Supporting Information for the manuscript

Platinum (II) phosphine complexes with acetylene ligand containing 1,4,5,8-naphthalenediimide: synthesis, crystal structure and electrochemistry

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SI.1. General information

In-house facilities were used for CHN and EI MS analysis. The following instruments were used: absorption spectra, a Cary 50 Bio UV-Visible spectrophotometer; luminescence spectra, a Perkin Elmer LS 50B spectrofluorimeter; ^{1}H NMR spectra (presented as δ in ppm and J in Hz), a Bruker 250 MHz spectrometer.

Electrochemical measurements were performed in freshly distilled dry CH_2Cl_2 under N_2 using 0.1 M of $(NBu_4)PF_6$ as a background electrolyte with an Ecochimie Autolab-100 potentiostat, using a three-electrode cell with Pt working (disc) and counter (wire) electrodes and an Ag/AgCl reference electrode. The potentiostat was operated using software package GPES v. 4.9 for Windows 2000. Scan rates in each experiment were varied between 10 and 500 mV/s. Ferrocene was used in each experiment as an internal standard. All potentials are quoted vs. Fc/Fc^+ couple.

Nanosecond flash photolysis studies were performed on a home-built set-up with a Nd:YAG laser (9 ns pulse width, energy 5 mJ, beam diameter 6 mm), a steady-state Xe lamp (Hamamatsu L 2273), and a Tektronix 3032B oscilloscope.

SI.2. Synthesis of Pt(dppe)Cl$_2$

$PtCl_2(DMSO)_2$ (150 mg, 0.36 mmol) and dppe (142 mg, 0.36 mmol) were stirred in CH_2Cl_2 (10 ml) under nitrogen for 24 hr at rt to give colourless solution. Addition of ether precipitated the product that was washed with ether and dried in vacuum. White solid – 232 mg (0.33 mmol, 92%) Calc. for $C_{26}H_{24}Cl_2P_2Pt\cdot(CH_2Cl_2)_{0.5}$ (M.W. 706.87): C, 45.03; H, 3.56. Found: C, 45.13; H, 3.30. The solvated molecule of CH_2Cl_2 was observed in ^{1}H NMR. ^{31}P NMR: 41.54 (s, $J_{\text{Pt-P}}$ 3620).

SI.3. Synthesis of Pt(dppf)Cl$_2$

$PtCl_2(DMSO)_2$ (100 mg, 0.24 mmol) and dppf (131 mg, 0.24 mmol) were stirred in CH_2Cl_2 (10 ml) under nitrogen for 24 hr at rt to give yellow solution. Addition of hexane and ether precipitated the product that was washed with ether and dried in vacuum. Orange solid – 188 mg (0.22 mmol, 92%). Calc. for $C_{34}H_{28}Cl_2P_2Pt\cdot(CH_2Cl_2)_{0.4}$ (M.W. 854.33): C, 48.36; H, 3.40. Found: C, 48.78; H, 3.56. The solvated molecule of CH_2Cl_2 was observed in ^{1}H NMR. ^{31}P NMR: 13.43 (s, $J_{\text{Pt-P}}$ 3766).

SI.4. X-ray crystallography

Data were collected on a Bruker Smart CCD area detector with Oxford Cryosystems low temperature system. Reflections were measured from a hemisphere of data collected of frames each covering 0.3 degrees in omega. All reflections were corrected for Lorentz and polarization effects and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections. The structure was solved by direct methods and refined by full matrix least squares methods on F^2. Complex scattering factors were taken from the program package SHELXTL [An integrated system for solving and refining crystal structures from diffraction data, Revision 5.1, Bruker AXS LTD] as implemented on an IBM PC. Hydrogen atoms were placed geometrically and refined with a riding model (including torsional freedom for methyl groups) and with U_{iso} constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

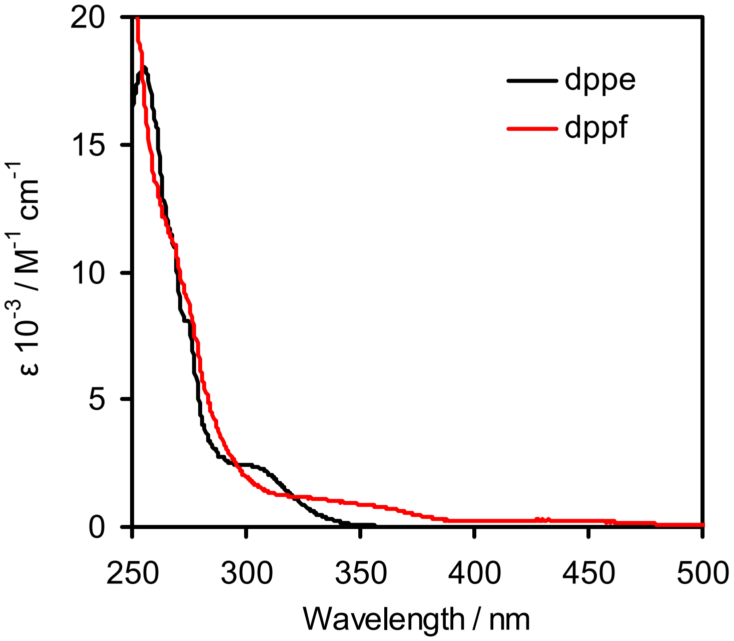

Fig. 1S. Absorption spectra of the precursor Pt(PP)Cl_2 complexes in CH_2Cl_2.

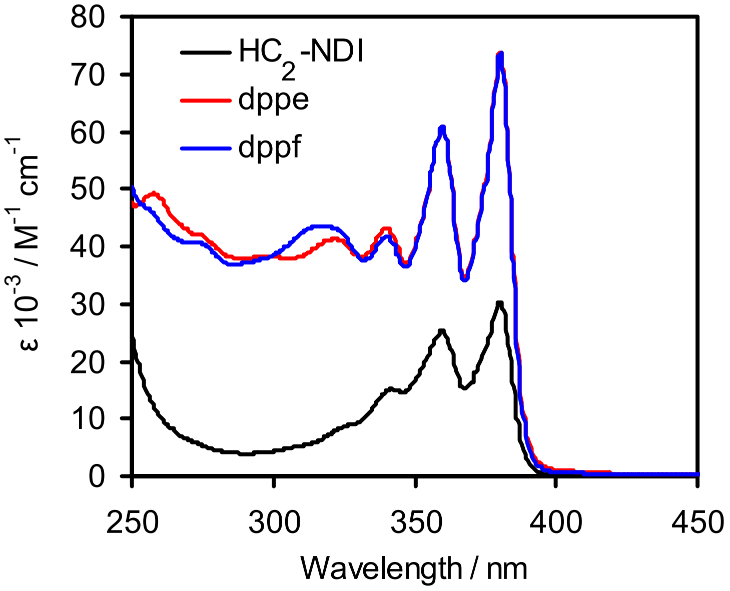

Fig. 2S. Absorption spectra of acetylene HC_2-NDI and its complexes Pt(PP)(C_2-NDI)$_2$ (PP = dppe or dppf) in CH_2Cl_2.

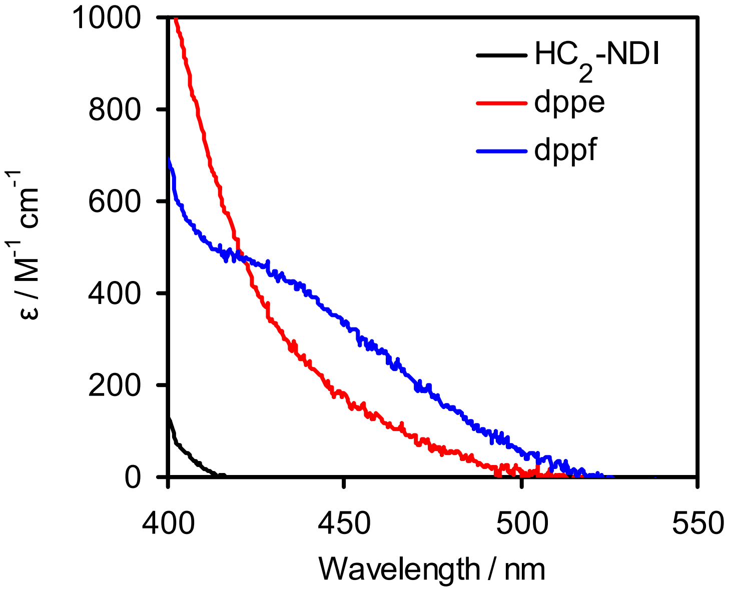

Fig. 3S. Absorption spectra above 400 nm of acetylene HC_2-NDI and its complexes Pt(PP)(C_2-NDI)$_2$ (PP = dppe or dppf) in CH_2Cl_2.