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Coordination self-assembly of tetranuclear Pt(II) macrocycles with organometallic backbone for sensing of acyclic dicarboxylic acids

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Abstract

Coordination self-assembly of a series of tetranuclear Pt(II) macrocycles containing organometallic backbone incorporating ethynyl functionality is presented. The 1 : 1 combination of a linear acceptor 1,4-bis[*trans*-$Pt(PEt_3)_2(NO_3)$(ethynyl)]benzene (**1**) with three different dipyridyl donor 'clips' ($\mathbf{L_a}$–$\mathbf{L_c}$) afforded three [2 + 2] self-assembled Pt^{II}_4 macrocycles (**2a**–**2c**) in quantitative yields, respectively [$\mathbf{L_a}$ = 1,3-bis(3-pyridyl)isothalamide; $\mathbf{L_b}$ = 1,3-bis(3-pyridyl)ethynylbenzene; $\mathbf{L_c}$ = 1,8-bis(4-pyridyl)ethynylanthracene]. These macrocycles were characterized by multinuclear NMR (^{1}H and ^{31}P); ESI-MS spectroscopy and the molecular structures of **2a** and **2b** were established by single crystal X-ray diffraction analysis. These macrocycles (**2a**–**2c**) are fluorescent in nature. The amide functionalized macrocycle **2a** is used as a receptor to check the binding affinity of aliphatic acyclic dicarboxylic acids. Such binding affinity is examined using fluorescence and UV-Vis spectroscopic methods. Solution state fluorescence study showed that macrocycle **2a** selectively binds (K_{SV} = 1.4 × 10^4 M^{-1}) maleic

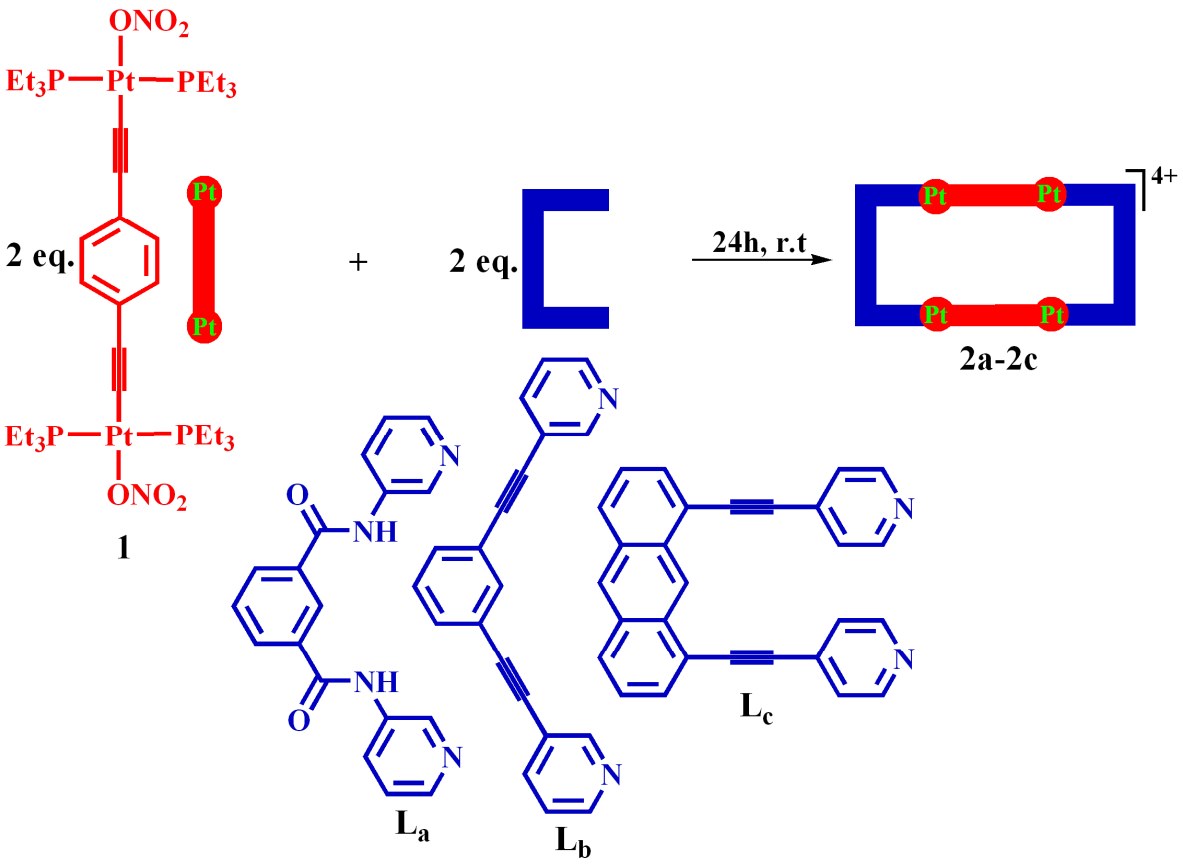
acid by subsequent enhancement in emission intensity. Other aliphatic dicarboxylic acids such as fumaric, succinic, adipic, mesaconic and itaconic acids caused no change in the emission spectra; thereby demonstrates its potential use as macrocyclic receptor in distinction of maleic acid from other aliphatic dicarboxylic acids.

Introduction

Self-assembly *via* coordination is a powerful tool to synthesize delicate supramolecular architectures of defined shapes and sizes.[1] Metal-ligand directional bonds between two or more predesigned molecular building units often furnish significant synthetic advantages such as fewer steps with very high yield of the target product and easy way to control the size and shape of the resulting supramolecular complexes.[2] A large number of finite two-dimensional (2D) and three-dimensional (3D) supramolecular polygons and polyhedra have been fabricated by employing this efficient coordination-driven self-assembly.[3] Among various known two-dimensional metallamacrocycles like square, rhomboid, triangle, rectangle, and polygons of higher symmetry, first two types dominate the literature. Despite their structural simplicity, rectangles are known to be less explored molecular polygons due to limitation of their synthesis from the readily available *cis*-blocked 90° acceptor. To overcome this difficulty, Stang *et al*. and others have established a novel way of designing rectangles by [2 + 2] self-assembly of a linear 180° ditopic building unit with a 'clip' type complementary building unit having bite angle of 0°.[4]

Furthermore, substantial efforts are being focused on incorporating suitable functional groups into the resulting supramolecular complexes in view to fabricate functional artificial molecular devices for potential applications in the field of optoelectronics. Among several functionality, incorporation of unsaturated ethynyl functional group enriches the resulting assemblies to be π-

electron rich and thus makes them luminescent for sensing applications.[5,6] Sensors for distinction of isomers are of special interest since in many cases isomers have similar chemical and physical properties.



Scheme 1. [2 + 2] Self-assembly of metallamacrocycles (**2a–2c**) using a Pt^{II}_2-organometallic 180° acceptor **1** in combination with ditopic donors ($\mathbf{L_a}$–$\mathbf{L_c}$).

Herein, we report the synthesis and characterization of a Pt^{II}_2 – organometallic 180° acceptor 1,4-bis[*trans*-$Pt(PEt_3)_2(NO_3)$(ethynyl)]benzene (**1**) and its [2 + 2] self-assembly with three different ditopic donor "clips" ($\mathbf{L_a}$–$\mathbf{L_c}$) to afford three rectangular metallamacrocycles **2a–2c** (Schemes 1). The [2 + 2] self-assembled rectangles (**2a–2c**) were characterized using various

spectroscopic techniques including structure determination of **2a-b** by single crystal X-ray diffraction. Furthermore, the ability of macrocycle **2a** as a receptor for dicarboxylic acids in solution has been demonstrated using fluorescence and UV-Vis titrations. Maleic acid and its *trans*-analogue (fumaric acid) are geometrical isomers with different orientation of the –COOH groups around C=C bond. Due to having amide functionality in proper fashion, macrocycle **2a** selectively recognized maleic acid by fluorescence enhancement over its isomeric fumaric acid and other dicarboxylic acids like succinic, adipic, mesaconic and itaconic acids. This result demonstrates a novel way of distinction of maleic acid from several other aliphatic acyclic dicarboxylic acids.

Experimental section

Materials and methods. The binuclear Pt^{II}_2 – acceptor **1** was synthesized under dry nitrogen atmosphere using standard Schlenk technique. All the required solvents were dried and distilled according to the standard literature procedures. 1,4-diiodobenzene, 1,3-dibromobenzene, isonicotinylchloride hydrochloride and 3-aminopyridine were purchased from Aldrich (USA) and were used as received without further purification. 1,3-bis(3-pyridyl)isophthalamide (**L_a**), 1,3-bis(3-pyridyl)ethynylbenzene (**L_b**) and 1,8-bis(4-pyridyl)ethynylanthracene (**L_c**) were synthesized following the reported procedures.[7] NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the NMR solvents: CD_3OD (3.33), CD_3NO_2 (4.33) and $CDCl_3$ (7.26). ^{31}P NMR were recorded at 121 MHz, and the chemical shifts (δ) are reported in ppm relative to external 85% H_3PO_4 at 0.00 ppm. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed in Bruker Daltonics (Esquire 300 Plus ESI model) using standard

spectroscopic grade solvents CH_3CN or CH_3OH. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Electronic absorption spectral measurement was done using Perkin Elmer LAMBDA 750 UV/visible spectrophotometer and fluorescence emission studies were carried out on HORIBA JOBIN YVON Fluoromax-4 spectrometer.

Synthesis of 1,4-bis[*trans*-Pt(PEt$_3$)$_2$I(ethynyl)]benzene (1a). 1,4-Diethynylbenzene (200.6 mg, 1.59 mmol) and *trans*-$(PEt_3)_2PtI_2$ (3.27 g, 4.77 mmol) were added to a 100 mL round bottom Schlenk flask. 40 mL of freshly distilled toluene and 20 mL of dry diethylamine were added to the above mixture through a glass syringe under nitrogen atmosphere. The mixture was stirred for 15 min at room temperature before 40 mg of CuI was added in one portion. After 36 h of stirring, the solvent was removed under vacuum and the resulting residue was purified by column chromatography (silica gel) using hexane/dichloromethane (8:2) as eluent. Yield: 850 mg, 43 %. Anal. Calcd for $C_{34}H_{64}I_2P_4Pt_2$: C, 32.91; H, 5.20. Found: C, 33.26; H, 5.49. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.12 (s, 4H), 2.19 (m, 24H, *CH*$_2$-PEt$_3$), 1.15 (m, 36H, *CH*$_3$-PEt$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 8.53 (s, $^1J_{Pt}$-P = 1737.0 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 130.8 (4C, phenyl), 125.9 (2C, phenyl), 101.0 (2C, ethynyl), 30.2 (2C, ethynyl), 17.2 (12C, *CH*$_2$-PEt$_3$), 8.7 (12C, *CH*$_3$-PEt$_3$). IR (neat): υ = 2114 cm^{-1} for ethynyl group.

Synthesis of 1,4-bis[*trans*-Pt(PEt$_3$)$_2$(NO$_3$)(ethynyl)]benzene (1). A 20 mL vial was charged with 148.9 mg (0.12 mmol) of 1,4-bis[*trans*-Pt(PEt$_3$)$_2$I(ethynyl)]benzene and 10 mL of chloroform. To the resulting solution was added 40.8 mg (0.24 mmol) of $AgNO_3$ in 5 mL methanol at once. After 3 h of stirring at room temperature in dark, AgI was filtered through celite using a glass fiber. To the concentrated filtrate (5 mL) cold diethyl ether was added to precipitate out **1** as off-white powder. Yield: 100 mg (75 %). Anal. Calcd for $C_{34}H_{64}N_2O_6P_4Pt_2$: C, 36.76; H, 5.81; N, 2.52; Found: C, 36.84; H, 5.87; N, 2.58. ^{1}H NMR ($CDCl_3$, 400 MHz): δ

7.07 (s, 4H), 1.92 (m, 24H, CH_2-PEt_3), 1.19 (m, 36H, CH_3-PEt_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 20.02 (s, $^1J_{Pt}$-P = 1856.86 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$/CD_3OD, 100 MHz): δ 131.2 (4C, phenyl), 125.8 (2C, phenyl), 104.1 (2C, ethynyl), 30.1 (2C, ethynyl), 14.8 (12C, CH_2-PEt_3), 8.8 (12C, CH_3-PEt_3). IR (neat): υ = 2124.7 cm^{-1} for ethynyl group. ESI-MS (m/z): 1048.6 [**1** − NO_3]$^+$.

Synthesis of 2a. To a stirred suspension of ditopic donor 1,3-bis(3-pyridyl)isophthalamide $\mathbf{L_a}$ (2.9 mg, 0.009 mmol) in 0.5 mL of methanol, was added a clear solution of Pt^{II}_2 acceptor **1** (10.0 mg, 0.009 mmol) in chloroform (0.5 mL) drop-by-drop. After stirring the reaction mixture at room temperature for 24 h in a closed 4 mL glass vial, the solution was concentrated to 0.5 mL. The product (**2a**) was isolated as off-white powder upon addition of diethyl ether (~5 mL) into the concentrated reaction mixture. Isolated yield = 86 %. Anal. Calcd for $C_{104}H_{156}N_{12}O_{16}P_8Pt_4$: C, 43.70; H, 5.50; N, 5.88. Found: C, 43.87; H, 5.79; N, 5.99. ^1H NMR ($CDCl_3$/CD_3OD, 400 MHz): δ 9.43 (s, 2H, phenyl-H_5), 8.36 (s, 4H, pyridyl-H1), 8.17 (s, 4H, phenyl-H_6), 8.13 (d, 4H, J = 7.6 Hz, pyridyl-H_2), 8.07 (m, 4H, pyridyl-H_3), 7.53 (m, 2H, phenyl-H_7), 7.05 (s, 8H, phenyl-H_a), 6.9 (d, 4H, J = 7.2 Hz), 1.70 (br, 48H, CH_2-PEt_3), 1.07 (br, 72H, CH_3-PEt_3). ^{31}P NMR ($CDCl_3$/CD_3OD, 121 MHz): δ 15.87 (s, $^1J_{Pt}$-P = 1742.64 Hz). IR (neat): υ(cm^{-1}) = 2124.7 (C≡C) and 1675.7 (C≡O). ESI-MS (m/z): 1366.41 [**2a** – $2NO_3^-$]$^{2+}$, 652.20 [**2a** – $4NO_3^-$]$^{4+}$.

Synthesis of 2b. Complex **2b** was synthesized in an analogous way as applied for **2a** using $\mathbf{L_b}$ instead of $\mathbf{L_a}$ and was isolated as off-white powder in 80% yield. Anal. Calcd for $C_{108}H_{152}N_8O_{12}P_8Pt_4$: C, 46.62; H, 5.51; N, 4.03. Found: C, 46.70; H, 5.48; N, 4.10. ^1H NMR (CD_3NO_2, 400 MHz): δ 8.96 (s, 4H, pyridyl-H_1), 8.80 (br, 4H, pyridyl-H_2), 8.24 (br, 4H, pyridyl-H_4), 7.85 (s, 2H, phenyl-H_5), 7.77 (br, 4H, phenyl-H_6), 7.72 (d, 4H, pyridyl-H_3, J = 7.6 Hz), 7.59 (m, 2H, phenyl-H_7), 7.25-7.19 (d, 8H, phenyl-H_a), 1.94 (m, 48H, CH_2-PEt_3), 1.23 (m, 72H, CH_3-

PEt_3). ^{31}P NMR (CD_3NO_2, 121 MHz): δ 15.96 (s, $^{1}J_{Pt}$ -P = 1719.89 Hz). IR (neat): υ(cm^{-1}) = 2123.3 for C≡C. ESI-MS (m/z): 864.87 [**2b** – $3NO_3^-$]$^{3+}$.

Synthesis of 2c. To a stirred suspension of ditopic donor 1,8-bis(4-pyridylethynyl)anthracene $\mathbf{L_c}$ (3.4 mg, 0.009 mmol) in acetone (0.5 mL) was added a clear solution of **1** (10.0 mg, 0.009 mmol) in chloroform (0.5 mL) drop-by-drop with continues stirring. Initially, a clear solution was formed, which upon further stirring at room temperature for 24 h yielded product as bright yellow precipitate. The solid product was isolated and washed several times with cold acetone and finally washed with diethyl ether. Isolated yield = 78 %. Anal. Calcd for $C_{124}H_{160}N_8O_{12}P_8Pt_4$: C, 49.93; H, 5.41; N, 3.76. Found: C, 50.21; H, 5.72; N, 3.91. ^1H NMR ($CDCl_3/CD_3OD$, 400 MHz): δ 9.14 (s, 2H, anthracene-H_5), 8.87 (d, 8H, pyridyl-H_α), 8.56 (s, 2H, anthracene-H_4), 8.15 (d, 4H, anthracene-H_3, J = 8.4 Hz), 7.99 (d, 4H, anthracene-H_1, J = 6.8 Hz), 7.89 (d, 8H, pyridyl-H_β, J = 6.0 Hz), 7.53 (m, 4H, anthracene-H_2), 7.11-7.04 (m, 8H, phenyl-H_a), 1.80 (m, 48H, CH_2-PEt_3), 1.14 (m, 72H, CH_3-PEt_3).^{31}P NMR (CD_3NO_2, 121 MHz): δ 15.83 (s, $^{1}J_{Pt}$ -P = 1728.60 Hz). IR (neat): υ(cm^{-1}) = 2123.3 for C≡C. ESI-MS (m/z): 1428.20 [**2c** – $2NO_3^-$]$^{2+}$, 931.87 [**2c** – $3NO_3^-$]$^{3+}$, 683.13 [**2c** – $4NO_3^-$]$^{4+}$.

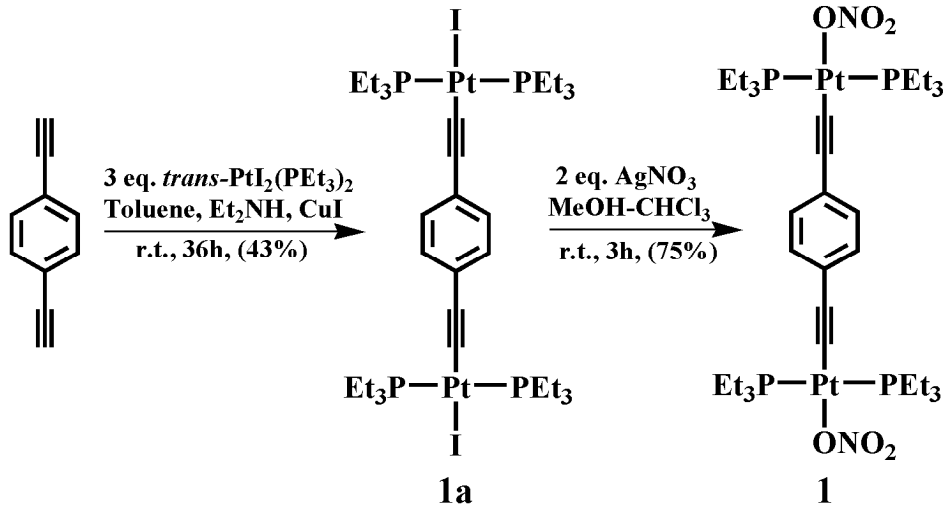
X-ray data collection and structure refinements. The diffraction data of **1a** was collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software. Intensity data were collected using graphite-monochromatic Mo-Kα radiation (0.7107 Å) at 150 K on a crystal as obtained after several attempts. The diffraction data were obtained using SMART/SAINT software[8] and the structures were solved by direct methods using the SHELX-97[9] incorporated in WinGX.[10] Empirical absorption corrections were applied with SADABS.[11a] All non-hydrogen atoms of **1a** were refined with anisotropic displacement coefficients. The diffraction data of macrocycles **2a** and **2b** were collected with with synchrotron radiation (**2a**; λ = 0.90000 Å, **2b**; λ

= 0.75000 Å) on a 2D Supramolecular Crystallography Beamline in ADSC Quantum-210 detector with a silicon (111) double-crystal monochromator at the Pohang Accelerator Laboratory, Korea. The ADSC Quantum-210 ADX program (Ver. 1.96)[12] was used for data collection and HKL2000 (Ver. 0.98.699)[13] was used for cell refinement, reduction, and absorption correction. The diffraction data were solved by direct methods using the SHELXTL-PLUS (ver 2008).[13] All non-hydrogen atoms were refined with anisotropic displacement coefficients except coordinated triethylphosphine at platinum metals and amide groups at ligand in complex **2a**. The data of complex **2a** is insufficient to refine the data set fully anisotropically and therefore the structure was determined as partial structure refinement. All non-hydrogen atoms were refined with anisotropic displacement coefficients in complex **2b**. Hydrogen atoms in both complexes (**2a** and **2b**) were assigned isotropic displacement coefficients, U(H) = 1.2U(C) or 1.5U (C-methyl), and their coordinates were allowed to ride on their respective carbons. The least-squares refinement of the structural model was performed under geometry constraint AFIX for phenyl groups of the complex **2a**, and under geometry restraints and displacement parameter restraints such as, DFIX, DANG, ISOR, SIMU and DELU for several atoms around PEt_3 groups residue in both the complexes. The final refinement of both complexes were performed with the modification of the structure factors for the electron densities of the solvents (complex **2a**; 470.9 Å^3, 15.4 % of the crystal volume, complex **2b**; 1336.6 Å^3, 20.9 % of the crystal volume, respectively) using the SQUEEZE option of PLATON. The refinement converged for complex **2a** at a final R1 = 0.1226 and wR2 = 0.6145 for 3671 reflections with I > 2σ (I); R1 = 0.1806 and wR2 = 0.3559 for all 5972 reflections and the largest difference peak and hole were 1.542 and -1.202 e•Å^3, respectively. The refinement converged for complex **2b** at a final R1 = 0.0578 and wR2 = 0.1748 for 10239 reflections with I > 2σ (I); R1 = 0.0729 and wR2 = 0.1834 for all 36378 reflections and the largest difference peak and hole were 1.889 and -2.086 e•Å^3, respectively.

Dicarboxylic acids binding study. Stock solutions (1 mM) of dicarboxylic acids such as maleic, fumaric, succinic, malonic, mesaconic, adipic and itaconic acid (1×10^{-3} M) in CH_3CN/CH_3OH (10:0.4, v/v) and that of macrocycle **2a** (1.0×10^{-4} M) in CH_3CN/CH_3OH (10:0.4, v/v) were prepared. 2 mL stock solution of **2a** was placed in a quartz cell of 1 cm width and dicarboxylic acid solution was added in an incremental fashion. Their corresponding fluorescence spectra were recorded at 298 K. Each titration was repeated at least two times to get consistent value. For all measurements λ_{exc} = 343 nm and the emission wavelength was monitored from 360–600 nm. Both excitation and emission slit widths were 5 nm. There was no considerable change in shape of the emission spectra except gradual enhancement of the fluorescence emission intensity upon addition of acid solution. Analysis of the normalized fluorescence intensity (I_0/I) as a function of increasing acid concentration ([G]) was well described by the Stern-Volmer equation $I_0/I = 1 + K_{SV}[G]$. The K_{SV} was calculated from the slope of the Stern-Volmer plot.

Results and discussion

Synthesis and characterization of the linear acceptor 1. Since the first report of Sonagashira *et al.* on coupling of terminal alkynes with aryl halides to make C−C bond using Pd(II) catalyst, large numbers of multinuclear organometallic complexes comprising ethynyl functionality have been synthesized.[14] Here, we utilized the coupling reaction of *trans*-$PtI_2(PEt_3)_2$ with the terminal alkynes as the key step to synthesize 180° acceptor **1**. As shown in Scheme 2, the 1,4-diethynylbenzene having two terminal alkynes was first reacted with 3.0 equivalents of *trans*-$PtI_2(PEt_3)_2$ to give 1,4-bis[*trans*-$Pt(PEt_3)_2(I)$(ethynyl)]benzene (**1a**) and its subsequent deiodination using 2.0 equivalents of silver nitrate ($AgNO_3$) in chloroform/methanol mixture under dark condition resulted in the isolation of acceptor **1** in high yield (75%).



Scheme 2: Schematic presentation of the synthesis of 1,4-bis[*trans*-$Pt(PEt_3)_2(NO_3)$(ethynyl)]benzene (**1**) from 1,4-diethynylbenzene and *trans*-$PtI_2(PEt_3)_2$.

The binuclear linear acceptor **1** was fully characterized by various spectroscopic techniques like IR, multinuclear NMR {^{1}H, ^{31}P and ^{13}C} and ESI-MS analysis. IR spectrum showed an intense peak at υ = 2124.74 cm^{-1} due to the ethynyl group (Fig. S1, Supporting Information). The diplatinum acceptor **1** showed a singlet at δ = 20.02 ppm with concomitant ^{195}Pt satellites ($^1J_{Pt}$-P = 1856.86 Hz) in the ^{31}P NMR spectrum (Fig. 1). The ^{1}H NMR spectrum exhibited a sharp singlet at δ = 7.07 ppm corresponding to the phenyl protons in the aromatic region (Fig. 1). The ^{13}C NMR spectrum of the acceptor **1** exhibited all the characteristics peaks correspond to phenyl, ethynyl and triethylphosphene units in the expected region in the range of δ = 131.2−8.27 ppm (Fig. S5, Supporting Information). Electrospray ionization (ESI-MS) mass spectrometric analysis of the linear acceptor **1** showed (Fig. S6, Supporting Information) peak at m/z = 1048.6 corresponds to the fragment [**1** – NO_3^-]$^+$. The experimental isotopic distribution pattern of this fragment was consistent with its charge state (Fig. S6, Supporting Information).

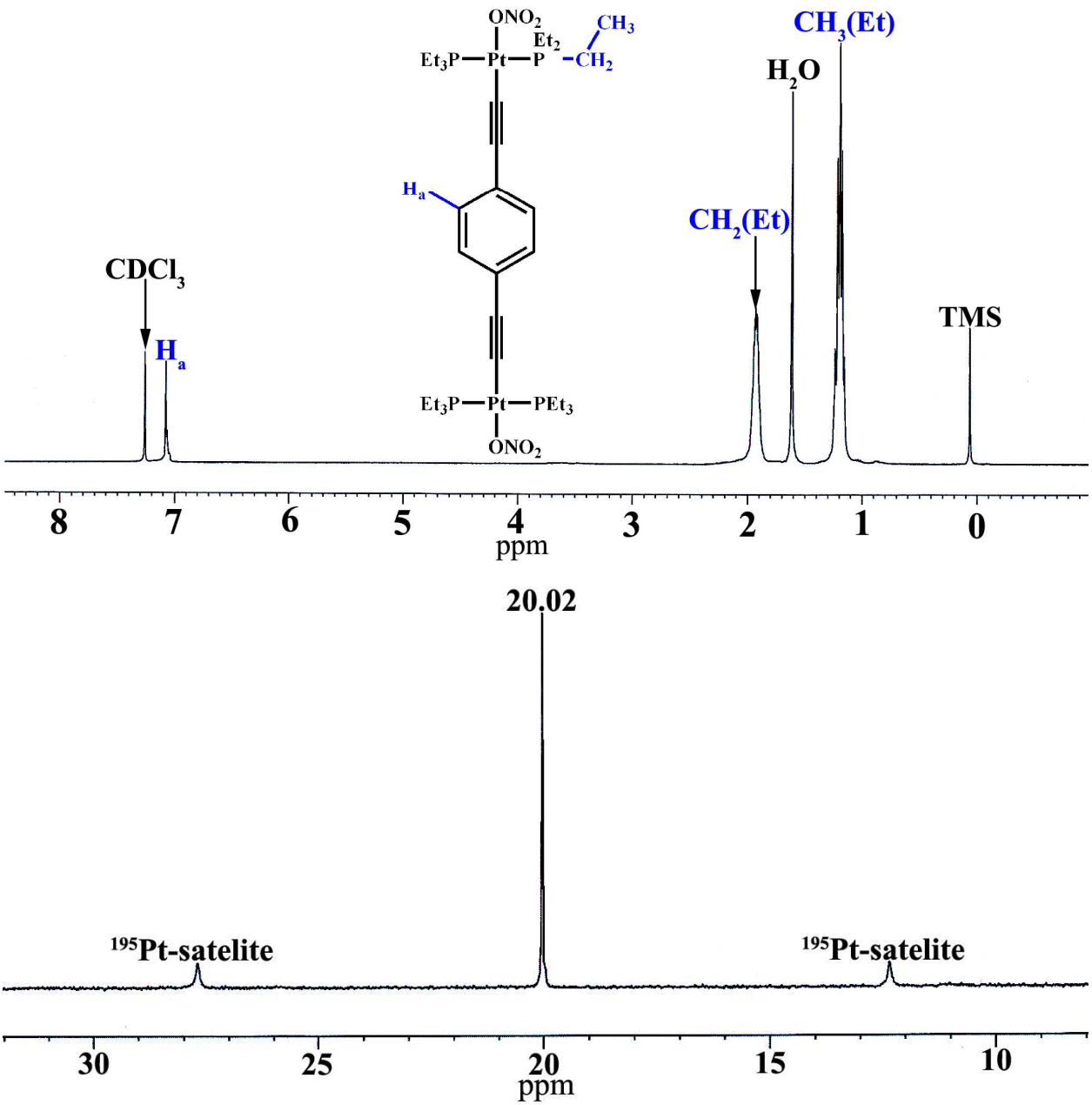


Fig. 1. ^{1}H (above) and ^{31}P NMR (below) spectra of the acceptor **1** recorded in $CDCl_3$ with the peak assignments.

Finally the formation of linear acceptor **1** was unambiguously established by single crystal X-ray diffraction analysis of the iodide analogue 1,4-bis[*trans*-Pt(PEt_3)$_2$I(ethynyl)]benzene (**1a**). Suitable single crystals of **1a** were obtained by slow evaporation of a solution of **1a** in dichloromethane/n-hexane (1/1) mixture at ambient temperature. The diiodide complex **1a** was crystallized in monoclinic *P* 21/n space group with two formula units in asymmetric unit. A ball & stick representation of the structure of **1a** (Fig. 2) shows that it is indeed a 180° linear building unit with Pt-phenyl-Pt angle being perfectly 180.0°. The coordination geometry around each Pt^{II} metal center is almost square-planar with I–Pt–P angles being in the range of 89.07°–91.47° and the C–Pt–P angles being in the range of 89.15°–90.33°. The Pt–I bond distance of 2.67 Å in **1a** is very close to the reported Pt–I distances in similar complexes.[15] Crystallographic data and refinement parameters are summarized in Table S1 (Supporting Information), while the selected bond lengths and angles are assembled in Table S2, Supporting Information**.**

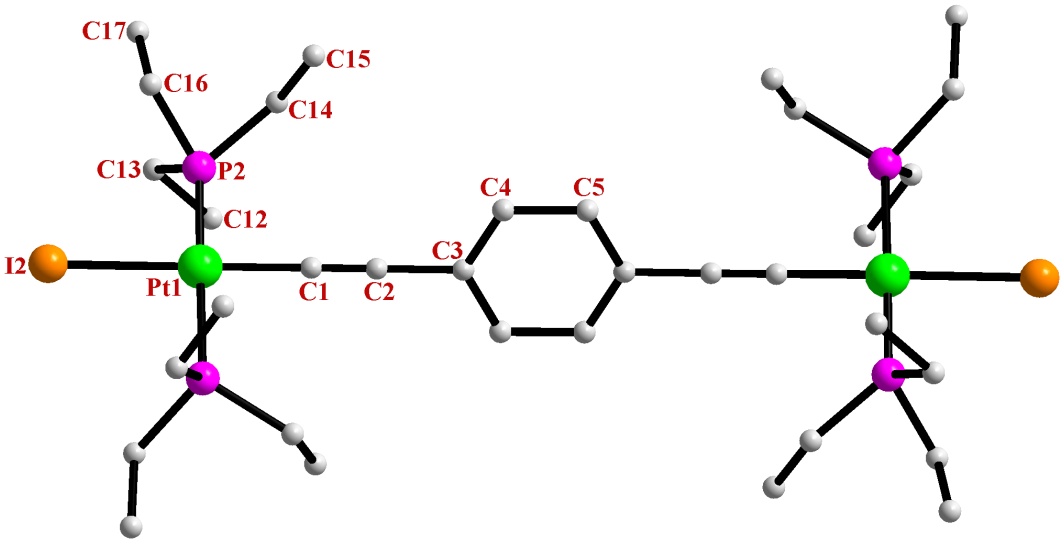


Fig. 2. Molecular structure of the 180° Pt^{II}_2- diiodide complex **1a** (color codes: green = Pt, orange = I, magenta = P, light grey = C). Hydrogen atoms are omitted for the sake of clarity.

Synthesis and characterization of the macrocycles 2a–2c. The Pt^{II}_2 – based linear acceptor **1** was treated separately with three different 'clip' type ditopic donors ($\mathbf{L_{a-c}}$) [$\mathbf{L_a}$ = 1,3-bis(4-pyridyl)isophthalamide; $\mathbf{L_b}$ = 1,3-bis(3-pyridyl)isophthalamide; $\mathbf{L_c}$ = 1,2-di(4-pyridyl)ethane] in 1 : 1 molar ratio in chloroform/methanol or acetone (1 : 1) mixture (4 mL) to obtain the [2 + 2] self-assembled metallamacrocycles (**2a–2c**) after 24 h of stirring at room temperature (Scheme 1). All the three self-assembled macrocycles were characterized by IR, multinuclear (^{1}H & ^{31}P) NMR as well as by ESI mass spectrometry. Multinuclear NMR (^{1}H, ^{31}P) spectra of the assemblies (**2a–2c**) were consistent with the formation of a single and symmetrical products (Fig. 3 and Supporting Informations). The ^{31}P NMR spectra of **2a**-**2c** exhibited sharp singlet [15.87 ppm (**2a**), 15.96 (**2b**), 15.83 ppm (**2c**)] shifted upfield with respect to the starting platinum building unit **1** (δ = 20.02 ppm) by 4.06 – 4.19 ppm**,** respectively. The upfield shifts of the phosphorous peaks indicated the ligand to Pt electron donation due to metal-ligand coordination. Moreover, decrease in coupling of the flanking ^{195}Pt satellites (ca. ΔJ = -1742.64 Hz for **2a**, ΔJ = -1719.89 Hz for **2b**, ΔJ = -1728.60 Hz for **2c**) with respect to the starting platinum building unit **1** ($^1J_{Pt}$-P = 1856.86 Hz) was consistent with the back donation from Pt(II) metal centers. In the ^{1}H NMR spectrum of the macrocycles **2a–2c**, hydrogen atoms of the pyridine rings exhibited small downfield shift due to the loss of electron density upon coordination of pyridine-N atom to platinum metal center (Fig. 3 and Supporting Informations).

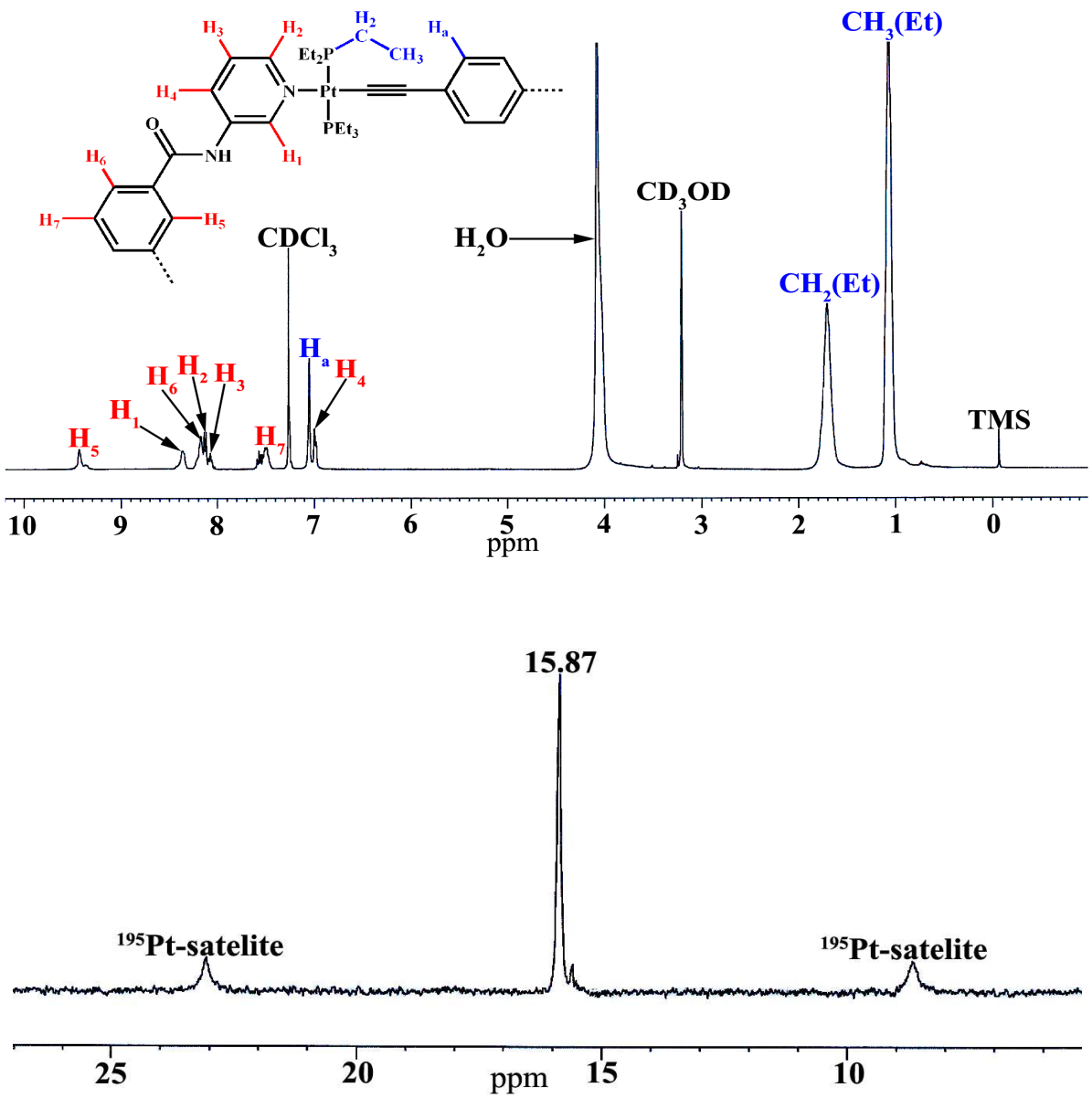


Fig. 3. ^{1}H (top) and ^{31}P NMR (bottom) spectra of the macrocycle **2a** recorded in $CDCl_3$-CD_3OD solvents mixture with the peak assignments.

The information about the composition of the resulted [2 + 2] self-assembled tetranuclear macrocycles **2a – 2c** was supported by ESI-MS spectrometric analysis, where multiple charged ions correspond to the expected macrocycles were observed (Supporting Information). ESI-MS experiments were performed on acetonitrile solution of the corresponding macrocycles. The

multiple charged molecular ions for **2a** at m/z = 1366.41 [**2a** – $2NO_3^-$]$^{2+}$, 652.20 [**2a** – $4NO_3^-$]$^{4+}$; for **2b** at m/z = 864.87 [**2b** – $3NO_3^-$]$^{3+}$; for **2c** at m/z = 1428.20 [**2c** – $2NO_3^-$]$^{2+}$, 931.87 [**2c** – $3NO_3^-$]$^{3+}$, 683.13 [**2c** – $4NO_3^-$]$^{4+}$, were observed. The experimentally observed isotopic distributions of the peaks corresponding to [**2a** – $2NO_3^-$]$^{2+}$, [**2a** – $4NO_3^-$]$^{4+}$, [**2b** – $3NO_3^-$]$^{3+}$ and [**2c** – $2NO_3^-$]$^{2+}$ fragments were consistent with their charge states (Supporting Information).

Molecular structures of the macrocycles 2a−2b. The X-ray diffraction quality single crystals of **2a** and **2b** were grown by slow vapor diffusion of diethyl ether into a dichloromethane/methanol (1:1) solution. The diffraction data (even using synchrotron radiation) of **2a** were not of good quality due to the unstable nature of the single crystals for very fast solvent evaporation. The crystallographic data for **2a** as partial structure determination is presented here. The gross connectivity of the building units and rectangular geometry of **2a** were established without any doubt from the obtained X-ray data set. Macrocycle **2a** was crystallized in triclinic *P*-1 space group with one formula unit in asymmetrical unit, whereas **2b** crystallized in monoclinic *P* 21/n space group with two formula units in asymmetrical unit. Single crystal X-ray diffraction analysis evidenced the formation of an expected [2 + 2] self-assembled Pt^{II}_4 rectangular macrocycles **2a** and **2b** with the dimensions of (0.9 nm × 3.0 nm) and (1.1 nm × 2.8 nm), respectively (Fig. 4). The lengths [3.0 nm (**2a**) and 2.8nm (**2b**)] and widths [0.9 nm (**2a**) and 1.1 nm (**2b**)] of the macrocycles are measured as the distances between the centroids of the opposite phenyl and pyridyl rings, respectively. The coordination geometry around each Pt-metal centers deviates slightly from the ideal square planar geometry due to the bulky PEt_3 groups. The P-Pt-C angles range between 85º−89º (**2b**), while the P-Pt-N angles range between 90º−94º (**2b**). Although, the single crystal X-ray diffraction analysis confirmed the formation of rectangular

geometry, we were not able to locate the $-NO_3^-$ counter anions of the macrocycles due to their high disorder, even though the data were collected at low temperature.

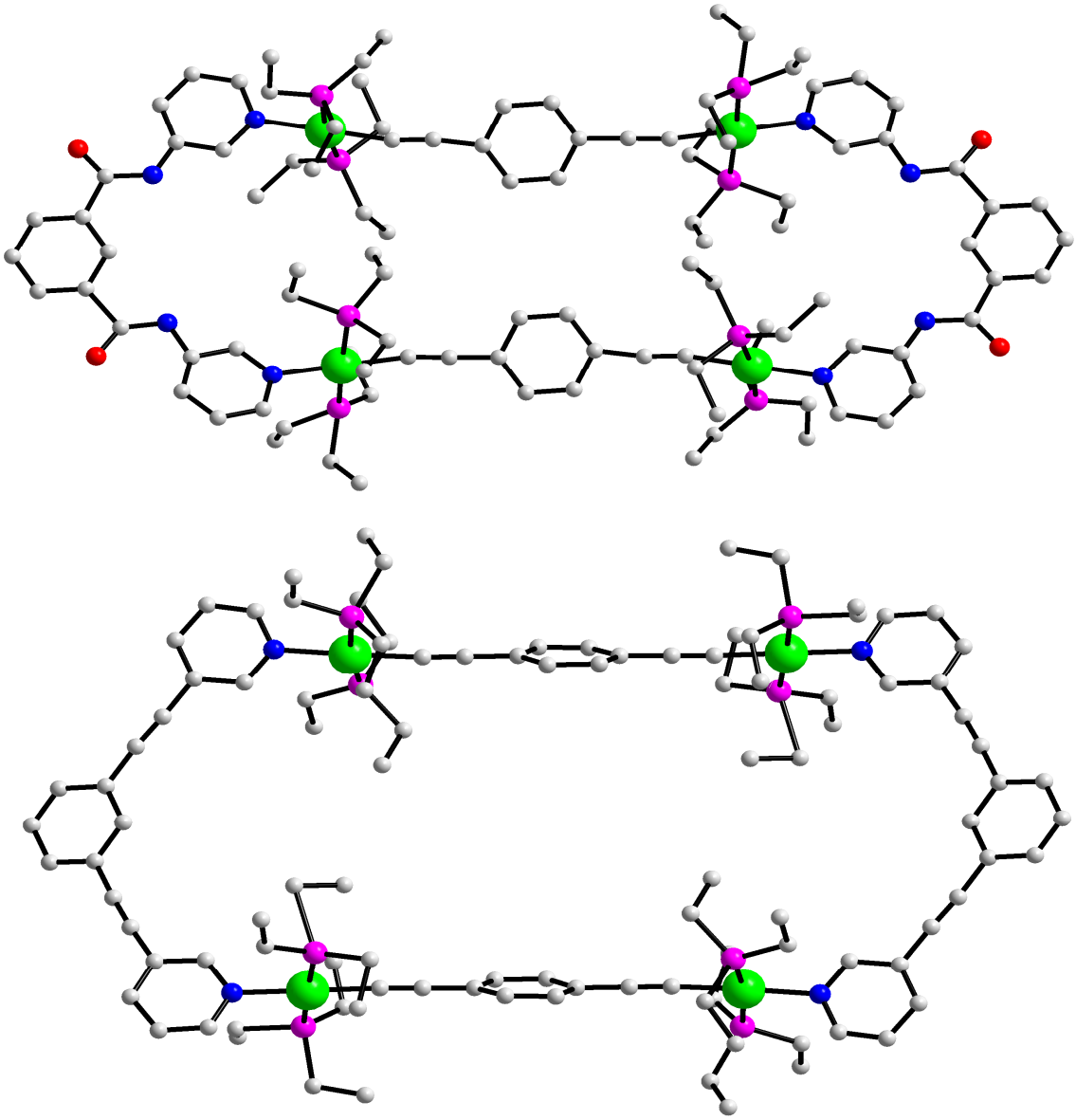


Fig. 4. X-ray crystal structures of the macrocycles **2a** (top) and **2b** (bottom): (color code) green = Pt, magenta = P, blue = N, red = O, light grey = C. The hydrogen atoms are removed for the sake of clarity.

Unfortunately, all efforts to obtain X-ray diffraction quality single crystals of **2c** were unsuccessful. However, the analysis of multinuclear NMR (^{1}H and ^{31}P) in concurrence with ESI-MS spectroscopic studies confirmed the formation of a [2 + 2] self-assembled tetranuclear macrocycle like **2a** & **2b**. In view to gain further information about the size and shape of this macrocycle, energy minimized structure of **2c** was obtained using molecular mechanics universal force field simulations (MMUFF).[16] A view of the optimized geometry of **2c** is depicted in Fig. 5.

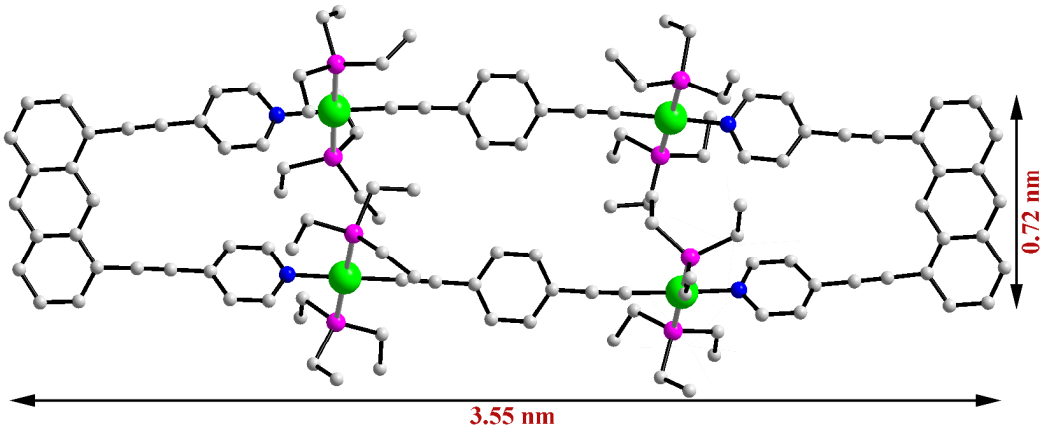


Fig. 5. A view of the energy minimized structure of **2c** (Color code; green = Pt, magenta = P, blue = N, red = O, light grey = C). The hydrogen atoms are removed for the sake of clarity.

UV–vis absorption and fluorescence studies. Photophysical data of the macrocycles (**2a – 2c**) are summarized in Table 1. The absorption spectra of the macrocycles **2a** – **2c** in CH_3CN (1.0×10^{-5} M) show peaks at λ = 261 nm, 278 nm and 344 nm (**2a**); λ = 282 nm, 301 nm and 346 nm (**2b**); λ = 261 nm, 345 nm, 392 nm and 416 nm (**2c**) (Fig. 6). The peaks in the range of 301–416 nm are tentatively assigned to metal to ligand charge transfer (MLCT), whereas the peaks in the range of 261–282 nm are ascribed to the intra/intermolecular π–π* transitions. All the three

synthesized macrocycles show high fluorescence characteristics in CH_3CN solution and their high luminescence behavior is basically attributed to the presence of unsaturated Pt-ethynyl functionality and extended π-conjugation (Fig. 6).

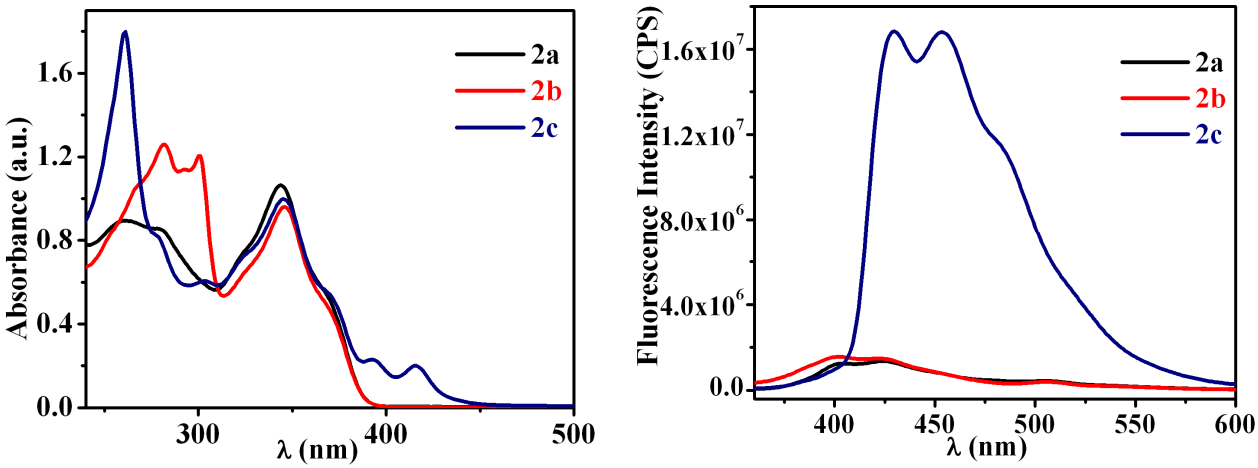


Fig. 6. UV-visible (left) and fluorescence (right) spectra of the macrocycles **2a** – **2c** recorded in CH_3CN solution (1.0×10^{-5} M) at room temperature.

Table 1. Photophysical data of the macrocycles **2a – 2c** in aerated CH_3CN solution.

Macrocycles	Absorption maxima λ_{max} (nm)	Molar extinction coefficient 10^3 ε M^{-1} cm^{-1} [λ_{max}(nm)]	Fluorescence emission maxima at 298K λ_{max}(nm)
2a	261, 278, 344	106 (344)	405, 424, 506 (sh)
2b	282, 301, 346	100 (346)	402, 422, 507 (sh)
2c	261, 345, 416	96 (345)	430, 454, 488 (sh)

Dicarboxylic acids binding study

The development of artificial receptors capable of signaling the presence analytes like anions, cations and neutral molecules has attracted great interest in recent time and efforts have been devoted in the modern supramolecular chemistry to develop various abiotic receptors.[17] In particular, the design and synthesis of suitable receptors for carboxylic acids (-COOH) and carboxylate anions ($-COO^-$) have been studied extensively due to their vital roles in various metabolic, biological and environmental processes.[18-19] Although several synthetic receptors are known for recognition of monocarboxylic acids, selective receptor for distinction of a di-/ multi-carboxylic acid from other members of the same homologue is appealing. In this regards, considerable interest has sparked among supramolecular chemists to find a suitable receptor for sensing multicarboxylic acids with particular attention being paid to fluorescent chemosensors due to its high sensitivity and fast response even at very low concentration of analytes.[20]

Accordingly, the newly designed molecular rectangle **2a** was used as a macrocyclic receptor to sense various aliphatic di-carboxylic acids for the following reasons: a) linking of aromatic hydrocarbons with Pt-ethynyl functionality develops luminescence behavior; b) amide-based 'clip' type donor was used to make an effective receptor site which could bind with anions through hydrogen bonding interaction; c) attachment of bulky PEt_3 groups with Pt(II) centers helps to avoid the intermolecular π-π stacking and hence prevents the possible self-quenching of intrinsic fluorescence behavior. The sensing behavior of receptor **2a** towards various dicarboxylic acids was monitored using fluorescence and UV-Vis absorption spectroscopy. The solution state fluorescence study shows that macrocycle **2a** (1.0×10^{-5} M) in CH_3CN/CH_3OH (10 : 0.4, v/v) doesn't undergo any significant change in its emission spectrum upon addition of different dicarboxylic acids such as fumaric, succinic, adipic, mesaconic and itaconic (9.0×10^{-5}

M) in CH_3CN/CH_3OH (10 : 0.4, v/v) (Fig. 7). Under identical condition, however, the addition of maleic acid (9.0×10^{-5} M) to a solution of receptor **2a** induced a fluorescence enhancement in the emission intensity (Fig. 7). The obvious reason for this increase in intensity of **2a** upon the addition of maleic acid over the other tested acids is attributed to its *cis*-configuration, which perfectly fits within the amide functionalized cleft.

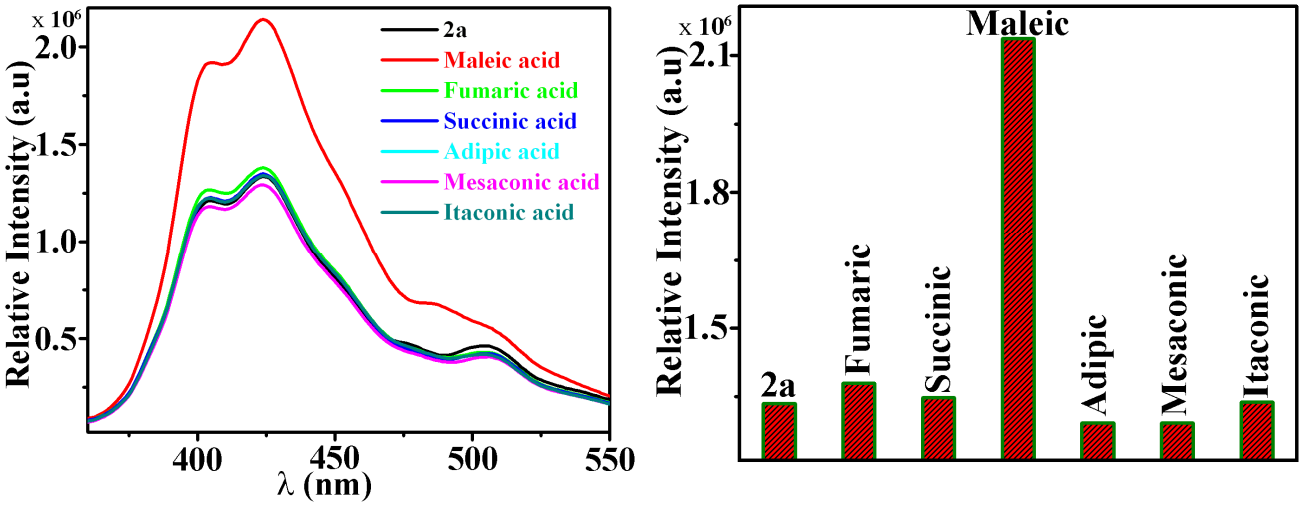


Fig. 7. Relative changes (left) in the initial fluorescence intensity of **2a** (1.0×10^{-5} M) upon addition of different dicarboxylic acids (9.0×10^{-5} M) in CH_3CN/CH_3OH (10:0.4, v/v) and their corresponding bar spectra (right).

Moreover, the gradual titration of CH_3CN/CH_3OH (10 : 0.4, v/v) solution of maleic acid with a solution of **2a** did not alter the shape of emission spectrum, except an enhancement in the initial emission intensity (Fig. 8). The final fluorescence enhancement factor (FEF = $I_{Maleic\ acid}/I_{2a}$) was approximately 1.6 times compared to the emission intensity of **2a**. The calculated Stern-Volmer

binding constant from the titration profile was K_{SV} = 1.4 ×10^4 M^{-1}. Binding assay calculation from the fluorescence titration data using the method of continuous variation (Jobs plot) indicated 1:2 mode of binding between **2a** and maleic acid (Fig. S14, Supporting Information). Macrocycle **2a** is composed of phenyl-ethynyl based fluorophore and amide based receptor. In the electronic excited states, there may be a strong electronic coupling via electron transfer from the acid-free amide receptor to the excited state of phenyl-ethynyl based fluorophore subunit. As a result, due to photoinduced electron transfer (PET) process, macrocycle **2a** shows moderate fluorescence emission (Fig. 8) in the acid-free situation.

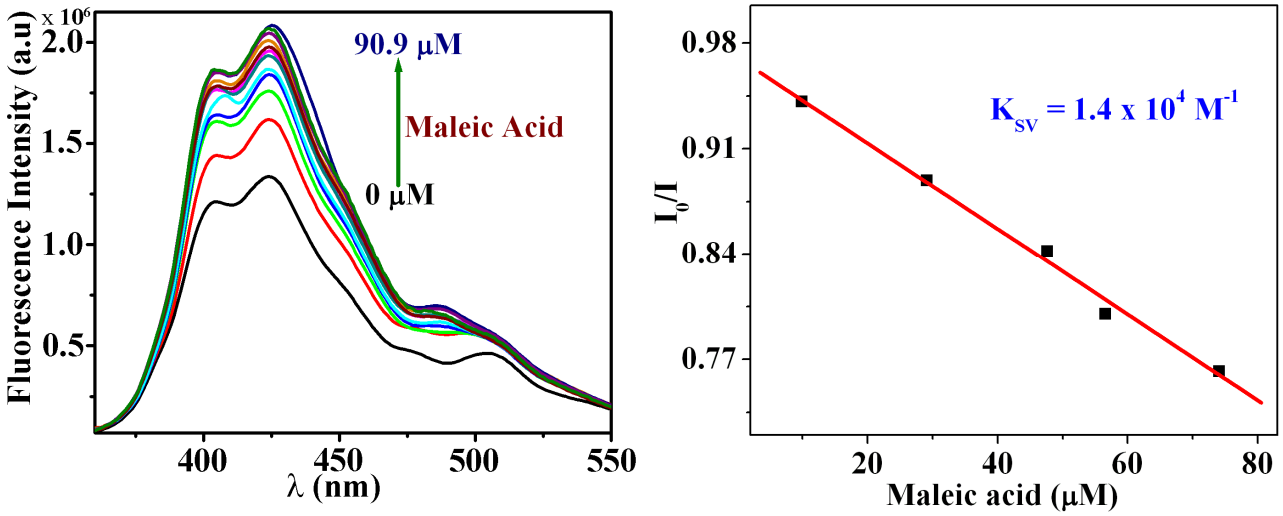


Fig. 8. Enhancement in the fluorescence intensity (left) of **2a** (1.0 × 10^{-5} M) upon the gradual addition of maleic acid (1.0 × 10^{-3} M) in CH_3CN/CH_3OH (10:0.4, v/v) solution and obtained Stern-Volmer plot (right).

However, the efficiency of PET process could be suppressed effectively upon binding of acid into the amide receptor through hydrogen bonding interaction. Such a suppression of the PET process results in an enhancement of emission intensity upon gradual addition of maleic acid solution.[1k, 18a] We also performed UV-vis absorption study check the binding affinity of **2a**

towards maleic acid using a CH_3CN/CH_3OH (10 : 0.4, v/v) solution (1.0×10^{-5} M) of the receptor **2a** and maleic acid (1.0×10^{-3} M) in CH_3CN/CH_3OH (10 : 0.4, v/v). Gradual addition of maleic acid in increasing concentration (0−69.7 μM) causes a noticeable enhancement in initial absorption along with a moderate red-shift (~4 nm) in the absorption spectra of **2a**, which indicates the existence of a strong interaction between **2a** and maleic acid (Fig. 9).

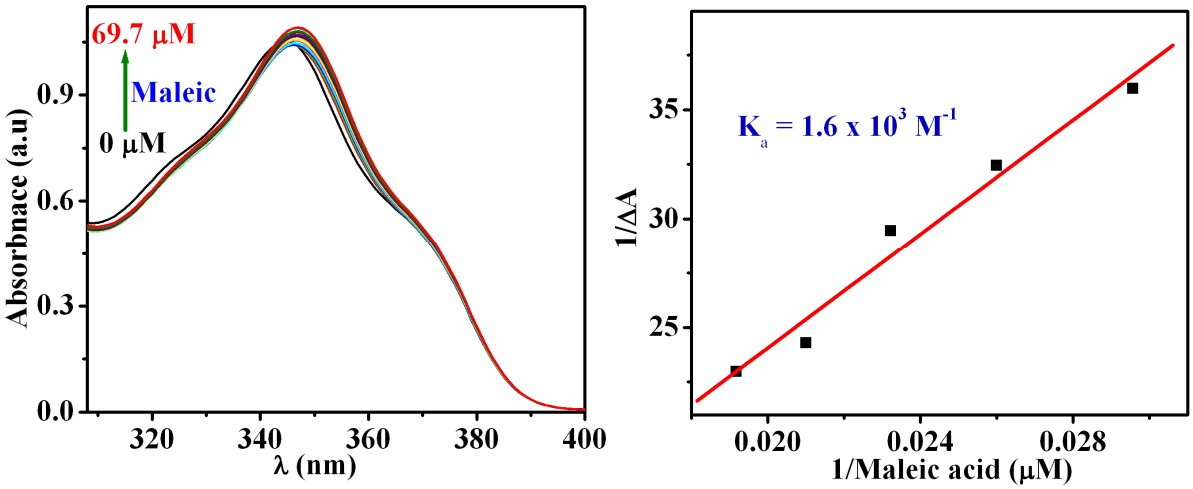


Fig. 9. Absorption spectral change (left) of **2a** (1.0×10^{-5} M) in CH_3CN/CH_3OH (10 : 0.4, v/v) upon titration with maleic acid in CH_3CN/CH_3OH (10 : 0.4, v/v) (0 – 69.7×10^{-6} M) at 25°C and corresponding Benesi-Hilderbrand plot (right).

Moreover, the appearance of a well–defined isobestic point centered at λ = 342 nm indicates a neat interconversion between the uncomplexed and complexed states (Fig. 9). A reciprocal plot of changes in the initial absorption intensity of **2a** upon increasing the concentration of the maleic acid yields a linear correlation and the binding constant $K_a = 1.6 \times 10^3$ M^{-1} was obtained from the slope and intercept of the plot.

Conclusions

We report here the use of a Pt^{II}_2-organometallic linear acceptor **1** in combination with several 'clip' type dipyridyl donors ($\mathbf{L_a}$–$\mathbf{L_c}$) to construct [2 + 2] self-assembled molecular rectangles (**2a**–**2c**) in good yields under mild condition. All these self-assembled macrocycles (**2a**–**2c**) were characterized by various spectroscopic techniques and molecular structures of the macrocycles **2a** & **2b** were obtained through X-ray diffraction analysis. Macrocycles (**2a**–**2c**) show luminescent characteristics in solution due to the presence of Pt-ethynyl functionality and extended π-conjugation. In addition, the amide functionalized macrocycle **2a** was tested as a macrocyclic receptor for various aliphatic acyclic dicarboxylic acids and the solution state fluorescence titration of **2a** with maleic acid caused an increase in emission intensity. Interestingly, no such perturbation in fluorescence intensity was observed when the titration was carried out with other dicarboxylic acids (fumaric, succinic, adipic, mesaconic and itaconic). Though, several receptors are known to recognize mono- or dicarboxylic acids,[18-20] receptor **2a** represents an interesting system for discrimination of maleic acid from other dicarboxylic acids.

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Supporting Information Available: Crystallographic details of **1a** and **2b**; IR, NMR (^{1}H and ^{31}P) and ESI-MS spectrum of **1**, **2a**–**2c** are available. CCDC-895738 and CCDC-895739 contain the supplementary crystallographic data of **1a** and **2b**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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TOC

Coordination self-assembly of tetranuclear Pt(II) macrocycles with organometallic backbone for sensing of acyclic dicarboxylic acids

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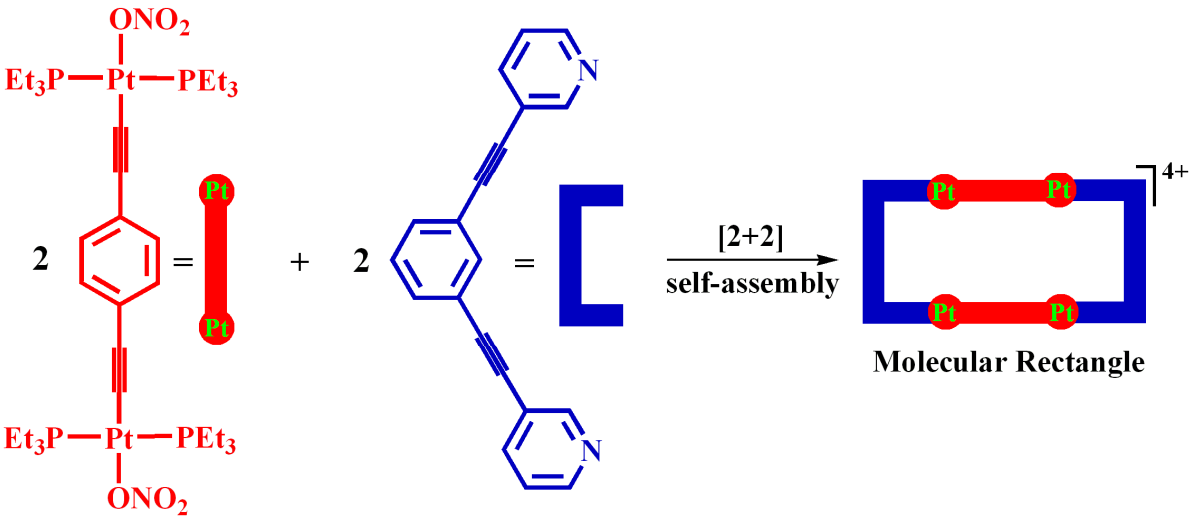

A series of Pt^{II}_4-metallamacrocycles has been synthesized using a Pt^{II}_2-organometallic 180° acceptor with several 'clip' type dipyridyl donors. One of the macrocycles containing amide functionality in proper orientation is tested as fluorescent sensor for discrimination of maleic acid from other acyclic dicarboxylic acids.