Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Photophysics and Non-Linear Absorption of Au(I) and Pt(II) Acetylide Complexes of a Thienyl-Carbazole Chromophore

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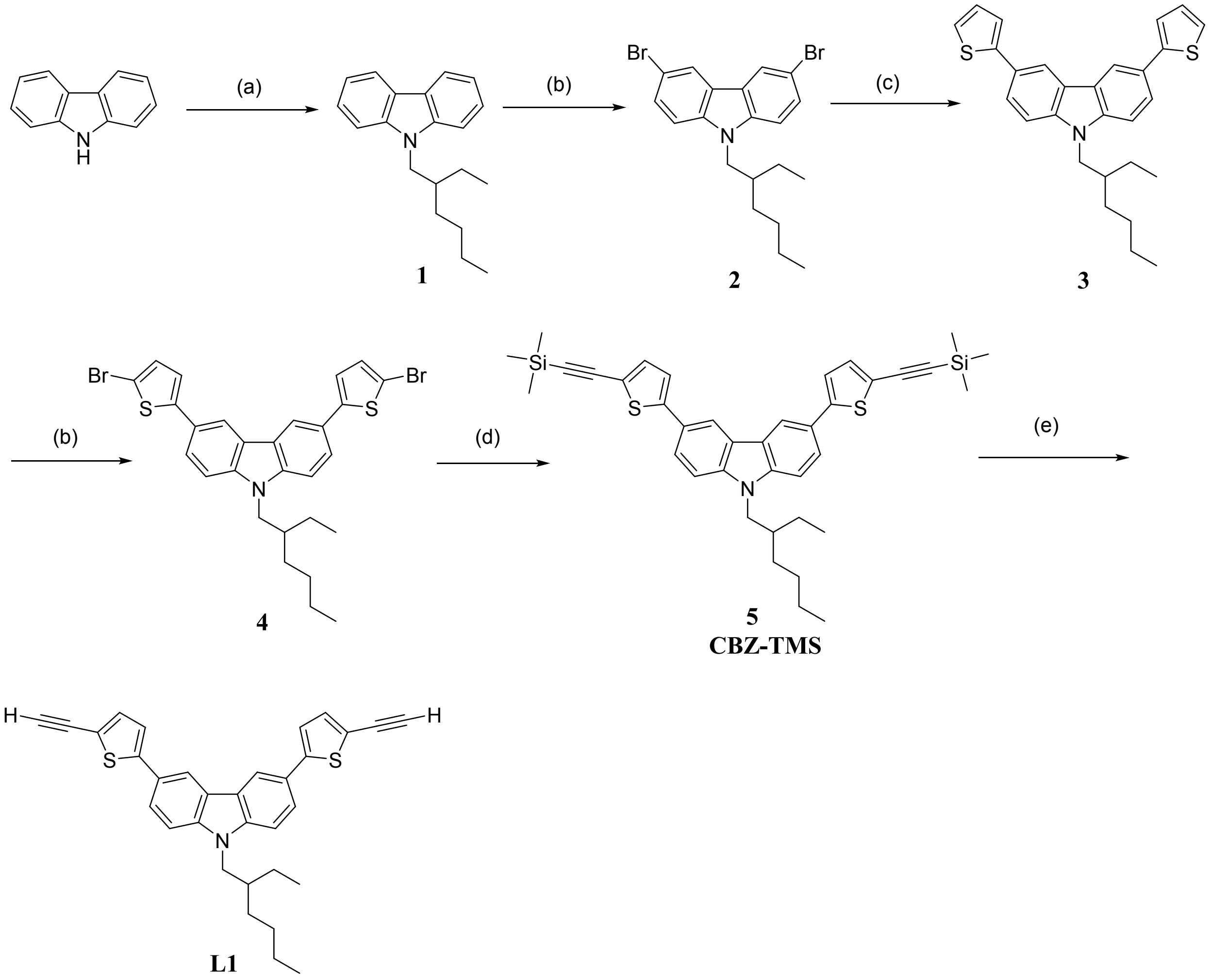
Content

I. General methods for synthesis. All reactions were performed under dry and argon atmosphere. THF was dried using solvent purification columns (Glass Contour). All other solvents were used without further purification unless specified. Chloro(trimethylphosphine)gold(I) was purchased from Sigma-Aldrich and used as received. Trimethylsilyl acetylene was purchased from GFS Chemical and was used as received. Potassium tetrachloroplatinate, tetrakis(triphenylphosphine)palladium (0) and bis(triphenylphosphine)palladium(II) dichloride were purchased from Strem Chemicals. Silica gel (230-400 mesh, 60 Å, Silicycle Inc.) was used for column chromatography. Compounds **2** and **4**[1] were synthesized according to the literature procedures. Compounds **1** and **3** were synthesized by modified literature procedures.[1] Cis-$Pt(PBu_3)_2Cl_2$ [2] and platinum complex **6** [3] were synthesized according to the literature procedures.

II. Synthetic procedures and scheme.

Scheme S1. Synthesis of **L1**.



(a) 2-Ethylhexyl bromide, aq. NaOH, Benzyltriethyl ammonium chloride, toluene, reflux, 15 h; **(b)** NBS, THF; **(c)** 2-(Tributylstannyl) thiophene, $Pd(PPh_3)_4$, DMF; **(d)** Trimethylsilyl acetylene, cis-$Pd(PPh_3)_2Cl_2$, CuI, Diisopropylamine/THF, 70°C ; **(e)** K_2CO_3, THF/MeOH, rt

9-(2-Ethylhexyl)-Carbazole (1)

Carbazole (5 g, 30 mmol) and 0.2 gm benzyltriethylammoniumchloride were dissolved in 25 mL of toluene and this light yellow colored suspension was deoxygenated by bubbling with argon for 30 minutes. To this suspension 17.5 gm of 50 w% NaOH (aq) was added at once and it was further deoxygenated for 30 minutes more, in the meanwhile the color of the solution changed to light brown from yellow. Then 2-ethylhexyl bromide (6.95 g, 36 mmol) was added to the reaction mixture dropwise, and then it was refluxed for 24 hours with vigorous stirring. The organic layer was separated from the aqueous layer and washed with water, brine solution and finally dried over anhydrous Na_2SO_4, filtered and concentrated. The crude yellow liquid was purified by silica gel column chromatography using hexane as eluent to give the titled compound as colorless oil (3 g, 37%). ^1H NMR (300 MHz, $CDCl_3$) : δ 8.22 (d, *J* = 7.7 Hz, 2H), 7.62-7.45 (m, 4H), 7.35 (t, $J = 7.4$ Hz, 2H), 4.29-4.14 (m, 2H), 2.18 (m, 1H), 1.55-1.33 (m, 8H), 1.06-0.97 (m, 6H).

3, 6-Bis(thiophene-2-yl)-9-(2-ethylhexyl)carbazole (3)

Compound **2** (3.74 g, 8.55 mmol) and 2-(tributylstannyl) thiophene (7.02 g, 18.81 mmol) were added to 40 mL of dry DMF and purged with argon for 45 minutes. $Pd(PPh_3)_4$ (420 mg, 4 mol %) was added to the reaction mixture under the flow of argon. The orange colored solution was refluxed under argon atmosphere which changed to dark color in an hour. The reflux was continued for 2 more days. The reaction mixture was poured over water and extracted with dichloromethane. The combined organic layer was extracted with brine and finally dried over anhydrous Na_2SO_4. It was filtered and the solvent was evaporated to dryness. The crude product was purified by column chromatography using silica gel as adsorbent and hexane as eluent to obtain **3** as greenish white solid (2 g, 53%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.31 (d, $J = 1.6$ Hz, 2H), 7.70 (dd, $J = 8.5$, 1.8 Hz, 2H), 7.38-7.30 (m, 4H), 7.24 (d, $J = 1.0$ Hz, 2H), 7.09 (dd, $J = 5.1$, 3.6 Hz, 2H), 4.17-4.07 (m, 2H), 2.08-1.99 (m, 1H), 1.42-1.18 (m, 8H) and 0.95-0.80 (m, 6H).

9-(2-Ethylhexyl)-3, 6-bis (5-((trimethylsilyl) ethynyl) thiophen-2-yl)carbazole (5)

Compound **4** (1.5 g, 2.49 mmol) was dissolved in 30 mL of diisopropylamine and THF (1:4) mixture and deoxygenated by bubbling argon for 45 minutes. Subsequently $Pd(PPh_3)_2Cl_2$ (35 mg, 2 mol %), CuI (20 mg, 4 mol %) were added to the reaction mixture under argon atmosphere and deoxygenated additionally for 30 more minutes. Then trimethylsilylacetylene (0.61 g, 6.23 mmol) was added and reaction mixture was heated at 70°C under inert atmosphere overnight. After confirming the consumption of starting material by TLC, the reaction mixture was evaporated to dryness and the crude product was purified by silica gel chromatography using hexane as eluent to give light yellow colored titled compound (1.43 g, 90.5%).

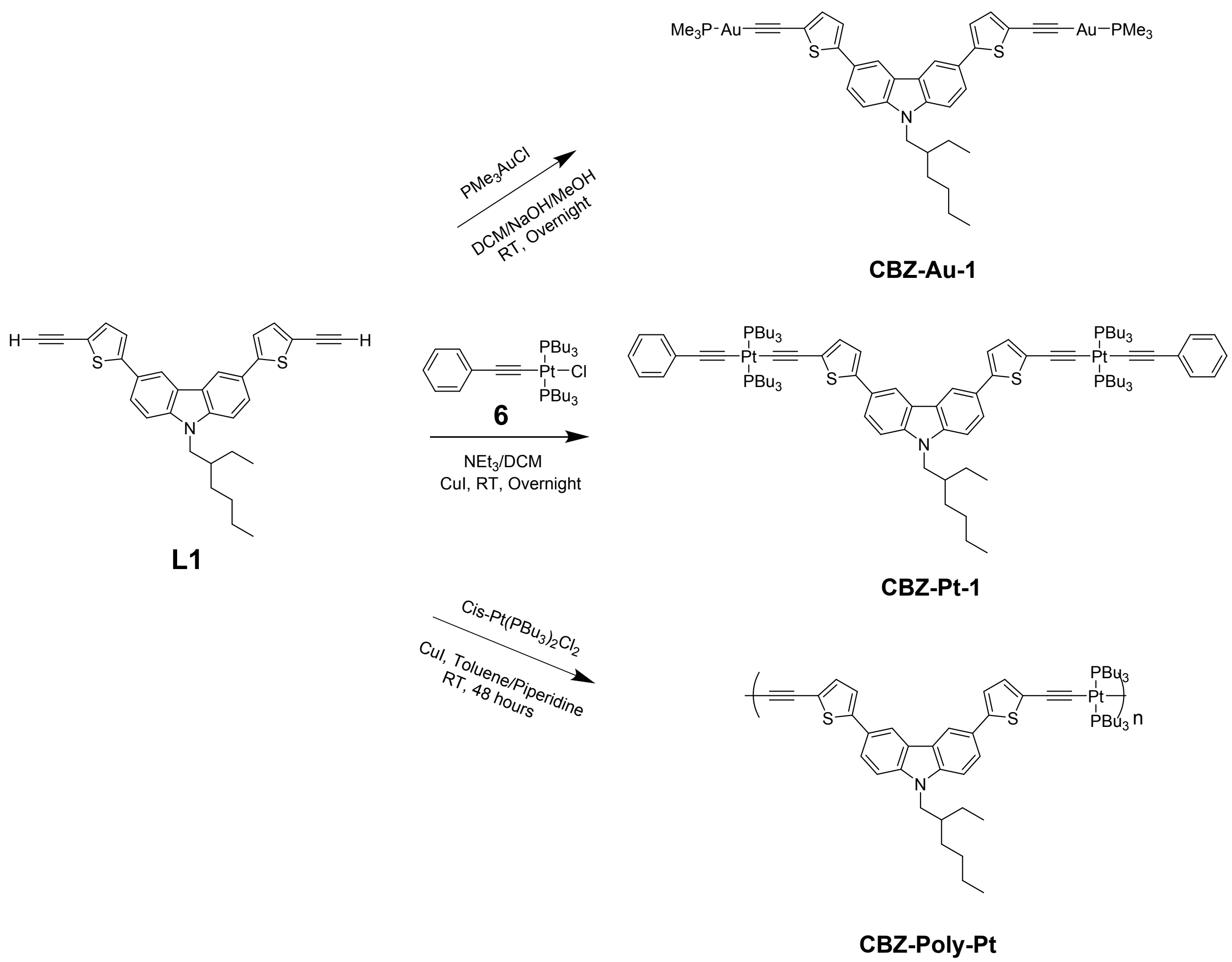
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (s, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.21 (m, 4H), 4.15 (d, *J* = 6.9 Hz, 2H), 2.15-1.95 (m, 1H), 1.48-1.17 (m, 8H) , 0.94-0.84 (m, 6H) and 0.27 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.41, 141.37, 134.10, 125.52, 124.77, 123.34, 122.01, 121.32, 118.14, 109.88, 99.35, 98.26, 47.89, 39.68, 31.21, 29.03, 24.59, 23.26, 14.26, 11.12 and 0.16 ($SiMe_3$).

Synthesis of L1

TMS protected compound **5** (200 mg, 0.314 mmol) was dissolved in 30 mL of MeOH/ THF (1:1) solvent mixture and purged with argon for 30 minutes. K_2CO_3 (216 mg, 1.57 mmol) was added to the reaction mixture and stirred it overnight under argon atmosphere shielded from the light with aluminum foil. The solvents were evaporated to dryness and the residue was dissolved in dichloromethane, washed three times with water and then brine solution. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and solvent was evaporated under vacuum to give the product as light yellow viscous oil (120 mg, 77%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, *J* = 1.6 Hz, 2H), 7.66 (dd, *J* = 8.5, 1.8 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 3.8 Hz, 2H), 7.18 (d, *J* = 3.8 Hz, 2H), 4.14 (m, 2H), 3.38 (s, 2H), 2.07-1.95 (m, 1H), 1.45-1.16 (m, 8H) and 0.91-0.81 (m, 6H). (Due to the instability of the compound ^{13}C NMR was not recorded).

Scheme S2. Synthesis of **CBZ-Au-1, CBZ-Pt-1** and **CBZ-Poly-Pt**.



Synthesis of CBZ-Au-1

Compound **L1** (40 mg, 0.0813mmol) was dissolved in 5 mL of dichloromethane and purged with argon for 30 minutes. PMe$_3$AuCl (50 mg, 0.163 mmol) was added to the reaction mixture under argon atmosphere. Then NaOMe (3 ml, 0.813 mmol) (prepared from dissolving 42.7 mg of NaOH in 25 ml of MeOH) was added, which caused formation of a bright yellow precipitate. The reaction mixture was stirred under inert atmosphere overnight. Then the solvent was evaporated to dryness and the yellow residue was dissolved in dichloromethane and passed through a plug of cotton to remove insoluble impurities. The filtrate was evaporated to 5 mL and methanol was added to obtain a yellow precipitate. The precipitate was centrifuged, washed with 20 ml of methanol, hexane and ether respectively and dried under vacuum to obtain 70 mg of complex in 84% yield.

^{1}H NMR (300 MHz, CDCl$_3$): δ 8.27 (s, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 3.8 Hz, 4H), 4.14 (d, *J* = 5.8 Hz, 2H), 2.04 (m, 1H), 1.53 (d, 18H), 1.33 (m, 8H) and 0.88 (m, 6H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 144.94, 141.07, 132.65, 126.05, 124.68, 123.76, 123.36, 121.82, 117.96, 109.62, 47.81, 39.65, 31.21, 29.05, 24.60, 23.25, 16.19, 15.71, 14.26, 11.12. ^{31}P NMR (121 MHz, CDCl$_3$) δ (ppm) 2.06. HRMS (APCI, [M+H]$^+$) *m*/*z* calcd for $C_{38}H_{45}Au_2NP_2S_2$ 1036.1873, found 1036.1912.

Synthesis of CBZ-Pt-1

Compound **L1** (64 mg, 0.13 mmol) and **6** (210 mg, 0.285 mmol) were dissolved in 50 mL of a dichloromethane/triethylamine mixture (1:1 v:v) and deoxygenated for 45 minutes by bubbling argon. After that 5 mg (26 mol %) of CuI was added and the reaction mixture was stirred under inert atmosphere overnight. The solvent was evaporated to dryness under vacuum, and the crude product was purified by silica gel column chromatography using 3:7 DCM/ hexane as an eluent to give the complex as a light yellow solid in 57% yield (140 mg).

^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ 8.29 (s, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.31-7.08 (m, 12H), 6.85 (s, 2H), 4.20 (d, *J* = 6.5 Hz, 2H), 2.17 (m, 25H), 1.65(m, 24H), 1.53 (m, 24H), 1.44-1.21 (m, 8H), 0.98 (m, 42H). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$): δ 142.2, 140.7, 130.9, 129.2, 128.5, 128.0, 126.4, 125.0, 124.3, 123.3, 121.7, 117.5, 115.3 (m), 109.5, 109.2, 107.8 (m), 101.6, 47.8, 39.7, 31.2, 29.1, 26.6, 24.6 (m), 24.2 (m), 23.3, 14.3, 14.1, 11.1 (due to superimposition two carbon is missing). ^{31}P NMR (121 MHz, CD_2Cl_2) δ 4.49 ($J_{Pt\text{-}P}$ = 2340 Hz). HRMS (APCI, $[M+H]^+$) *m/z* calcd for $C_{96}H_{145}NP_4Pt_2S_2$ 1890.9078, found 1890.9134.

Synthesis of CBZ-Poly-Pt

The ligand **L1** (90 mg, 0.183 mmol) and *cis*-Pt(PBu_3)$_2$$Cl_2$ (123 mg, 0.183 mmol) was dissolved in 10 mL of piperidine and toluene solvent mixture (1:1) and deoxygenated for 45 minutes by bubbling argon. CuI (5 mg) was added to the reaction mixture and it was stirred at room temperature under argon for 48 hours. The yellow viscous liquid was passed through a short neutral alumina column and filtrate was evaporated to dryness to give a yellow colored film. The residue was dissolved in 5 mL of chloroform and poured it over 200 mL of cold methanol. The obtained yellow precipitate was centrifuged and the supernatant was removed. The obtained polymer was purified by repeated precipitations (2 times), which resulted in 90 mg of the polymer in 44% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.25 (bs, 2H), 7.66 (d, 2H), 7.33 (d, 2H), 7.13 (bd, 2H), 6.86 (bd, 2H), 4.15 (d, 2H), 2.32-1.94 (m, 13H), 1.78-1.4 (m, 24H), 1.36 (m, 8H) and 1.1-0.81 (m, 24H).

^{31}P NMR (121 MHz, $CDCl_3$): δ 4.41 ($J_{Pt\text{-}P}$ = 2335.3 Hz).

GPC: M_w = 24800, M_n = 9400 g/mol, PDI = 2.6

III. NMR Spectra

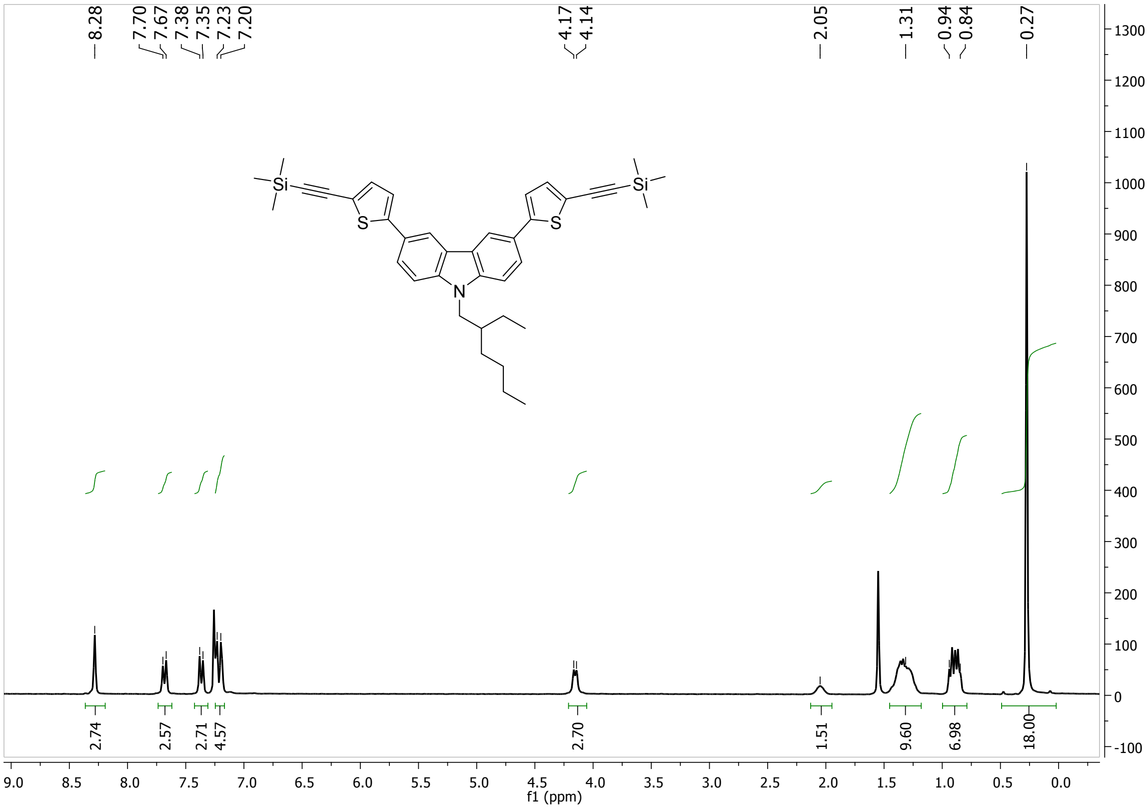


Figure S1. ^{1}H NMR (300 MHz, CDCl$_3$) of **CBZ-TMS.**

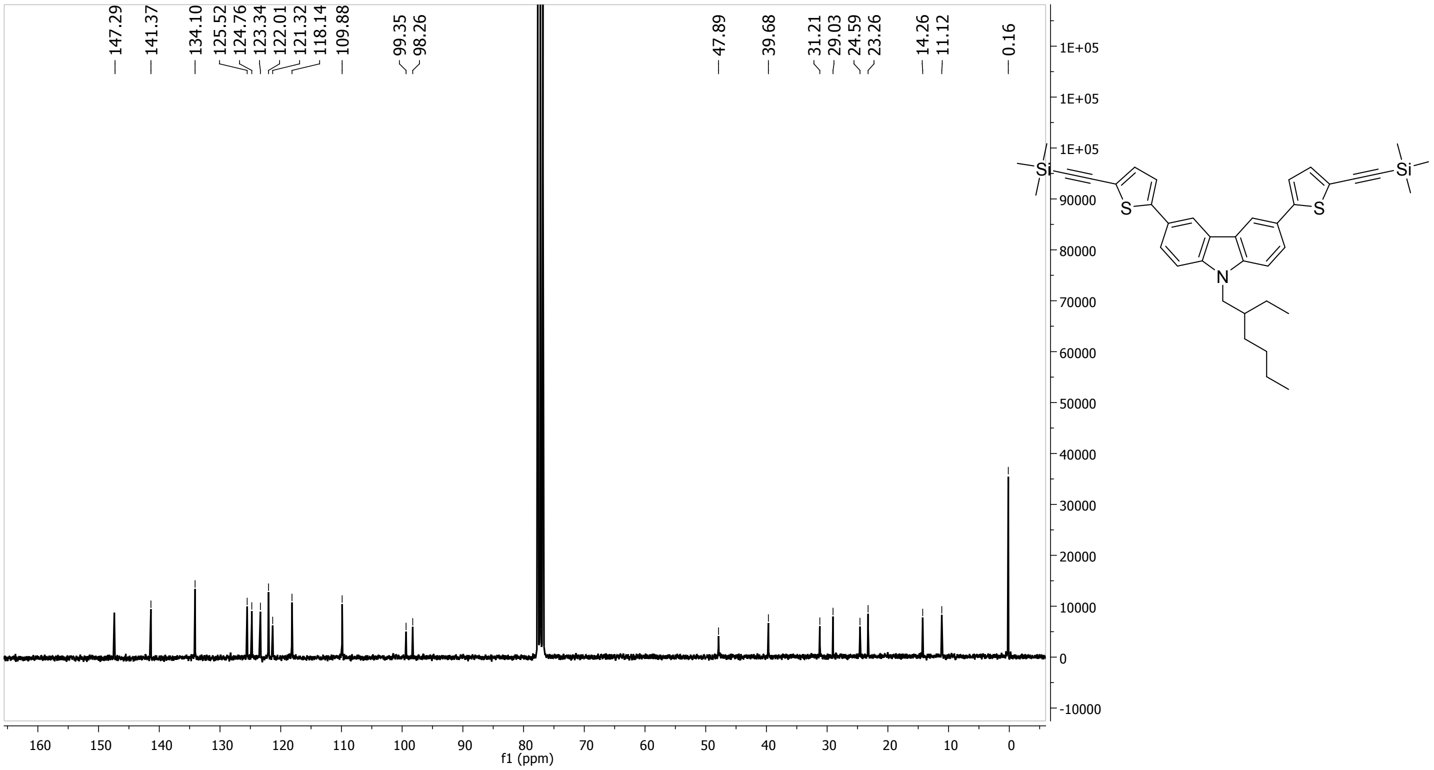


Figure S2. ^{13}C NMR (300 MHz, CDCl$_3$) of **CBZ-TMS.**

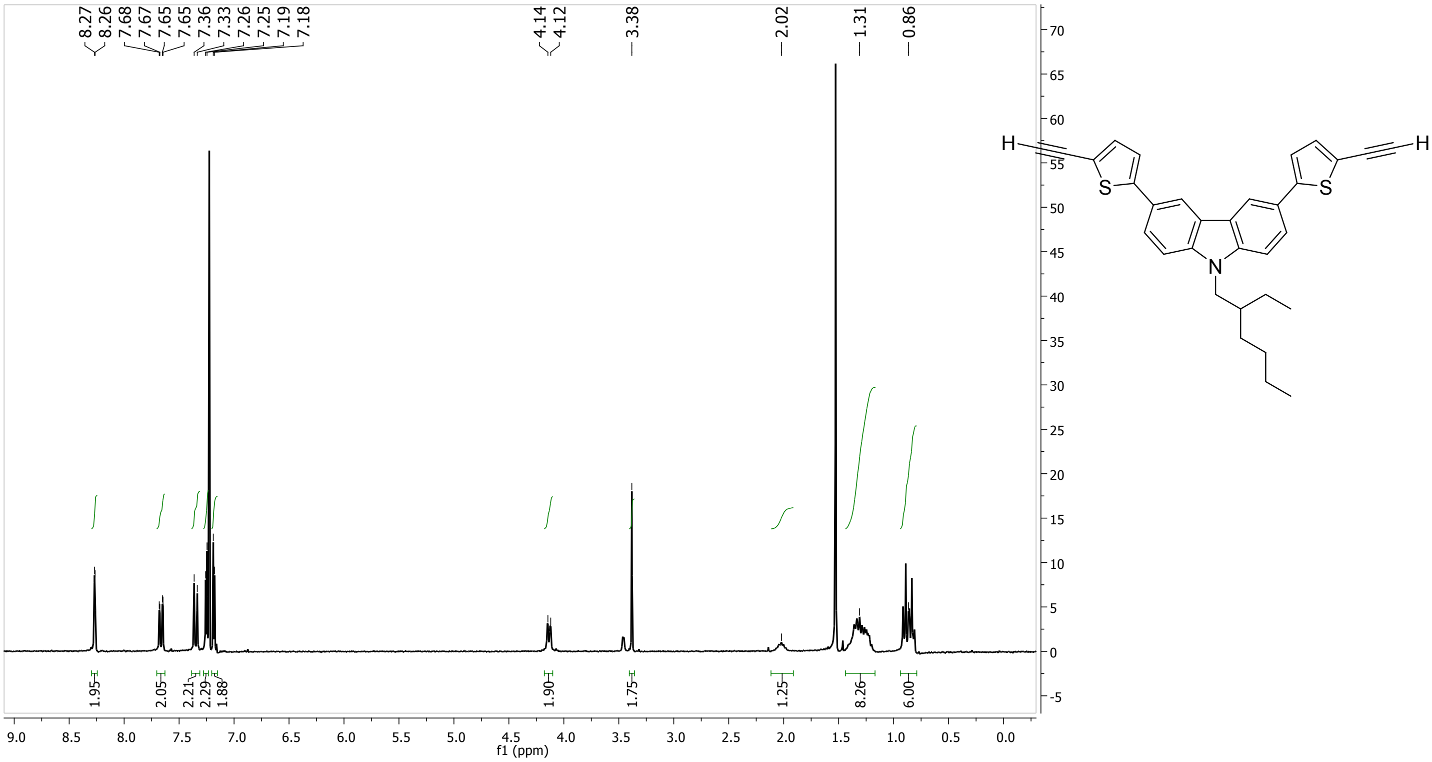


Figure S3. ^{1}H NMR (300 MHz, CDCl$_3$) of **L1.**

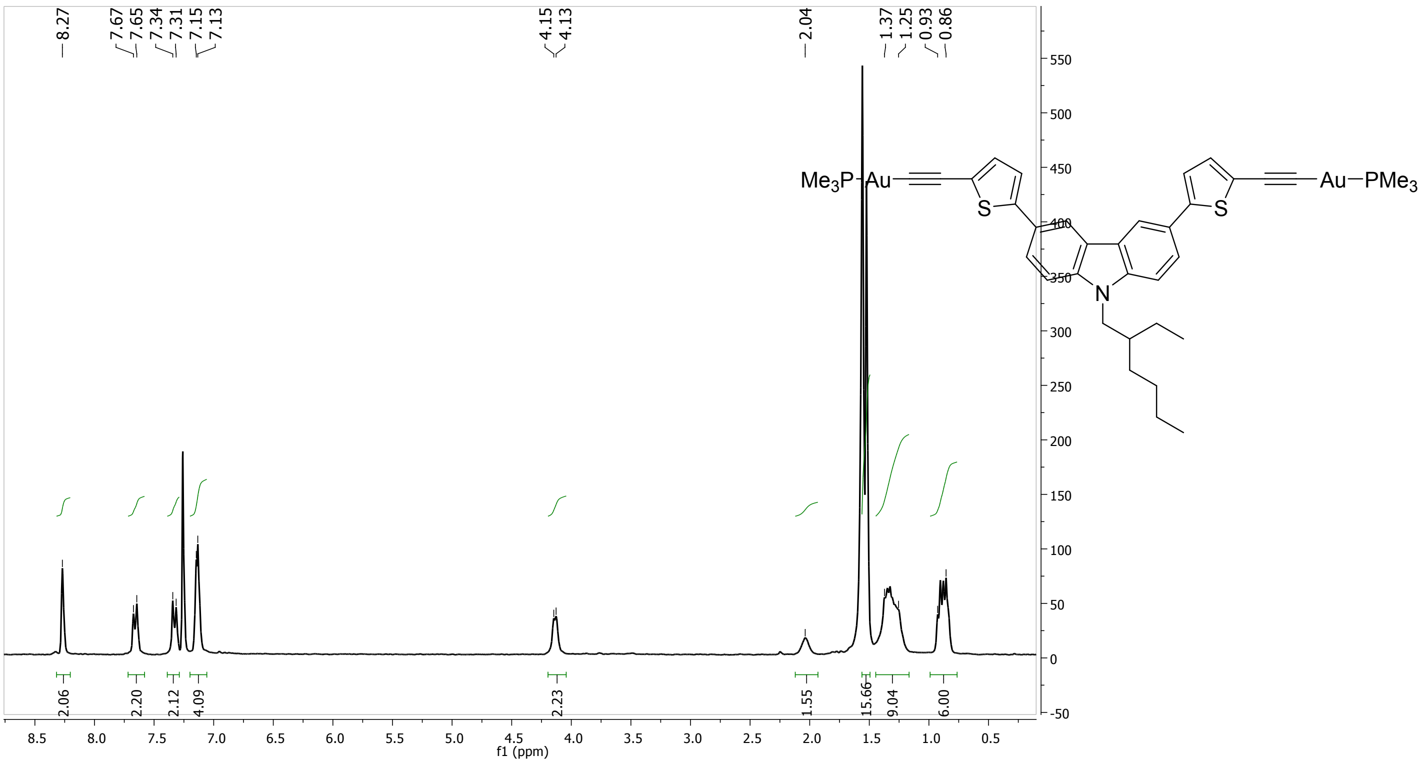


Figure S4. ^{1}H NMR (300 MHz, CDCl$_3$) of compound **CBZ-Au-1.**

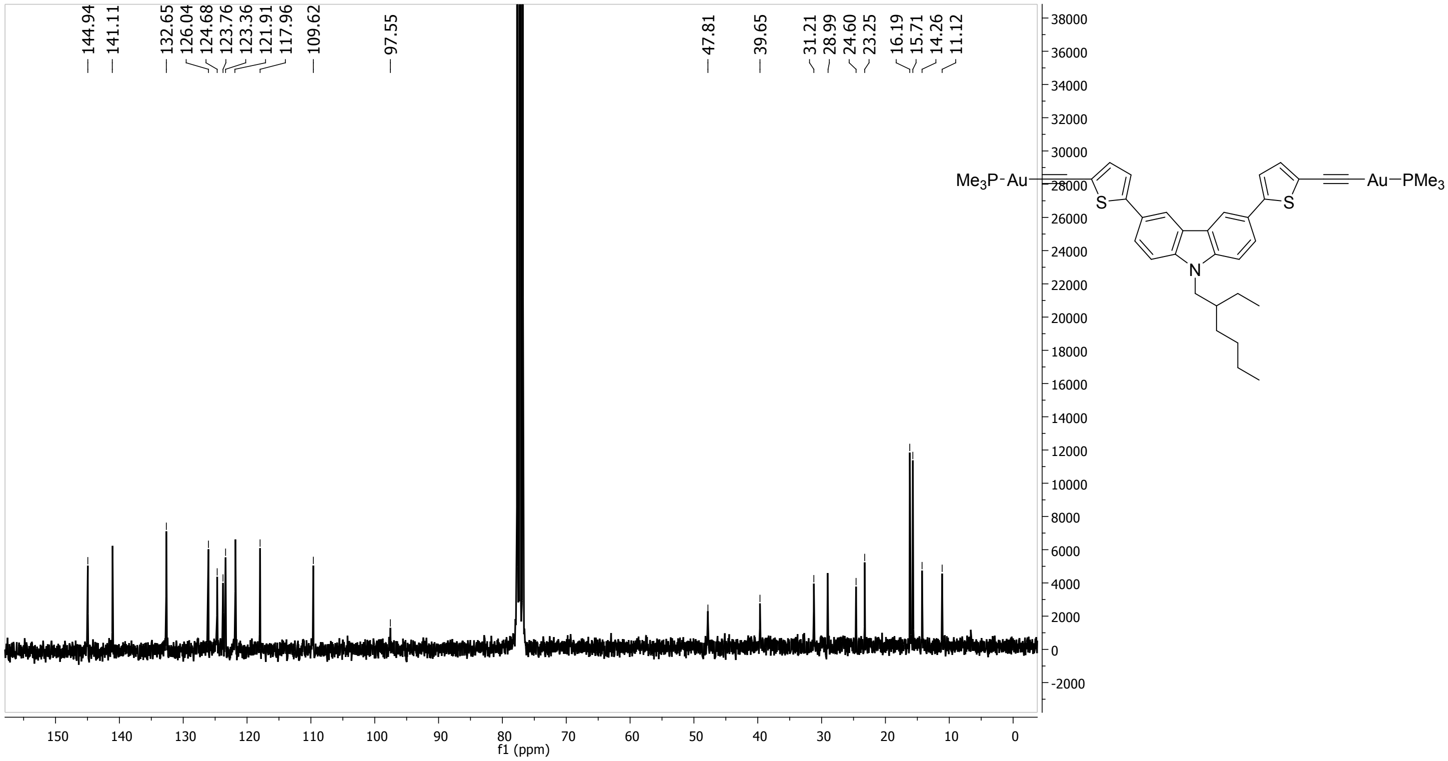


Figure S5. ^{13}C NMR (75 MHz, CDCl$_3$) of compound **CBZ-Au-1**.

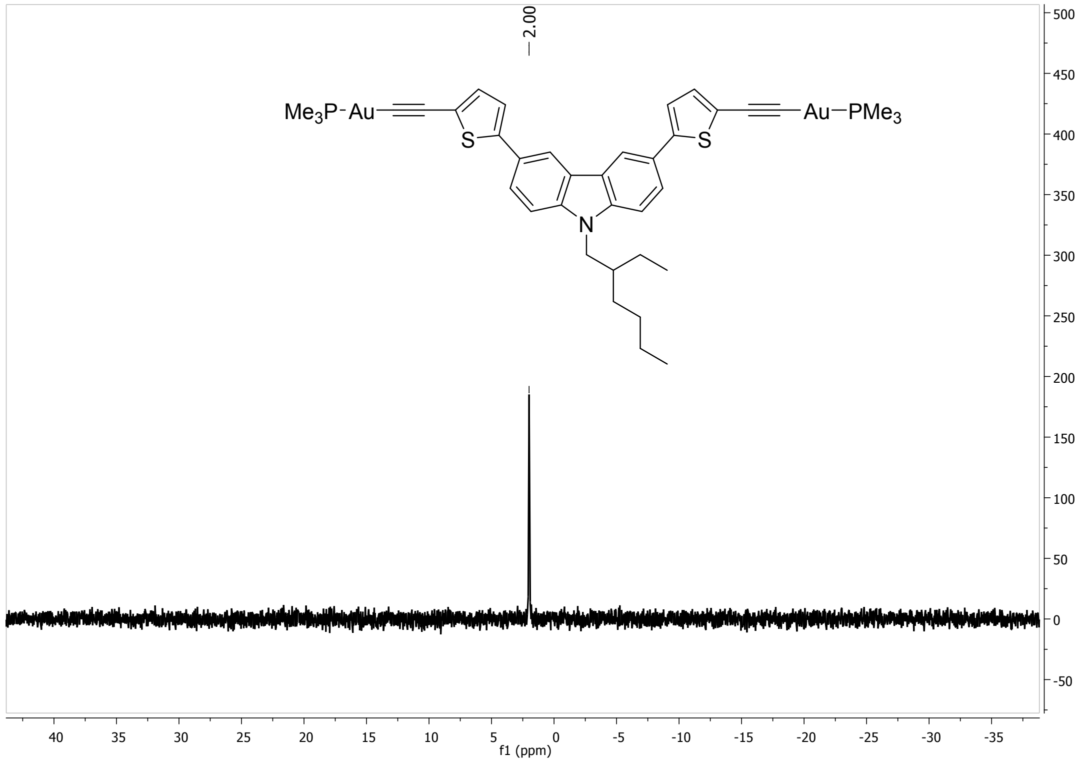


Figure S6. ^{31}P NMR (121 MHz, $CDCl_3$) of compound **CBZ-Au-1**.

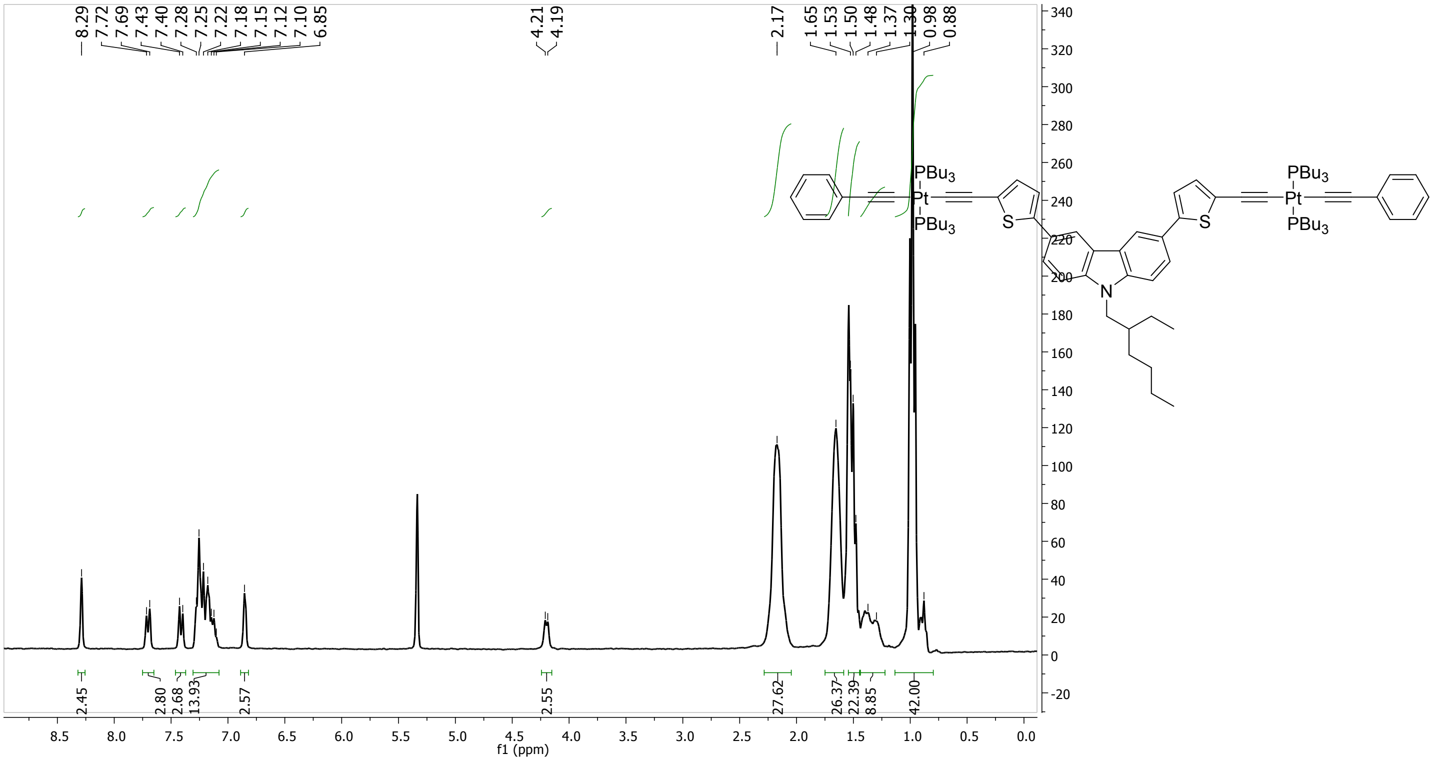


Figure S7. ^{1}H NMR (300 MHz, CD_2Cl_2) of compound **CBZ-Pt-1.**

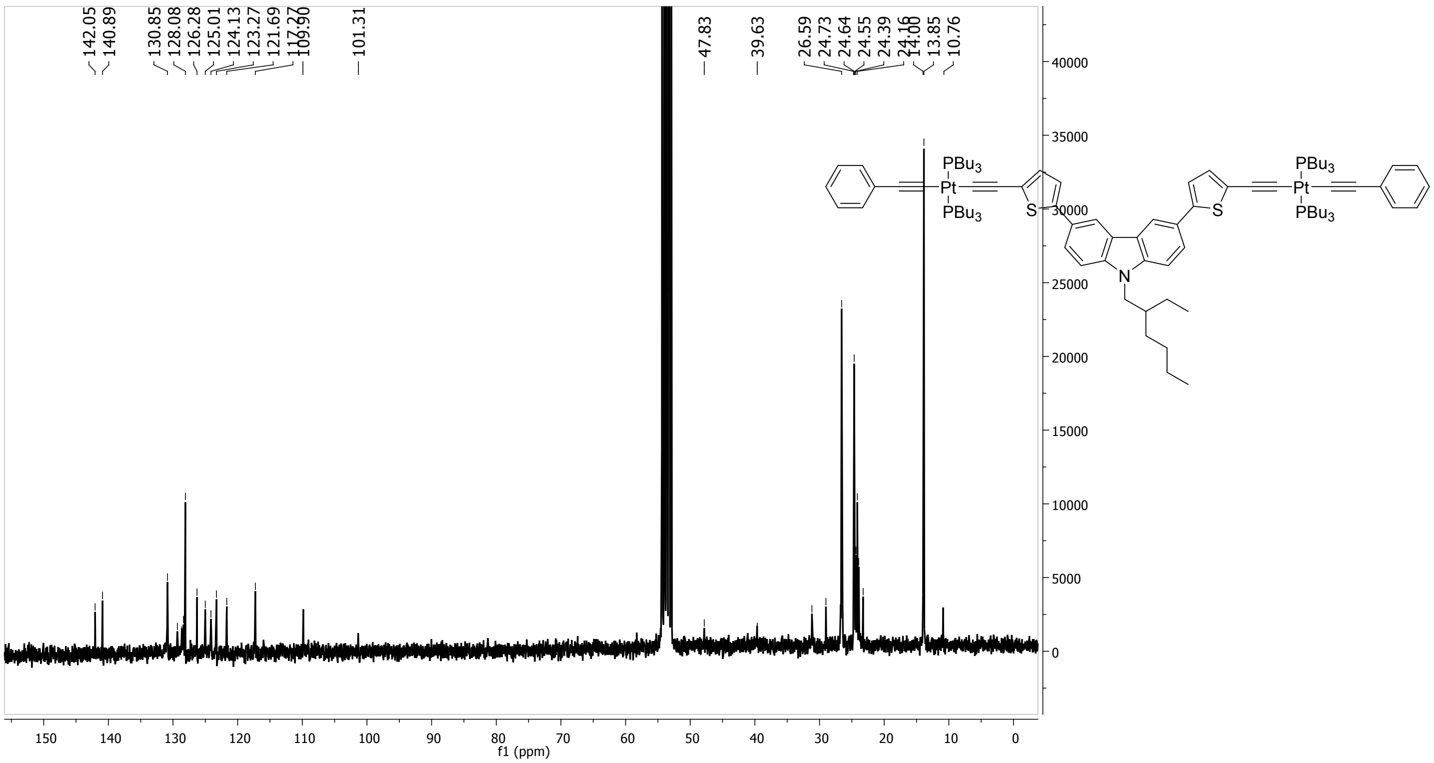


Figure S8. ^{13}C NMR (75 MHz, CD_2Cl_2) of compound **CBZ-Pt-1**.

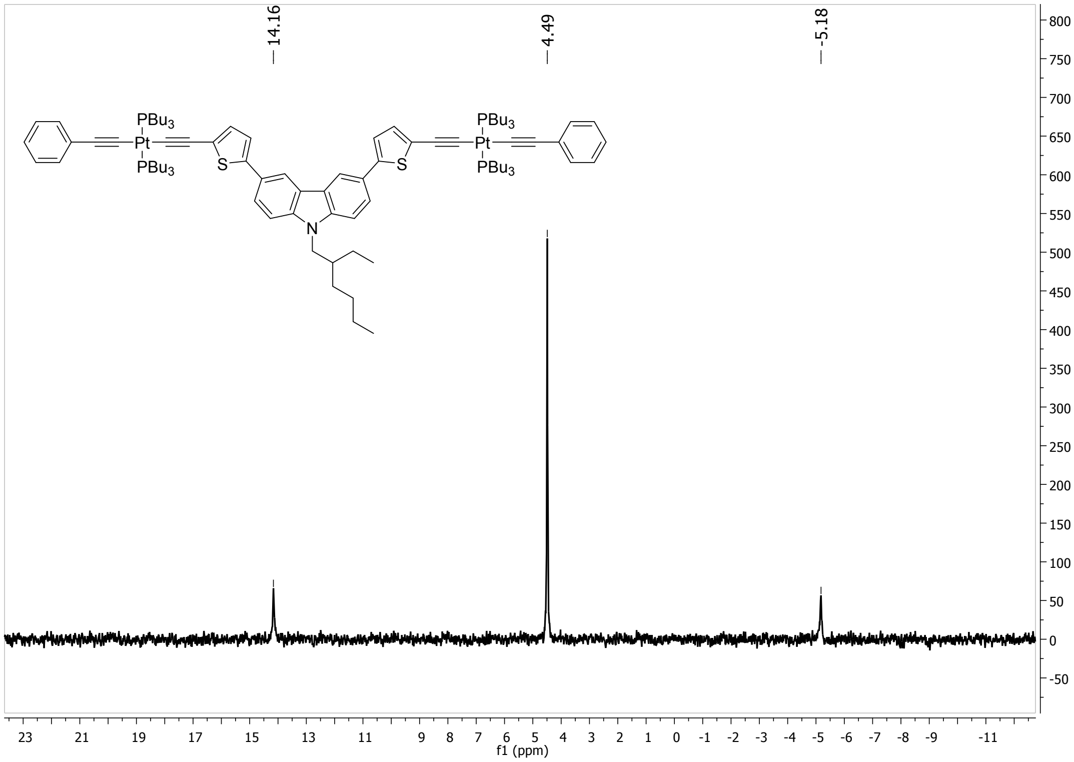
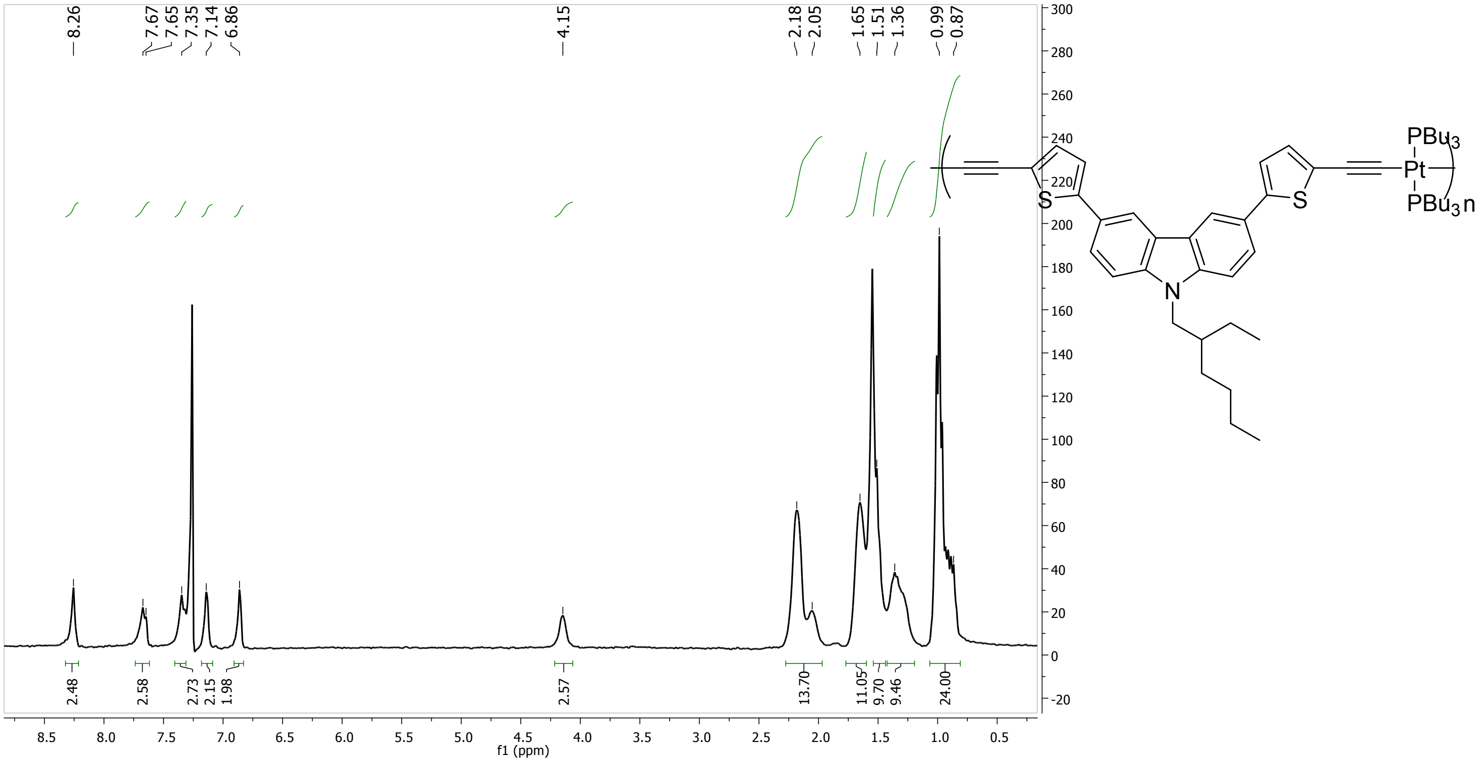


Figure S9. ^{31}P NMR (121 MHz, CD_2Cl_2) of compound **CBZ-Pt-1**.



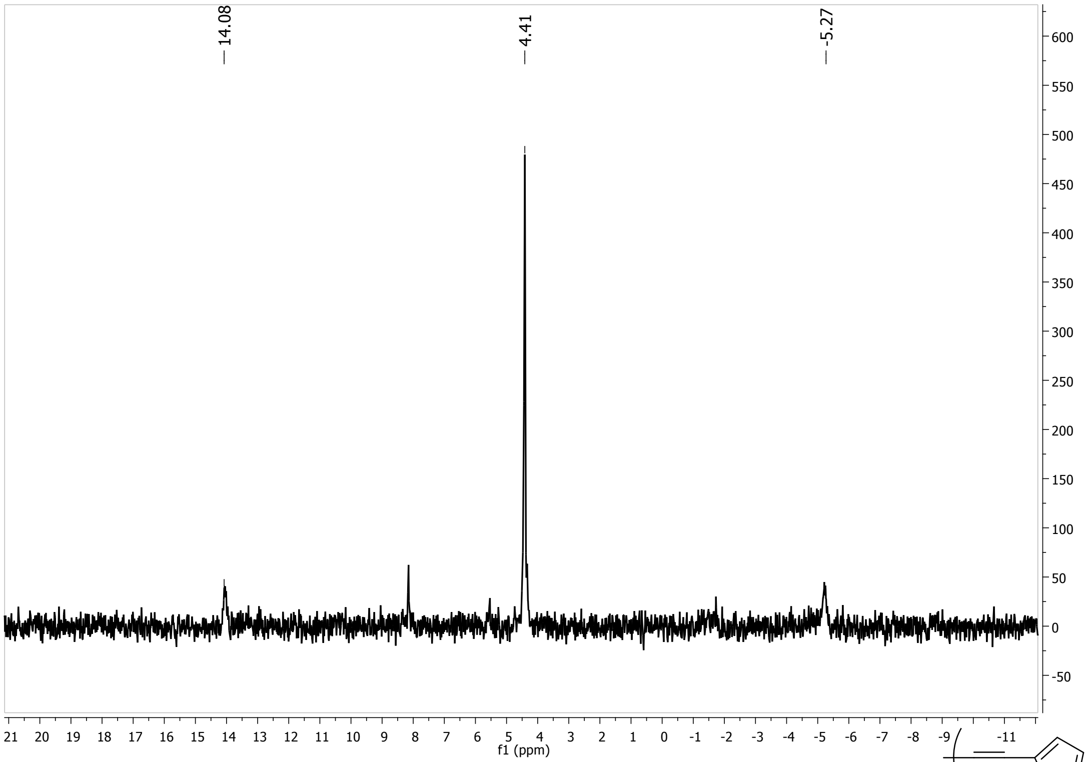


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) of compound **CBZ-Poly-Pt.**

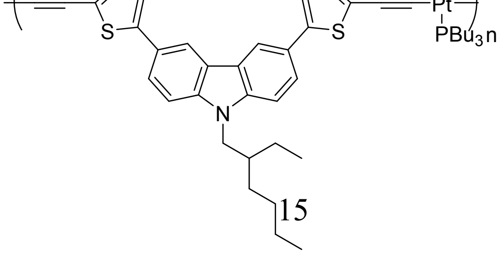


Figure S11. ^{31}P NMR (121 MHz, CDCl$_3$) of compound **CBZ-Poly-Pt.**

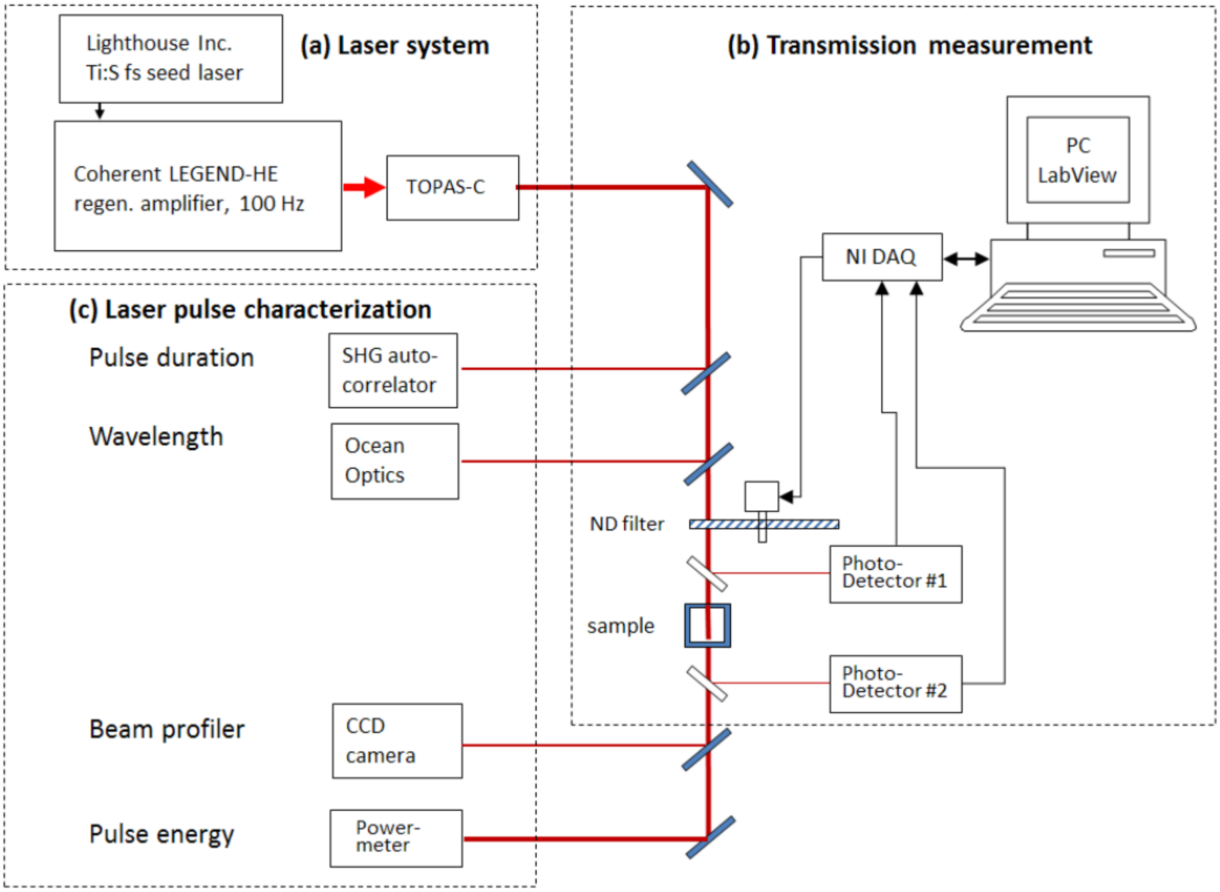


Figure S12: Experimental setup for measuring femtosecond NLT. (a) Laser system comprising femtosecond optical parametric amplifier pumped by femtosecond Ti:Sapphire regenerative laser amplifier; (b) LabVIEW-controlled measurement system that varies the power by rotating a circular ND filter and digitizes the signals from the photodetectors #1 and #2; (c) the instrumentation to measure the wavelength, the pulse duration, the pulse energy and the spatial intensity profile of the laser beam.

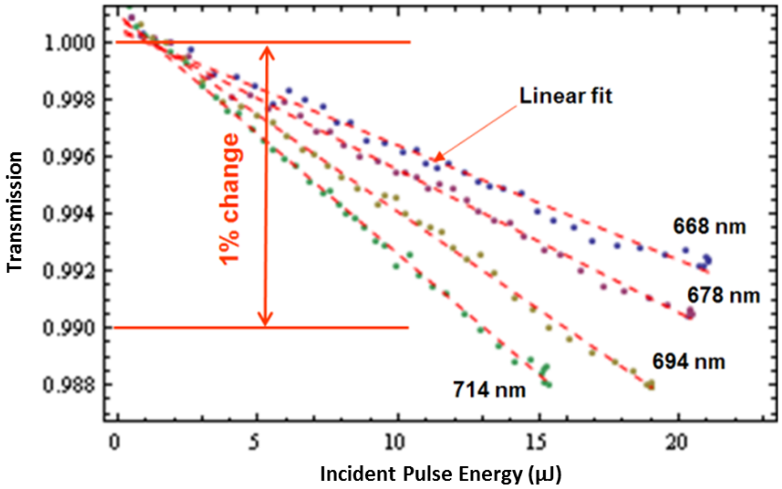


Figure S13: Exemplary measured transmission as a function of the incident laser pulse energy at different wavelengths. Dashed lines represent linear fits to the data. The distance between two red horizontal lines corresponds to transmission change of 1%.

IV. References.

1. V. Promarak and S. Ruchirawat, *Tetrahedron*, 2007, 63, 1602-1609.
2. G. G. Dubinina, R. S. Price, K. A. Abboud, G. Wicks, P. Wnuk, Y. Stepanenko, M. Drobizhev, A. Rebane and K. S. Schanze, *J. Am. Chem. Soc.*, 2012, 134, 19346-19349.
3. T. Cardolaccia, A. M. Funston, M. E. Kose, J. M. Keller, J. R. Miller and K. S. Schanze, *J. Phys. Chem. B*, 2007, 111, 10871-10880.