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# Self-Assembly of Metallamacrocycles Using a Dinuclear Organometallic Acceptor: Synthesis, Characterization, and Sensing Study

Sankarasekaran Shanmugaraju, Sachin A. Joshi, and Partha Sarathi Mukherjee*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

Supporting Information

**ABSTRACT:** A dinuclear organometallic acceptor 4,4′-bis[*trans*-Pt($PEt_3$)$_2$($O_3SCF_3$)(ethynyl)]biphenyl (**1**) containing Pt-ethynyl functionality is synthesized. Multinuclear NMR ($^1$H, $^{31}$P, and $^{13}$C), infrared (IR), and electrospray ionization mass spectrometry (ESI-MS) including single-crystal X-ray diffraction analysis established the formation of **1**. Equimolar treatment of acceptor **1** separately with three different "clip" type ditopic donors ($L_a$−$L_c$) yielded [2 + 2] self-assembled three metallamacrocycles **2a**−**2c**, respectively. These macrocycles were characterized by various spectroscopic techniques, and their sizes/shapes were obtained through geometry optimization using molecular mechanics universal force field (MMUFF) simulations. Attachment of unsaturated ethynyl functionality to biphenyl building unit helped to make the macrocycles (**2a**−**2c**) $\pi$-electron rich and thereby fluorescent in nature. Furthermore, **2c** in solution has been examined to be suitable for sensing electron-deficient nitroaromatic like picric acid, which is often considered as a secondary chemical explosive. The fluorescence study of **2c** showed a marked quenching of initial emission intensity upon titrating with picric acid (PA), and it exhibited the largest fluorescence quenching response with high selectivity among various other electron deficient aromatic compounds tested.


## INTRODUCTION

Several synthetic protocols have been developed for the synthesis of previously unthinkable large macromolecules.[1−3] In the meantime, metal−ligand coordination driven self-assembly of supramolecular architectures of defined shapes and sizes has witnessed rapid growth due to its potential applications.[4] The basic principle of such self-assembly relies on proper designing of information encoded building units that fulfill the requirements for selective molecular recognition. Moreover, such a self-assembly approach provides an opportunity to obtain even macromolecules of expected shapes, sizes, and functionality. The power and versatility of metal−ligand coordination have been used extensively in the past few years to synthesize several complex architectures.[5] As far as two-dimensional macrocycles are concerned; several architectures like molecular triangles, squares, and rhomboids are very common compared to molecular rectangles. However, Stang and co-workers have established a novel approach of designing rectangle via two-component self-assembly of a clip-type acceptor and linear donor.[6] Subsequently, large numbers of $Pd^{II}$/$Pt^{II}$, $Re^{I}$, and $Ru^{II}$ based molecular rectangles are also reported by several others in the recent past.[7] Interestingly, Stang's complementary approach of designing rectangles using a linear acceptor and clip-type of donor is not explored well.[6m]

Furthermore, the design of suitable chemical sensor for the detection and elimination of trace chemical explosives is a challenging task in the field of chemical sensors.[8,9] Substantial efforts have been devoted in the recent past for the protection of lives and control of environmental pollutions. Trinitrotoluene (TNT) and picric acid (PA) are common components in many buried landmines. Hence, designing suitable sensors for their detection is a challenging task to synthetic chemists.[10] An easy way of functionalization of coordination assemblies is by incorporating suitable functional groups.[8] As the nitroaromatic explosives are electron deficient in nature due to the presence of electron withdrawing $-NO_2$ group/s, our approach is to design molecular assemblies which are $\pi$-electron rich by incorporating ethynyl functionality.

Herein, we report the synthesis and characterization of a new $Pt_2^{II}$−organometallic 180° acceptor 4,4′-bis[*trans*-Pt($PEt_3$)$_2$-($O_3SCF_3$)(ethynyl)]biphenyl (**1**) and its [2 + 2] self-assembly with three different ditopic "clip" type donors ($L_a$−$L_c$) to afford rectangular metallamacrocycles **2a**−**2c** [$L_a$ = 1,3-bis(3-pyridyl)isothalamide; $L_b$ = 1,3-bis(3-pyridyl)ethynylbenzene; $L_c$ = 1,8-bis(4-pyridyl)ethynylanthracene] (Scheme 1).

All the three macrocycles **2a**−**2c** show luminescent behavior in solution as expected due to the presence of Pt-ethynyl functionality and extended $\pi$-conjugation along the backbones.

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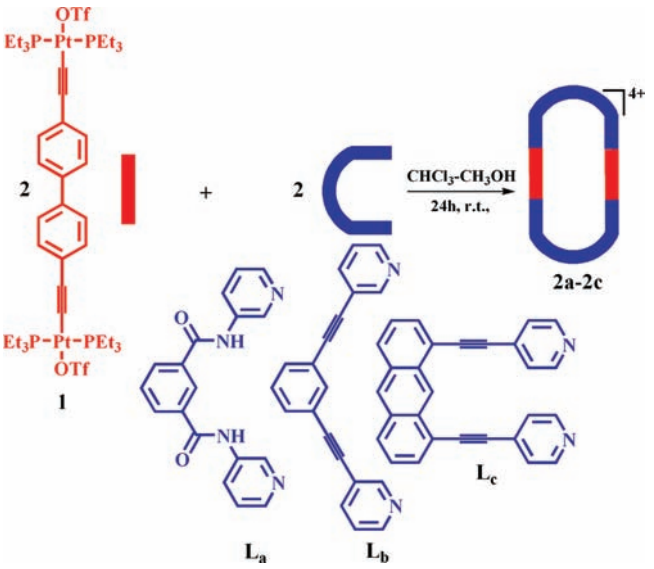
**Scheme 1. [2 + 2] Self-Assembly of Metallamacrocycles (2a−2c) Using a New Organometallic Linear Acceptor 1 in Combination with Three Different Ditopic Donors ($L_a$−$L_c$)**




Anthracene functionalized extended $\pi$-conjugated macrocycle **2c** is tested to be a fluorescent sensor for electron-deficient nitroaromatic such as picric acid (PA). Fluorescence study showed a marked quenching of initial fluorescence intensity of the macrocycle (**2c**) upon gradual addition of picric acid (PA) with a detection limit of even at the parts per billion level in solution.

## EXPERIMENTAL SECTION

**Materials and Methods.** The $Pt_2^{II}$−acceptor **1** was synthesized under dry nitrogen atmosphere using standard Schlenk technique. Solvents were dried and distilled according to the standard literature procedure. 4,4′-Dibromobiphenyl, 1,3-dibromobenzene, isonicotinylchloride hydrochloride, and 3-aminopyridine were purchased from Aldrich (USA) and were used without further purification. 1,3-Bis(3-pyridyl)isophthalamide[11] (**$L_a$**), 1,3-bis(3-pyridyl)ethynylbenzene[12] (**$L_b$**), and 1,8-bis(4-pyridyl)ethynylanthracene[13] (**$L_c$**) were synthesized following the reported procedures. NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts ($\delta$) in $^1$H NMR spectra are reported in parts per million (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) and $CDCl_3$ (7.26). $^{31}$P NMR spectra were recorded at 120 MHz, and the chemical shifts ($\delta$) are reported in ppm relative to external 85% $H_3PO_4$ at 0.00 ppm. $^{13}$C NMR were recorded at 100 MHz, and the chemical shifts ($\delta$) are reported in ppm relative to external $CDCl_3$ at 77.8−77.2 ppm. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed in a Bruker Daltonics spectrometer 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 4,4′-Bis[*trans*-Pt(PEt$_3$)$_2$I(ethynyl)]biphenyl.** 4,4′-Diethynylbiphenyl (400.4 mg, 1.98 mmol) and *trans*-$(PEt_3)_2PtI_2$ (3.38 g, 4.94 mmol) were added to a 100 mL round-bottom Schlenk flask. A 40 mL portion 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 at room temperature, a small amount of $Et_2NH_2^+I^-$ was started to precipitate out. 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: 980 mg, 38%. Anal calcd (%) for $C_{40}H_{68}I_2P_4Pt_2$: C, 36.48; H, 5.20. Found (%): C, 36.77; H, 5.29. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.46 (d, 4H, $J$ = 8.0 Hz), 7.34 (d, 4H, $J$ = 8.0 Hz), 2.22 (m, 24H, $CH_2$−$PEt_3$), 1.17 (m, 36H, $CH_3$−$PEt_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 120 MHz): $\delta$ 8.63 (s, $^1J_{Pt}$-P = 1720.9 Hz). $^{13}$C{$^1$H} NMR ($CDCl_3$, 100 MHz): $\delta$ 138.3 (2C, biphenyl), 131.5 (4C, biphenyl), 127.8 (2C, biphenyl), 126.88 (4C, biphenyl), 100.7 (2C, ethynyl), 31.4 (2C, ethynyl), 17.2 (12C, $CH_2$-$PEt_3$), 8.8 (12C, $CH_3$-$PEt_3$). IR: $\nu$ = 2117.5 cm$^{-1}$ for ethynyl group.

**Synthesis of 4,4′-Bis[*trans*-Pt(PEt$_3$)$_2$(O$_3$SCF$_3$)(ethynyl)]biphenyl (1).** A 20 mL Schlenk flask was charged with 290 mg (0.22 mmol) of 4,4′-bis[*trans*-Pt$(PEt_3)_2$I(ethynyl)]biphenyl and 10 mL of dry dichloromethane. A 118.7 mg (0.46 mmol) portion of $AgO_3SCF_3$ was added at once to the resulting solution. After 12 h of stirring at room temperature in dark under a stream of nitrogen, the suspension was passed through Celite using glass frit to remove AgI. The concentrated solution (2 mL) was triturated with cold *n*-pentane (5 mL) to isolate **1** as an off-white powder. Yield: 184 mg (60%). Anal calcd (%) for $C_{42}H_{68}F_6O_6P_4Pt_2S_2$: C, 37.06; H, 5.04. Found (%): C, 37.42; H, 5.30. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.46 (d, 4H, $J$ = 8.0 Hz), 7.27 (d, 4H, $J$ = 8.0 Hz), 2.06 (m, 24H, $CH_2$-$PEt_3$), 1.24 (m, 36H, $CH_3$-$PEt_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 120 MHz): $\delta$ 22.00 (s, $^1J_{Pt}$-P = 1773.0 Hz). $^{13}$C{$^1$H} NMR ($CDCl_3$/$CD_3OD$, 100 MHz): $\delta$ 139.0 (2C, biphenyl), 131.7 (4C, biphenyl), 126.8 (4C, biphenyl), 122.3 (2C, biphenyl), 119.1 (2C, $^-O_3SCF_3$), 103.1 (2C, ethynyl), 30.0 (2C, ethynyl), 14.4 (12C, $CH_2$−$PEt_3$), 8.5 (12C, $CH_3$-$PEt_3$). IR: $\nu$(cm$^{-1}$) = 2114.7 and 1253.52 for C≡C and C—F (OTf), respectively. ESI-MS ($m/z$): 1212.16 [**1** − $O_3SCF_3^-$]$^+$, 531.58 [**1** − $2O_3SCF_3^-$]$^{2+}$.

**General Procedure for the Synthesis of Macrocycles 2a−2c.** To a suspension of the corresponding ditopic donors ($L_a$−$L_c$) in methanol (2 mL) was added a clear solution of the $Pt_2^{II}$ acceptor **1** in chloroform (2 mL) drop-by-drop with continuous stirring in a 1:1 molar ratio. After stirring the reaction mixture at room temperature for 24 h in a closed 4 mL glass vial, the clear solution was concentrated to 0.5 mL and the products were isolated in pure form upon triturating with cold diethyl ether (∼5 mL).

**Synthesis of the Macrocycle 2a.** The 180° acceptor **1** (5.4 mg, 0.004 mmol) and 1,3-bis(3-pyridyl)isophthalamide **$L_a$** (1.3 mg, 0.004 mmol) were reacted in chloroform/methanol (1:1) solvent mixture to obtain **2a**. Isolated yield: 86%. Anal calcd for $C_{120}H_{164}F_{12}N_8O_{16}P_8S_4Pt_4$: C, 42.91; H, 4.92; N, 3.34. Found: C, 43.26; H, 4.63; N, 3.58. $^1$H NMR ($CDCl_3$/$CD_3OD$, 400 MHz): $\delta$ 9.34 (s, 2H, phenyl-$H_5$), 8.17−8.12 (m, 8H, pyridyl-$H_{1,2}$), 8.10 (d, 4H, phenyl-$H_6$, $J$ = 8.4 Hz), 7.62−7.43 (m, 6H, pyridyl-$H_3$ and phenyl-$H_7$), 7.38 (d, 8H, biphenyl-$H_\alpha$, $J$ = 8.0 Hz), 7.32 (d, 4H, pyridyl-$H_4$, $J$ = 8.0 Hz), 7.20 (d, 8H, biphenyl-$H_\beta$, $J$ = 8.0 Hz), 1.72 (m, 24H, $CH_2$-ethyl), 1.07 (m, 36H, $CH_3$-ethyl). $^{31}$P NMR ($CDCl_3$/$CD_3OD$, 120 MHz): $\delta$ 15.93 (s, $^1J_{Pt}$-P = 1730.4 Hz). IR: $\nu$(cm$^{-1}$) = 2118.9 and 1249.2 for C≡C and C—F (OTf), respectively. ESI-MS ($m/z$): 1530.49 [**2a** − $2O_3SCF_3^-$]$^{2+}$, 1412.49 [**2a** − $2O_3SCF_3^-$ − $2PEt_3$]$^{2+}$, 852.65 [**2a** − $3O_3SCF_3^-$ − $3PEt_3$]$^{3+}$, 690.74 [**2a** − $4O_3SCF_3^-$]$^{4+}$, 631.74 [**2a** − $4O_3SCF_3^-$ − $2PEt_3$]$^{4+}$.

**Synthesis of the Macrocycle 2b.** The acceptor **1** (5.4 mg, 0.004 mmol) and 1,3-bis(3-pyridyl)ethynylbenzene **$L_b$** (1.1 mg, 0.004 mmol) were reacted in chloroform/methanol (1:1) solvent mixture to obtain **2b**. Isolated yield: 80%. Anal calcd for $C_{124}H_{160}F_{12}N_4O_{12}P_8S_4Pt_4$: C, 45.37; H, 4.91; N, 1.71. Found: C, 45.42; H, 5.28; N, 1.75. $^1$H NMR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($CDCl_3/CD_3OD$, 400 MHz): $\delta$ 8.64 (s, 4H, pyridyl-$H_1$), 8.59 (d, 4H, pyridyl-$H_2$, $J$ = 4.8 Hz), 8.09 (d, 4H, pyridyl-$H_4$, $J$ = 7.2 Hz), 7.92 (s, 2H, phenyl-$H_5$), 7.66 (d, 4H, phenyl-$H_6$, $J$ = 6.0 Hz), 7.59−7.56 (m, 4H, pyridyl-$H_3$), 7.41 (d, 8H, biphenyl-$H_\alpha$, $J$ = 8.4 Hz), 7.32 (m, 2H, pyridyl-$H_7$), 7.22 (d, 8H, biphenyl-$H_\beta$, $J$ = 8.4 Hz), 1.75 (m, 24H, $CH_2$-ethyl), 1.09 (m, 36H, $CH_3$-ethyl). $^{31}$P NMR ($CDCl_3/CD_3OD$, 120 MHz): $\delta$ 15.87 (s, $^1J_{Pt}$-P = 1717.6 Hz). IR: $\nu$($cm^{-1}$) = 2124.62 and 1262.02 for C≡C and C—F (OTf), respectively. ESI-MS ($m/z$): 1492.48 [**2b** − $2O_3SCF_3^-$ − $PEt_3$]$^{2+}$, 1378.20 [**2b** − $2O_3SCF_3^-$ − $2PEt_3$]$^{2+}$, 1215.48 [**2b** − $2O_3SCF_3^-$ − $5PEt_3$ + $2H_2O$]$^{2+}$, 1139.30 [**2b** − $2O_3SCF_3^-$ − $6PEt_3$]$^{2+}$, 748.65 [**2b** − $3O_3SCF_3^-$ − $5PEt_3$]$^{3+}$, 671.74 [**2b** − $4O_3SCF_3^-$]$^{4+}$.

**Synthesis of the Macrocycle 2c.** Acceptor **1** (5.4 mg, 0.004 mmol) and 1,8-bis(4-pyridyl)ethynylanthracene $\mathbf{L_c}$ (1.5 mg, 0.004 mmol) were reacted in chloroform/methanol (1:1) solvent mixture to obtain **2c** in 78% isolated yield. Anal calcd for $C_{140}H_{168}F_{12}N_4O_{12}P_8S_4Pt_4$: C, 48.27; H, 4.86; N, 1.61. Found: C, 48.53; H, 4.99; N, 1.88. $^1$H NMR ($CDCl_3/CD_3OD$, 400 MHz): $\delta$ 9.24 (s, 2H, anthracene-$H_6$), 9.06 (s, 2H, anthracene-$H_7$), 8.69 (d, 4H, pyridyl-$H_1$, $J$ = 8.4 Hz), 8.52 (d, 4H, pyridyl-$H_2$, $J$ = 10.0 Hz), 8.10 (d, 4H, anthracene-$H_3$, $J$ = 8.4 Hz), 7.94 (d, 4H, anthracene-$H_4$, $J$ = 6.8 Hz), 7.81 (d, 4H, anthracene-$H_5$, $J$ = 10.0 Hz), 7.38 (d, 8H, biphenyl-$H_\alpha$, $J$ = 7.2 Hz), 7.21 (d, 8H, biphenyl-$H_\beta$, $J$ = 7.6 Hz), 1.75 (m, 24H, $CH_2$-ethyl), 1.09 (m, 36H, $CH_3$-ethyl). $^{31}$P NMR ($CDCl_3/CD_3OD$, 120 MHz): $\delta$ 15.80 (s, $^1J_{Pt}$ -P = 1738.4 Hz). IR: $\nu$($cm^{-1}$) = 2118.9 and 1260.6 for C≡C and C—F (OTf), respectively. ESI-MS ($m/z$): 1533.59 [**2c** − $2O_3SCF_3^-$ − $PEt_3$]$^{2+}$, 1474.54 [**2c** − $2O_3SCF_3^-$ − $2PEt_3$]$^{2+}$, 1012.06 [**2c** − $3O_3SCF_3^-$]$^{3+}$, 721.79 [**2c** − $4O_3SCF_3^-$]$^{4+}$, 633.29 [**2c** − $4O_3SCF_3^-$ − $3PEt_3$]$^{4+}$.

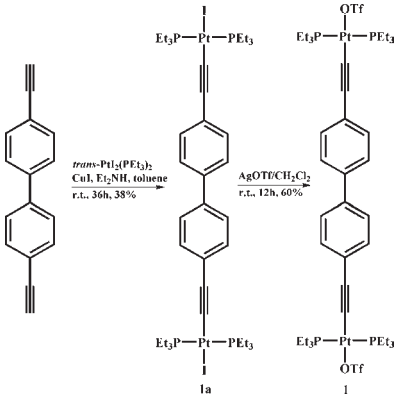
**X-ray Data Collection and Structure Refinements.** The diffraction data of **1a** were collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software.[14] Intensity data were collected using graphite-monochromatic Mo−K$\alpha$ radiation (0.7107 Å) at 150 K on a crystal as obtained after several attempts. The structure was solved by direct methods using the SHELX-97[15] incorporated in WinGX.[16−18] Empirical absorption corrections were applied with SADABS.[19] All the non-hydrogen atoms were refined with anisotropic displacement coefficients. Though the quality of structure solution was not very good due to poor quality of the crystal, the linear nature of the linker was clear without any doubt. Hydrogen atoms were assigned isotropic displacement coefficients $U$(H) = 1.2$U$(C) or 1.5$U$(C-methyl), and their coordinates were allowed to ride on their respective carbons.

**Fluorescence Quenching of 2c by Picric Acid.** A 2 mL stock solution ($8.0 \times 10^{-7}$ M) of the macrocycle **2c** in $CHCl_3$−$CH_3OH$ (1:1) was placed in a quartz cell of 1 cm width, and the picric acid stock solution ($1.0 \times 10^{-3}$ M) in $CH_3OH$ was added into it in an incremental fashion. The whole titration experiment was carried out at 298 K, and each titration was repeated at least three times to get concordant value. For all measurements the macrocycle **2c** was excited at $\lambda_{ex}$ = 360 nm, and their corresponding emission wavelengths were monitored from $\lambda_{em}$ = 370 nm onward. For all the measurements, both excitation and emission slit widths were 5 nm. There was no change in shape of the emission spectra except efficient quenching of the initial emission intensity of **2c** upon successive addition of picric acid solution. Analysis of the normalized fluorescence emission intensity ($I_0/I$) as a function of increasing quencher concentration [Q] was well-described by the Stern−Volmer equation $I_0/I = 1 + K_{SV}[Q]$. The Stern−Volmer binding constant ($K_{SV}$) was calculated from the slope of the Stern−Volmer plot.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of the Linear Acceptor 1.** Since the pioneering work of Sonagashira et al. on coupling of terminal alkynes with aryl-halides, large numbers of multinuclear organometallic complexes comprising ethynyl functionality have been synthesized.[20,21] Here, we utilized the coupling reaction of *trans*-$PtI_2(PEt_3)_2$ with the terminal alkynes as the key step to synthesize a 180° acceptor (Scheme 2).

**Scheme 2. Schematic Representation of the Synthesis of 4,4′-Bis[*trans*-$Pt(PEt_3)_2(O_3SCF_3)$(ethynyl)]biphenyl (1) from 4,4′-Dethynylbiphenyl and *trans*-$PtI_2(PEt_3)_2$**



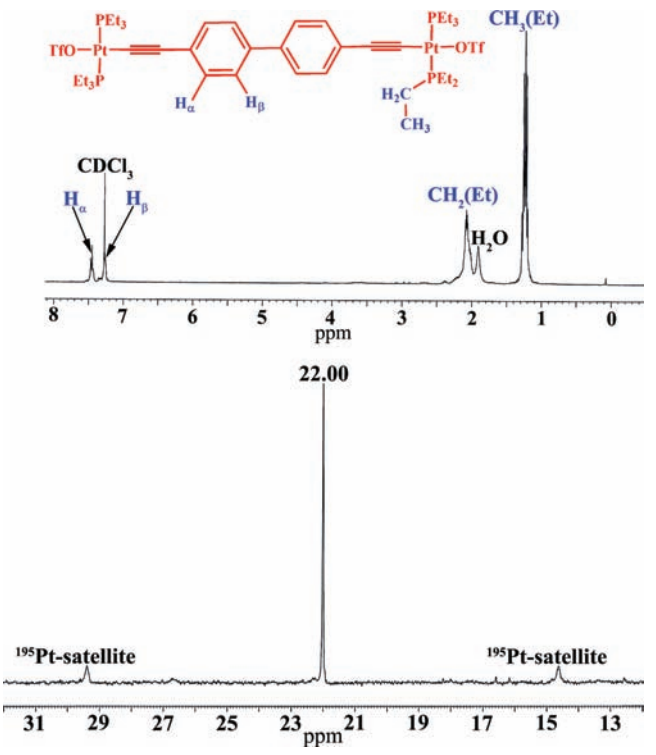




**Figure 1.** $^1$H (above) and $^{31}$P NMR (below) spectra of the acceptor **1** recorded in $CDCl_3$ with the peak assignments.

4,4′-Diethynylbiphenyl having two terminal alkynes was first reacted with 2.5 equiv of *trans*-$PtI_2(PEt_3)_2$ to give 4,4′-bis[*trans*-$Pt(PEt_3)_2$(I)(ethynyl)]biphenyl (**1a**), and its subsequent deiodination using 2.1 equiv of silver triflate (AgOTf) in dry dichloromethane under a stream of nitrogen atmosphere produced acceptor **1** in high yield (Scheme 2).

The linear acceptor **1** was fully characterized by various spectroscopic techniques like IR, multinuclear NMR {$^1$H, $^{31}$P, and $^{13}$C}, and ESI-MS analyses. IR spectrum showed an intense peak at $\nu$ = 2144.7 $cm^{-1}$ due to the ethynyl group (Figure S1,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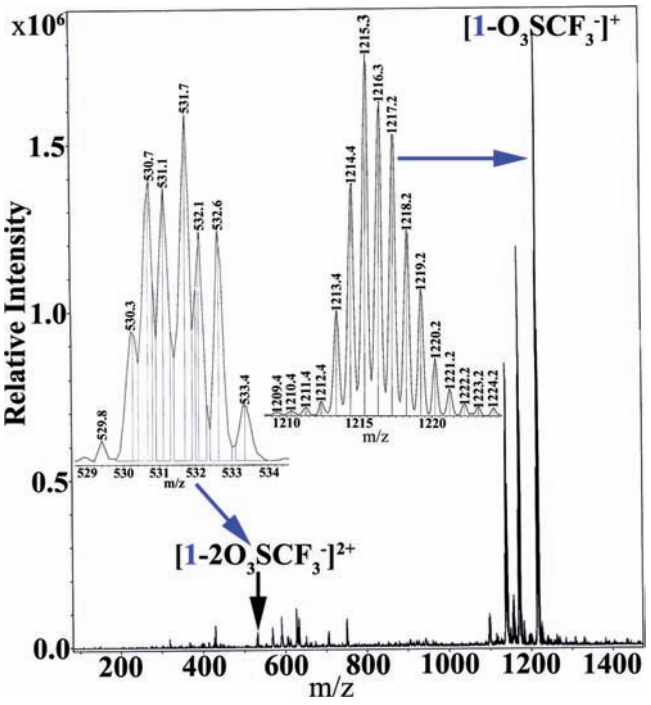


**Figure 2.** ESI-MS spectrum of the acceptor **1** recorded in acetonitrile. (inset) Experimentally observed isotopic distribution for $[\mathbf{1} - O_3SCF_3^-]^+$ and $[\mathbf{1} - 2O_3SCF_3^-]^{2+}$ fragments.

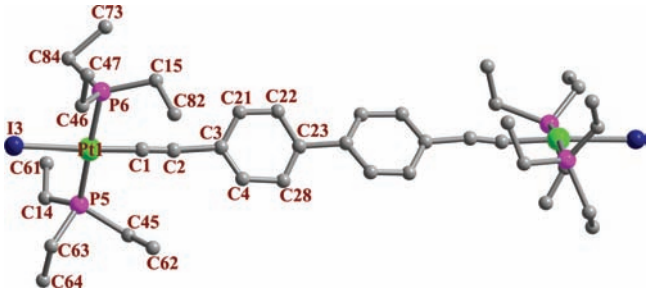


**Figure 3.** Molecular structure of the linear $Pt_2^{II}$—diiodide complex **1a**: (color codes) green = Pt, purple = I, magenta = P, gray = C. Hydrogen atoms are omitted for the sake of clarity.

Supporting Information). The diplatinum acceptor **1** showed a singlet at $\delta$ = 22.00 ppm with concomitant $^{195}$Pt satellites ($^1J_{Pt\text{-}P}$ = 1773.0 Hz) in the $^{31}$P NMR spectrum (Figure 1). The $^1$H NMR spectrum exhibited a set of doublets in the range of $\delta$ = 7.46−7.25 ppm corresponding to the biphenyl protons in the aromatic region (Figure 1). Electrospray ionization (ESI-MS) mass spectrometric analysis of the linear acceptor **1** showed (Figure 2) peaks at $m/z$ = 1212.16 and 531.58 corresponding to the fragments $[\mathbf{1} - O_3SCF_3^-]^+$ and $[\mathbf{1} - 2O_3SCF_3^-]^{2+}$, respectively. The experimental isotopic distribution patterns of these fragments matched well with their corresponding charged state (Figure 2).

Finally the formation of linear acceptor **1** was unambiguously established by X-ray single crystal diffraction study of the iodide analogue 4,4′-bis[*trans*-Pt(PEt$_3$)$_2$I(ethynyl)]biphenyl (**1a**). Suitable single crystals were obtained by slow evaporation of a solution of **1a** in dichloromethane/*n*-hexane (1/1) mixture at ambient temperature. **1a** was crystallized in triclinic $\overline{P}1$ space

**Table 1. Crystallographic Data and Refinement Parameters of 1a**

| | **1a** |
|---|---|
| empirical formula | $C_{40}H_{68}I_2P_4Pt_2$ |
| formula weight | 1316.8 |
| crystal system | triclinic |
| space group | $\overline{P}1$ |
| $T$, K | 150 |
| $\lambda$ (Mo K$\alpha$), Å | 0.71073 |
| $a$, Å | 16.804(3) |
| $b$, Å | 17.587(3) |
| $c$, Å | 17.973(3) |
| $\alpha$, deg | 105.619(9) |
| $\beta$, deg | 90.102(9) |
| $\gamma$, deg | 105.726(9) |
| $V$, Å$^3$ | 4907.9(15) |
| $Z$ | 4 |
| $\rho_{calcd}$, g cm$^{-1}$ | 1.804 |
| $\mu$, mm$^{-1}$ | 7.110 |
| GOF[a] | 0.940 |
| $R1$[b] $[I > 2\sigma(I)]$ | 0.0187 (16346) |
| $wR2$[c] $[I > 2\sigma(I)]$ | 0.0693 (16384) |

[a] GOF = $\{\Sigma[w(F_0^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where $n$ and $p$ denotes the number of data points and the number of parameters, respectively. [b] $R1 = (\Sigma||F_0| - |F_c||)/\Sigma|F_0|$. [c] $wR2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_0^2) + (aP)^2 + (bP)]$ and $P = [\max(0, F_0^2) + 2F_c^2]/3$.

group with four formula units per asymmetric unit. A balls and sticks representation of the structure (Figure 3) shows that it is indeed a linear building unit with a Pt—biphenyl—Pt angle of approximately 178.43°. The dihedral angle between the phenyl rings of the biphenyl unit is about 14.91°. The coordination geometry around each $Pt^{II}$ metal center is almost square-planar with I—Pt—P angles in the range of 91.21—95.52° and C—Pt—P angles in the range of 85.38—90.70°. The Pt—I bond distances of 2.65 Å and 2.66 Å in **1a** are very close to the reported Pt—I distances in other complexes.[22] Crystallographic data and refinement parameters are summarized in Table 1, while the selected bond parameters are assembled in Table 2.

**Synthesis and Characterization of the 2 + 2 Metallamacrocycles (2a−2c).** The geometry of the resulting macrocycles is generally determined by the bite angles of the predesigned complementary building blocks. According to the "directional bonding approach" and "symmetry interaction" model, a molecular rectangle can be self-assembled via two different synthetic pathways.[4c] One method is three-component [4 + 2 + 2] self-assembly of a cis-blocked 90° acceptor and two different linear ditopic donors of 180° bite angle. The second approach is two-component [2 + 2] self-assembly of a linear 180° ditopic subunit and a clip-type building unit of 0° bite angle between their binding sites. Following this design methodology, exclusive formation of several cationic as well as neutral planar molecular rectangles has been realized by Stang et al. and others.[6,7] The second approach is expected to be entropically more favorable over the first approach since less building units are required to design a molecular rectangle. Here, we report a complementary approach to Stang's one to generate cationic rectangles using linear acceptor and donor clip under mild reaction condition (Scheme 1).[6m,13] The equimolar combination of a linear 180°


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**Table 2. Selected Bonds Distances (Å) and Angles (deg) for 1a**

| | | | | | |
|---|---|---|---|---|---|
| | | | 1a | | |
| Pt(1)−C(1) | 1.818(5) | Pt(1)−P(6) | 2.1214(11) | Pt(1)−P(5) | 2.3402(10) |
| Pt(1)−I(3) | 2.6515(6) | Pt(4)−C(7) | 1.846(6) | Pt(4)−P(1) | 2.1283(15) |
| Pt(4)−P(2) | 2.3356(11) | Pt(4)−I(2) | 2.6598(6) | | |
| C(1)−Pt(1)−P(6) | | 85.39(13) | C(1)−Pt(1)−P(5) | | 88.30(12) |
| P(6)−Pt(1)−P(5) | | 171.68(5) | C(1)−Pt(1)−I(3) | | 175.35(17) |
| P(6)−Pt(1)−I(3) | | 95.52(3) | P(5)−Pt(1)−I(3) | | 91.21(3) |
| C(7)−Pt(4)−P(1) | | 90.7(2) | C(7)−Pt(4)−P(2) | | 85.8(2) |
| P(1)−Pt(4)−P(2) | | 175.71(6) | C(7)−Pt(4)−I(2) | | 175.14(16) |
| P(1)−Pt(4)−I(2) | | 92.23(3) | P(2)−Pt(4)−I(2) | | 91.47(4) |
| C(35)−P(1)−Pt(4) | | 126.7(2) | C(12)−P(1)−Pt(4) | | 121.68(13) |
| C(87)−P(1)−Pt(4) | | 95.7(5) | C(67)−P(2)−Pt(4) | | 105.5(2) |
| C(34)−P(2)−Pt(4) | | 116.00(17) | C(13)−P(2)−Pt(4) | | 116.3(3) |
| C(46)−P(6)−Pt(1) | | 121.45(17) | C(2)−C(1)−Pt(1) | | 173.7(4) |

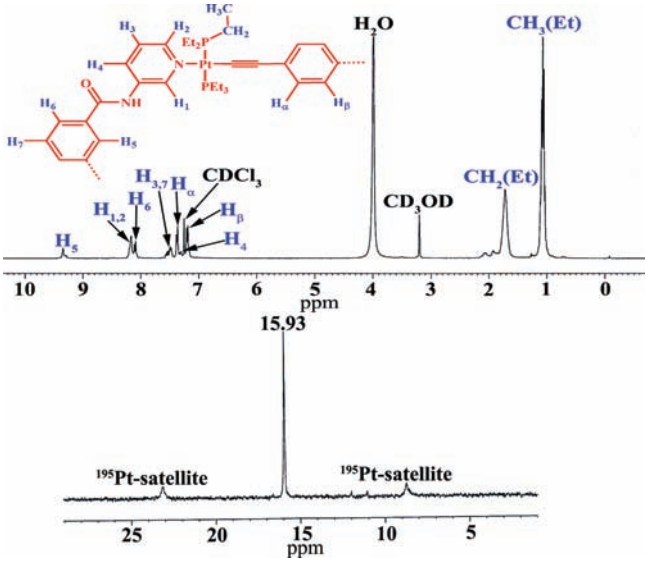


**Figure 4.** $^{1}$H (top) and $^{31}$P NMR (bottom) spectra of the amide-based macrocycle **2a** recorded in $CDCl_3-CD_3OD$ solvent mixture with the peak assignments.

acceptor **1** separately with three different ditopic clip-type donors $\mathbf{L_{a-c}}$ in a chloroform−methanol solvent mixture (1:1) yielded cationic tetranuclear molecular rectangles (**2a**−**2c**), respectively, after 24 h of stirring at room temperature (Scheme 1). All the self-assembled macrocycles were fully characterized by IR, NMR ($^{1}$H and $^{31}$P), and ESI-MS analyses. The formation of products were initially monitored by multinuclear NMR ($^{1}$H and $^{31}$P) spectroscopy and were consistent with the formation of a single and symmetrical product in all the cases (Figure 4 and Supporting Informations). The $^{31}$P $\{^{1}$H$\}$ NMR spectra of **2a**, **2b**, and **2c** exhibited sharp singlet (ca. 15.93 ppm for **2a**; 15.87 ppm for **2b**; and 15.63 ppm for **2c**), which are upfield shifted with respect to the starting diplatinum acceptor **1** by 6.06, 6.12, and 6.37 ppm, respectively with the appearance of concomitant platinum satellites (Figure 4 and Supporting Information). Upfield shift of the phosphorus peaks is indicative of ligand to Pt(II) coordination. Moreover, a significant decrease in the coupling of flanking $^{195}$Pt satellites (ca. $^{1}J_{Pt}$-P = 1730.4 Hz for **2a**; $^{1}J_{Pt}$-P = 1717.6 Hz for **2b**; $^{1}J_{Pt}$-P = 1738.4 Hz for **2c**) compared to the starting acceptor **1** ($^{1}J_{Pt}$-P = 1773.0 Hz) is consistent with electron back-donation from Pt(II) centers and imparting further support of ligand to metal coordination. Likewise, the appearance of sharp and single set of $^{1}$H NMR signals suggested the formation of symmetrical products. In the $^{1}$H NMR spectrum of each macrocycles (**2a**−**2c**), hydrogen atoms of the pyridine rings exhibited small downfield shift relative to uncoordinated $\mathbf{L_{a-c}}$ due to the loss of electron density upon coordination of the pyridine-N to Pt(II) centers (Figure 4 and Supporting Informations). The sharp signals in both $^{1}$H and $^{31}$P NMR spectra as well as high solubility of the resulting macrocycles in common organic solvents ruled out the possibility of forming any polymeric analogue.

Although, the initial characterization of these metallacycles using multinuclear ($^{1}$H and $^{31}$P) NMR spectroscopy suggested ligand to metal coordination, it does not furnish any information about the exact composition and nuclearity of the resulting macrocycles. ESI-mass spectrometry is a well-accepted soft-ionization technique to determine the composition of charged species in solution.[23] Formation of [2 + 2] self-assembled tetranuclear rectangular macrocycles **2a**−**2c** was supported by ESI-MS spectrometric analysis, where multiply charged ions corresponding to the expected macrocycles were observed (Figure 5 and Supporting Information). ESI-MS experiments were performed on an acetonitrile solution of the corresponding macrocycles. The multiply charged molecular ions for **2a** at $m/z$ = 1530.49 [**2a** − $2O_3SCF_3^-$]$^{2+}$, 1412.49 [**2a** − $2O_3SCF_3^-$ − $2PEt_3$]$^{2+}$, 852.65 [**2a** − $3O_3SCF_3^-$ − $3PEt_3$]$^{3+}$, 690.74 [**2a** − $4O_3SCF_3^-$]$^{4+}$, 631.74 [**2a** − $4O_3SCF_3^-$ − $2PEt_3$]$^{4+}$; for **2b** at $m/z$ = 1492.48 [**2b** − $2O_3SCF_3^-$]$^{2+}$, 1374.48 [**2b** − $2O_3SCF_3^-$ − $2PEt_3$]$^{2+}$, 1215.48 [**2b** − $2O_3SCF_3^-$ − $5PEt_3$ + $2H_2O$ ]$^{2+}$, 1138.48 [**2b** − $2O_3SCF_3^-$ − $6PEt_3$]$^{2+}$, 748.65 [**2b** − $3O_3SCF_3^-$ − $5PEt_3$]$^{3+}$, 671.74 [**2b** − $4O_3SCF_3^-$]$^{4+}$; for **2c** at $m/z$ = 1533.59 [**2c** − $2O_3SCF_3^-$ − $PEt_3$]$^{2+}$, 1474.54 [**2c** − $2O_3SCF_3^-$ − $2PEt_3$]$^{2+}$, 1012.06 [**2c** − $3O_3SCF_3^-$]$^{3+}$, 721.79 [**2c** − $4O_3SCF_3^-$]$^{4+}$, 633.29 [**2c** − $4O_3SCF_3^-$ − $3PEt_3$]$^{4+}$ were observed. The experimentally observed isotopic distributions of the peaks corresponding to the [**2a** − $2O_3SCF_3^-$]$^{2+}$ and [**2b** − $2O_3SCF_3^-$]$^{2+}$ fragments were consistent with their charge states (Figure 5 and Supporting Information). So, the ESI-MS results are consistent with the formation of [2 + 2] self-assembled products. The only


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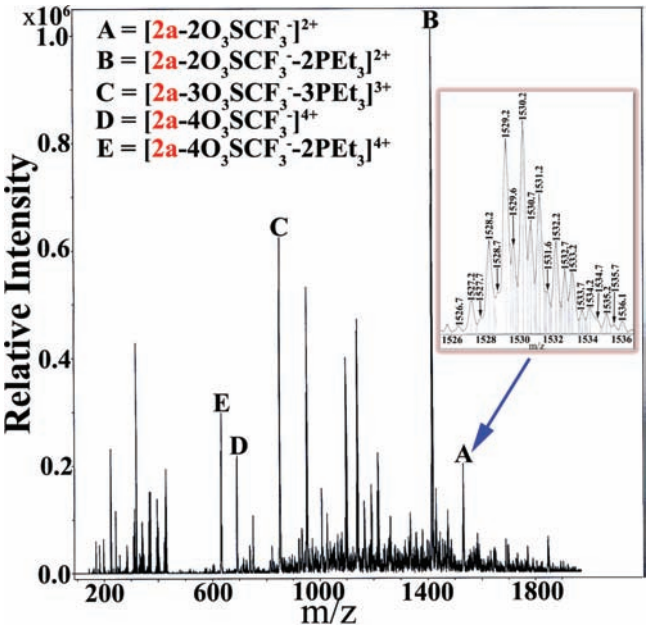


**Figure 5.** ESI-MS spectrum of the macrocycle **2a** recorded in $CH_3CN$. (inset) Experimentally observed isotopic distribution pattern of the fragment $[\mathbf{2a} - 2O_3SCF_3^-]^{2+}$.

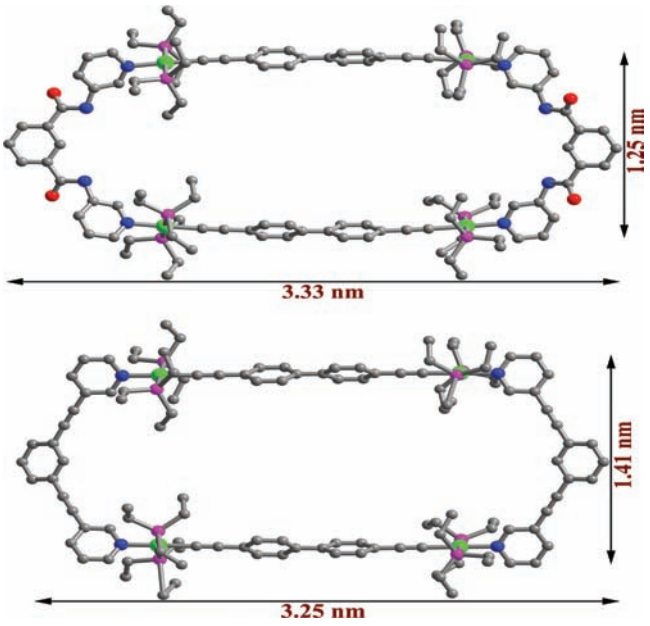


**Figure 6.** Energy minimized structures of the macrocycles **2a** (top) and **2b** (bottom): (color code) green = Pt, magenta = P, blue = N, red = O, gray = C. The hydrogen atoms are removed for the sake of clarity.

possible structure for such [2 + 2] combination of a clip-type donor and a linear acceptor is molecular rectangle.

Unfortunately, all efforts to obtain X-ray diffraction quality single crystals of the macrocycles have been unsuccessful. However, the analysis of multinuclear NMR ($^1H$ and $^{31}P$) in concurrence with ESI-MS spectroscopic studies supported the formation of [2 + 2] self-assembled macrocycles. In view to gain further insight into the structural characteristics of the newly designed macrocycles, energy minimized structures of the macrocycles (**2a**−**2c**) were obtained using molecular mechanics universal force field simulation (MMUFF).[24] Perspective views of the energy minimized structures of the macrocycles **2a**−**2b** and **2c** are depicted in Figure 6 and Supporting Information, respectively. The optimized structures of the macrocycles indicated the formation of rectangular geometry with overall dimensions of 3.33 nm ×1.25 nm, 3.25 nm ×1.37 nm, and 3.98 nm ×0.72 nm for **2a**, **2b**, and **2c**, respectively. Notably, although the simulated structure of **2c** adopts a perfect rectangular geometry, macrocycles **2a** and **2b** assume more of an oval shape (Figure 6).

**UV−vis Absorption and Fluorescence Studies of the Macrocycles.** Photophysical data of the macrocycles (**2a**−**2c**) are summarized in Table 3. The absorption spectra of the macrocycles **2a**−**2c** in DMF ($1.0 \times 10^{-6}$ M) show peaks at $\lambda$ = 282 and 343 nm for **2a**; $\lambda$ = 288, 306, and 343 nm for **2b**; $\lambda$ = 288, 343, and 422 nm for **2c** (Figure 7). The peaks in the range of 306−343 nm are tentatively assigned to MLCT, whereas the peaks in the range of 282−288 nm are ascribed to the intra/intermolecular $\pi-\pi^*$ transitions. All the three macrocycles show high fluorescence characteristics in DMF solution, and their high luminescence behavior is basically attributed to the presence of unsaturated Pt-ethynyl functionality and extended $\pi$-conjugation (Figure 7). Solution state emissive quantum yields of the macrocycles **2a**−**2c** were determined to be 0.03 for **2a**; 0.02 for **2b**, and 0.12 for **2c**, respectively, relative to anthracene ($\Phi$ = 0.27 in ethanol) as a standard.

**Table 3. Photophysical Data of the Macrocycles 2a−2c in Aerated DMF Solution**

| macrocycles | absorption maxima $\lambda_{max}$ (nm) | molar extinction coefficient $10^4$ $\varepsilon$ $M^{-1}$ $cm^{-1}$ [$\lambda_{max}$ (nm)] | fluorescence emission maxima at 298 K $\lambda_{max}$ (nm) | quantum yield[a] ($\Phi$) |
|---|---|---|---|---|
| **2a** | 282, **343** | 786 (343) | **394**, 542 | 0.03 |
| **2b** | 288, 302, **343** | 1004 (343) | **400**, 542 | 0.02 |
| **2c** | 288, **343**, 422 | 870 (343) | **433**, 458, 491 (sh) | 0.12 |

[a] Using anthracene ($\Phi_f$ = 0.27) as a standard in ethanol at room temperature. Values in bold represent the highest absorption ($\lambda_{abs}$) and emission ($\lambda_{em}$) maxima, respectively.

**Fluorescence Quenching Based Detection of Picric Acid.** Picric acid is a common chemical used frequently in several organic transformations and in leather/dye industries as a pigment.[25] Due to its high rate of thermal expansion upon initiation with external stimuli, picric acid has long been used as important component in manufacturing of explosives and rocket fuels.[26] It is proved that the long time exposure to the vapor of picric acid can cause headaches, anemia, and liver injury.[27] Versatile use of picric acid made it a significant environmental pollutant and attracted much attention to design suitable sensors for its detection. Several detection methods have been proposed including classical chemical methods.[28] However, these methods are not well-suited due to expensive instrumentation and lack of selectivity and sensitivity. The substitution of strong electron withdrawing $-NO_2$ groups to the phenyl ring makes picric acid into an electron-poor analyte. Thus, the probable mechanism of sensing involves the formation of a nonfluorescent charge-transfer (CT) complex between the electron-poor picric acid (quencher) and electron-rich fluorophore (donor). This leads to its detection by subsequent quenching of initial fluorescence intensity of the fluorophore. $\pi$-Electron-rich


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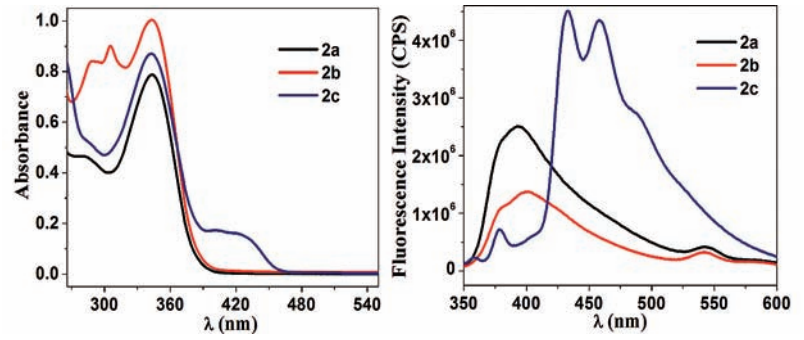


**Figure 7.** UV−visible (left) and fluorescence (right) spectra of the macrocycles **2a**−**2c** recorded in DMF solution ($1.0 \times 10^{-6}$ M) at room temperature.

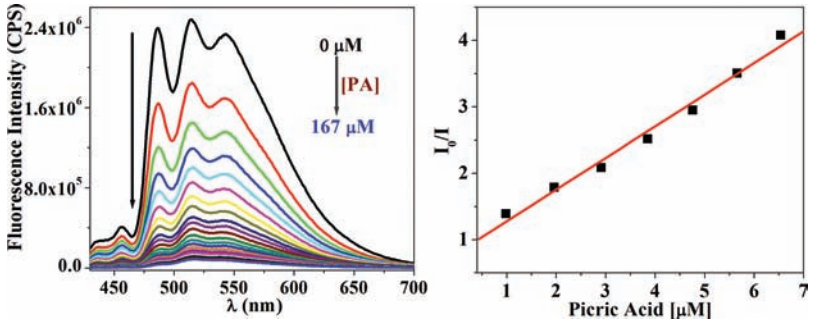


**Figure 8.** Fluorescence quenching (left) of **2c** ($8.0 \times 10^{-7}$ M) with picric acid ($1.0 \times 10^{-3}$ M) in chloroform−methanol solution and the obtained Stern−Volmer plot (right).

luminescent cages have been tested recently as sensors for electron poor explosives constituents.[5j,12] Two important criteria need to be considered in designing suitable fluorophores to sense the electron-deficient analytes. First, fluorophore should be $\pi$-electron-rich and highly oriented to enable effective $\pi-\pi$ stacking with an electron-poor quencher. Second, a fluorophore must be grafted with a bulky substituent on the peripheral to prevent the intermolecular excimer formation through $\pi-\pi$ interactions. Polycyclic aromatic hydrocarbons like anthracene, pyrene, etc. and their derivatives have been used as fluorescence sensors because of their strong electron donor ability and strong luminescence characteristics.[29] On the basis of these intrinsic electronic properties, we have synthesized an anthracene-based finite molecular rectangle **2c** to use as fluorescence sensors for picric acid. The linking of anthracene and ethynyl moieties can enhance the electron donating ability of the macrocycles and thus increase the efficiency of the fluorescence quenching by the oxidative quencher. Moreover, the attachment of bulky triethylphosphine ($-PEt_3$) groups to the Pt-metal centers can prevent the excimer formation between the adjacent macrocycles, thereby maintaining the spectroscopic stability in the solution.

To demonstrate the ability of macrocycle **2c** to sense picric acid, we first performed fluorescence quenching titration experiments of **2c** with picric acid (PA) in solution. Upon gradual addition of picric acid to a $CHCl_3-CH_3OH$ (1:1) solution of the macrocycle, the initial fluorescence intensity of the macrocycle was quenched rapidly (Figure 8). There was no change in the shape of the emission spectra except marked quenching of the initial emission intensity upon an increasing concentration of picric acid. The reason for the observed quenching of initial fluorescence intensity of the macrocycle is due to the efficient ground state charge-transfer (CT) complex formation between the $\pi$-electron-rich macrocycle and electron-poor picric acid. A linear Stern−Volmer plot was obtained from the fluorescence quenching titration profile, and Stern−Volmer quenching constants ($K_{SV} = 5.0 \times 10^6\ M^{-1}$) were determined from the slope of the plot (Figure 8). According to the Stern−Volmer equation, a linear plot may be observed if either static or dynamic quenching process is dominant. However, the static quenching mechanism involves the formation of a ground state nonfluorescent charge-transfer (CT) complex, whereas dynamic quenching adopts the excited state electron transfer from fluorophore to oxidative quencher or collision. In this case, macrocycle **2c** forms a stable ground-state CT complex with picric acid as judged by electronic absorption spectroscopy including marked visual color change and excited state lifetime measurement in response to the quencher concentrations. To further prove the formation of a charge-transfer (CT) complex between **2c** and picric acid, we have carried out a typical $^1H$ NMR titration experiment. A pale yellow solution of picric acid (PA) was mixed with macrocycle **2c** in 4:1 molar ratio in 0.6 mL of $CDCl_3$. Upon complex formation, significant upfield shift of the proton resonance of both picric acid and macrocycle **2c** was noticed and subsequent dilution of the NMR sample solution with $CDCl_3$ (0.2 mL each time) caused a gradual downfield shifting of proton resonance of picric acid (Figure S12, Supporting Information).

The observed downfield shift of the picric acid peak is presumably due to the shifting of equilibrium position from the bound charge-transfer state to an unbound state of picric acid. We have also carried out the electronic absorption spectral measurement of macrocycle **2c** with picric acid. A significant increase in the initial absorption intensity of **2c** was noticed upon


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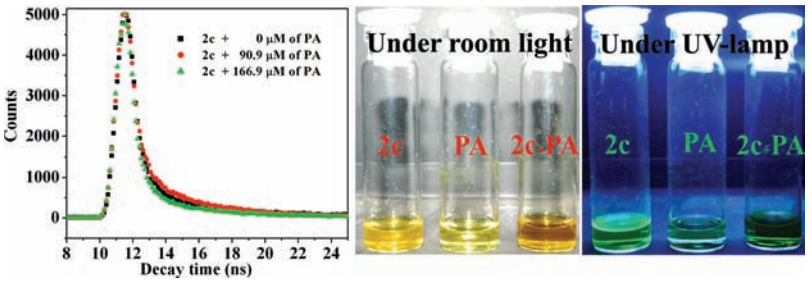


**Figure 9.** Excited-state lifetime analysis of the macrocycle **2c** (left) with respect to increasing the concentration of picric acid (0−166.9 $\mu$M) at room temperature and a sharp visual color change (right) of **2c** upon exposing with picric acid in $CHCl_3/CH_3OH$ solvent mixture.

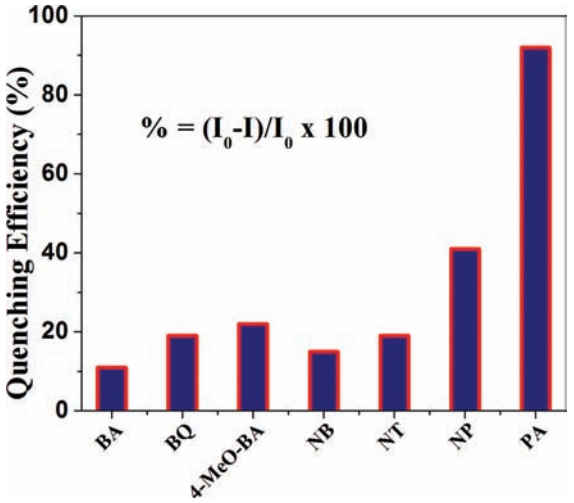


**Figure 10.** Relative fluorescence quenching of the macrocycle **2c** observed upon addition of various analytes: BA = benzoic acid, BQ = benzoquinone, 4-MeBA = 4-methoxybenzoic acid, NB = nitrobenzene, NT = nitrotoluene, NP = nitrophenol, PA = picric acid.

gradual addition of picric acid in methanol ($1.0 \times 10^{-3}$ M) to a chloroform−methanol solution of ($8.0 \times 10^{-7}$ M) **2c** at room temperature (Figure S14, Supporting Information). The considerable change of initial absorption intensity including a sharp visual color change (Figure 9) of **2c** upon the gradual addition of picric acid are indicative of the formation of ground state charge-transfer (CT) complex between macrocycle **2c** and picric acid quencher. Furthermore, the excited-state lifetime of the macrocycle **2c** ($\tau$ = 4.0 ns) was unchanged upon increasing the concentration of picric acid quencher, which also supported that the fluorescence quenching of macrocycle **2c** mainly follows the static quenching mechanism via ground-state charge transfer complex formation (Figure 9).

In order to verify the sensitivity of the macrocycle to sense picric acid at lower concentration, we carried out the fluorescence quenching titration with picric acid at parts per billion (ppb) concentrations. The obtained result shows that this particular macrocycle (**2c**) can sense the presence of picric acid even at the ppb level of concentration (Figure S13, Supporting Information). In addition, we have also examined the effect of other electron deficient aromatic compounds on initial fluorescence intensity of the macrocycle **2c** in order to ascertain the selectivity toward a picric acid quencher. The obtained results are shown in Figure 10, which reveal that macrocycle **2c** shows very high quenching response toward picric acid over other tested analytes like BA = benzoic acid, BQ = benzoquinone, 4-MeBA = 4-methoxybenzoic acid, NB = nitrobenzene, NT = nitrotoluene, NP = nitrophenol. Although, the reduction potential of these tested analytes are not significantly different from picric acid, we think that the observed higher quenching response of picric acid is, probably due to the strong dipolar or electrostatic interactions of electron-poor picric acid with the $\pi$-electron-rich macrocycle.

## CONCLUSIONS

In conclusion, we report here a biphenyl based $Pt_2^{II}$−organometallic linear acceptor **1**, and its equimolar combination with several ditopic donors ($\mathbf{L_a}$−$\mathbf{L_c}$) to yield [2 + 2] self-assembled molecular rectangles **2a**−**2c**. All the self-assembled macrocycles (**2a**−**2c**) were characterized by various spectroscopic techniques and energy minimized structures of the macrocycles were obtained using force-field simulation. Macrocycles (**2a**−**2c**) show luminescent characteristics in solution due to the presence of Pt-ethynyl functionality and extended $\pi$-conjugation. Furthermore, due to its strong electron donating ability and strong luminescent characteristic, anthracene derived macrocycle **2c** has been tested as fluorescent sensor for electron-poor analyte like picric acid in solution. The solution phase fluorescence intensity of **2c** was quenched efficiently and selectively upon exposing to picric acid, which is one of the common chemical constituents found in many chemical explosives.

## ASSOCIATED CONTENT

**Supporting Information.** Crystallographic details of **1a**, IR spectra of **2a**−**2c**, NMR ($^1$H and $^{31}$P) spectra, and ESI-MS spectrum of macrocycle **2b** and **2c**. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: psm@ipc.iisc.ernet.in. Fax: 91-80-2360-1552. Tel.: 91-80-2293-3352.

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