 2H; thienyl-H), 2.43 (t, J = 7.5 Hz, 4H; CH₂), 1.49 (m, 4H; CH₂), 1.34-1.20 (36H; CH₂), 0.88 (t, J = 6.8 Hz, 6H; CH₃).

3,3'-Bis(dodecyl)-5,5'-bis(trimethylsilylethynyl)bithiophene (10) 3,3'-Bis(dodecyl)-5,5'-dibromo-bithiophene (9) (0.25 g, 0.37 mmol) was dissolved in 10 ml of degassed triethylamine, followed by the addition of copper(I) iodide (5 mg, 0.026 mmol) and bis(biphenylphosphine)palladium dichloride (25 mg, 0.035 mmol). After 5 minutes of stirring, trimethylsilylacetylene (0.085 g, 0.12 ml, 0.85 mmol) was added into the reaction mixture and it was heated at reflux for 2 hours under N₂ flow. After that, 2 M HCl (10 ml) was added to quench the reaction and

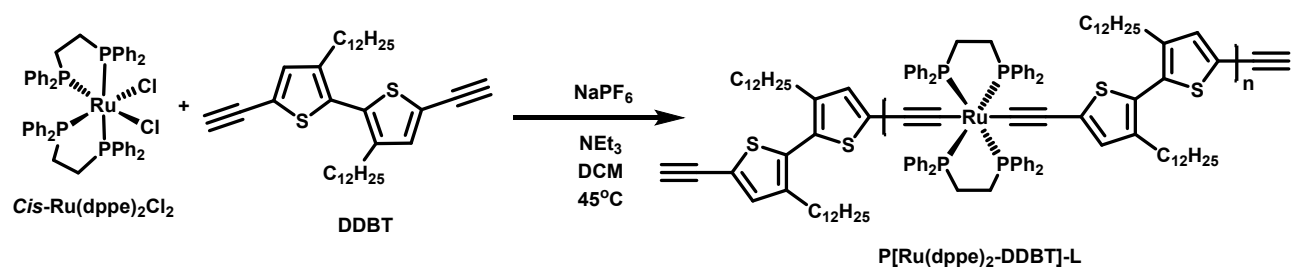
diethyl ether was used to extract the crude product. The organic phases were combined, dried with MgSO_4 and the solvent removed *in vacuo*. The crude product was purified by column chromatography with *n*-hexane as eluent to afford (**10**) as a yellow oil (0.22 g, 0.32 mmol, 85%). ^1H NMR (500 MHz, CDCl_3) δ : 7.09 (s, 2H; thienyl-H), 2.43 (t, $J = 7.4$ Hz, 4H; CH_2), 11.48 (m, 4H; CH_2), 1.34-1.20 (36H; CH_2), 0.88 (t, $J = 6.8$ Hz, 6H; CH_3), 0.25 (s, 18H; $\text{Si}(\text{CH}_3)_3$).

(3,3'-Didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (L1) 3,3'-Bis(dodecyl)bithiophene (**8**) (1.3 g, 2.3 mmol, 90% purity assumed) was dissolved in anhydrous tetrahydrofuran (30 ml) in a 100 ml two-necked round-bottom flask. The reaction was cooled to -78 °C and *n*-butyllithium (3.2 ml, 5.1 mmol, 2.2 eq.) was added dropwise into the reaction mixture. The mixture was stirred at low temperature for 1 hour under N_2 flow, and then allowed to warm to room temperature. After stirring at room temperature for 30 minutes, the solution was again cooled down to -78 °C and trimethyltin chloride (5.1 ml, 5.1 mmol, 2.2 eq.) was added dropwise into the mixture. The solution color turned from orange to yellow after a few minutes. The reaction was stirred overnight under N_2 atmosphere, and then the crude product was extracted with diethyl ether 3 times. The organic phases were combined, washed with brine and dried by MgSO_4 . All organic solvent was removed first by rotary evaporator and then using a vacuum pump. The obtained yellow solid was dissolved in a minimal amount of isopropanol for recrystallization. The resulting white powder was washed with cold isopropanol to give (**8**) (0.83 g, 1 mmol, 43%). ^1H NMR (500 MHz, CDCl_3) δ : 7.02 (s and d, $^3J_{\text{SnH}} = 27.9$ Hz, 2H; thienyl-H), 2.52 (t, $J = 7.4$ Hz, 4H; CH_2), 1.56 (m, 4H; CH_2), 1.32-1.20 (36H; CH_2), 0.85 (t, $J = 6.9$ Hz, 6H; CH_3), 0.36 (s and d, $^2J_{\text{SnH}} = 56.3$ Hz, 18H; $\text{Sn}(\text{CH}_3)_3$).

(3,3'-Didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(ethyne-1,2-diyl)bis(trimethylstannane) (L2) 3,3'-Didodecyl-5,5'-diethynyl-2,2'-bithiophene (**DBBT**) (0.2 g, 0.4 mmol) was dissolved in dry toluene (10 ml) in a 25 ml two-necked round-bottom flask. (Dimethylamino)trimethyltin(IV) (0.17 g, 0.14 ml, 0.84 mmol) was added dropwise, and the reaction stirred overnight at 80°C under N_2 atmosphere. All volatiles were removed *in vacuo*, yielding the product (**12**) as brown oil. Since the substance is not stable in the presence of moisture, only a fast 60 MHz ^1H NMR measurement was carried out before subsequent reaction steps. The peak corresponding to the ethynyl proton could no longer be detected, indicating a high conversion rate. ^1H NMR (60 MHz, CDCl_3) δ : 7.05 (2H; thienyl-H), 2.44 (t, 4H; CH_2), 1.54-1.24 (40H; CH_2), 0.85 (t, 6H; CH_3), 0.36 (18H; $\text{Sn}(\text{CH}_3)_3$).

3,3'-Didodecyl-5,5'-diethynyl-2,2'-bithiophene (DBBT) 3,3'-Bis(dodecyl)-5,5'-bis(trimethylsilylethynyl)-bithiophene (**10**) (0.7 g, 1 mmol) was added into a 50 ml one-necked round-bottom flask and diluted with dichloromethane (20 ml). After that, a freshly prepared KOH solution (0.33 g, 5 mmol in 20 ml of methanol) was added and the reaction mixture stirred for 3 hours at room temperature. The reaction was quenched with water and extracted with dichloromethane. All organic phases were combined, washed with water and brine, and then dried with MgSO_4 . The solvent was removed *in vacuo*, and the resulting crude product purified by flash column chromatography with *n*-hexane as eluent to yield the title compound (0.4 g, 0.7 mmol, 73%). ^1H NMR (500 MHz, CDCl_3) δ : 7.13 (s, 2H; thienyl-H), 3.37 (s, 2H; ethynyl-H), 2.45 (t, $J = 7.5$ Hz, 4H; CH_2), 1.50 (m, 4H; CH_2), 1.35-1.20 (36H; CH_2), 0.88 (t, $J = 6.8$ Hz, 6H; CH_3).

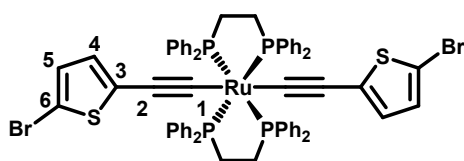
Synthesis – P[Ru(dppe)₂-DDBT]-L



P[Ru(dppe)₂-DDBT]-L The precursors **DDBT** (82.6 mg, 0.15 mmol) and *cis*-Ru(dppe)₂Cl₂ (131 mg, 0.135 mmol) were added into a 50 ml two-necked round-bottom flask, followed by the addition of NaPF₆ (69.3 mg, 0.4 mmol), DCM (24 ml) and NEt₃ (0.23 ml, 1.62 mmol). The reaction mixture was heated at 45°C for 3 days under N₂ flow. The crude mixture was precipitated in *n*-hexane, followed by re-dissolving in DCM and precipitation in acetonitrile. A yellow solid was obtained (20 mg).

NMR studies

Trans-[Ru(dppe)₂(TBr)₂]



Trans-[Ru(dppe)₂(TBr)₂]

¹H NMR (500 MHz, CDCl₃): 7.41 (m, 16H; *o*-Ph), 7.20 (t, 7.6 Hz, 8H; *p*-Ph), 7.01 (t, 7.6 Hz, 16H; *m*-Ph), 6.74 (d, 3.7 Hz, 2H; 5), 5.99 (d, 3.7 Hz, 2H; 4), 2.57 (m, 8H; P(CH₂)₂P).

¹³C NMR (125 MHz, CDCl₃) δ: 141.3 (m, 1), 136.4 (m; *i*-Ph), 134.0 (*o*-Ph), 133.4 (3), 129.1 (5), 128.8 (*p*-Ph), 127.2 (*m*-Ph), 124.7 (4), 108.5 (2), 103.5 (6), 31.4 (m; P(CH₂)₂P).

³¹P NMR (202 MHz, CDCl₃) δ: 53.7.

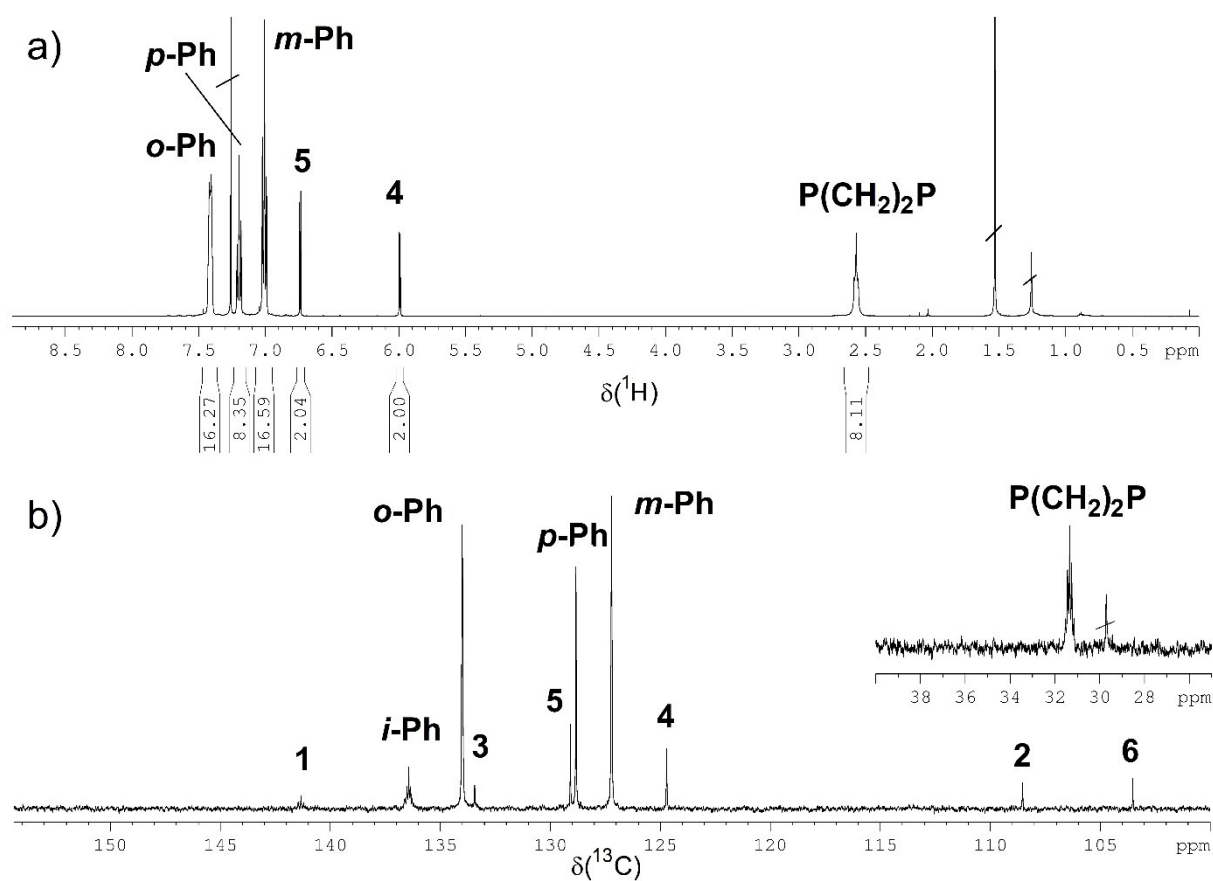
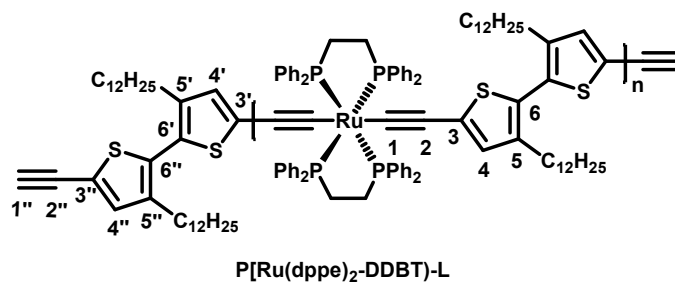


Figure S1. ¹H (a) and ¹³C NMR spectrum (b) of *trans*-[Ru(dppe)₂(TBr)₂].

P[Ru(dppe)₂-DDBT]-L



¹H NMR (500 MHz, CD₂Cl₂) δ: 7.55 (m, 16H; *o*-Ph), 7.27 (m, 8H; *p*-Ph), 7.12 (m, 16H; *m*-Ph), 6.28 (br s, 2H; 4), 2.71 (8H; P(CH₂)₂P), 2.63 (4H; 7), 1.70 (4H; 8), 1.5-1.2 (36H; 9-17), 0.88 (6H, 18).

¹³C NMR (125 MHz, CD₂Cl₂) δ: 141.0 (5), 138.8 (1), 137.4 (*i*-Ph), 134.5 (*o*-Ph), 131.0 (3), 129.1 (*p*-Ph), 127.6 (*m*-Ph), 127.2 (4), 124.4 (6), 109.7 (2), 32.3 (17), 31.7 (m, P(CH₂)₂P), 31.5 (8), 30.5-29.7 (9-15), 29.5 (7), 23.1 (17), 14.3 (18).

³¹P NMR (202 MHz, CD₂Cl₂) δ: 51.6.

Assigned endgroup signals

¹H NMR (500 MHz, CD₂Cl₂): 7.20 (4''), 6.22 (4'), 3.45 (1'').

¹³C NMR (125 MHz, CD₂Cl₂): 141.0 (5', 5''), 135.2 (4''), 132.2 (3'), 121.3 (6'), 120.6 (3''), 109.5 (2'), 81.5 (1''), 77.2 (2'').

The degree of polymerization can be calculated by the following equation:

$DP_{\text{NMR}} = (I_{4+4'} - I_{1''})/I_{1''}$, where I_n is the integral signal intensity of the corresponding proton n.

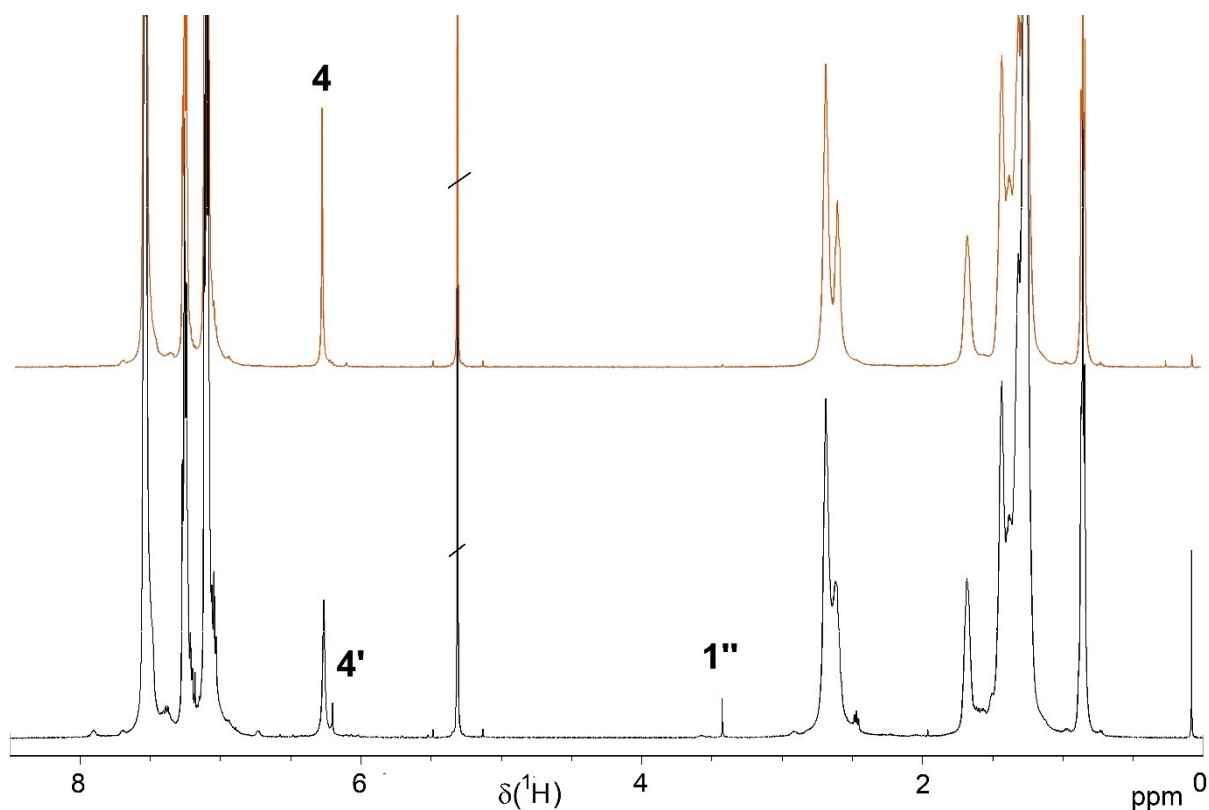
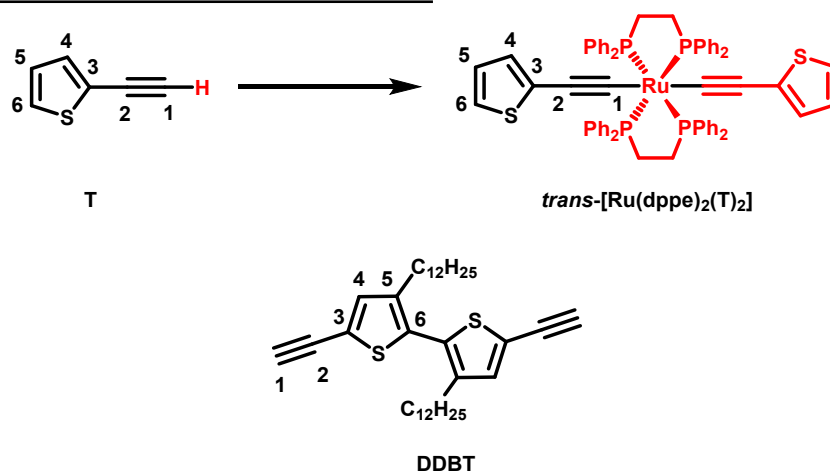


Figure S2. ^1H NMR spectra of a high-molecular-weight $\text{P}[\text{Ru}(\text{dppe})_2\text{-DBBT}]$ (red) and low-molecular-weight $\text{P}[\text{Ru}(\text{dppe})_2\text{-DBBT}]\text{-L}$ (black); solvent: CD_2Cl_2 .

The assignment of ^{13}C NMR signals of non-protonated carbons was hampered by missing correlations in the HMBC spectrum. Therefore, the signal assignment is based on chemical shift increment calculation. Appropriate substituent chemical shift increments were determined from the ^{13}C NMR data of 2-ethynylthiophene (**T**) and *trans*- $[\text{Ru}(\text{dppe})_2(\text{T})_2]$, in which the ethynyl proton is replaced by $\text{Ru}(\text{dppe})_2\text{T}$.

Calculation of substituent ^{13}C chemical shift increments



T - ^{13}C NMR (125 MHz, CD_2Cl_2) δ : 133.4 (4), 127.9 (6), 127.3 (5), 122.2 (3), 81.4 (1), 77.0 (2).

Trans-[Ru(dppe)₂(T)₂] - ¹³C NMR (125 MHz, CD₂Cl₂) δ: 138.0 (m; 1), 137.2 (m; *i*-Ph), 134.4 (*o*-Ph), 132.2 (3), 129.0 (*p*-Ph), 127.4 (*m*-Ph), 126.3 (5), 124.7 (4), 120.0 (6), 109.0 (2), 31.7 (m; P(CH₂)₂P).

DDBT - ¹³C NMR (125 MHz, CD₂Cl₂) δ: 143.4 (5), 135.1 (4), 130.1 (6), 122.2 (3), 82.1 (1), 76.9 (2), 32.2, 30.8, 30.0, 29.9, 29.7, 29.6, 29.0, 23.0, 14.2 (all C₁₂H₂₅).

¹³C chemical shift effect on C₁ – C₆ due to substitution of proton by **Ru(dppe)₂** moiety (solvent: CD₂Cl₂): Δδ (C₁) = +56.6 ppm; Δδ (C₂) = +32.0 ppm; Δδ (C₃) = +10.0 ppm; Δδ (C₄) = -8.7 ppm; Δδ (C₅) = -1.0 ppm; Δδ (C₆) = -7.9 ppm

Calculation of ¹³C chemical shifts of P[Ru(dppe)₂-DDBT]

Applying these increments on the ¹³C NMR data of the ligand DDBT results in the following estimated chemical shifts for carbons C₁ – C₆ of **P[Ru(dppe)₂-DDBT]** and finally in a complete signal assignment:

Table S1. Calculated and observed ¹³C chemical shifts values of **P[Ru(dppe)₂-DDBT]**.

Carbon	Calculated values	Observed values
C ₁	82.1 + 56.6 = 138.7 ppm	138.8 ppm
C ₂	76.9 + 32.0 = 106.9 ppm	109.7 ppm
C ₃	122.2 + 10.0 = 132.2 ppm	131.0 ppm
C ₄	135.1 - 8.7 = 126.4 ppm	127.2 ppm
C ₅	143.4 - 1.0 = 142.4 ppm	141.0 ppm
C ₆	130.1 - 7.9 = 122.2 ppm	124.4 ppm

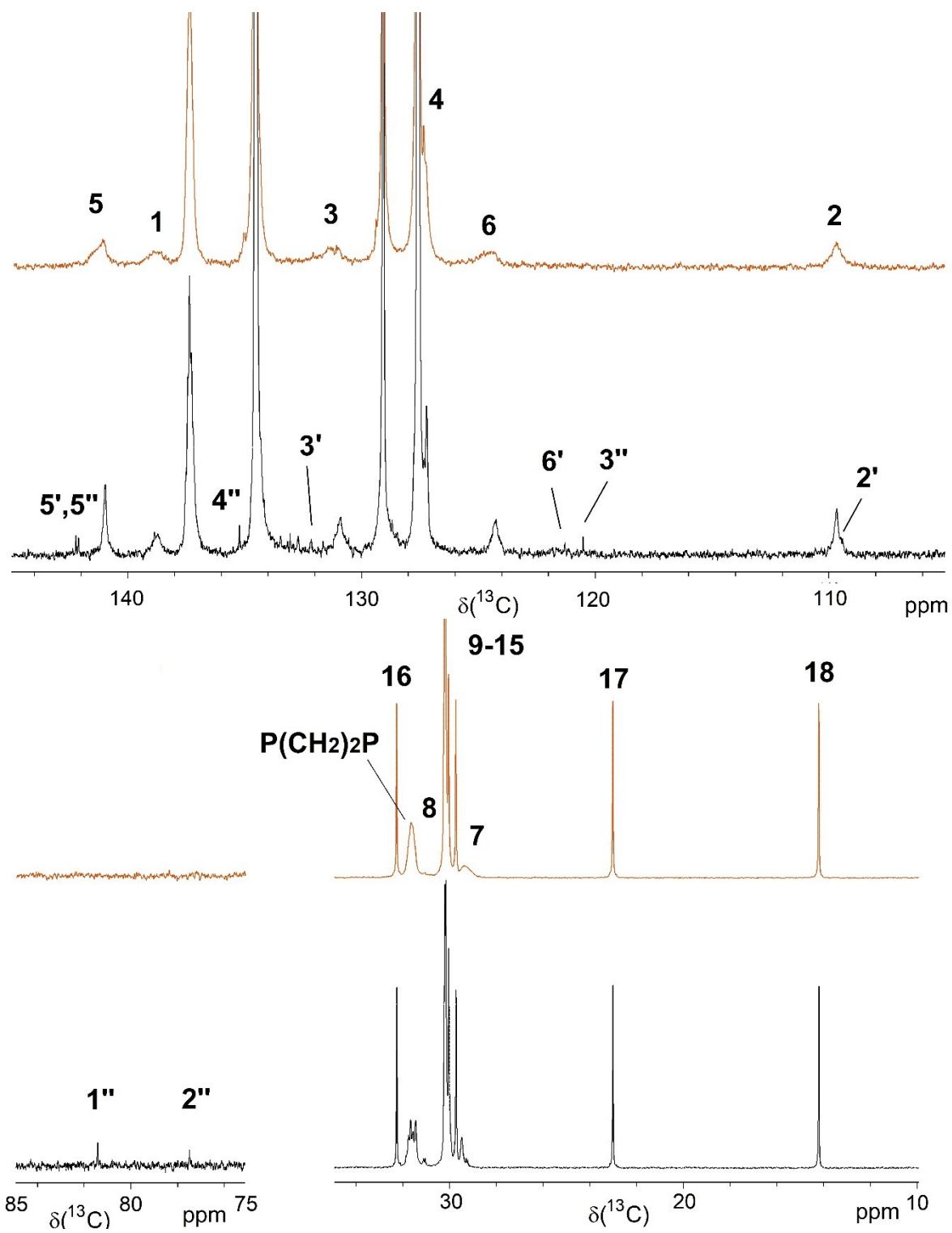


Figure S3. ^{13}C NMR spectra of high-molecular-weight $\text{P}[\text{Ru}(\text{dppe})_2\text{-DBBT}]$ (red) and low-molecular-weight $\text{P}[\text{Ru}(\text{dppe})_2\text{-DBBT}]\text{-L}$; solvent: CD_2Cl_2 .

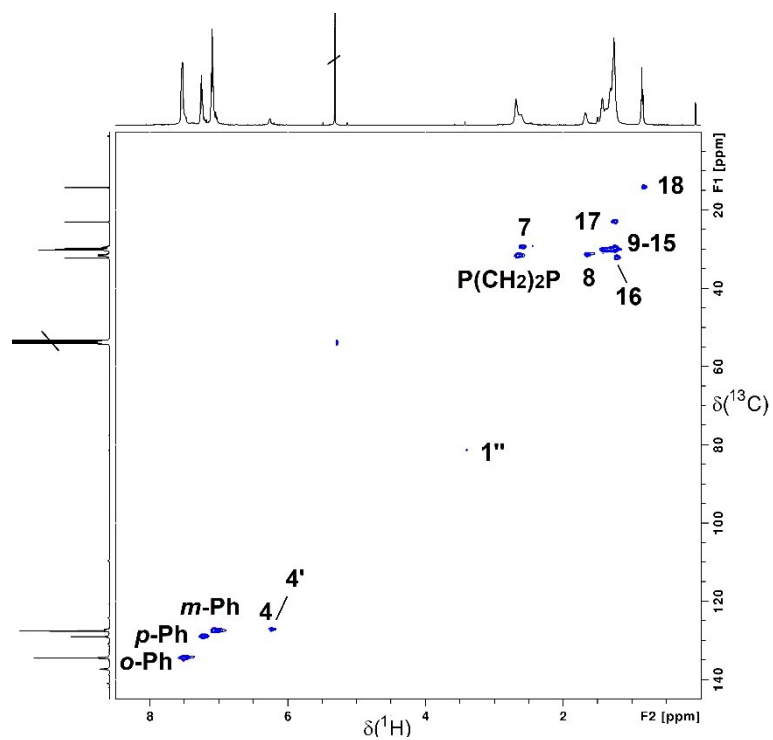


Figure S4. HSQC spectrum of low-molecular-weight $P[Ru(dppe)_2-DBBT]-L$; solvent: CD_2Cl_2 .

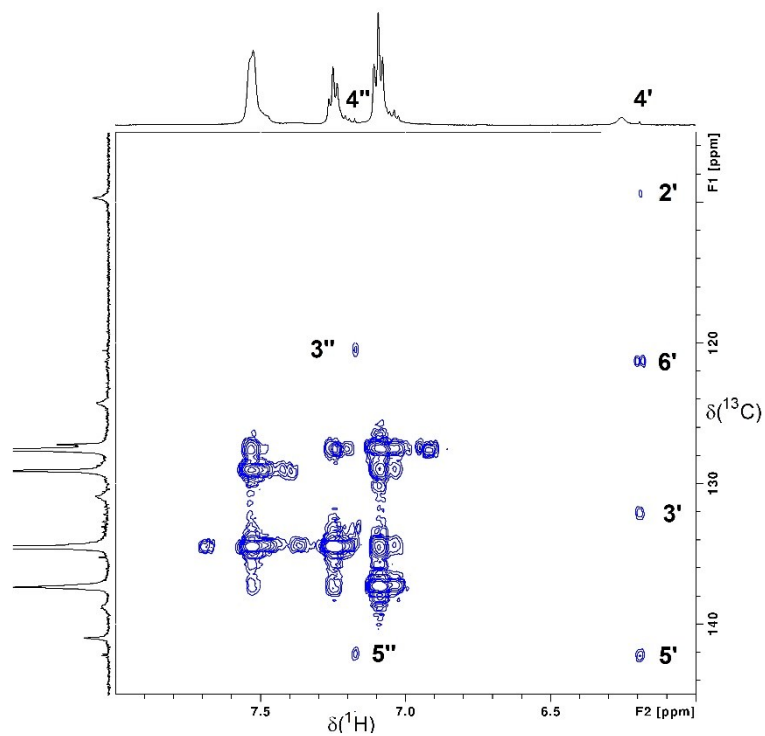


Figure S5. HMBC spectrum (region) of low-molecular-weight $P[Ru(dppe)_2-DBBT]-L$; solvent: CD_2Cl_2 .

GPC – monitoring

Table S2. GPC results at different time interval.

Entry	M_w (kg mol ⁻¹)	M_n (kg mol ⁻¹)	PDI
P[Ru(dppe) ₂ -DDBT]-24h	620	180	3.5
P[Ru(dppe) ₂ -DDBT]-48h	690	240	2.8
P[Ru(dppe) ₂ -DDBT]-72h	640	220	2.9
P[Ru(dppe) ₂ -DDBT] final product after purification	360	80	4.5

Monitoring procedure

1 ml of reaction mixture was sampled every 24 hours, injected into 50 ml of *n*-hexane, followed by suction filtration. The powder was collected, and a 1 mg/ml solution was prepared. This solution was passed through a 0.2 μm filter before injection into the column. All the M_w , M_n and PDI values were calculated within the calibration points. According to Table S2, the polymerization is completed after 48 hours. Further heating did not increase the molecular weight. After purification, a drastic change of molecular weight according to GPC is observed, indicating the presence of conglomerates during the GPC monitoring.

FTIR studies

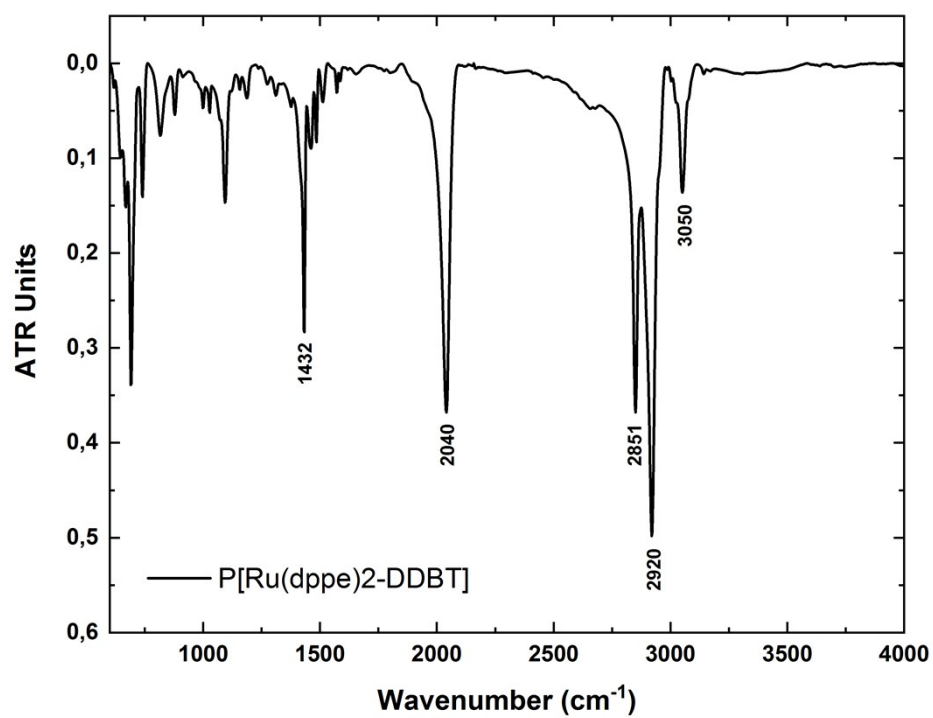


Figure S6. FTIR spectrum of P[Ru(dppe)₂-DDBT].

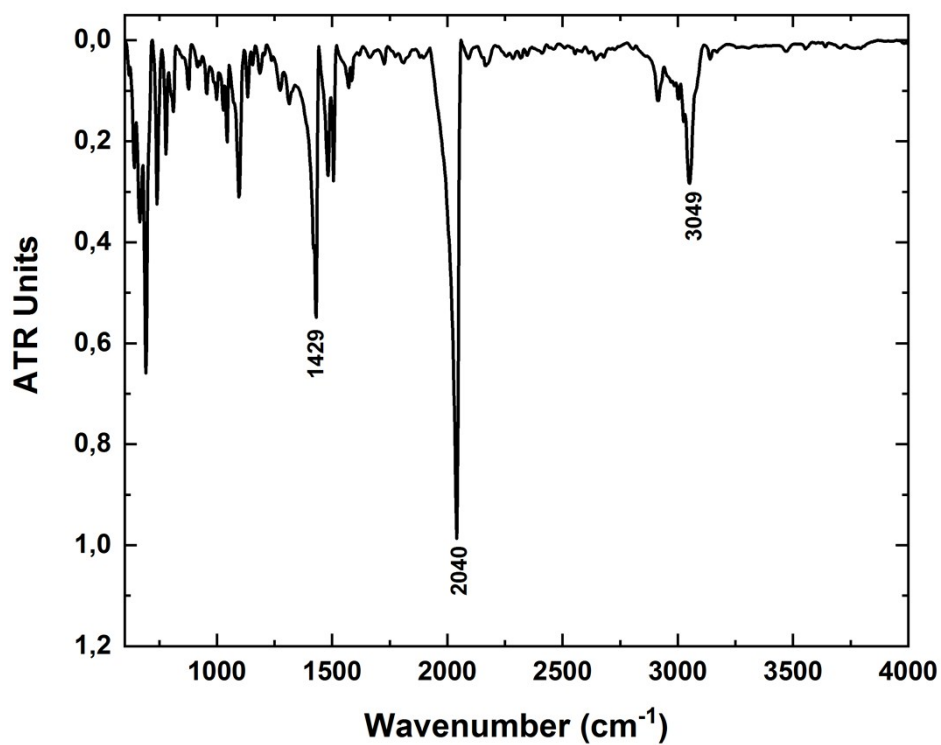


Figure S7. FTIR spectrum of *trans*-[Ru(dppe)₂(TBr)₂].

X-ray crystallography of *trans*-[Ru(dppe)₂(TBr)₂]

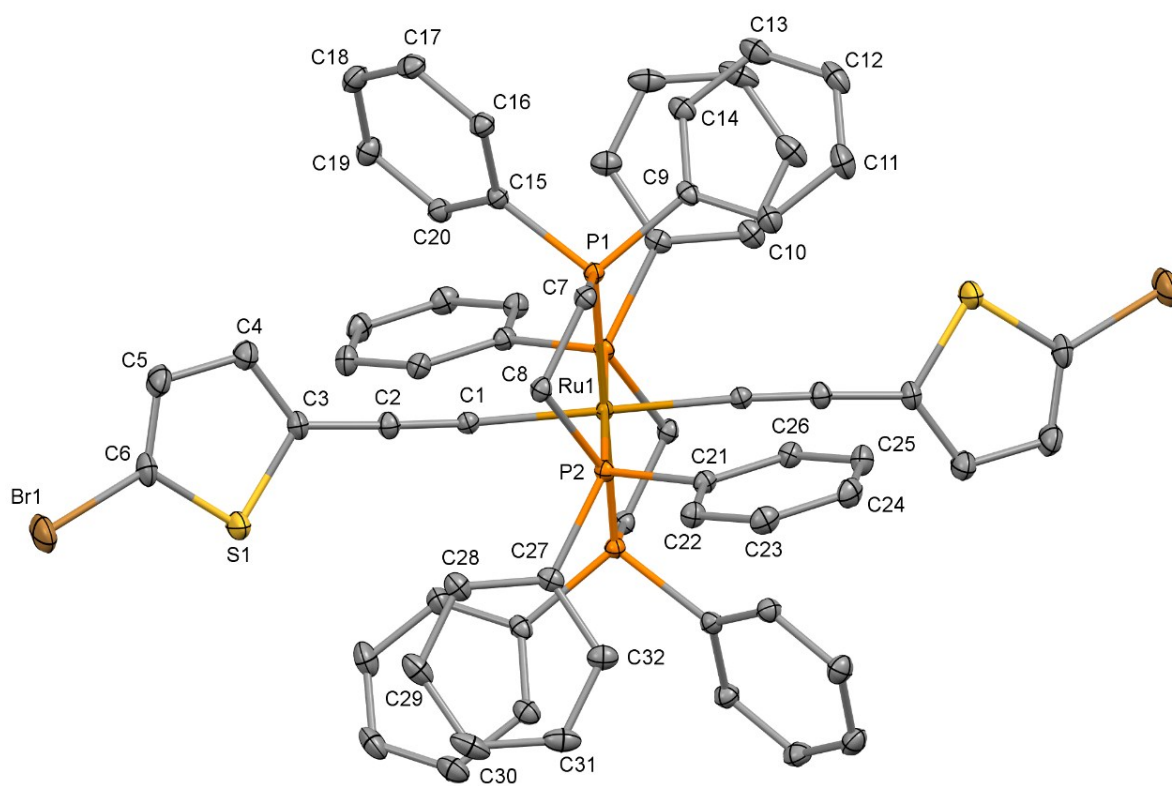


Figure S8. Molecular structure of *trans*-[Ru(dppe)₂(TBr)₂]. The thermal ellipsoids are drawn at the 30 % probability level. All H atoms are omitted for clarity. The Ru center lies on a center of inversion, only half of the molecule was refined, the second part being reproduced by a symmetry operation.

Table S3. Crystal data and structure refinement parameters for *trans*-[Ru(dppe)₂(TBr)₂].

<i>trans</i> -[Ru(dppe) ₂ (TBr) ₂].	
CCDC number	CCDC 1942075
Empirical formula	C ₆₄ H ₅₂ Br ₂ P ₄ RuS ₂
Formula weight	1269.94
Temperature/K	160(1)
Crystal system	triclinic
Space group	P-1
a/Å	9.3882(2)
b/Å	12.9082(2)
c/Å	13.5032(3)
α/°	117.037(2)
β/°	96.017(2)
γ/°	103.315(2)
Volume/Å ³	1376.31(5)
Z	1
ρ _{calc} /g/cm ³	1.532
μ/mm ⁻¹	6.129
F(000)	642.0
Crystal size/mm ³	0.14 × 0.07 × 0.02
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.574 to 148.978
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 15, -16 ≤ l ≤ 16
Reflections collected	29985
Independent reflections	5629 [R _{int} = 0.0277, R _{sigma} = 0.0194]
Data/restraints/parameters	5629/0/331
Goodness-of-fit on F ²	1.061
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0312, wR ₂ = 0.0833
Final R indexes [all data]	R ₁ = 0.0318, wR ₂ = 0.0837
Largest diff. peak/hole / e Å ⁻³	1.29/-1.44

MALDI-TOF-MS study

Table S4. Parameters for positive and negative reflectron and positive linear mode MALDI measurements.

Parameter	Linear positive mode
m/z range	0 - 200k
Sample rate	0.5
Shots per measurement	1000
Matrix suppression	Off
Measurements per spectra	20
Random walk	Off
Detector gain	100x
Electronic gain	Enhanced
Realtime smooth	High
Laser-frequency	1000 Hz
Laser-size	Large

Calibration

High molecular weight area (1k - 14k m/z)

At the beginning of each set of high molecular weight MALDI-TOF-MS measurements in linear positive mode, the instrument was calibrated as described in literature^{14,15}.

Sample plate cleaning procedure

The sample plate was cleaned before every new series of measurements using the following procedure, which was slightly changed compared to literature¹⁴:

1. Wipe sample plate with wet paper tissue (each once: chloroform, acetonitrile, acetone);
2. Clean with a sponge/steel-polishing solution "Mr Muscle, Stahl-Fix classic" ©SC Johnson.
3. Ultra-sonication for 10 min at rt in Milli-Q H₂O / acetonitrile (100 ml / 50 ml);
4. Rinse with 50 ml acetonitrile;
5. Ultra-sonication for 10 min at rt in acetone / tetrahydrofuran (100 ml / 50 ml);
6. Rinse with 50 ml tetrahydrofuran;
7. Rinse with 50 ml acetone;
8. Ultra-sonication for 10 min at rt in chloroform / ethanol (100 ml / 50 ml);
9. Rinse with 50 ml ethanol;
10. Rinse with 50 ml chloroform.

Sample preparation

Dried-droplet method

The samples were prepared with the dried-droplet method on a standard sample plate (Bruker "MTP 384 target plate ground steel BC" Part-No.: 8280784)^{16,17}. The polymeric analyte **P[Ru(dppe)₂-DDBT]-L** and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as secondary matrix were dissolved in toluene. The additive sodium trifluoroacetate (NaTFA) was dissolved in ethanol. The matrix and analyte were mixed with a ratio of 10:1 plus 1 vol.-% NaTFA (e.g. 100 µl matrix - 10 µl analyte - 1 µl NaTFA). Finally, the mixed solution was dropped on the sample plate (V = 1 µl) and dried in air (~ 1 min)¹⁸.

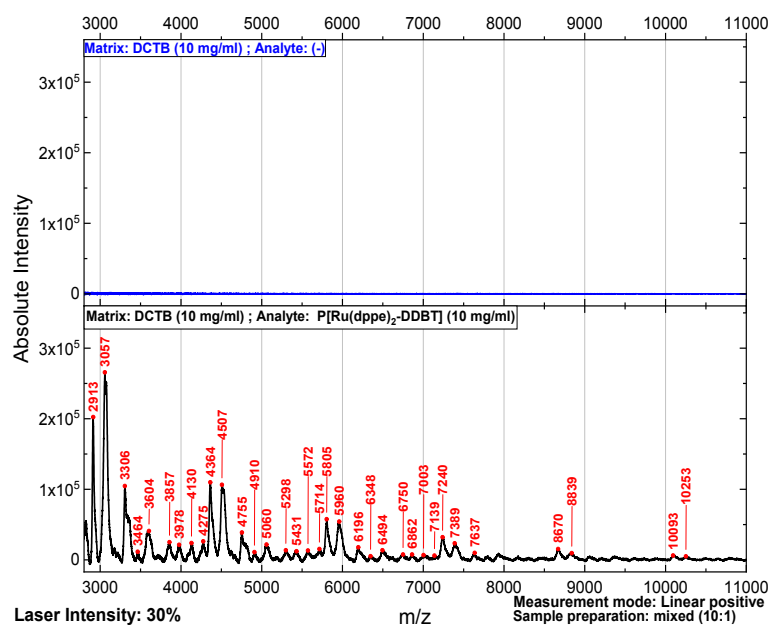


Figure S9. Linear mode MALDI-TOF mass spectra of pure matrix DCTB (blue) and matrix DCTB mixed with analyte **P[Ru(dppe)₂-DDBT]-L** (black).

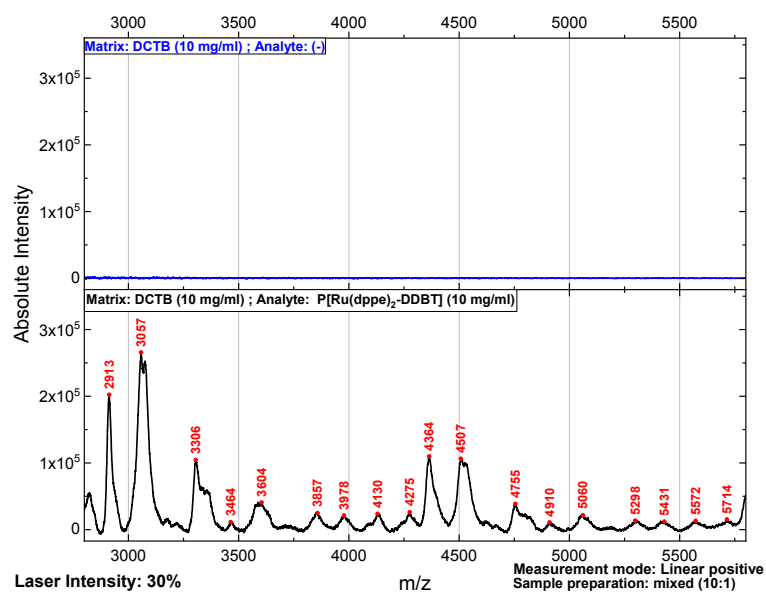


Figure S10. Linear mode MALDI-TOF mass spectra of pure matrix DCTB (blue) and matrix DCTB mixed with analyte **P[Ru(dppe)₂-DDBT]-L** (black). The spectra are zoomed for a better visibility of the repeating unit.

Table S5. Tentative assignment of endgroups (red) for the polymer **P[Ru(dppe)₂-DDBT]-L** (black) including clustered cations (green). Abbreviations: Ru = Ru(dppe)₂; BT = 3,3'-bis(dodecyl)bithiophenyl, TMS = trimethylsilyl, ACN = acetonitrile.

Observed signal	Suggested structure	Suggested molar weight ± Error
2913	BT-C≡C-[Ru-C≡C-BT-C≡C]-Ru-ACN	2909 ± 4
3057	TMS-C≡C-BT-C≡C-[Ru-C≡C-BT-C≡C]-Ru-C≡C-BT-Eth + K⁺	3052 ± 5
3306	TMS-C≡C-BT-[C≡C-Ru-C≡C-BT]₂-C≡C + K⁺	3302 ± 4
3464	C≡C-BT-[C≡C-Ru-C≡C-BT]₂-C≡C + Na⁺	3463 ± 1
3604	Br-BT-C≡C-[Ru-C≡C-BT-C≡C]₂-TMS + K⁺	3608 ± 4
3857	Cl-[Ru-C≡C-BT-C≡C]₂-Ru-Cl	3860 ± 3
4130	ACN-[Ru-C≡C-BT-C≡C]₂-Ru-C≡C-BT-C≡C	4129 ± 1

Cyclic voltammetry and UV-vis absorption studies

Cyclic voltammetric studies

Cyclic voltammogram of *trans*-[Ru(dppe)₂(TBr)₂] was recorded on IviumSoft with a three-electrode system containing Pt disc working electrode (WE), Pt wire counter electrode (CE) and Ag/Ag⁺ reference electrode (RE). During CV measurements, 0.1M of n-Bu₄NPF₆ in dichloromethane was used as supporting electrolyte and ferrocene was used as the internal reference. The measurement was done in ambient condition under N₂ flow.

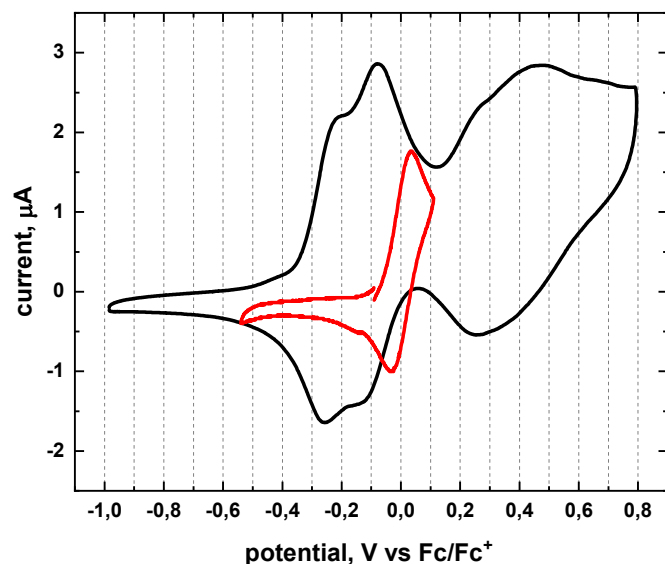


Figure S11. Cyclic voltammogram of *trans*-[Ru(dppe)₂(TBr)₂] (red) and P[Ru(dppe)₂-DDBT] (black) in 0.1 M n-Bu₄NPF₆ in DCM.

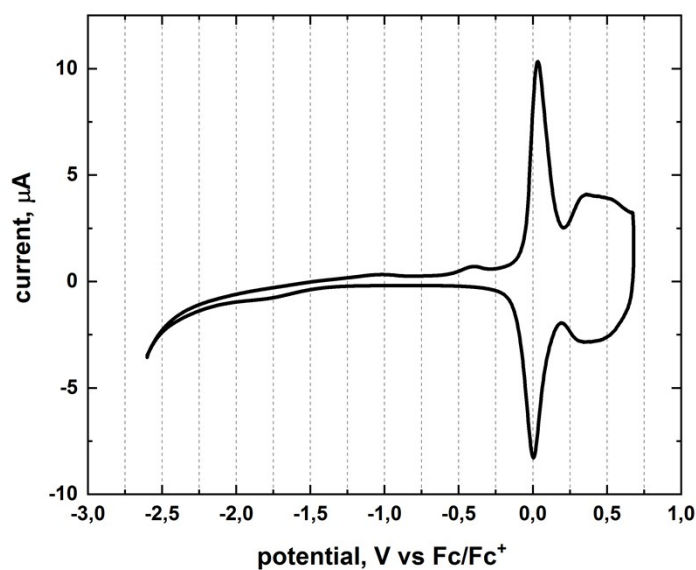


Figure S12. Cyclic voltammogram of P[Ru(dppe)₂-DDBT] thin-film from -3.0 V to 1 V.

UV-vis absorption of P[Ru(dppe)₂-DDBT]

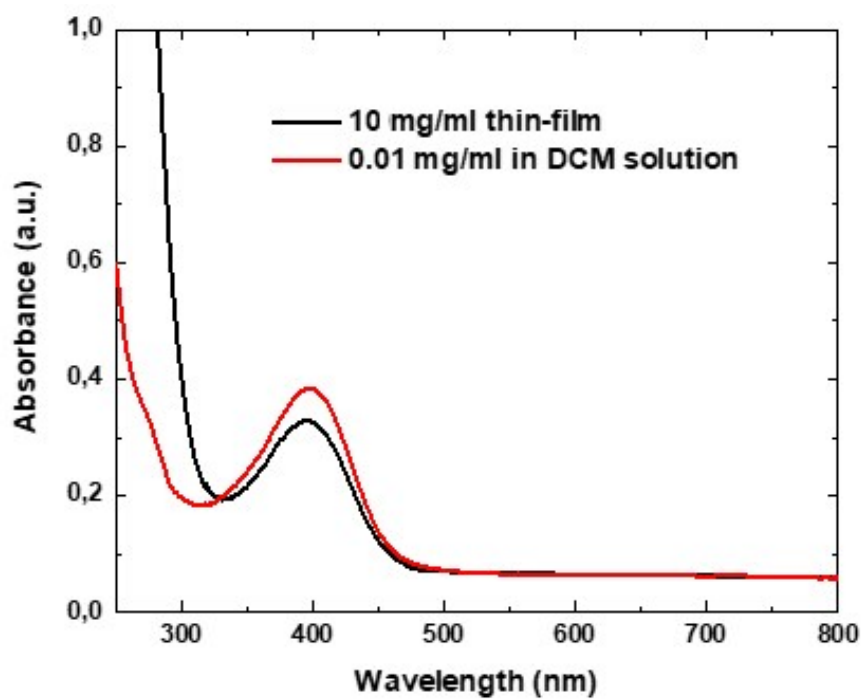


Figure S13. UV-vis absorption spectra of P[Ru(dppe)₂-DDBT] thin-film (black curve) and in DCM solution (red curve).

AFM images

OTS surface treatment procedures

SiO₂ was sonicated in reagent grade acetone and isopropanol for 10 minutes in each solvent. After that, the wafers were cleaned using an ozone cleaner for 30 minutes. Chloroform was used to wash away remaining organic contaminants. The cleaned wafers were transferred to the glovebox, and soaked in a freshly prepared solution of 5 % v/v *n*-octadecyltrichlorosilane (OTS) for 24 hours. Then the wafers were rinsed with toluene and sonicated in toluene for 10 min. Finally, the treated wafers were baked in a vacuum oven at 120°C for 20 minutes.

Spin-coating

Solutions of **P[Ru(dppe)₂-DDBT]** (5 mg ml⁻¹) were prepared in chloroform (film-C), chlorobenzene (film-CBz), 1,2-dichlorobenzene (film-dCBz) and tetrachloroethane (film-TCE). The solutions were allowed to stir for 15 minutes before spin-coating. 8 drops of each solvent were used to cover the whole surface.

The following spin-coating parameters were used:

Rotation per minute = 1000 rpm

Acceleration = 500 rpm s⁻¹

Duration = 60 seconds

Thickness and roughness results

Table S6. Thickness and roughness of different films.

Entry	Thickness results (nm)	Roughness (Sa)	Surface area difference in %
Film-C	58.2	0.494	0.03
Film-CBz	15.9	0.474	0.06
Film-dCBz	7.4	0.883	0.27
Film-TCE	No film	0.860	2.18

The prepared films (except film-TCE) are homogenous according to the scale bars (Figure S14). The difference of thickness may be due to different wettability of the solvents on the OTS-treated surface.

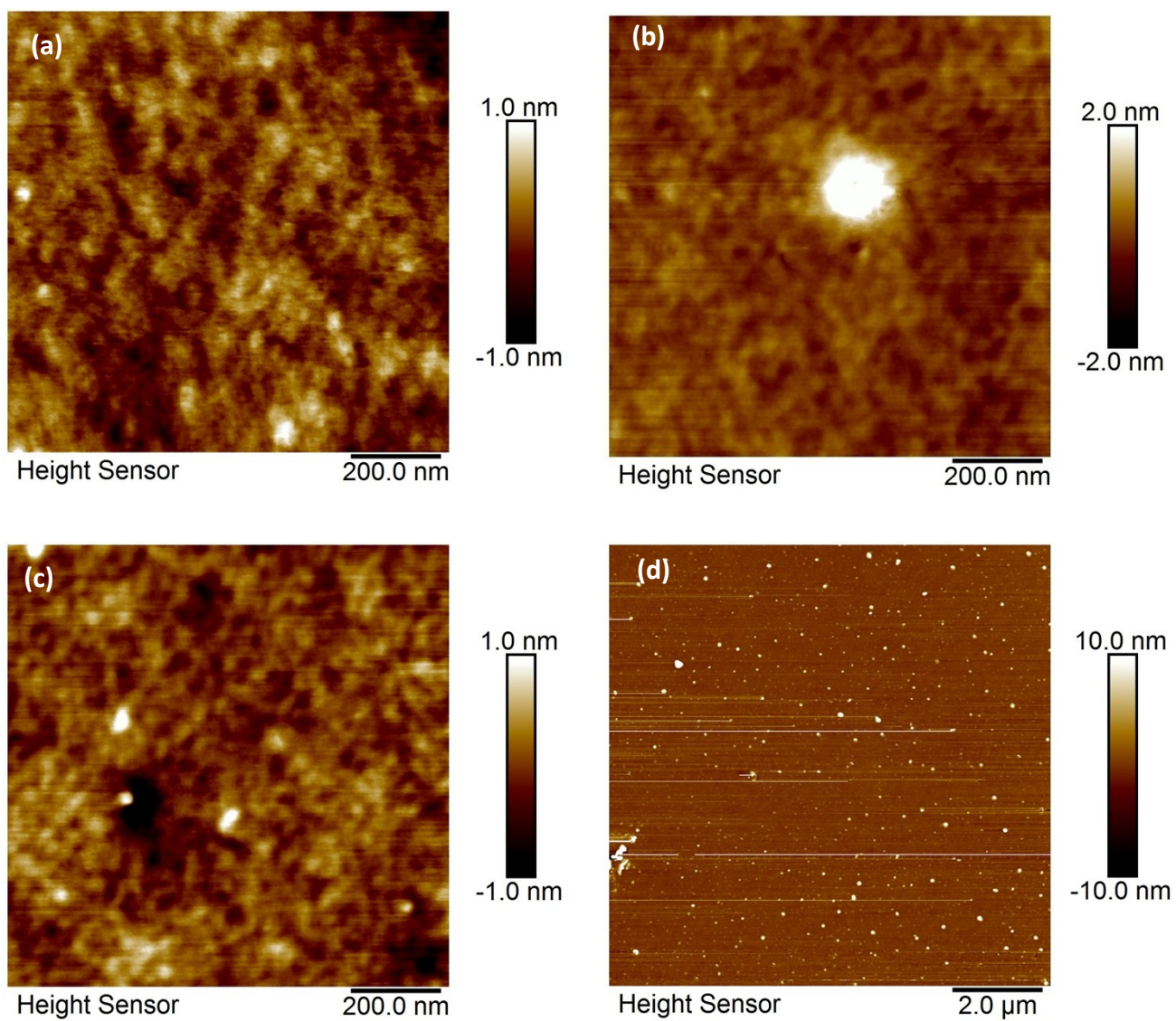


Figure S14. AFM images of (a) film-C (chloroform), (b) film-CBz (chlorobenzene), (c) film-dCBz (1,2-dichlorobenzene) and (d) film-TCE (tetrachloroethane).

TGA and DSC

TGA:

The sample size was 5.07 mg. The TGA analysis took place under nitrogen atmosphere with the isothermal for 10 min and Ramp 10.00 K/min to 750.00 °C.

DSC:

The sample size was 4.15 mg. The analysis was carried out with the following method:

Sampling interval 0.80 sec/pt

Equilibrate at -90.00°C

Isothermal for 5.00 min

1: Ramp 10.00 K/min to 300.00°C

Isothermal for 0.20 min

2: Ramp 10.00 K/min to -90.00°C

Isothermal for 5.00 min

3: Ramp 10.00 K/min to 300.00°C

Sample	Weight (mg)	Weight loss after 10' at RT (%)	T _{max} of derivative weight (°C)	T _{final} of decomp. Step (°C)	Weight loss at T _{final} (%)	Residue 750°C (%)
P[Ru(dppe) ₂ -DDBT]	5.071	0	65	90	0,05	49.7
			210	240	0,4	
			386	410	22,9	
			436	to 750	26,9	

Table S7. Results of TGA analysis of P[Ru(dppe)₂-DDBT].

Table S8. Results of DSC analysis of **P[Ru(dppe)₂-DDBT]**.

Sample	Weight (mg)	mode	T _g (°C)	Δc _p (J/gK)	Int. limit (°C)	ΔH (J/g)	T _m or T _{c,m} (°C)	T _{c,o} (°C)	peak-height W/g
P[Ru(dppe) ₂ -DDBT]	4.147	1 st heating	overlapped						
		2 nd heating	72	0.25					

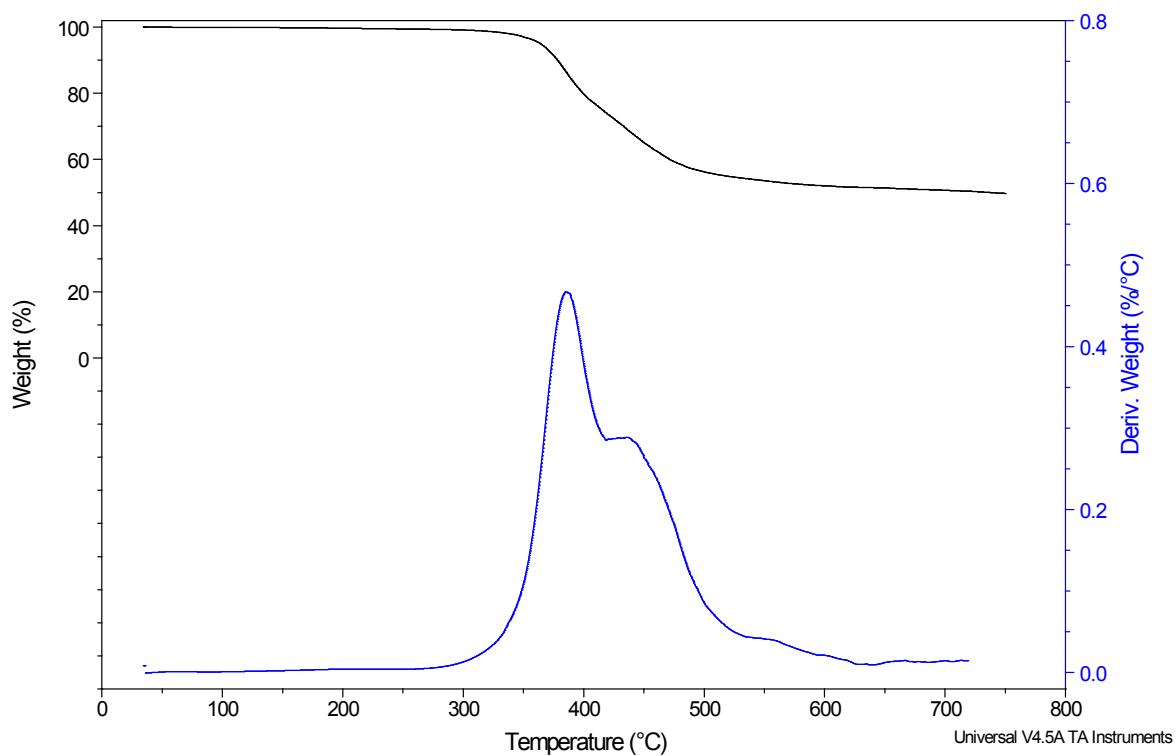


Figure S15. TGA analysis of **P[Ru(dppe)₂-DDBT]**.

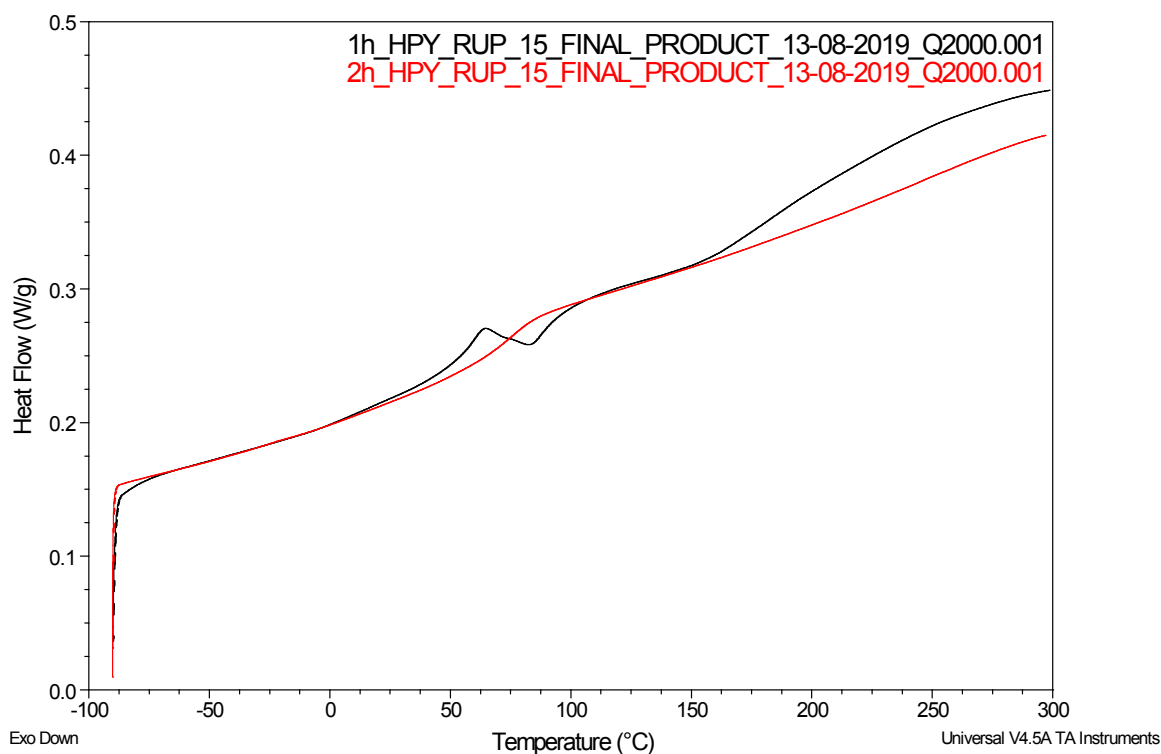


Figure S16. DSC analysis of **P[Ru(dppe)₂-DBBT]**.

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