Introduction

Chemists have long desired to develop molecular ensembles with diverse shapes, sizes, and functionalities in order to mimic complex biological systems and also to explore such systems for practical applications. The rapid development of synthetic methodologies has made it possible to synthesize various intricate macrocycles/cages, which have found significant importance for the applications in drug delivery, sensing, catalysis and host–guest chemistry. However, the conventional covalent (C–C bond formation) synthesis of such molecules often involves multi-step reactions and hence found to be laborious, time consuming and results in low yield of the targeted products. Thus, it remains a constant challenge for the scientific community to introduce alternative synthetic methodologies targeting minimum synthetic difficulties to achieve desired products with maximum possible yields. In light of this, coordination-driven self-assembly has become one of the powerful strategies for one-pot synthesis of desired molecular architectures in high yield. The stable coordination geometry of square planar Pd(II) and Pt(II) metal ions and their dynamic metal–ligand coordination bond formation with N/O-donors gives them the potential to achieve thermodynamically stable single products over several kinetically driven possibilities, as nicely described in the ‘Molecular library’ by Stang et al. But the rapid development of the field demands the design and synthesis of more sophisticated and unprecedented molecular architectures beyond the existing molecular library. For this purpose, the use of flexible building blocks is a popular approach to achieve unusual structural features. Though a large number of rigid/semi-rigid donors has been extensively used for this purpose, the use of flexible metal-acceptors is very rare. Our group has been actively involved in this field to develop efficient self-assembled 2D/3D architecture for the sensing of nitroaromatic explosives, small molecules and various anions. The present study introduces a novel benzil-based semi-rigid bisplatinum(II) acceptor bisPt-NO$_3$ which was utilized to obtain four new [2 + 2] metallamacrocycles (M$_1$–M$_4$) in almost quantitative yields by heating with equimolar amounts of the imidazole based ditopic donors (L$_1$–L$_4$) of different size and rigidity in 1:1 chloroform/acetone solvent mixture (Scheme 1). All the macrocycles were fully characterized by multinuclear NMR and ESI-MS spectrometry. Semi-empirical PM6 geometry optimization was carried out for all the four macrocycles to illuminate their structures.
Experimental Section

Materials and Methods

The bisplatinum intermediate bisPt-I was synthesized under dry nitrogen atmosphere using standard Schlenk techniques. All the solvents were dried and freshly distilled prior to the reactions. The starting materials 4,4'-dibromobenzonitrile, imidazole, anthracene, carbazole, dibromo-p-xylene, dibromo-m-xylene and other reagents were purchased from various commercial sources and used without further purification. All four donors (L₁–L₄) were synthesized by following literature procedures.[8]

NMR spectra were recorded in a Bruker 400 MHz spectrometer and the chemical shifts are reported in ppm with respect to standard reference tetramethylsilane (Me₄Si; δ = 0.00 ppm) or the solvent peaks arising due to their incomplete deuteration (δ = 7.26 for CDCl₃, δ = 194.40 for CD₃CN in case of ¹H NMR). ESI-MS spectra were recorded in an Agilent 6538 Ultra-High Definition (UHD) Accurate Mass Q-TOF spectrometer. IR experiments were done in a Bruker ALPHA FTIR spectrometer. A Perkin-Elmer Lambda 750 UV/Vis spectrophotometer was used for recording absorbance spectra, while the emission spectra was obtained using HORIBA Jovin Yvon Fluoromax-4 spectrometer. HPLC grade solvents were used for UV/Vis and fluorescence spectroscopic studies.

Synthesis of 4,4'-Diethynylbenzil (1)

An oven-dried 100 mL two-neck round bottom flask was charged with 4,4'-dibromobenzonitrile (2.0 g, 5.43 mmol), trans-[PtCl₂(PPh₃)₂] (0.114 g, 0.16 mmol) and Cu (0.031 g, 0.16 mmol) and 70 mL of dry NεT, under nitrogen atmosphere. Then triphenylphosphine (0.114 g, 0.16 mmol) with CuI (0.0074 g, 0.038 mmol) was placed in an oven-dried Schlenk flask and 15 mL dry toluene-di-isopropyl ether. The mixture was added to the chloroform solution of the reaction (as monitored by TLC), the solvent was evaporated completely and the crude product was purified by column chromatography in silica gel matrix using 1:1 chloroform–hexane mixture to obtain pure desilylated 4,4'-diethynylbenzil (1) as a pale brown powder (86%). Anal calc.: C, 39.23; H, 5.98; N, 7.37. Found: C, 39.27; H, 5.92; N, 7.40.

Synthesis of bisPt-I

A mixture of 4,4'-diethynylbenzil (1; 1.00 g, 0.38 mmol), trans-[PtI₂(PPh₃)₂] (0.796 g, 1.16 mmol) and CuI (0.031 g, 0.16 mmol) was added to an oven-dried Schlenk flask and 15 mL dry toluene-di-isopropyl ether. The mixture was stirred for 24 h at room temperature under nitrogen atmosphere until TLC confirmed the completion of the reaction. The solvent was evaporated completely and the crude product was purified by silica-gel column chromatography using 1:1 ethyl acetate–hexane mixture as eluent to get iodide analogue bisPt-I as yellow solid in 64% yield (Scheme 2). Anal calc.: C, 39.23; H, 5.98; N, 7.37. Found: C, 39.23; H, 5.98; N, 7.37. The ⁱH NMR (CDCl₃, 400 MHz): δ = 7.83 (d, J = 8.82 Hz, 4H, Ar-H), 7.34 (d, J = 8.78 Hz, 4H, Ar-H), 3.33 (s, 2H, alkylene-He): ¹³C NMR (CDCl₃, 100 MHz): δ = 193.42, 133.13, 132.84, 132.57, 130.37, 130.13, 104.18, 100.30, 0.23. A solution of 4,4'-trimethylysilyl-1,3-benzil (1.5 g, 3.72 mmol) in dichloromethane–methanol (1:1) mixture was stirred with potassium carbonate (515 mg, 3.72 mmol) for 2 h at room temperature. The solvent was evaporated completely and the solid residue was filtered through silica gel chromatography in silica gel by eluting with cold diethyl ether.

Spectral data of bisPt-NO₂: ¹H NMR (CDCl₃, 400 MHz): δ = 7.83 (d, 4H, Ar-H), 7.28 (d, 4H, Ar-H), 1.91 (m, 24H, CH₂-), 1.19 (m, 36H, CH₃-). ³¹P NMR (CDCl₃): δ = 20.21.

Synthesis of M₁

Reaction of carbozal-based donor L₄ (4.76 mg, 0.0145 mmol) with bisPt-NO₂ gave macrocycle M₁ in an isolated yield of 86%. Anal calc.: C, 37.24; H, 5.36; N, 5.67. Found: C, 37.25; H, 5.34; N, 5.65.

Synthesis of M₂

Reaction of donor L₃ (3.45 mg, 0.0145 mmol) with bisPt-NO₂ gave the corresponding M₂ in an isolated yield of 83%. Anal calc.: C, 37.24; H, 5.36; N, 5.67. Found: C, 37.24; H, 5.37; N, 5.66.

Synthesis of M₃

Macrocycle M₃ was isolated in almost quantitative yield by the reaction of L₂ (3.45 mg, 0.0145 mmol) with bisPt-NO₂. Anal calc.: C, 37.24; H, 5.36; N, 5.67. Found: C, 37.24; H, 5.35; N, 5.65.

Synthesis of M₄

Macrocycle M₄ was isolated in almost quantitative yield by the reaction of L₁ (3.45 mg, 0.0145 mmol) with bisPt-NO₂. Anal calc.: C, 37.24; H, 5.36; N, 5.67. Found: C, 37.24; H, 5.35; N, 5.66.

Scheme 2. Schematic representation of the synthesis of 4,4'-bis[trans-Pt(PPh₃)₂(NO₂)]ethynil]benzil (bisPt-NO₂) from 4,4'-diethynylbenzil (1) and trans-PtI₂(PPh₃)₂.
[M−3NO−]3+, 678.73 [M−4NO−]4+. IR (υ/cm−1): 2965.38, 2114.79, 1660.97.

Synthesis of M

Macrocycle M was obtained by the reaction of 1,4-MeCN (4.9 mg, 0.0145 mmol) with bisPt-NO3 in 77% isolated yield. Anal. calcd for C31H24N4O5P2: C, 51.83; H, 3.59; N, 5.55. Found: C, 51.36; H, 3.49; N, 5.50. IR (υ/cm−1): 3061.57, 2996.60, 2113.69, 2662.72.

X-ray Data Collection and Structure Refinements

A suitable single crystal of the iodide analogue bisPt-I was mounted on a crystal mounting loop after coating with paratone oil and diffraction on a Bruker SMART APEX CCD diffractometer using graphite-monochromatic Mo-Kα radiation (0.7107 Å) at 293 K. The structure was solved by direct methods using SHELX-97 software incorporated with WINGX package. [9] Empirical absorption corrections were applied with SADABS. All the non-hydrogen atoms were refined with anisotropic displacement coefficients while the hydrogen atoms were fixed to their geometric positions suggested by the program.

Results and Discussion

Design, Synthesis and Characterisation of bisPt-NO3

Design of a bisplatinum(II) acceptor compatible with various type of donors can be obtained by incorporating a ‘not so rigid’ backbone which will allow the acceptor to adjust its binding sites in accordance with the incoming donor coordination environment. However, the restricted flexibility will retain its characteristic structural coding as a building unit. After thorough survey of the literature, the benzil moiety has been judiciously selected for this purpose due to its unique structural features (long C–C bond of ~1.54 Å and conformational flexibility) as earlier reported for some of its derivatives. [10] The C=O groups in the benzil moiety are found to reside in different planes as a consequence of the strong electronic repulsion between the oxygen atoms which make ‘cis’ conformation highly unfavourable. On the other hand, the strong electron withdrawing nature of the oxygen restricts the delocalization of electron density between two C=O moieties effectively imposing ‘only’ single bond character to the carbonyl C–C bond, resulting in a twisted geometry intermediate between cis and trans conformations of the benzil moiety.

To synthesize the desired bisplatinum acceptor bisPt-NO3, 4,4′-dibromobenzil was first converted to 4,4′-diethynylbenzil (1) by a Sonogashira coupling reaction with trimethylsilylacetylene followed by desilylation of the alkyne groups with potassium carbonate.

Subsequently, 4,4′-dithylnylbenzil 1 was incorporated with two platinum centres by Cu(i)-catalysed metal insertion reaction with trans-Pt2(PEt3)2 to obtain the iodide analogue bisPt-I in 64% yield (Scheme 2). bisPt-I was fully characterised by multi-nuclear (1H, 13C, 31P) NMR spectroscopy, IR and ESI-MS spectrometry. The 1H NMR spectrum consists of two doublets in the aromatic region (δ = 7.32 ppm, δ = 7.32 ppm, δ = 7.32 ppm, δ = 7.32 ppm, δ = 7.32 ppm), along with two multiplets in the upfield region (δ = 2.25, δ = 2.25, δ = 2.25, δ = 2.25, δ = 2.25), showing the twisted conformation in the solid state. Hydrogen atoms are omitted for clarity.

Table 1. Crystallographic data and structure refinement parameters for bisPt-I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C31H24N4O5P2</td>
</tr>
<tr>
<td>Crystal formula</td>
<td>1372.82</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C</td>
</tr>
<tr>
<td>λ(Mo Kα) Å</td>
<td>0.71073</td>
</tr>
<tr>
<td>a, Å</td>
<td>39.683(14)</td>
</tr>
<tr>
<td>b, Å</td>
<td>8.831(3)</td>
</tr>
<tr>
<td>c, Å</td>
<td>14.908(5)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90.0</td>
</tr>
<tr>
<td>β, deg</td>
<td>90.0</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90.0</td>
</tr>
<tr>
<td>V, Å3</td>
<td>5198(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>ρ, g cm−3</td>
<td>1.754</td>
</tr>
<tr>
<td>μ, mm−1</td>
<td>6.717</td>
</tr>
<tr>
<td>GOF</td>
<td>1.226</td>
</tr>
<tr>
<td>R1, (I &gt; 2σ(I))</td>
<td>0.0380</td>
</tr>
<tr>
<td>wR2</td>
<td>0.1181</td>
</tr>
</tbody>
</table>

*GOF = {Σ[w(Fo2−Fo)2] / (n−p)}1/2, where n and p denotes the number of data points and the number of parameters, respectively.

Fig. 1. 1H (left) and 31P (right) NMR spectra of bisPt-I recorded in CDCl3.

Fig. 2. Crystal structure of bisPt-I showing the twisted conformation in solid state. Hydrogen atoms are omitted for clarity.
Supramolecular chemistry

ceptor bisPt-NO₃ was synthesized by treating bisPt-I with 2.1 equiv. silver nitrate in a chloroform–methanol mixture, which was also characterized by multinuclear NMR spectroscopy (Supplementary Data, Fig. S9, S10). Interestingly, exchange of iodine caused a shift in the peak position from δ = 8.72 ppm to δ = 20.21 ppm in the 31P NMR spectrum.

The diffraction quality single crystals were obtained by the slow evaporation of dichloromethane–hexane solution of bisPt-I at room temperature. bisPt-I crystallised in monoclinic crystal system in the C2/c space group (Table 1). The solid-state structure shows that the two C=O groups of the benzil moiety are not exactly trans-oriented, instead twisted along the C–C bond possessing a torsional angle of –113.50(3)° (ΦO-C-C-O). Moreover, the C–C bond distance is 1.535(16) Å and hence suggesting single bond character (Table 2).

The two platinum centres are 16.240(89) Å apart from each other describing a ~122° bite angle with respect to the centroids of the carbonyl carbon atoms making it a unique building block. The phosphorous atoms of the trans-blocking PEt₃ groups are situated outside the benzoyl plane at an angle of around 35°.

### Synthesis and Characterisation of [2 + 2] Self-assembled Metallamacrocycles (M₁−M₄)

In order to check the versatility of the acceptor bisPt-NO₃ to become amenable for a range of donor systems, four imidazole-based ditopic donors (L₁−L₄) with different shapes, sizes and flexibility were selected to self-assemble their corresponding [2 + 2] metallamacrocycles. While L₄ being a carbazole-based rigid donor possessing an almost 90° donor angle, the L₂–L₃ donors are rather flexible in their coordination directionality. L₄ is functionalised with a fluorescent anthracene backbone.

In a general synthetic methodology, the iodide analogue bisPt-I was converted in situ to its nitrate analogue bisPt-NO₃ and then treated separately with an equivalent amount of the donors L₁−L₄ by heating overnight in chloroform–acetone solvent mixture to obtain self-assembled macrocycles M₁−M₄ (Scheme 1). The sharp single peak, along with two satellite peaks, in the 31P(¹H) NMR spectra appeared in the shielded region compared to the acceptor bisPt-NO₃ due to the enhanced platinum to phosphorous back donation upon ligand coordination demonstrating the formation of a single product in each case (Figs 3 and S12–S19, Supplementary Data).

Diffusion ordered spectroscopy (DOSY) of M₄ showed single diffusion coefficient for all the peaks and further
confirmed its purity (Fig. S20). The stoichiometry of the building blocks in $\text{M}_3$--$\text{M}_4$ were determined from the ESI-MS spectra where in each case the isotopic distribution patterns of the peaks matched with their respective theoretical patterns corresponding to the expected $[2 + 2]$ assemblies (Figs 4 and S22–S25). ESI-MS spectra of $\text{M}_3$ showed three sharp peaks at $m/z = 1508.48$, 984.65 and 722.98 (Fig. S22) corresponding to $[\text{M}_3^{-2\text{NO}_2}]^{4+}$, $[\text{M}_3^{-3\text{NO}}]^{4+}$ and $[\text{M}_3^{-4\text{NO}_2}]^{4+}$ fragments, respectively. Similarly for $\text{M}_3$ and $\text{M}_4$ (having identical molecular formulae), ESI-MS peaks were obtained at $m/z = 1418.50(\text{M}_2)$ and 1418.45($\text{M}_1$) (theoretical value = 1418.45), 926.75($\text{M}_3$) and 926.64($\text{M}_4$) (theoretical value = 925.64), 678.75($\text{M}_3$) and 678.73($\text{M}_4$) (theoretical value = 678.73) corresponding to the $[\text{M}_3/\text{M}_4^{-2\text{NO}_2}]^{4+}$, $[\text{M}_3/\text{M}_4^{-3\text{NO}}]^{4+}$ and $[\text{M}_3/\text{M}_4^{-4\text{NO}_2}]^{4+}$ fragments, respectively (Supplementary Data, Figs S23, S24). All the four macrocycles absorbed at 353 nm owing to the $\pi-\pi^*$ transition of the ethynyl acceptor (Fig. S29). $\text{M}_3$ shows strong fluorescence due to the presence of anthracene moiety with characteristic triple humped curve in the emission spectra (Fig. S30).

In order to investigate their structural nature, semi-empirical geometry optimizations using PM6 method were carried out which show $\text{M}_3$ forming a beautiful flat ring-shaped architecture where the furthest stretch is about 3.90 nm between the ethyl groups (Fig. 5) and also having inner diameters of 2.43 nm and 1.58 nm respectively. The $\text{M}_2$, $\text{M}_3$ and $\text{M}_4$ have similar kind of architectures where aromatic backbones of the donors are oriented perpendicular to the longer diagonal axis (Figs 5, S31–S34). Interestingly, $\text{M}_4$ has little bending near the acceptor sites shaping the molecule in a boat-like geometry (Fig. S34). In all the cases triethylphosphine groups were oriented outwards from the ring to release steric strain. The torsional angles associated with the acceptor (both $\Phi_{\text{C}_1/\text{C}_2/\text{C}_3}$ and $\Phi_{\text{C}_1/\text{C}_2/\text{C}_3}$) significantly vary in four structures over a range from 132.6° to 140.7° for $\Phi_{\text{C}_1/\text{C}_2/\text{C}_3}$ and from 133.2° to 139.4° for $\Phi_{\text{C}_1/\text{C}_2/\text{C}_3}$, which reflects the flexible donor binding capability of the acceptor bisPt-NO$_4$ (Table S1 Supplementary Data).

**Conclusions**

In conclusion, we have synthesized a new benzil-based semi-rigid Pt$_2$-organometallic acceptor bisPt-I and its nitrate analogue bisPt-NO$_4$ in high yields. Multinuclear NMR, and X-ray diffraction analysis of bisPt-I, unequivocally confirmed their formation. The benzil functionality was chosen due to its long carbon–carbon C–C bond and to investigate the effect of semi-rigidity on controlling the shape and size of final supramolecular architectures. The presence of unsaturated ethynyl functionality imparts further stability to keep the final molecular architectures intact under various experimental conditions. The stoichiometry (1:1) combination of bisPt-NO$_4$ with a series of ditopic imidazole donors ($\text{L}_1$–$\text{L}_3$) resulted in the formation of $[2 + 2]$ self-assembled metallacycles $\text{M}_1$–$\text{M}_4$ in quantitative yields. The purity and selective formation of $[2 + 2]$ metallacycles in each case was verified by various spectroscopic techniques and structural information of these assemblies was obtained through geometry optimisation with the PM6 semi-empirical method. To the best of our knowledge, these metallamacrocycles are the first examples of discrete supramolecular architectures obtained from benzil-based semi-rigid organometallic acceptor via metal–ligand coordination. Our group is now actively working to design various types of flexible/semi-rigid organometallic Pt(II) acceptors to generate a library of unprecedented functional metallamacrocycles.

**Supplementary Data**

Supplementary Data containing NMR, ESI MS, and electronic spectra and optimized coordinates is provided. CCDC 966747 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Acknowledgements**

B. R. is grateful to IISc Bangalore for a research fellowship. P.S.M thanks the Department of Science and Technology (DST), India, for financial support in the form of a Swarnajayanti fellowship.

Received: July 7, 2015

---

**References**


