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PAPER

Self-assembly of neutral and cationic Pd^{II} organometallic molecular rectangles: synthesis, characterization and nitroaromatic sensing†

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Design and synthesis of three novel [2 + 2] self-assembled molecular rectangles **1–3** *via* coordination driven self-assembly of predesigned Pd(II) ligands is reported. 1,8-Diethynylanthracene was assembled with *trans*-$Pd(PEt_3)_2Cl_2$ in the presence of CuCl catalyst to yield a neutral rectangle **1** *via* Pd–C bond formation. Complex **1** represents the first example of a neutral molecular rectangle obtained *via* C–Pd coordination driven self-assembly. A new Pd_2^{II} organometallic building block with 180° bite-angle 1,4-bis[*trans*-(ethynyl)$Pd(PEt_3)_2(NO_3)$]benzene (**M²**) containing ethynyl functionality was synthesized in reasonable yield by employing Sonagashira coupling reaction. Self-assembly of **M²** with two organic clip-type donors (**L²–L³**) afforded [2 + 2] self-assembled molecular rectangles **2** and **3**, respectively [**L²** = 1,8-bis(4-pyridylethynyl)anthracene; **L³** = 1,3-bis(3-pyridyl)isophthalamide]. The macrocycles **1–3** were fully characterized by multinuclear NMR and ESI-MS spectroscopic techniques, and in case of **1** the structure was unambiguously determined by single crystal X-ray diffraction analysis. Incorporation of Pd-ethynyl bonds helped to make the assemblies π-electron rich and fluorescent in nature. Complexes **1–2** showed quenching of fluorescence intensity in solution in presence of nitroaromatics, which are the chemical signatures of many commercially available explosives.

Introduction

Chemists' desire to design and synthesize a target macromolecule dates back to the time when the synthetic organic chemistry started. Obtaining a molecule with expected shape, size and functionality *via* conventional covalent bond formation requires multistep reaction which is laborious, time consuming and generally ends in poor yield of the target product. In recent years, chemists have put an enormous effort in developing a directional self-assembly approach as an efficient route to construct larger and more complex molecules.[1] This self-assembly process is a spontaneous association of precursors guided by one or more interactions like H-bonding, π–π interaction, van der Waals forces, metal–ligand coordination *etc.* Self-assembly *via* coordination has been manifested as a useful and powerful protocol for the construction of predesigned and well-defined architectures.[1,2] The success of the process codes in the use of rigid precursors with appropriate shapes and symmetries. The rigid square planar coordination environment of Pd(II) and Pt(II) has long been utilized as favorite acceptors to engineer 2D and 3D architectures in this field. Unlike nitrogen-donors, oxygen-donor linkers are less common in the construction of large supramolecular structures of these metal ions.[3] In most of the cases, discrete and defined structures of these metals are constructed using *cis*-blocked Pd(II)/Pt(II)-acceptors as 90° building units. It is obvious that constructions of various typical architectures like hexagon, pentagon, dodecahedron *etc.* cannot be derived from these 90° *cis*-blocked Pd(II)/Pt(II) building units. For such architectures, shape-selective appropriate acceptors are required. Interestingly, though several shape selective Pt(II)-acceptors have been reported to achieve such typical 2D/3D-architectures,[4] shape selective polypalladium acceptors are yet to be explored.

In a recent communication we have reported the first example of a neutral Pd_4-molecular rectangle from a new shape-selective Pd_2 organometallic molecular "clip" (**M¹**) upon treatment with fumarate as a linear donor (Scheme 1).[5] If the design principle is appropriate, a complementary approach must give similar architecture. Here, we report three new Pd(II)-molecular rectangles **1–3** obtained in a complementary self-assembly of our previous approach using linear metal acceptors in combination with organic donor "clips"(Scheme 1). The neutral Pd_2-molecular rectangle (**1**) was constructed in an one-pot synthesis from 1,8-diethynylanthracene (**L¹**) and *trans*-$Pd(PEt_3)_2Cl_2$. Complex **1** represents the first example of a molecular rectangle obtained *via* Pd-carbon coordination driven self-assembly. Moreover, **1** is proved to be much more fluorescent compared to the previously

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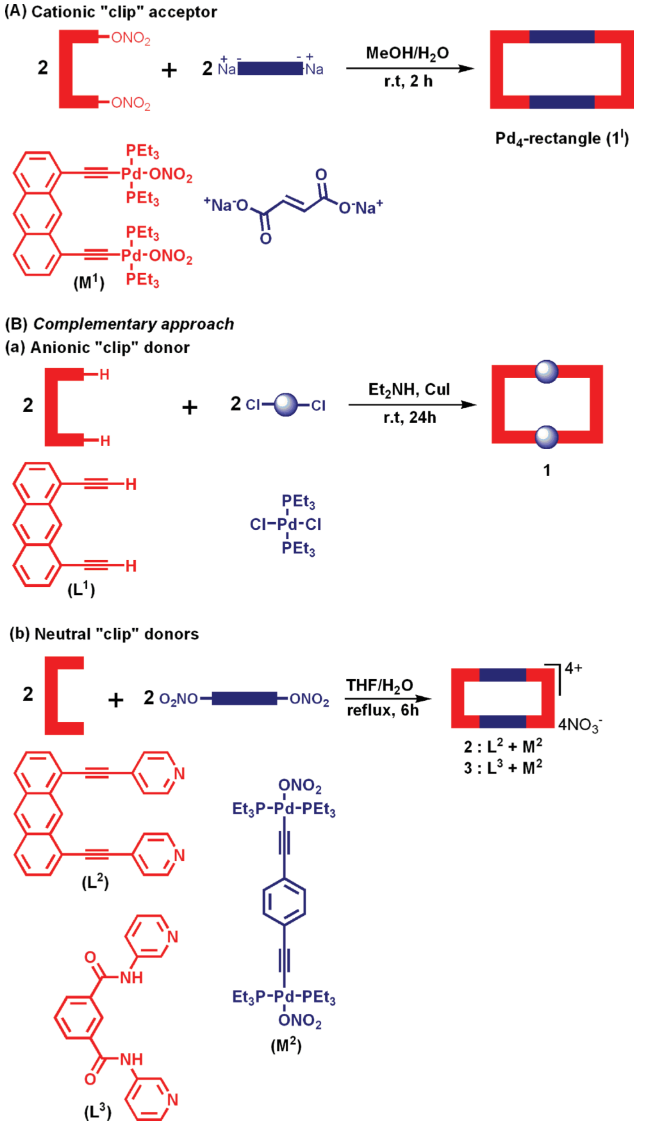
† Electronic supplementary information (SI) available: Stern–Volmer plots for the titration of complexes **1** and **2** with picric acid. ¹H NMR spectra of 1,4-bis[*trans*-(ethynyl)$Pd(PEt_3)_2(NO_3)$]benzene and **M²**. ESI-MS spectra of **M²**, **2**, **3** and emission, IR spectra of complex **3**. CCDC reference number 790087 (**1**). For SI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01048k



Scheme 1 [2 + 2] Self-assembled Pd(II)-based molecular rectangles.

reported Pd_2 organometallic molecular "clip" $\mathbf{M^1}$ and the neutral Pd_4 molecular rectangle (**1′**; Scheme 1).[5] To explore this complementary approach of designing molecular rectangle, we report here a linear Pd_2 organometallic acceptor 1,4-bis[*trans*-(ethynyl)Pd$(PEt_3)_2(NO_3)$]benzene ($\mathbf{M^2}$) and its self-assembly of two cationic Pd_4-molecular rectangles (**2**) and (**3**) using clip-type organic donors 1,8-bis(4-ethynylpyridyl)anthracene ($\mathbf{L^2}$) and 1,3-bis(3-pyridyl)isophthalamide ($\mathbf{L^3}$), respectively. Rectangles **1** and **2** exhibited selective fluorescence quenching in solution in presence of electron deficient nitroaromatics, which are well known chemical constituents of many commercial explosives.

Experimental

Materials and methods

All chemicals used in this work were purchased from commercial sources and used without further purification. Solvents were distilled by standard methods prior to use. The complexes *trans*-Pd$(PEt_3)_2Cl_2$,[6] 1,4-diethynylbenzene,[7] 1,8-diethynylanthracene ($\mathbf{L^1}$),[8] 1,8-bis(4-ethynylpyridyl)anthracene ($\mathbf{L^2}$),[9] 1,3-bis(3-pyridyl)isophthalamide ($\mathbf{L^3}$)[10] were prepared following the reported procedures. KBr phase IR spectra of the complexes were recorded in the range of 4500–400 cm^{-1} using a Perkin Elmer Lambda-35 spectrometer. ^1H and ^{31}P NMR spectra were recorded in a Bruker 400 MHz spectrometer. $^{31}P\{H\}$ chemical shifts are reported relative to an external, unlocked sample of H_3PO_4 ($\delta = 0.0$ ppm), while ^1H NMR chemical shifts are referenced to TMS. Electrospray ionization mass (ESI-MS) experiments were done using a Bruker Daltonics (Esquire 300 Plus ESI model). Elemental analyses were performed using a Perkin–Elmer 2400 CHNS analyzer.

Fluorescence quenching titration study. Stock solutions of the nitroaromatic quenchers (1.0×10^{-3} M) in $CHCl_3$ and that of rectangles **1–2** (1.0×10^{-6} M) in THF or $CHCl_3$ were prepared. A 2 mL stock solution (1.0×10^{-6} M) of the rectangles (**1–2**) was placed in a quartz cell of 1 cm width and nitroaromatic stock solution (1.0×10^{-3} M) was added in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated at least three times to get concordant value. For all measurements both the rectangles (**1–2**) were excited at λ_{ex} = 320 nm and emissions above 330 nm were monitored. Both excitation and emission slit width were 5 nm for rectangle **1** and 1 nm for rectangle **2**. There was no change in shape of the emission spectra except significant gradual quenching of the initial fluorescence emission intensity of rectangles (**1–2**) upon titration with electron deficient nitroaromatic quenchers. Analysis of the normalized fluorescence emission intensity (I_0/I) as a function of increasing quenchers concentration ([Q]) was well described by the Stern–Volmer equation $I_0/I = 1 + K_{SV}[Q]$. The Stern–Volmer binding constant was calculated from the slope of the Stern–Volmer plot.

Synthesis of 1,8-bis[*trans*-(ethynyl)Pd$(PEt_3)_2(NO_3)$]-anthracene ($\mathbf{M^1}$). To a stirred solution of 1,8-bis[*trans*-(ethynyl)Pd$(PEt_3)_2$(Cl)]anthracene[5] (525.3 mg, 0.54 mmol) in 30 mL of degassed $CHCl_3$ was added dry and degassed methanolic solution (15 mL) of silver nitrate (273.1 mg, 1.6 mmol) under nitrogen atmosphere. The reaction mixture was stirred at ambient temperature for 24 h in absence of light and then filtered through celite. The filtrate and washings were concentrated to ~3 mL and cold diethyl ether was added to precipitate out ($\mathbf{M^1}$) as brown solid in a 60% (332 mg) isolated yield. Anal. Calcd. for $C_{42}H_{68}N_2O_6P_4Pd_2$: C, 48.80; H, 6.63; N, 2.71; Found: C, 48.45; H, 6.90; N, 2.50.^1H NMR (400 MHz; $CDCl_3$): δ (ppm) = 9.24 (s, 1H), 8.37 (s, 1H), 7.84 (d, 2H), 7.48 (d, 2H), 7.38–7.34 (m, 2H), 1.95–1.85(m, 24H), 1.34–0.98 (m, 36H). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.4 MHz): 19.17 (s). ESI-MS: m/z = 970.32 $[M^1 - NO_3]^+$.

Synthesis of 1,4-bis[*trans*-(ethynyl)Pd$(PEt_3)_2(NO_3)$]benzene ($\mathbf{M^2}$). To a 100 mL round bottom Schlenk flask 1, 4-diethynylbenzen (0.5 mg, 3.97 mmol) and *trans*-Pd$(PEt_3)_2Cl_2$ (4.15 g, 10.04 mmol) were added under N_2-atmosphere. 75 mL of dried and degassed Et_2NH was syringed into the flask. After 10 min stirring, CuCl (40 mg, ~10 mol%) was added at a time under nitrogen atmosphere. Immediately yellow precipitate appeared and on stirring it assumed brown reaction mixture. After 48 h stirring, solvent was removed under vacuum to get brown solid. The crude solid was column chromatographed through silica gel (60–120 mesh) with CH_2Cl_2 as eluent. The complex 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene was eluted as the first fraction in 80% (2.79 g) isolated yield. Efforts to obtain suitable single crystals were failed. Needle shaped very thin crystals were obtained on slow evaporations of the THF solution of the complex. Though the single crystal X-ray diffraction data were not of publishable quality, the connectivity of the constituents was clear to conclude the linear structure of 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene. Anal. Calcd. for $C_{34}H_{64}Cl_2P_4Pd_2$: C, 46.38; H, 7.33; Found: C, 46.63; H, 7.69. ^{1}H NMR (400 MHz; $CDCl_3$): δ((ppm) = 7.13 (d, 4H), 1.94–2.01 (m, 24H), 1.15–1.26 (m, 36H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz): 18.04 (s). IR (KBr): $\nu(C\equiv C)$ = 2114.7 cm^{-1}.

To a stirred solution of 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]-benzene (220 mg, 0.25 mmol) in 25 mL of degassed $CHCl_3$ was added degassed methanolic solution (15 mL) of silver nitrate (127.3 mg, 0.75 mmol) under nitrogen atmosphere. The reaction mixture was stirred for further 24 h in absence of light, and filtered through celite-545. The filtrate and washings were concentrated to ~2 mL and cold diethyl ether was added to isolate **M²** as brown solid with 50% (117 mg) isolated yield. Anal. Calcd. for $C_{34}H_{64}Pd_2N_2O_6P_4$: C, 43.74; H, 6.91; N, 3.00; Found: C, 43.99; H, 7.28; N, 2.93. ^{1}H NMR (400 MHz; $CDCl_3$): δ ((ppm) = 7.11 (d, 4H), 1.83–1.87 (m, 24H), 1.17–1.25 (m, 36H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz): 19.9 (s). ESI-MS (*m*/*z*): 871.6, [$\mathbf{M^2}$ – NO_3^-]$^+$; 404.8, [$\mathbf{M^2}$ – 2NO_3^-]$^{2+}$.

Synthesis of the rectangle (1). To a 50 mL Schlenk flask 1, 8-diethynylanthracene (200.0 mg, 0.885 mmol) and *trans*-Pd(PEt_3)$_2Cl_2$ (364.4 mg, 0.881 mmol) were added under an atmosphere of N_2. 25 mL of dry and degassed Et_2NH was syringed into the flask. CuCl (10 mg, ~10 mol%) was added at a time after 10 min stirring. Immediately greenish yellow gelatinous fluorescent precipitate appeared and on stirring it changed to deep greenish yellow fluorescent mixture. Solvent was removed under reduced pressure after 24 h stirring to get greenish yellow solid. The crude solid was eluted on preparative TLC plate with n-hexane–toluene (20/80 v/v) solvent mixture as eluent. Complex **1** was eluted as the first fraction and it was extracted with THF and the solvent was evaporated to dryness to yield **1** as greenish yellow solid with 80% (401 mg) isolated yield. The X-ray diffraction quality crystals were obtained upon slow evaporation of the THF solution. Anal. Calcd. for $C_{60}H_{76}P_4Pd_2$: C, 63.55; H, 6.76; Found: C, 63.27; H, 6.92. ^{1}H NMR (400 MHz; $CDCl_3$): δ((ppm) = 9.68 (s, 2H), 8.34 (s, 2H), 7.9 (d, 4H), 7.49 (d, 4H), 7.32–7.36 (m, 4H), 2.01–2.34 (m, 48H), 1.22–1.30 (m, 72H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz): 14.4 (s). IR (KBr): $\nu(C\equiv C)$ = 2087.8 cm^{-1}. UV-Vis (THF) λ_{max} (ε) [nm (cm^{-1}M^{-1})]: 268 (18967), 366 (1139), 384 (1679), 406 (2890), 430 (3285). Emission (THF) λ_{max}: 358, 375, 392, 440, 465, 495.

Synthesis of the rectangle (2). To a THF solution of **L²** (10 mg, 0.026 mmol) was added drop wise a solution of **M²** (25.0 mg, 0.026 mmol) in THF–H_2O solvent mixture. The reaction mixture was refluxed with stirring for 6 h and the solvent was removed under reduced pressure. Diethyl ether was added to the dry mass to obtain **2** as brown solid in 76% (26.2 mg) yield. Anal. Calcd. for $C_{124}H_{160}N_8P_8Pd_4O_{12}$: C, 56.67; H, 6.14; N, 4.26; Found: C, 57.01; H, 5.99; N, 4.10. ^{1}H NMR (400 MHz; $CDCl_3$): δ ((ppm) = 9.48 (s, 2H), 8.54 (broad, [2H_4 +8H_α]), 8.12 (d, 4H), 7.87–7.89 (m, 4H). 7.40 (d, 8H), 7.11 (d, 8H), 1.97–1.98 (m, 48H), 1.19–1.23 (m, 72H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz): 19. 8 (s). IR (KBr); $\nu(C\equiv C)$ (cm^{-1}): 2202.5; 2111.9. UV-Vis (THF) λ_{max} (ε) [nm (cm^{-1}M^{-1})]: 268 (18967),366 (1139), 384 (1679), 406 (2890), 430 (3285). Emission (THF) λ_{max}: 358, 375, 392, 440, 465, 495. ESI-MS *m*/*z*: 1251.6, [**2** – 2NO_3^-]$^{2+}$/2; 1246.63, [**2** – NO_3^- + 3H_2O]$^+$; 844.74, [**2** – 3NO_3^- + 3MeOH]$^{3+}$/3; 836.2, [**2** – 3NO_3^-]$^{3+}$/3; 610.3, [**2** – 4NO_3^- + 2MeOH]$^{4+}$/4.

Synthesis of the rectangle (3). To a slurry of **L³** in THF (10 mg, 0.03 mmol) a solution of **M²** (28.0 mg, 0.03 mmol) in THF–H_2O solvent mixture was added drop wise. The reaction mixture was refluxed with continuous stirring for 6 h. Upon completion, the reaction mixture was dried under vacuum to dryness and washed with diethyl ether to obtain **3** as brown solid with 56% (21 mg) isolated yield. Anal. Calcd. for $C_{104}H_{156}N_{12}P_8O_{16}Pd_4$: C, 49.89; H, 6.28; N, 6.71; Found: C, 50.22; H, 5.96; N, 6.89. ^{1}H NMR (400 MHz; $CDCl_3$): δ ((ppm) = 10.96 (brad, NH), 10.79 (s, 4H),9.40 (d, 4), 9.07(d, 4H), 8.73 (d, 4H). 7.58 (m, 4H), 6.91 (d, 8H), 1.64–1.78 (m, 48H), 1.08–1.18 (m, 72H). ^{31}P{^{1}H} NMR ($CDCl_3$, 121.4 MHz): 17.8 (s). IR (KBr); $\nu(C\equiv C)$ (cm^{-1}): 2207.5; 2112.9. Emission (THF) λ_{max}: 430, 456, 485. ESI-MS *m*/*z*: 1189.95, [**3** – 2NO_3^-]$^{2+}$/2; 1071.95, [**3** – 3NO_3^- – 2PEt_3]$^{2+}$/2; 772.63, [**3** – 3NO_3^-]$^{3+}$/3; 564.00, [**3** – 4NO_3^-]$^{4+}$/4; 528.22, [**3** – 4NO_3^- – 2PEt_3 + 3MeOH]$^{4+}$/4.

X-ray crystallographic studies

X-ray diffraction quality single crystals of **1** were obtained by slow evaporation of its THF solution. Several efforts to obtain suitable single crystals of 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene were failed and only very thin crystals were obtained finally. Though the quality of diffraction data was not publishable, gross connectivity of the components was conclusive. The complex was crystallized in triclinic crystal system with $P\bar{1}$ space group having cell parameters a = 7.1069(4) Å, b = 8.8519(5) Å, c = 33.0829(18) Å, α = 89.169(5)°, β = 87.412(4)° and γ = 87.898(4)°. The diffraction data of **1** were collected with synchrotron radiation (λ = 0.71073 Å) using wiggler beamline 4A at Pohang Accelerator Laboratory. This multipole wiggler has 28 magnet poles with 2.02 tesla and its periodic length and gap size are 14 cm and 14 mm, respectively. A fast speed CCD was installed for multi-wavelength anomalous diffraction (MAD) experiments in the energy range of 6–18 keV. *SADABS*[11] program was use for empirical absorption correction. The structure was solved by direct methods (*SHELXS-97*) and standard Fourier techniques, and refined on F^2 using full matrix least squares procedures (*SHELXL-97*)[12] incorporated in *WinGX*.[13] Structural illustrations were drawn using *POV-Ray*. The aromatic hydrogen atoms were located and refined anisotropically. Other hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to either 1.5 (methyl hydrogen atoms) or 1.2 (all other hydrogen atoms) times the thermal parameter of the carbon atoms to which they were attached.

Results and discussions

Synthesis and characterisation

The neutral Pd_2 organometallic molecular rectangle **1** was synthesized in an one-pot self-assembly using 1,8-diethynylanthracene and *trans*-Pd(PEt$_3$)$_2$Cl$_2$ in presence of CuCl catalyst under inert atmosphere *via trans*-metallation reaction (Scheme 1). On addition of CuCl catalyst into the stirred yellow solution of 1,8-diethynylanthracene (**L^1**) and *trans*-Pd(PEt$_3$)$_2$Cl$_2$ in dry and degassed HNEt$_2$, greenish yellow gelatinous precipitate started to appear. The progress of the reaction was monitored by TLC and though almost 90% reaction was completed within 4–5 h, complete consumption of the starting materials needed ~24 h. Exclusive formation of **1** was only achieved when 1 : 1 molar ratio of **L^1** and *trans*-Pd(PEt$_3$)$_2$Cl$_2$ was maintained. Though a zig-zag 1D polymer is also an expected product from the reaction of such a small "clip" 1,8-diethynylanthracene (**L^1**) in combination with a sterically crowded *trans*-Pd(PEt$_3$)$_2$Cl$_2$, isolation of **1** in good yield is surprising. Formation of Pd$_2$ organometallic rectangle may be a consequence of kinetic *versus* thermodynamic control.

The ^{31}P NMR spectrum (Fig. 1) of complex **1** showed a singlet at 14.4 ppm. An upfield shift of ^{31}P peak ($\Delta\delta = 3.55$ ppm) in complex **1** compared to the starting material *trans*-Pd(PEt$_3$)$_2$Cl$_2$ indicated complex formation. Moreover, considerable downfield shift ($\Delta\delta = 0.24$ ppm) of the peak corresponding to H$_5$ (Fig. 1) in the ^{1}H NMR spectrum of **1** compared to **L^1** is due to a decrease in electron density upon its (**L^1**) coordination to Pd. A sharp singlet in the ^{31}P NMR spectrum and one set of peaks in the ^{1}H NMR spectrum of **1** indicate the formation of a single and symmetrical product (Fig. 1). In a recent communication we reported a neutral carboxylate-based Pd$_4$-molecular rectangle.[5] The present neutral Pd$_2$ rectangle (**1**) is a unique example of an organometallic rectangle obtained *via* Pd–C bond directed self-assembly in a single step (Scheme 1).

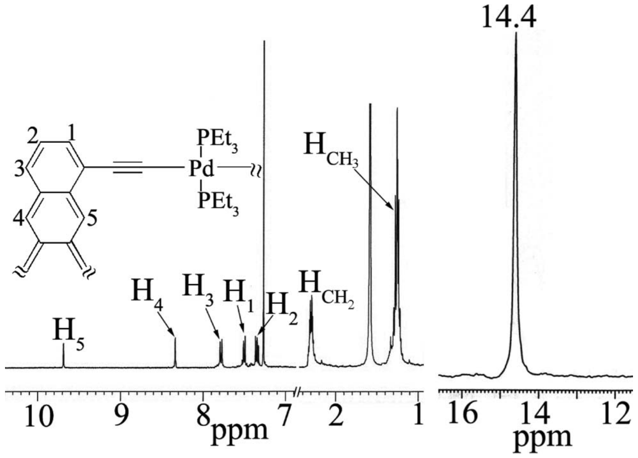
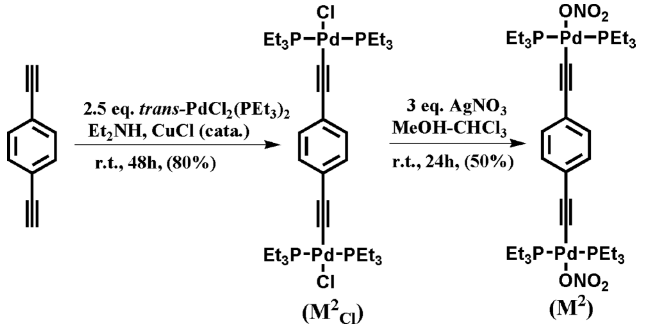


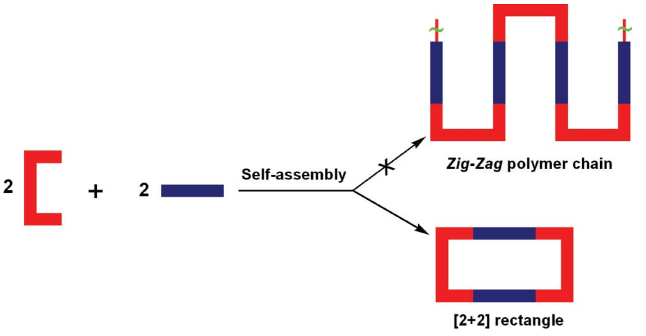
Fig. 1 ^{1}H (left) and ^{31}P (right) NMR spectra of complex **1**.



Scheme 2 Synthesis of the linear organometallic Pd$_2$ acceptor **M^2**.

To extend this methodology of building molecular rectangles with different functionality, we have designed a Pd$_2$ organometallic linear ditopic acceptor **M^2**. Treatment of 1,4-diethynylbenzene with 2.5 equivalents of *trans*-Pd(PEt$_3$)$_2$Cl$_2$ in the presence of a catalytic amount of CuCl in an inert atmosphere in dry HNEt$_2$ afforded 1,4-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]benzene (Scheme 2). The reaction was monitored by TLC and it was found to be over upon 24 h stirring at room temperature. After completion of the reaction, the reaction mixture was dried and 1,4-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]benzene was purified by column chromatography (silica gel) using CH$_2$Cl$_2$ as eluent. In the ^{1}H NMR spectrum of 1,4-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]benzene, disappearance of ethynyl protons as well as appearance of one set of aromatic protons (Fig. S1, SI†) indicated its exclusive formation. Though the quality of single crystal X-ray data of this chloride analogue was not publishable, the formation of expected linear 1,4-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]benzene was conclusive.

The chloride derivative 1,4-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]-benzene was treated with 3 equivalents of AgNO$_3$ in a MeOH–CHCl$_3$ mixture in the absence of light (Scheme 2). Immediate formation of AgCl as well as a change in color of the solution from yellow to orange–red indicated the progress of the reaction. The mixture was filtered through celite bed after 24 h stirring and the filtrate was concentrated to minimum volume followed by trituration with a cold n-hexane–diethyl ether mixture to obtain **M^2** as the yellowish brown solid with 50% isolated yield. The ^{31}P NMR spectrum of **M^2** showed a single peak considerably downfield shifted compared to the chloride derivative (Fig. 2). Downfield shift of the peaks in the ^{1}H NMR spectrum of **M^2** compared to its chloride derivative also supports its formation (Fig. 2). Elemental analyses and finally the ESI-MS experiment supported the formation of **M^2** by the appearance of two prominent peaks corresponding to [**M^2** – NO$_3^-$]$^+$ (871.6) and [**M^2** – 2NO$_3^-$]$^{2+}$ (404.8). Experimental isotopic distribution pattern of the peak corresponding to [**M^2** – NO$_3^-$]$^+$ fragment matched well with the expected pattern (Fig. 2 and SI†). In principle, self-assembly of a ditopic donor "clip" in combination with a linear acceptor may either allow the formation of a [2 +2] self-assembled molecular rectangle or a zig-zag polymeric chain or a mixture of them (Scheme 3).



Scheme 3 Possible structures from the combination of a "clip" and a linear linker.

Formation of both discrete rectangle as well as polymeric analogue is reported upon treatment of a donor "clip" with linear linkers.[14,6] Interestingly, the reaction of linear Pd$_2$ acceptor

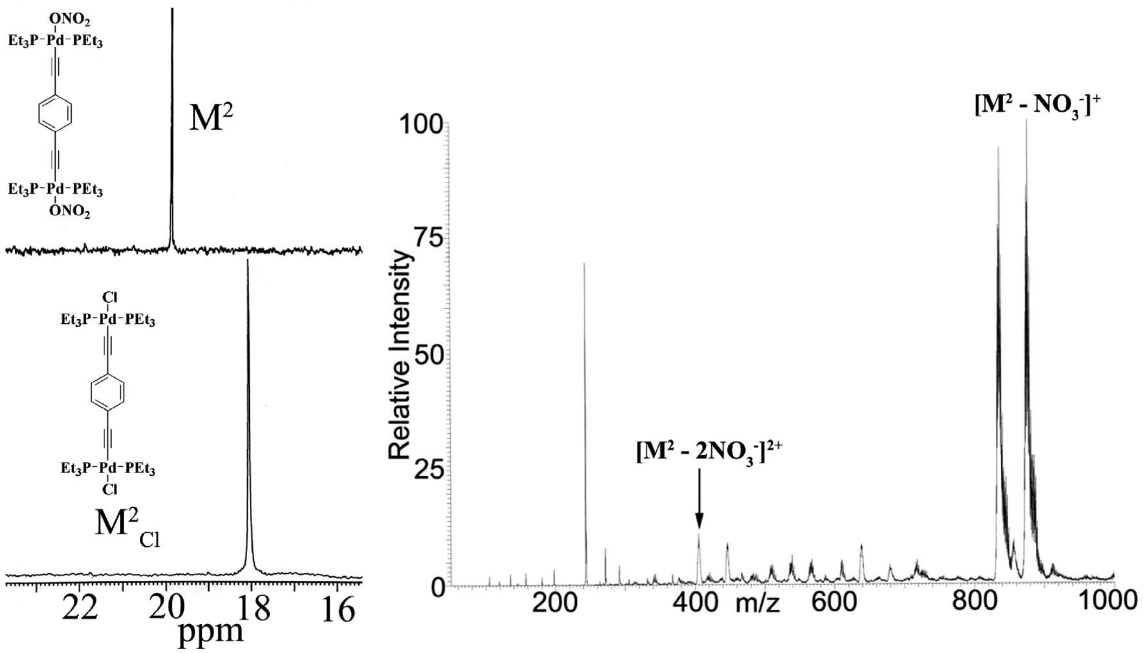


Fig. 2 ^{31}P NMR spectra of **M^2** and 1,4-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]benzene (left) and ESI-MS of **M^2** (right).

(**M^2**) with the "clip" **L^2** or **L^3** favored the exclusive formation of macrocyclic analogue **2** or **3**, respectively (Scheme 3). The cationic rectangle (**2**) was synthesized upon treatment of the Pd$_2$ acceptor **M^2** with the donor "clip" **L^2**. An immediate color change of the solution of **M^2** dissolved in THF–H$_2$O solvent mixture from orange to dark red upon addition of yellow THF solution of **L^2** was noticed. The ^{31}P NMR spectrum showed a single peak at 19.8 ppm, slightly upfield shifted (Δδ = 0.1 ppm) compared to **M^2** (Fig. 3). Clear downfield shift of the peak corresponding to the H$_\alpha$ in the ^{1}H NMR spectrum (Fig. 3) compared to starting material **L^2** indicated coordination of pyridyl nitrogen to the Pd(II) centre. Overall, the NMR analysis indicated the formation of a single and symmetrical product.

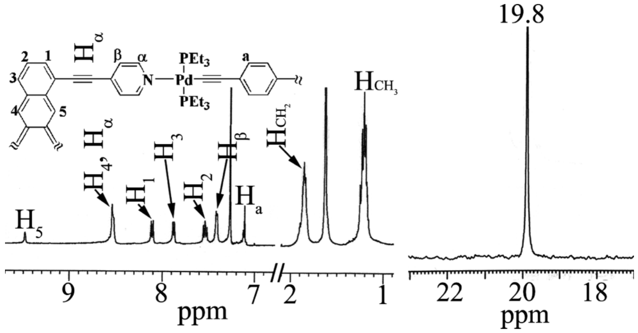


Fig. 3 ^{1}H (left) and ^{31}P (right) NMR spectra of complex **2**.

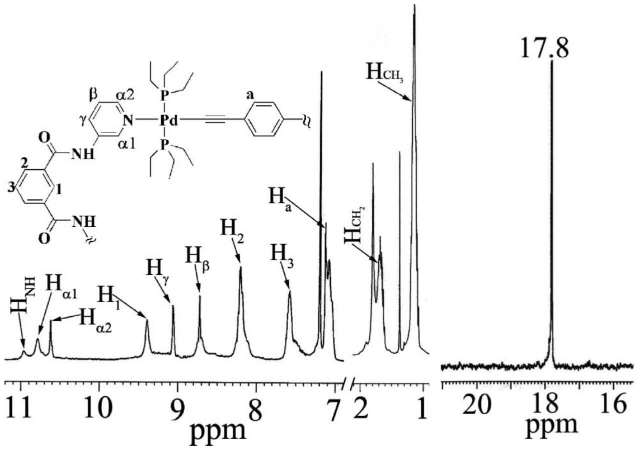


Fig. 4 ^{1}H (left) and ^{31}P (right) NMR spectra of complex **3**.

Similarly, the cationic rectangle (**3**) was obtained upon treatment of **M^2** with the organic "clip" **L^3**. Ligand **L^3** in THF was treated with an orange solution of **M^2** in THF–H$_2$O solvent mixture. Finally, after refluxing for 4 h the whole reaction mixture turned into a transparent solution. The ^{31}P NMR spectrum showed a single peak at 17.8 ppm, which is considerably upfield shifted (Δδ = 2.02 ppm) compared to **M^2** (Fig. 4). In addition to the large upfield shift of the peak in the ^{31}P NMR spectrum, significant downfield shifts of the peaks corresponding to the H$_{\alpha1}$ and H$_{\alpha2}$ in the ^{1}H NMR spectrum (Fig. 4) of the complex indicated coordination of pyridyl nitrogen to the Pd(II). Formation of a single and symmetrical product was conclusive from ^{31}P & ^{1}H NMR spectra.

ESI-MS analyses for complexes **2** and **3** (SI†) supported the formation of [2 + 2] self-assembled rectangles by the appearance of a series of prominent peaks for [**2**/**3** – (NO$_3^-$)$_n$]$^{n+}$ fragments. For complex **2**, the prominent peaks at *m*/*z* = 1251.6, 1246.6, 844.7, 813.7 and 610.3 were assigned to [**2** – 2NO$_3^-$]$^{2+}$/2, [**2** – NO$_3^-$ + 3H$_2$O]$^+$, [**2** – 3NO$_3^-$ + 3MeOH]$^{3+}$/3, [**2** – 3NO$_3^-$]$^{3+}$/3 and [**2** – 4NO$_3^-$ + 2MeOH]$^{4+}$/4, respectively. While for complex **3**, the prominent peaks at *m*/*z* = 1189.9, 1071.9, 772.6 and 564.0 were assigned to [**3** – 2NO$_3^-$]$^{2+}$/2, [**3** – 3NO$_3^-$ – 2PEt$_3$]$^{2+}$/2, [**3** – 3NO$_3^-$]$^{3+}$/3 and [**3** – 4NO$_3^-$]$^{4+}$/4, respectively.

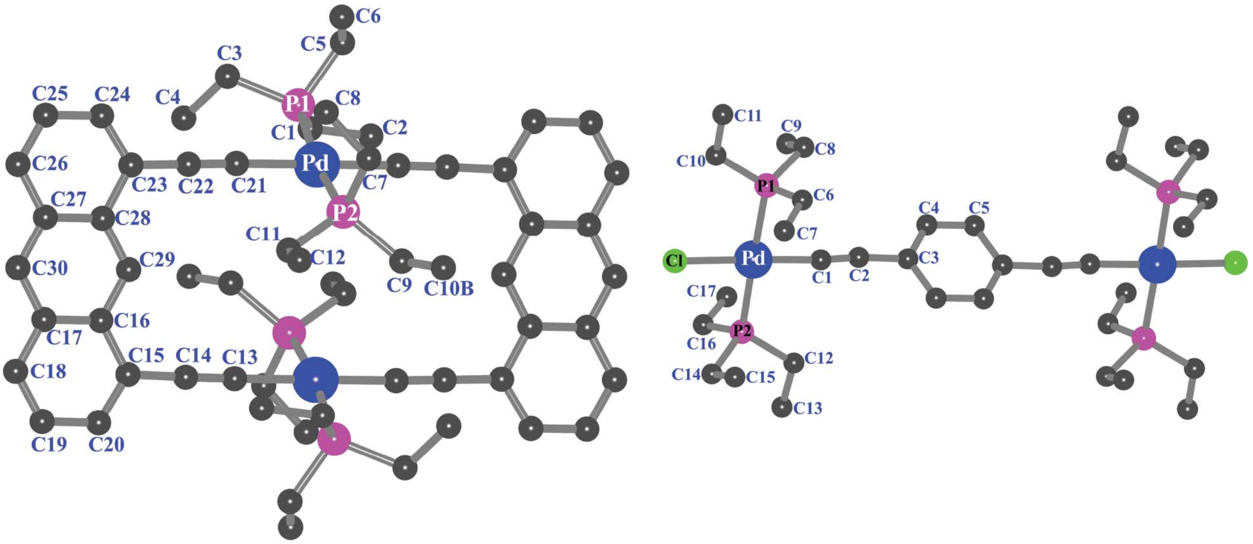


Fig. 5 Ball & stick models of the solid state single crystal structures of complex **1** (left) and 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene (right). H-atoms are omitted for clarity. Color codes: blue = Pd, purple = P, green = Cl, gray = C.

Table 1 Crystallographic data and refinement parameters of **1**

Formula	$C_{60}H_{66}P_4Pd_2$
fw, g mol^{-1}	1123.81
Crystal system	Monoclinic
Space group	$P121/c1$
T/K	150
a/Å	9.935(2)
b/Å	20.917(4)
c/Å	12.996(3)
α (°)	90
β (°)	102.57(2)
γ (°)	90
V/Å^3	2636(9)
Z	2
ρ_c/g cm^{-3}	1.416
μ/mm^{-1}	0.840
collected reflections	6618
unique reflections	12406
R_{int}	0.0237
Final $R1^a$, $wR2^b$ ($I \geq 2\sigma$)	0.0388, 0.0977
R_1, wR_2 (all data)	0.0558, 0.1042
GOF on F^2	0.997

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ with P is $[2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$.

Description of crystal structures

Molecular structures of complex **1** and 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene were unambiguously proved by single crystal X-ray data analysis. The solid state molecular structures of **1** and 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene based on single crystal X-ray diffraction studies are shown in Fig. 5. Crystallographic data and refinement parameters of **1** are presented in Table 1 and selected bond parameters are assembled in Table 2. The quality of X-ray data of 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene was not good enough for publication. Hence the molecular view of this linker as obtained from the poor quality data set is only presented here. The solid state structure of **1** belongs to the monoclinic system with $C2/c$ space group where the asymmetric unit contains half of a formula unit and full structure is $C2$ symmetry generated. The linker 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene was crystallized in triclinic $P\bar{1}$ space group with two formula units in asymmetric unit.

In the molecular rectangle **1**, two Pd(II) centres are placed at the mid points of the longer arms of the rectangle with dimensions 7.30 Å × 14.97 Å (Fig. 6). The distance between the two palladium centres is 5.13 Å while the distance between the H_1 and H_8 of the anthracene moiety is 4.99 Å. Moreover, two 1,8-diethynylanthracene moieties and two palladium centres are perfectly coplanar. Thus complex **1** represents a rare example of a rigid and regular molecular rectangle. Though the *trans*-coordinated ethynyl moieties and palladium centers are almost co-linear (the angle of $C_{C\equiv C}$–Pd–$C_{C\equiv C}$ = 178°), the *trans*-coordinated PEt_3 groups are deviated from the ideal square planar geometry with P–Pd–P angle = 171°. Moreover, the $C_{C\equiv C}$–Pd–P angles are in the range of 82–92°.

Surprisingly, the arms of the chloride analogue of $\mathbf{M^1}$ are neither parallel nor co-planar (Fig. 6). Two arms are oriented in such a fashion that one Pd(II)-centre lies above the plane containing the anthracene moiety while the other one lies below this plane. Moreover, the palladium metal centres are considerably pulled down from their respective ideal square planar geometry. Interestingly, the directions of the two Pd–Cl bonds are mutually divergent (divergent angle = 26°) enough compared to the parallel (divergent angle = 0°) ethynyl "arms" of 1,8-diethynylanthracene. But the solid state structure of 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene showed almost square planar geometry around the palladium metal centres (Fig. 6).

Almost square planar environment around Pd(II) centers in conjunction with coplanarity of the ethynyl moieties makes **1** a perfect rectangle. The C≡C bond distances in complex **1** are C(13)–C(14) = 1.209(4) and C(21)–C(22) = 1.204(4) Å, respectively. C–Pd distances are measured to be Pd(1)–C(13) = 2.005(3) Å and Pd(1)–C(21) = 2.016(3) Å. In case of organometallic clip 1,8-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]anthracene the C≡C and C–Pd

Table 2 Selected bond distances (Å) and angles (°) for **1**

Pd(1)–C(13)	2.005(3)	Pd(1)–C(21)	2.016(3)	Pd(1)–P(2)	2.3126(9)
Pd(1)–P(1)	2.3178(8)	P(1)–C(5)	1.827(3)	P(1)–C(3)	1.827(3)
C(13)–C(14)	1.209(4)	C(21)–C(22)	1.204(4)		
C(13)–Pd(1)–C(21)	178.02(11)		C(13)–Pd(1)–P(2)	87.70(8)	
C(21)–Pd(1)–P(2)	90.56(8)		C(13)–Pd(1)–P(1)	88.99(8)	
C(21)–Pd(1)–P(1)	92.59(8)		P(2)–Pd(1)–P(1)	170.63(2)	
C(22)–C(21)–Pd(1)	178.3(2)				

Symmetry transformations used to generate equivalent atoms: #1 –x + 1,–y,–z + 1.

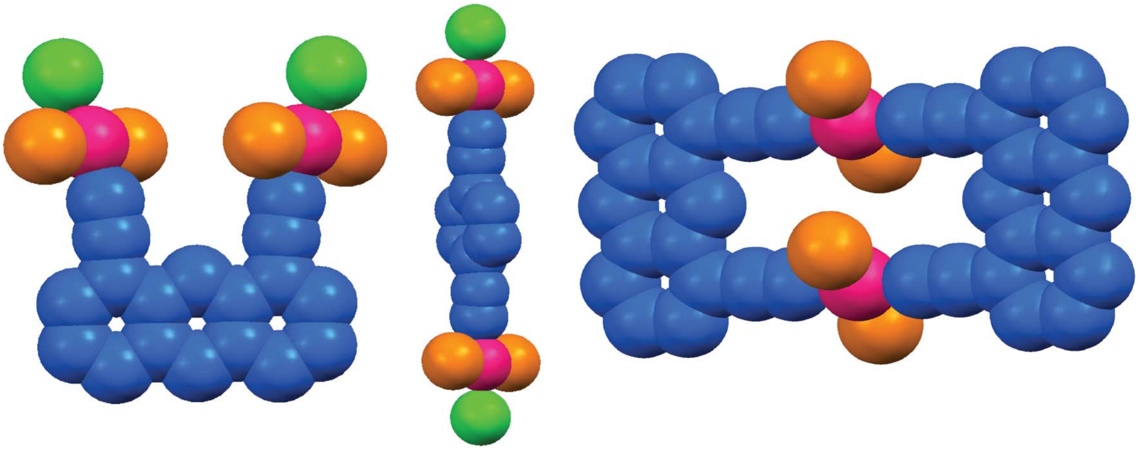


Fig. 6 Space-filled models of the solid state single crystal structures of 1,8-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]anthracene (left), 1,4-bis[*trans*-(ethynyl)Pd(PEt_3)$_2$(Cl)]benzene (middle) and **1** (right). The H atoms and Et groups are omitted for clarity. Colour codes: pink = Pd, orange = P, green = Cl, blue = C.

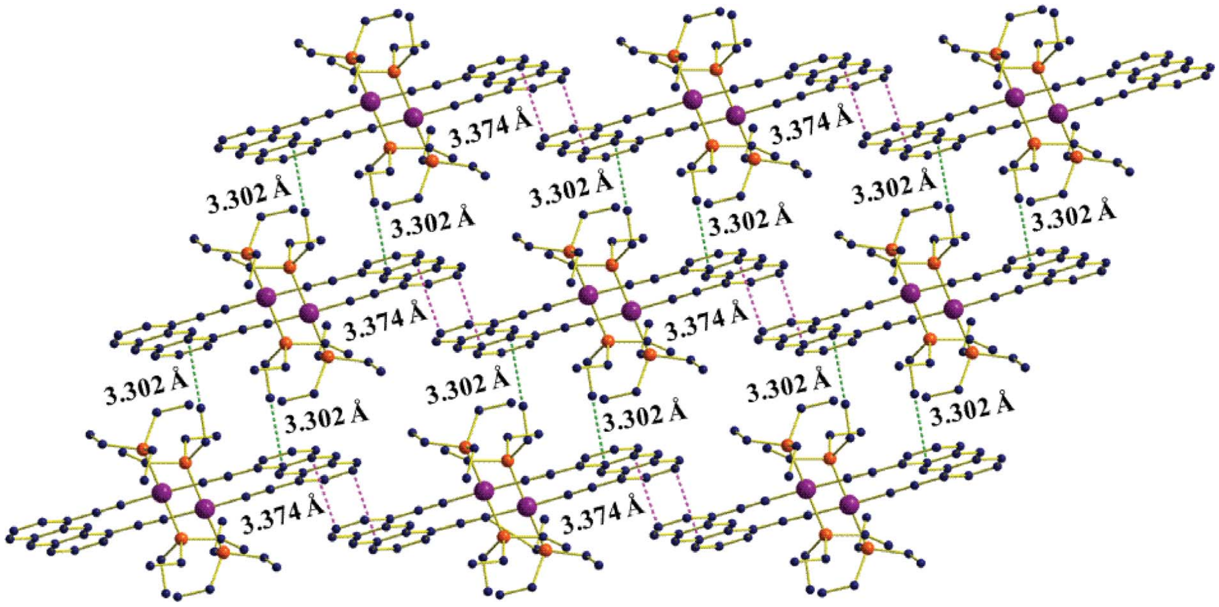


Fig. 7 Solid state packing diagram of complex **1** viewed along the crystallographic *b* axis. H-atoms are omitted for clarity.

bond lengths were measured to be 1.205(7) Å and 1.949(6) Å, respectively. A close look along the crystallographic b axis revealed that the adjacent rectangles are not packed in perfectly parallel fashion; rather they packed in head and tail fashion (Fig. 7) to form 1D chain *via* π–π type interaction between the anthracene moieties. The anthracene moieties of the adjacent molecules are 3.374 Å apart. The neighbouring chains are again packed by C–H···π interaction between the C–H of ethyl group and anthracene moiety of the neighbouring chain. Overall packing results in 1D channels as viewed along the *c*-axis (SI†).

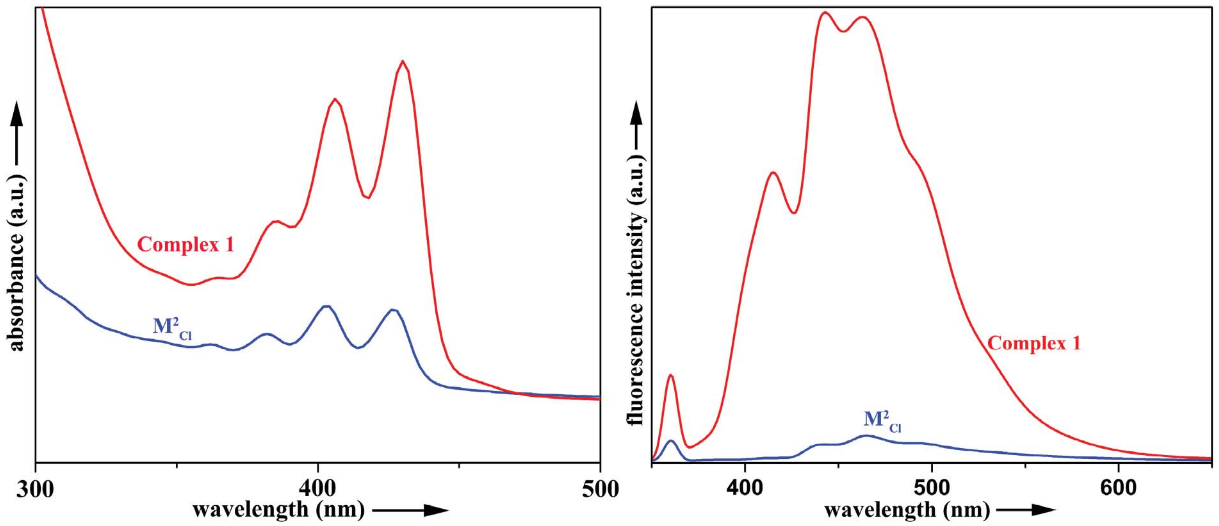


Fig. 8 Absorption (left) and emission (right) spectra of complex **1** and 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene recorded in 1.0×10^{-3} M solutions in THF.

UV-Vis absorption spectroscopic analysis

The UV-Vis absorption and emission spectroscopic studies of complex **1** and 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene were carried out in a 1.0×10^{-3} M solution in HPLC grade THF. Complex **1** showed four prominent absorption bands with absorption maxima at λ_{max} 364 nm, 384 nm, 406 nm and 432 nm (Fig. 8). A similar spectral pattern was observed in the case of 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene with absorption maxima at 360 nm, 380 nm, 404 nm and 426 nm. The spectral nature of both complexes **1** and 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene is similar to the characteristic absorption spectrum of the anthracene moiety and thereby indicating prominent intra-ligand (IL) π–π* electronic transition.[15,16] The red-shift of the absorption bands in complex **1** compared to 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene indicates lowering of HOMO–LUMO energy gap, which is probably due to intermolecular π–π interaction between the neighboring molecules. Excitation at 320 nm in both cases displayed emission spectra similar to the characteristic emission spectrum of the anthracene moiety.[17] Moreover, a phosphorescence band appears at significantly lower energy region compared to the fluorescence band in the photoluminescence spectrum.[18] Absence of such low energy band in the luminescence spectra of both complexes **1** and 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene indicated the insignificant intersystem crossing (IC) phenomenon in their excited state and thereby increasing their fluorescence behavior. Interestingly, the emission intensity of **1** was measured to be ~ 2×10^2 times larger than that of 1,8-bis[*trans*-(ethynyl) Pd(PEt$_3$)$_2$(Cl)]anthracene at emission maximum ~ 440 nm (Fig. 8). Such large difference in emission intensity can be attributed to two plausible factors. On one hand, complex **1** has two electron-rich anthracene fluorophore units and on the other hand, because of the presence of the heavy element chloride in 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene the fluorescence intensity is lower.

Recently, we have shown that the emission intensity of a fumarate-based neutral Pd$_4$-rectangle (**1′**) was almost twice that of 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene.[5] Such increase was presumably due to the presence of more anthracene-fluorophore units in complex **1′** compared to 1,8-bis[*trans*-(ethynyl)Pd(PEt$_3$)$_2$(Cl)]anthracene. The considerably lower emission intensity of **1′** compared to **1** is probably because of the interruption of π-electron delocalization throughout the molecular skeleton due to the lack of proper p_π orbital on the coordinated fumarate-oxygen. The emission intensity of complex **2** is almost two times larger than that of the organic "clip" **L**^{2} (Fig. 9). This is presumably, again, because of the larger number of fluorophores. The IR spectrum of the "clip" 1,8-bis[*trans*-(ethynyl) Pd(PEt$_3$)$_2$(Cl)]anthracene (Fig. 9) showed a sharp peak[5] corresponding to the symmetric stretching frequency of the ethynyl moiety ($\nu_{C\equiv C}$) at 2101 cm^{-1}. The considerable red-shift ($\Delta\nu_{C\equiv C}$ = 14 cm^{-1}) of $\nu_{C\equiv C}$ in the IR spectrum of complex **1** (Fig. 9) indicated an increase in π-electron delocalization. Moreover, almost no change in UV-Vis spectra as well as less red-shifts of the ethynyl stretching frequencies ($\nu_{C\equiv C}$) in the IR spectra of both the Pd$_4$ rectangles **2** (Fig. 9) and **3** (SI†) indicated weak π-electron delocalization throughout the molecular skeleton.

Fluorescence quenching based detection of nitroaromatics is very important because of huge applications in security.[19] π-electron rich organic polymers are proven to be efficient redox sensors for oxidizing explosives.[20] Polyethynyl compounds with porous structures have been investigated as potential fluorescent sensors for nitroaromatics, which are the chemical signatures of many explosives. Nitroaromatics are electron deficient in nature and substitution of electron withdrawing nitro groups on the aromatic ring lowers the energy of the empty π* orbitals, thereby making them good electron acceptors. Keeping these factors in mind the rectangles **1–2** were designed for two reasons: a) Pd-ethynyl functionality was introduced to make the assemblies fluorescent and to make them π electron rich; b) PEt$_3$ groups help to avoid intermolecular stacking and thus prevent the chance of self-quenching of fluorescence. Both complexes **1** and **2** showed potential nitroaromatic sensing by fluorescence quenching phenomenon. These two complexes can selectively sense electron deficient nitroaromatics in micromolar concentration level.

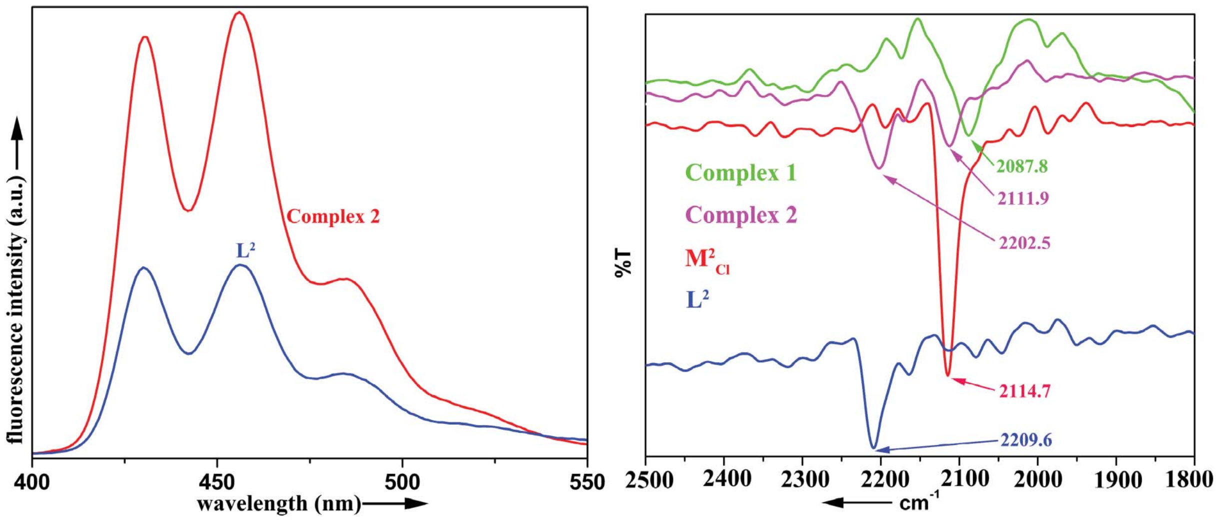


Fig. 9 Emission spectra (left) recorded with 10^{-3} M solution in $CHCl_3$ at room temperature and the solid phase IR spectra (right).

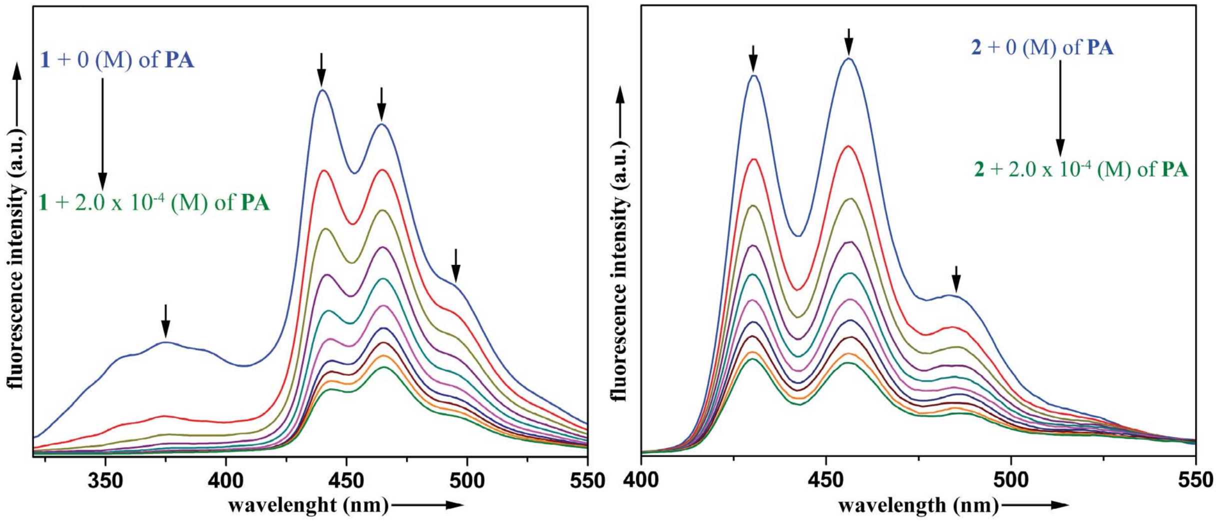


Fig. 10 Quenching of fluorescent intensity of 1×10^{-6} M solutions of **1** (left) and **2** (right) upon gradual addition of 1×10^{-3} M picric acid solution in $CHCl_3$.

Titration of a 1.0×10^{-6} M solution of complex **1** (in THF) or **2** (in $CHCl_3$) with a 1×10^{-3} M $CHCl_3$ solution of picric acid (PA) showed a gradual decrease in the initial fluorescence intensity (Fig. 10). In the case of complex **1**, the spectral band near emission maxima 375 nm completely quenched upon addition of 150 μL of 1.0×10^{-3} M PA into 2000 μL of 1.0×10^{-6} M solution of **1**. While the bands near emission maxima 440 nm, 465 nm and 495 nm gradually decayed on gradual addition of picric acid quencher (Fig. 10). In the case of complex **2** the bands near emission maxima at 430 nm, 457 nm and 485 nm were gradually died down upon gradual addition of a 1.0×10^{-3} M $CHCl_3$ solution of the PA into 1×10^{-6} M solution of **2** in $CHCl_3$. Analysis of the normalized fluorescence intensity (I_0/I) as a function of quencher concentration [Q] was carried out by the Stern–Volmer equation $I_0/I = 1 + K_{SV}[Q]$. The Stern–Volmer constant (K_{SV}) in this case was calculated to be 3.1×10^4 (±0.0016) M^{-1} (for the titration of **1** with PA) and 1.9×10^4 (±0.0011) M^{-1} (for the titration of **2** with PA) (SI†). The selectivity of **1** and **2** (Fig. 11) towards nitroaromatics was carried out with a series of electron deficient compounds. It was found that only electron deficient nitroaromatics were able to quench the fluorescence of both complexes **1** and **2**.

Surprisingly, though benzoic acid (BA) or anthraquinone (AQ) are electron deficient, their efficiency towards quenching of fluorescence intensity of **1** or **2** was not much noticeable due to their low reduction potential value.[21]

Conclusion

We have synthesized three Pd^{II} molecular rectangles **1–3** among which rectangle **1** is fully characterized by spectroscopic and single crystal X-ray diffraction studies while the other two are characterized by spectroscopic studies. Though synthesis of molecular rectangles using "clip" type acceptor in combination with linear donor is well established, the present paper reports a complementary approach of designing rectangle using "clip" type donor with linear acceptor. Complex **1** represents the

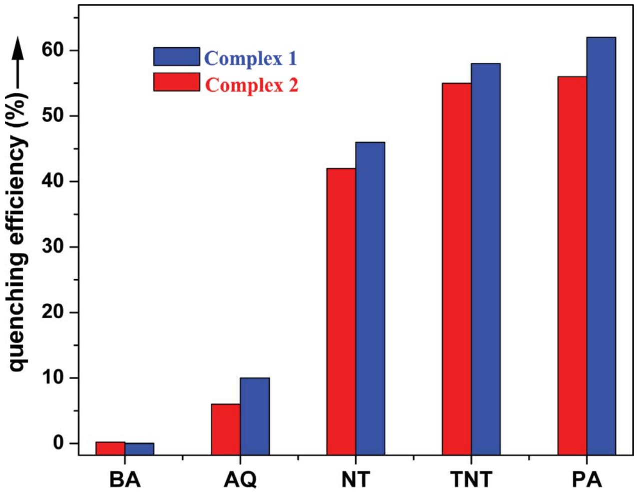


Fig. 11 Quenching efficiency of the analytes. Color codes: blue (**1**), red (**2**). Abbreviations: BA = benzoic acid, AQ = anthraquinone, NT = 4-nitrotoluene, TNT = 1,3,5-trinitrotoluene, PA = picric acid.

first example of a neutral rectangle obtained using Pd–C bond coordination as a driving force. In addition to this neutral Pd_2 molecular rectangle, two more cationic rectangles have been prepared using an organometallic linear donor 1,4-bis[*trans*-(ethynyl)Pd$(PEt_3)_2(NO_3)$]benzene. Furthermore, we have demonstrated that the self-assembly of building blocks possessing ethynyl functionalities can endow suitable architectures with interesting properties, such as increased electron density and fluorescence. Complexes **1–2** showed fluorescence behavior and the fluorescence intensity in solution phase was quenched efficiently and selectively in the presence of electron deficient nitroaromatics, which are the common chemical constituents of many commercially available explosives. Because of the neutral nature of the rectangle **1**, there exists anion free open space to accommodate electron deficient nitroaromatics. Hence complex **1** showed to be a better receptor for nitroaromatics compared to complex **2**. Moreover, due to the anionic nature of the donor ethynyl clip, rectangle **1** is neutral and more electron rich compared to the cationic analogue **2**, thereby showing better sensitivity towards electron deficient nitroaromatics.

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