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Self-Assembly in Inorganic Chemistry

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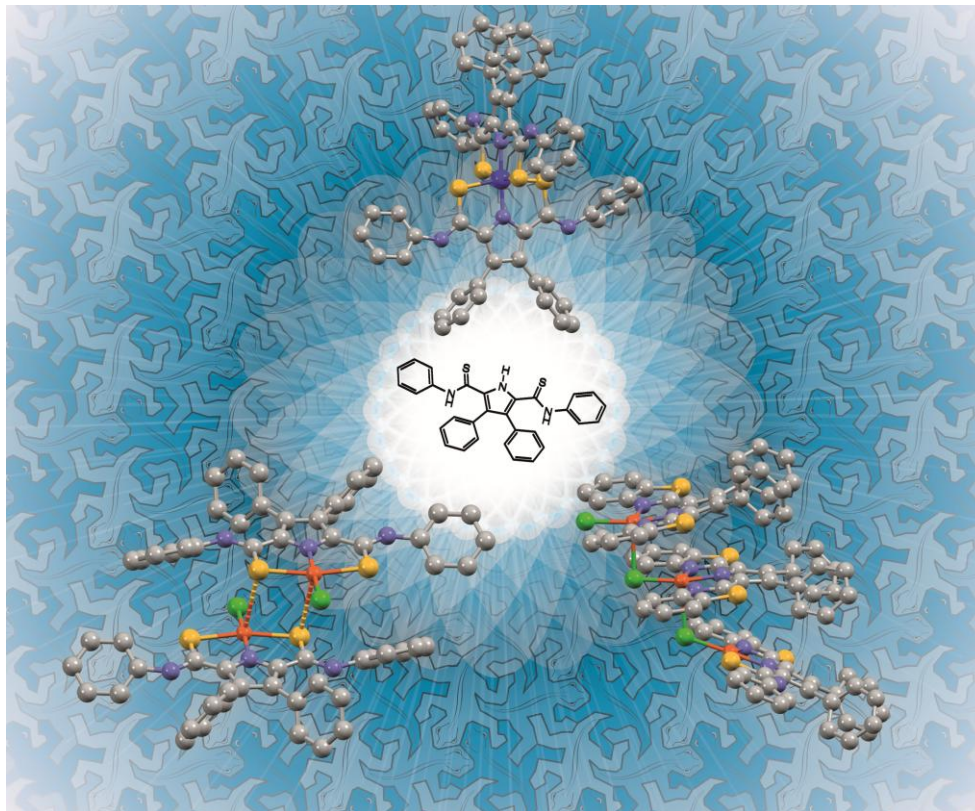


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Coordination-driven self-assembly of 2D-metallamacrocycles using a shape-selective Pt^{II}₂-organometallic 90° acceptor: design, synthesis and sensing study†

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Synthesis of a series of two-dimensional metallamacrocycles *via* coordination-driven self-assembly of a shape-selective Pt^{II}₂-molecular building unit incorporating carbazole-ethynyl functionality is described. An equimolar (1 : 1) combination of a Pt^{II}₂-organometallic 90° acceptor, **1**, with rigid linear ditopic donors (**L_a** and **L_b**) afforded [4 + 4] self-assembled octanuclear molecular squares, **2** and **3**, in quantitative yields, respectively [**L_a** = 4,4'-bipyridine; **L_b** = *trans*-1,2-bis(4-pyridyl)ethylene]. Conversely, a similar treatment of **1** with an amide-based unsymmetrical flexible ditopic donor, **L_c**, resulted in the formation of a [2 + 2] self-sorted molecular rhomboid (**4a**) as a single product [**L_c** = N-(4-pyridyl)isonicotinamide]. Despite the possibility of several linkage isomeric macrocycles (rhomboid, triangle and square) due to the different connectivity of **L_c**, the formation of a single and symmetrical molecular rhomboid (**4a**) as the only product is an interesting observation. All the self-assembled macrocycles (**2**, **3** and **4a**) were fully characterized by multinuclear NMR (¹H and ³¹P) and ESI-MS analysis. Further structural insights about the size and shape of the macrocycles were obtained through energy minimization using density functional theory (DFT) calculations. Decoration of the starting carbazole building unit with Pt-ethynyl functionality enriches the assemblies to be more π-electron rich and luminescent in nature. Macrocycles **2** and **3** could sense the presence of electron deficient nitroaromatics in solution by quenching of the initial intensity upon gradual addition of picric acid (PA). They exhibited the largest quenching response with high selectivity for nitroaromatics compared to several other electron deficient aromatics tested.

Introduction

In last few years, several functional nanoscopic metallamacrocycles of well defined sizes and shapes have evoked significant attention due to their potential for applications as chemosensors, catalysts, molecular vessels for trapping reactive intermediates and in host-guest chemistry study.¹ Among the various synthetic protocols utilized for the synthesis of metallamacrocycles, the metal mediated directional self-assembly has proven to be a very simple and highly efficient way for the construction of several fascinating architectures.² The most exciting factor for exploring metal–ligand directional self-assembly over traditional covalent synthesis is the ease of it to synthesize large structures in a single step using proper building units. It is noteworthy that Pd(II) and Pt(II) have long been the favorite choices for the purpose of

designing several molecular architectures because of their rigid square-planar coordination environment.^{3–5} A widely used class of donors for these acceptors are based on symmetrical polypyridyl with a few exceptions where the carboxylate based flexible oxygen donors have also been used to design neutral supramolecular architectures.³ Furthermore, the utilization of flexible linkers in the self-assembly event may often generate a pseudo-rigid molecular assembly with a large internal cavity, which further can be used to selectively encapsulate guest molecules of suitable shape/size and functionality.⁴ The first coordination driven self-assembly of a molecular square was reported by Fujita *et al.* in 1990. Since then a large number of molecular squares have been synthesized from 90° angular *cis*-blocked metal acceptor with equimolar amount of linear ditopic donor.⁶ However, in some cases the effort to synthesize a molecular square from a *cis*-blocked 90° acceptor in combination with a bulky ditopic donor were unsuccessful; instead they resulted in the formation of an oligomeric product because of the steric demands of bulky donors.² One possible way to overcome the steric hindrance of these bulky linkers is to synthesize a “shape-selective” acceptor with 90° directionality but the acceptor sites are far apart so as to reduce steric repulsion among the approaching

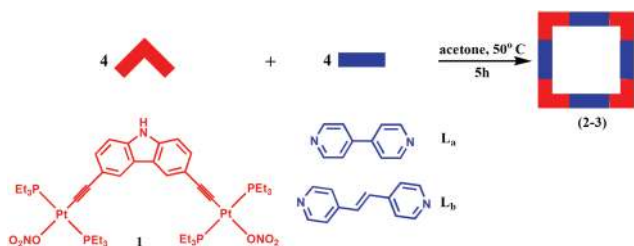
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† Electronic supplementary information (ESI) available: IR, NMR (¹H and ³¹P) and ESI-MS spectra of **2** including fluorescence quenching titration profile for **2** with picric acid. See DOI: 10.1039/c1dt10790a

donors.⁷ In continuation of our efforts of synthesizing suitable shape-selective acceptors, we have recently reported a new Pt^{II}-organometallic building block with 90° geometry and its [2 + 2] self-assembled macrocycles employing different flexible ditopic donors.⁸ As far as the application is concerned, significant progress has been made in the past few years on incorporating suitable functional groups into the resulted molecular assemblies in view of making artificial functional nanoscale molecular devices.⁹

Detection of trace analytes is a challenge in the field of chemical sensors and substantial efforts have been devoted in recent years to the development of suitable sensors for chemical explosives. The supersensitive detection of hidden chemical explosives is an essential needs for the protection of lives and variety of security related-applications.¹⁰ Among several known chemical explosives, nitro (-NO₂) derivatives like trinitrotoluene (TNT), dinitrotoluene (DNT) and picric acid (PA) are the common constituents in many buried landmines.¹¹ Among various transduction methods used, the fluorescence quenching, in particular, is considered to be an efficient tool for sensing chemical explosives in recent years owing to its high sensitivity and short response time.^{12,13}

Herein, we report the formation of two [4 + 4] metalla-macrocycles (**2** and **3**) by coordination-driven self-assembly of a shape-selective Pt^{II}-organometallic 90° acceptor 3,6-bis[*trans*-Pt(PEt₃)₂(NO₃)(ethynyl)]carbazole (**1**) and two linear ditopic donors (**L_a** and **L_b**) [**L_a** = 4,4'-bipyridine; **L_b** = *trans*-1,2-bis(4-pyridyl)ethylene] (Scheme 1). A similar combination of acceptor **1** with an amide-based flexible ditopic donor **L_c** [**L_c** = N-(4-pyridyl)isonicotinamide] yielded a [2 + 2] self-assembled molecular rhomboid as a single product in solution rather than the formation of several linkage isomeric complexes as expected due to the different connectivity of unsymmetrical linker **L_c**. Initially, the formation of self-assembled macrocycles was monitored by various spectroscopic techniques like IR, multinuclear NMR (¹H and ³¹P{¹H}) including ESI-MS spectrometric analysis and further structural analysis about the size and shape of the resulted macrocycles was obtained through energy minimization using DFT study. All the macrocycles exhibit luminescent behavior in solution due to the presence of Pt-ethynyl functionality and macrocycles **2** and **3** were tested as optical sensors for electron-deficient nitroaromatic compounds (NAC). The solution state emission intensity of the macrocycles **2** and **3** was quenched efficiently in the presence of nitroaromatic compounds. Interestingly, the non-responsive nature of macrocycles **2** and **3**, upon mixing of other electron-deficient aromatic compounds like benzoquinone, 4-methoxybenzoic acid and benzoic acid, make them suitable as selective sensing materials for nitroaromatics.



Scheme 1 [4 + 4] self-assembly of molecular squares **2** and **3** via an organometallic 90° acceptor **1** and linear ditopic donors (**L_a**–**L_b**).

Experimental section

Materials and methods

The building block 3,6-bis[*trans*-Pt(PEt₃)₂(NO₃)(ethynyl)]carbazole (**1**) was synthesized following our previously reported procedure under dry nitrogen atmosphere using standard Schlenk technique.⁸ All the solvents were dried and freshly distilled prior to reactions following the standard literature procedures. 4,4'-bipyridine (**L_a**), *trans*-1,2-bis(4-pyridyl)ethylene (**L_b**), 3,6-dibromocarbazole, isonicotinylchloride hydrochloride and 4-aminopyridine were purchased from Aldrich (USA) and used without further purification. N-(4-pyridyl)isonicotinamide (**L_c**) was synthesized following the reported procedure.¹⁴ All the nitroaromatic compounds (NAC) and other quenchers including benzoic acid (BA), anthraquinone (AQ), 4-methoxybenzoic acid (4-MeOBA) were of analytical grade and used as received without further purification. All the solvents used for photophysical studies were of spectroscopic grade. NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts (δ) in ¹H NMR spectra are reported in ppm relative to tetramethylsilane (Me₄Si) as internal standard (0.0 ppm) or proton resonance resulting from incomplete deuteration of the NMR solvents: CD₃NO₂ (4.33), CDCl₃ (7.26), CD₃CN (1.94) and CD₃OD (3.33). ³¹P NMR were recorded at 120 MHz and the chemical shifts (δ) are reported in ppm relative to external 85% H₃PO₄ at 0.00 ppm. High resolution ESI-MS spectral analyses of the self-assembled macrocycles were recorded on a Bruker Daltonics esquire 300 spectrometer using standard spectroscopic grade solvents (CH₃OH or CH₃CN/CH₃NO₂). IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer and electronic absorption spectra data were collected from Perkin Elmer LAMBDA 750 UV/visible spectrophotometer. Fluorescence emission studies were carried out on HORIBA JOBIN YVON Fluoromax-4 spectrometer.

General procedure for the synthesis of **2**, **3** and **4a**

To a stirred solution of the corresponding linear ditopic donor (**L_a**–**L_c**) in acetone (2 mL) was added a clear solution of the 90° acceptor **1** in acetone (2 mL) in 1 : 1 molar ratio. The initial suspension turns into a clear solution, which upon further stirring at 50 °C for 5 h, yielded the product as a precipitate. The solid product was washed several times with acetone and diethylether.

Macrocycle **2**

Building block **1** (24.0 mg, 0.02 mmol) and 4,4'-bipyridine **L_a** (3.1 mg, 0.02 mmol) were reacted in acetone (4 mL) to obtain **2**. Isolated yield: 86%. Anal. Calcd for C₂₀₀H₃₀₀N₂₀O₂₄P₁₆Pt₈: C, 44.28; H, 5.57; N, 5.16. Found: C, 44.63; H, 5.32; N, 5.41. ¹H NMR (CD₃OD, 400 MHz): δ 8.99 (d, 16H, Py-H _{α} , J = 16.2 Hz), 8.83 (s, 4H, NH-carbazole), 8.21 (s, 8H, H _{a} -carbazole), 7.98 (d, 16H, Py-H _{β} , J = 16.4 Hz), 7.45 (m, 16H, H _{b,c} -carbazole), 1.90 (m, 96H, CH₂-ethyl), 1.22 (m, 144H, CH₃-ethyl). ³¹P NMR [CH₃NO₂ (CDCl₃ external), 120 MHz]: δ 17.09 (s, ¹J_{Pt-P} = 1721.4 Hz). IR (KBr): ν = 2120.4 cm⁻¹ for ethynyl group. ESI-MS (m/z): 1294.21 [2 – 4NO₃⁻]⁴⁺, 1264.71 [2 – 4NO₃⁻ – PEt₃]⁴⁺, 1022.97 [2 – 5NO₃⁻]⁵⁺, 975.77 [2 – 5NO₃⁻ – 2PEt₃]⁵⁺, 842.14 [2 – 6NO₃⁻]⁶⁺, 802.80 [2 – 6NO₃⁻ – 2PEt₃]⁶⁺, 696.12 [2 – 7NO₃⁻ – PEt₃]⁷⁺, 616.10 [2 – 8NO₃⁻]⁸⁺.

Macrocycle 3

Building block **1** (24.0 mg, 0.02 mmol) and **L_b** (3.6 mg, 0.02 mmol) were reacted in acetone (4 mL) to obtain **3**. Isolated yield: 82%. Anal. Calcd. for C₂₀₈H₃₀₈N₂₀O₂₄P₁₆Pt₈: C, 45.18; H, 5.61; N, 5.07. Found: C, 44.83; H, 5.76; N, 4.82. ¹H NMR (CD₃OD, 400 MHz): δ 8.80 (d, 16H, Py-H_α, *J* = 17.6 Hz), 8.56 (s, 4H, NH-carbazole), 7.93 (d, 16H, Py-H_β, *J* = 14.4 Hz), 7.76 (s, 8H, H_a-carbazole), 7.36 (m, 16H, H_{b,c}-carbazole), 6.58 (s, 8H, H-ethylene), 1.91 (m, 96H, CH₂-ethyl), 1.25 (m, 144H, CH₃-ethyl). ³¹P NMR (CD₃OD, 120 MHz): δ 15.90 (s, ¹*J*_{Pt-P} = 1723.08 Hz). IR (KBr): ν = 2120.3 cm⁻¹ and 1610.4 cm⁻¹ for ethynyl and ethylene groups, respectively. ESI-MS (*m/z*): 1320.24 [**3** - 4NO₃]⁴⁺, 1290.74 [**3** - 4NO₃ - PEt₃]⁴⁺, 859.49 [**3** - 6NO₃]⁶⁺, 727.80 [**3** - 7NO₃]⁷⁺, 647.12 [**3** - 8NO₃ + H₂O]⁸⁺, 629.12 [**3** - 8NO₃]⁸⁺.

Macrocycle 4a

Building block **1** (24.0 mg, 0.02 mmol) and **L_c** (4.0 mg, 0.02 mmol) were reacted in acetone (4 mL) to obtain **4a**. Isolated yield: 80%. Anal. Calcd. for C₁₀₂H₁₅₂N₁₂O₁₄P₈Pt₄: C, 43.78; H, 5.47; N, 6.01. Found: C, 43.62; H, 5.26; N, 6.34. ¹H NMR (CD₃NO₂, 400 MHz): δ 8.98 (broad, 4H, Py-H_α), 8.64 (d, 4H, Py-H_{α2'}, *J* = 5.48 Hz), 8.27 (broad, 4H, Py-H_β), 8.16 (d, 4H, Py-H_{β2}, *J* = 5.84 Hz), 8.06 (s, 4H, H_a-carbazole), 7.46 (m, 8H, H_{b,c}-carbazole), 1.97 (m, 48H, CH₂-ethyl), 1.26 (m, 72H, CH₃-ethyl). ³¹P NMR (CD₃NO₂, 120 MHz): δ 16.42 (s, ¹*J*_{Pt-P} = 1729.2 Hz), 15.77 (s, ¹*J*_{Pt-P} = 1716.6 Hz). IR (KBr): ν = 2123.20 cm⁻¹, 1691.1 cm⁻¹ and 3218.09 cm⁻¹ for ethynyl, amide-CO and amide-NH groups, respectively. ESI-MS (*m/z*): 1337.24 [**4a** - 2NO₃]²⁺, 1314.24 [**4a** - 2NO₃ - PEt₃ + 2H₂O]²⁺, 870.82 [**4a** - 3NO₃]³⁺, 637.62 [**4a** - 4NO₃]⁴⁺.

Fluorescence quenching study

A 2 mL stock solution (1.0 × 10⁻⁶ M) of the macrocycle (**2** or **3**) in DMF was placed in a quartz cell of 1 cm width and the quencher stock solution (1.0 × 10⁻³ M) 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 macrocycles were excited at λ_{ex} = 324 nm and their corresponding emission wavelengths were monitored from λ_{em} = 368 nm onwards. For all the measurements both excitation and emission slit widths were 5 nm. Appearance of a new broad peak at ~480 nm for **2** and ~469 nm for **3** was noticed upon the gradual addition of picric acid along with the significant fluorescence quenching of initial fluorescence intensity of the macrocycles (**2** and **3**). Analysis of the normalized fluorescence emission intensity (*I*₀/*I*), as a function of increasing quenchers concentration [*Q*], was well described by the Stern–Volmer equation: *I*₀/*I* = 1 + *K*_{SV}[*Q*]. The Stern–Volmer binding constant was calculated from the slope of the Stern–Volmer plot.

Results and discussions

Synthesis and characterization of [4 + 4] self-assembled molecular squares **2** and **3**

In general, a molecular square can be prepared by [4 + 4] self-assembly of a *cis*-blocked 90° acceptor with a rigid linear donor. Although, a large number of tetranuclear molecular squares are

known, a higher nuclear square is very rare in the literature because of the difficulty in synthesis of multimetallic acceptor units.^{1–4} We report here the synthesis of Pt^{II}₈ octanuclear molecular squares using a shape-selective bimetallic Pt^{II}₂-building block. The mixing of a 90° acceptor, **1**, separately with two linear ditopic donors, **L_{a-b}**, in 1 : 1 molar ratio in acetone (4 mL) resulted in the formation of two cationic octanuclear molecular squares (**2** and **3**) after 5 h of stirring at 50 °C in high yields, respectively (Scheme 1). Both the molecular squares were fully characterized by IR, multinuclear NMR (¹H and ³¹P) and ESI-MS analysis. The formation of molecular squares was initially monitored by multinuclear NMR (¹H and ³¹P) and was consistent with the formation of a single and symmetrical product in both the cases (Fig. 1 and supporting information†).

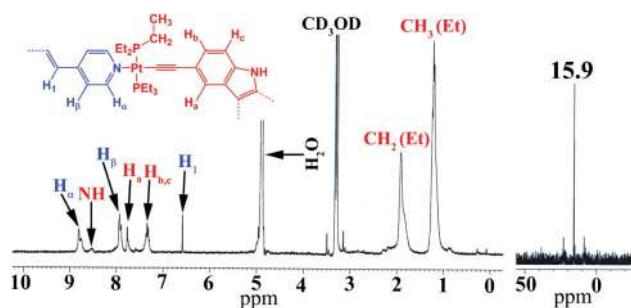


Fig. 1 ¹H (left) and ³¹P NMR (right) spectra of the molecular square **3** recorded in CD₃OD with the peak assignments.

The ³¹P {¹H} NMR spectra of **2** and **3** exhibited a sharp singlet (*ca.* 17.09 ppm for **2** and 15.90 ppm for **3**), which are shifted upfield with respect to the starting di-platinum 90° acceptor, **1**, by 3.0 ppm and 4.2 ppm, respectively, with the appearance of concomitant platinum satellites (Fig. 1 and supporting information†). Upfield shift of the phosphorous peaks indicated a ligand to Pt(II) electron donation due to coordination. Moreover, a significant decrease in coupling of flanking ¹⁹⁵Pt satellites (*ca.* Δ*J* = -1721.40 Hz for **2**, Δ*J* = -1723.08 Hz for **3**) compared to the starting 90° acceptor **1** (Δ*J* = -1848.36 Hz) is consistent with electron back donation from Pt-metal centers and imparting further support to the ligand to metal coordination. Likewise, the appearance of simple and sharp ¹H NMR signals indicated the formation of symmetrical macrocycles. In the ¹H NMR spectrum of each assembly, hydrogen atoms of the pyridine rings exhibited small downfield shifts (for α protons Δδ = 0.30–0.28 ppm; for β protons Δδ = 0.29–0.08 ppm) relative to uncoordinated **L_{a-b}** due to the loss of electron density that occurs upon coordination of the pyridine-N atom to the Pt(II) metal centers (Fig. 1 and supporting information†). The sharp NMR signals in both ¹H and ³¹P along with their high solubility of the resulted macrocycles in common organic solvents like CH₃NO₂, CHCl₃, CH₃OH, and CH₃CN ruled out the possibility of any polymer formation.

Formation of [4 + 4] self-assembled octanuclear macrocycles **2** and **3** was further attested by ESI-MS spectrometric analysis, where multiply charged ions corresponding to macrocycles were observed (Fig. 2 and supporting information†). The ESI-MS experiments were performed in an acetonitrile/nitromethane (4 : 1) mixture of the corresponding macrocycles. The multiply charged molecular ions for **2** at *m/z* = 1294.21 [**2** - 4NO₃]⁴⁺, 1264.71 [**2** - 4NO₃ - PEt₃]⁴⁺, 1022.97 [**2** - 5NO₃]⁵⁺, 975.77 [**2**

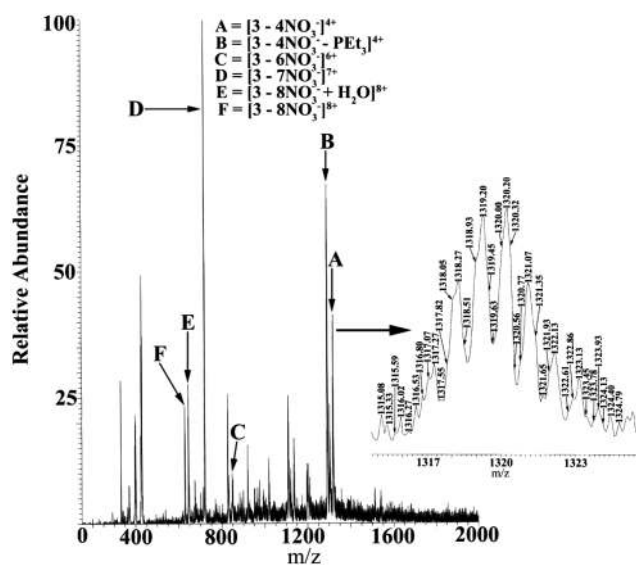


Fig. 2 ESI-MS spectrum of the macrocycle **3** recorded in $\text{CH}_3\text{CN}/\text{CH}_3\text{NO}_2$. Inset: isotopic distribution pattern of the fragment $[\text{3} - 4\text{NO}_3^-]^+$.

– $5\text{NO}_3^- - 2\text{PtEt}_3^+$, 842.14 $[\text{2} - 6\text{NO}_3^-]^{6+}$, 802.80 $[\text{2} - 6\text{NO}_3^- - 2\text{PtEt}_3]^{6+}$, 696.12 $[\text{2} - 7\text{NO}_3^- - \text{PtEt}_3]^{7+}$, 616.10 $[\text{2} - 8\text{NO}_3^-]^{8+}$; for **3** at m/z 1320.24 $[\text{3} - 4\text{NO}_3^-]^{4+}$, 1290.74 $[\text{3} - 4\text{NO}_3^- - \text{PtEt}_3]^{4+}$, 859.49 $[\text{3} - 6\text{NO}_3^-]^{6+}$, 727.80 $[\text{3} - 7\text{NO}_3^-]^{7+}$, 647.12 $[\text{3} - 8\text{NO}_3^- + \text{H}_2\text{O}]^{8+}$, 629.12 $[\text{3} - 8\text{NO}_3^-]^{8+}$ were found in the mass spectra and experimental isotopic distribution of the peak corresponding to $[\text{3} - 4\text{NO}_3^-]^{4+}$ fragment was consistent with the charge state (Fig. 2). Thus, the ESI-MS spectrometry confirmed the formation of octanuclear molecular squares.

Unfortunately, all efforts to obtain X-ray diffraction quality single crystals of macrocycles **2** and **3** have so far been unsuccessful. However, the analysis of multinuclear NMR (^1H and ^{31}P) in conjunction with ESI-MS spectroscopic studies confirmed the formation of $[4 + 4]$ self-assembled molecular squares. In view to gain further insights into the structural characteristics of the newly designed macrocycles, energy minimization of the macrocycles (**2** and **3**) has been done using density functional theory (DFT) calculations. The B3LYP functional was used for the DFT calculations, which were performed with the Gaussian 03 program. Two basis sets were employed, 6-31G for lighter elements (C, H, N, and O) and LanL2DZ for the heavier elements (Pt and P). A perspective view of the optimized structures of the macrocycles (**2** and **3**) is depicted in Fig. 3. An energy minimized view of the molecules indicated the formation of square-type macrocycles with the dimensions of $29.48 \text{ \AA} \times 29.36 \text{ \AA}$ for **2** and $31.69 \text{ \AA} \times 31.67 \text{ \AA}$ for **3**, respectively.

Synthesis and characterization of $[2 + 2]$ self-sorted molecular rhomboid (**4a**)

So far we have discussed the $[4 + 4]$ self-assembly phenomena involving a rigid 90° acceptor **1** and rigid symmetrical linear bipyridyl linkers L_a and L_b for the formation of molecular squares. In order to test the effect of ligand strength on the geometry of self-assembled products and to probe the self-selection of single linkage isomeric molecular entities, we have employed a nonsymmetric flexible ditopic donor L_c with the same 90° acceptor **1**. Because of

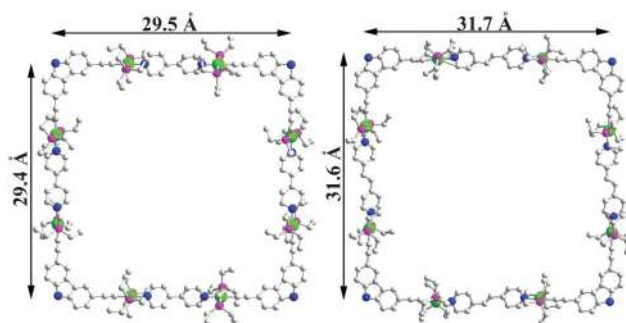


Fig. 3 Energy minimized structures of the macrocycles **2** (left) and **3** (right) (green = Pt, magenta = P, blue = N, red = O, grey = C). The hydrogen atoms have been removed for the sake of clarity.

the presence of flexible amide functional group as spacer between two coordinating pyridyl moieties, L_c can adopt two conformers, one with linear binding mode and other with angular binding mode (Fig. 4).

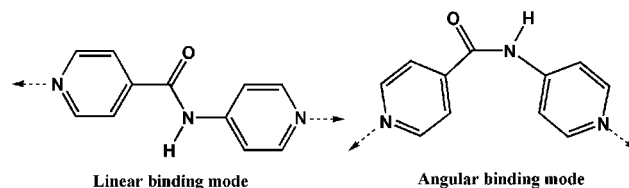
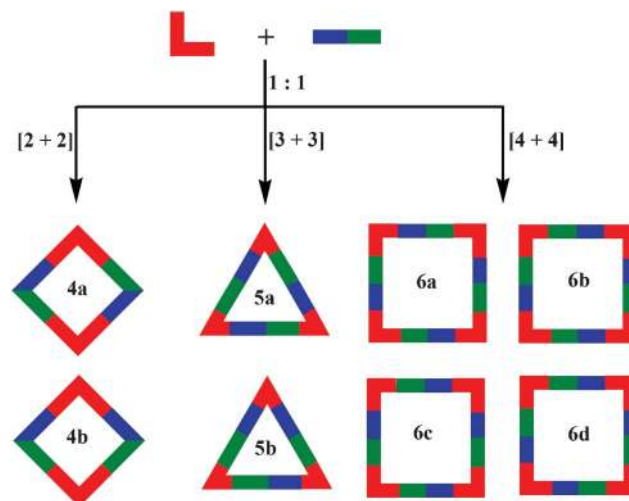


Fig. 4 Two possible linear (*trans*-) and angular (*cis*-) conformers of linker L_c .

One can envisage that self-assembly of such a flexible ambidentate ditopic donor and a rigid 90° acceptor may result in four linkage isomeric molecular squares (**6a–6d**) or two linkage isomeric molecular triangles (**5a–5b**) or two linkage isomeric molecular rhomboids (**4a–4b**) (Scheme 2). Due to different bonding connectivity, different isomers may display different characteristic NMR spectrum.¹⁵



Scheme 2 Possible macrocyclic linkage isomers from one-pot self-assembly of a 90° acceptor and a linear flexible ambidentate donor in 1 : 1 molar ratio.

^{31}P NMR study can give initial insight of the reaction mixture. Each metal center in the isomers **4a–4b**, **5a** and **6a** or **6d** is

coordinated to two different binding sites of two different linkers and hence in their ^{31}P NMR spectrum two equally intense peaks are expected. In the same way, such connectivity analysis results in four different peaks with intensity ratio 2 : 2 : 1 : 1 for the complex **5b**, four different peaks with intensity ratio 1 : 1 : 1 : 1 for complexes **6b** and **6c** in their corresponding ^{31}P NMR spectrum. But, to our surprise, treatment of the 90° acceptor **1** with the donor **L_c** in 1:1 molar ratio in acetone medium at 50°C after 5 h stirring resulted in exclusive formation of molecular rhomboid **4a** as judged by multinuclear (^1H and ^{31}P) NMR and ESI-MS spectrometric analysis (Scheme 3).



Scheme 3 [2 + 2] self-assembly of molecular rhomboid **4a** via an organometallic 90° acceptor, **1**, and a linear flexible ambidentate ditopic donor (**L_c**).

On addition of pale yellow acetone (2 mL) solution of **1** into a white slurry of **L_c** in acetone (2 mL) at 50°C , immediate consumption of the suspended particles and subsequent appearance of fluorescent yellow precipitate indicated the progress of the reaction. After stirring for 5 h, the reaction mixture was cooled down to room temperature and the precipitate was washed several times with cold acetone and cold diethyl ether to obtain pure macrocycle as yellow solid. Appearance of two sharp peaks at $\delta = 16.42$ ppm and 15.77 ppm with intensity ratio 1 : 1 with concomitant satellite peaks in the ^{31}P NMR spectrum (Fig. 5) of the bulk material primarily indicated self-selection of a single linkage isomeric macrocycle among **4a**, **4b**, **5b**, **6a** and **6d**. Moreover, the observed two peaks in ^{31}P NMR spectrum are

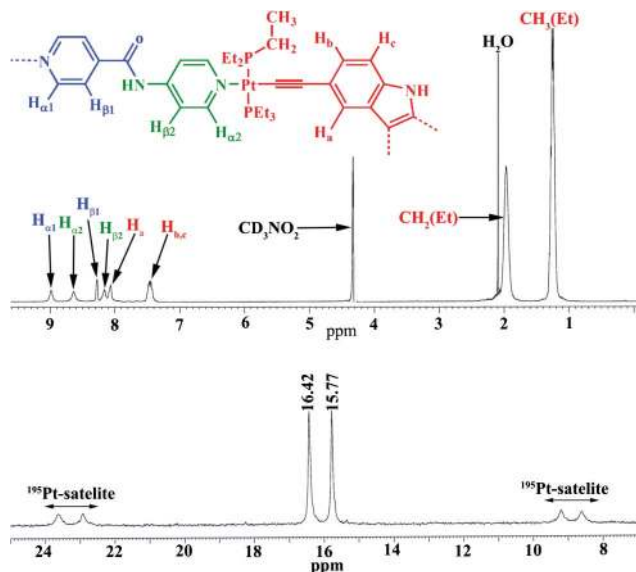


Fig. 5 ^1H NMR (above) and ^{31}P NMR (below) spectra of the molecular rhomboid **4a** recorded in CD_3NO_2 with the peak assignments.

considerably upfield shifted with respect to the starting acceptor **1** and thereby indicated ligand to metal coordination.

However, the ESI-MS spectrometric analysis of the reaction mixture indirectly supported the formation of [2 + 2] self-sorted molecular rhomboids (**4a** or **4b**) and ruled out the formation of other possible linkage isomeric macrocycles (**5a**, **6a** and **6d**). Although, ^{31}P NMR and ESI-MS spectroscopic analysis indirectly confirmed the presence of symmetrical and [2 + 2] self-sorted macrocycle, these techniques are helpless to distinguish the isomeric rhomboid **4a** and **4b** since, in both cases, two peaks of equal intensity are expected. Appearance of two peaks in the ^{31}P , and based on the previous results using nonsymmetrical linkers, we expect the formation of symmetrical isomer **4a** as a single product.^{30,3p,3r}

The electrospray ionization mass spectrometric (ESI-MS) analysis showed multiple charged molecular ions for [2 + 2] self-sorted molecular rhomboid (**4a**) (Fig. 6). The prominent peaks in the ESI-MS at the $m/z = 1337.24$, 1314.24 , 870.82 and 637.62 are assigned to $[\mathbf{4a} - 2\text{NO}_3^-]^{2+}$, $[\mathbf{4a} - 2\text{NO}_3^- - \text{PEt}_3 + 2\text{H}_2\text{O}]^{2+}$, $[\mathbf{4a} - 3\text{NO}_3^-]^{3+}$ and $[\mathbf{4a} - 4\text{NO}_3^-]^{4+}$ charged fragments, respectively. The experimentally observed isotopic distribution of the fragments $[\mathbf{4a} - 2\text{NO}_3^-]^{2+}$ and $[\mathbf{4a} - 3\text{NO}_3^-]^{3+}$ clearly supported the charge states and thus is in support of the [2 + 2] self-assembly (Fig. 6). The geometry of the rhomboidal structure of **4a** was predicted through computational simulation using DFT study (Supporting information†).

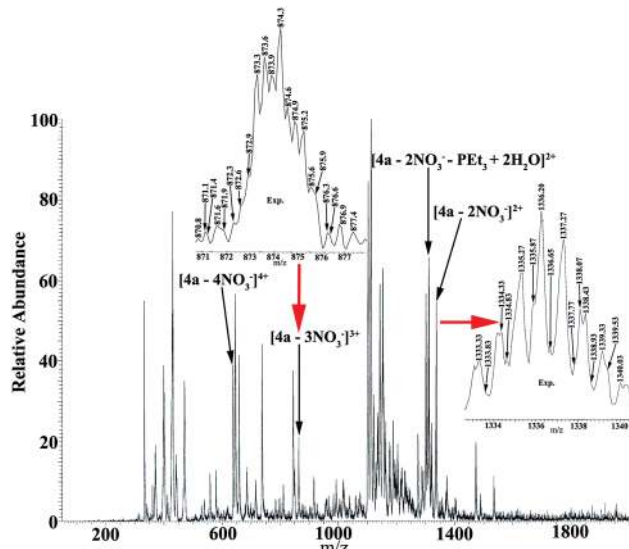


Fig. 6 ESI-MS spectrum of **4a** recorded in $\text{CH}_3\text{CN}/\text{CH}_3\text{NO}_2$. Inset represents the observed isotopic distribution corresponding to $[\mathbf{4a} - 2\text{NO}_3^-]^{2+}$ and $[\mathbf{4a} - 3\text{NO}_3^-]^{3+}$ fragments.

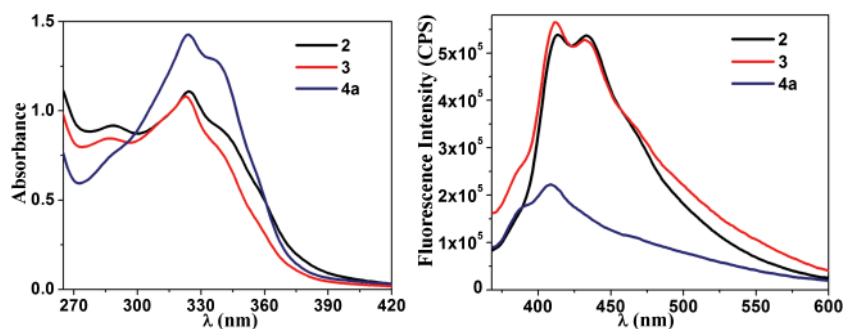
UV-Vis absorption and fluorescence studies of the macrocycles

Photophysical data of the macrocycles (**2**, **3** and **4a**) are summarized in Table 1. The absorption spectra of the macrocycles (**2**, **3** and **4a**) in DMF (1.0×10^{-6} M) show peaks at $\lambda = 288$ nm, 324 nm and 341 nm for macrocycle **2**, $\lambda = 287$ nm, 322 nm and 340 nm for **3** and $\lambda = 286$ nm, 324 nm and 337 nm for **4a** (Fig. 7). The peaks in the range of 322 – 324 nm are tentatively assigned to metal to ligand charge transfer (MLCT), whereas the peaks in the range of 286 – 288 nm are ascribed to the intra/intermolecular π - π^* transitions. The emissions spectral

Table 1 Photophysical data of macrocycles **2**, **3** and **4a** in aerated DMF solution

Macrocycles	Absorption maxima λ_{max} (nm)	Molar extinction coefficient $10^4 \epsilon \text{ M}^{-1} \text{ cm}^{-1} [\lambda_{\text{max}} \text{ (nm)}]$	Fluorescence emission maxima at 298 K λ_{max} (nm)	Quantum Yield ^a (Φ)
2	288, 324 , 341 (sh)	111 (324)	413, 433	0.006
3	287, 322 , 340 (sh)	108 (322)	412 , 432	0.016
4a	386, 324 , 337 (sh)	143 (324)	388, 409	0.042

^a Using anthracene ($\Phi_f = 0.27$) as the fluorescence standard in ethanol at room temperature. Values in bold in columns II and IV represent the highest absorption (λ_{abs}) and emission (λ_{em}) maxima, respectively.

**Fig. 7** UV-visible (left) and fluorescence (right) spectra of macrocycles **2**, **3** and **4a** recorded in DMF solution ($1.0 \times 10^{-6} \text{ M}$) at room temperature.

(Fig. 7) data of macrocycles **2**, **3** and **4a** recorded in DMF ($1.0 \times 10^{-6} \text{ M}$) at room temperature are listed in Table 1. The observed emission patterns of the macrocycles are almost similar in nature and their high luminescence characteristic is attributed to the presence of unsaturated Pt-ethynyl functionality in the backbone. All the macrocycles were excited at $\lambda_{\text{ex}} = 324 \text{ nm}$ and their corresponding emission wavelengths were monitored from $\lambda_{\text{em}} = 368 \text{ nm}$. Both excitation and emission slit widths were 5 nm. The solution state emissive quantum yields of molecular squares **2**, **3** and **4a** were determined to be 0.006 for **2**, 0.016 for **3** and 0.042 for **4a** respectively, relative to that of anthracene ($\Phi = 0.27$ in ethanol).

Fluorescence quenching based detection of nitroaromatics

As discussed earlier, researchers have been focusing their effort in recent years on fluorescence quenching based detection of nitroaromatics for security and environmental reasons. The basic mechanism of sensing nitroaromatics involves the formation of a non-fluorescent charge-transfer (CT) complex between the electron poor nitroaromatics (quencher) and electron donor (fluorophore) or excited state electron transfer from the fluorophore to the electron deficient analyte. This leads to their detection by subsequent quenching of initial fluorescence intensity of the fluorophore. Several π -electron-rich fluorophores such as conjugated organic/inorganic polymers and various small molecule based aromatic fluorophores have been used greatly as potential candidates with high sensitivity for the nitroaromatics sensing.¹⁶

Despite their highly sensitive detection of explosives, the real time monitoring of the polymeric materials is limited, due to their multi-step conventional covalent synthesis, which is time consuming, laborious and usually ends in low yield of the targeted sensor materials. Two important criteria need to be considered in designing new fluorophores. Firstly, fluorophore should be π -electron-rich and highly oriented to enable the effective π - π

stacking with electron poor nitroaromatics. Secondly, fluorophore must be grafted with bulky substituent on the peripheral to prevent the intermolecular excimer formation through π - π interactions. Carbazole and its derivatives are appealing for this purpose because of their strong electron donor ability and high thermal stability.¹⁷ Based on this intrinsic electronic property, here we have synthesized several carbazole-based discrete metallamacrocycles to use as fluorescence sensors for explosive components. We report that the incorporation of carbazole and ethynyl moieties can enhance the electron donating ability of the macrocycles and thus increases the efficiency of the fluorescence quenching by oxidative nitroaromatic explosives. Moreover, the attachment of bulky triethylphosphine ($-\text{PEt}_3$) groups to the Pt-metal centers would prevent the excimer formation between the adjacent macrocycles; thereby maintaining the spectroscopic stability in the solution.

To demonstrate the ability of **2** and **3** for sensing nitroaromatic explosives, we first performed fluorescence quenching titration experiments of macrocycles (**2** and **3**) with picric acid (PA) in solution. Upon gradual addition of picric acid to a DMF solution of the macrocycles, the initial fluorescence intensity was quenched rapidly (Fig. 8 and supporting information†). Along with the efficient quenching of emission intensity, a new low-energy band at $\lambda = \sim 480 \text{ nm}$ for **2** and $\lambda = \sim 469 \text{ nm}$ for **3** appeared upon increasing concentration of picric acid. Like conjugated polymer based sensors, we believe that the reason for the observed quenching of initial fluorescence intensity and appearance of new low-energy band is attributed to the ground state charge-transfer (CT) complex formation between π -electron-rich macrocycles and electron-poor picric acid. An upward curvature type of Stern–Volmer plot was obtained from the fluorescence quenching titration profile. Quenching constants (K_{SV}) were determined from the slope of the plot (Fig. 8 and supporting information†). The Stern–Volmer binding constants $K_{\text{SV}} = 2.0 \times 10^4 \text{ M}^{-1}$ for **2** and $5.0 \times 10^4 \text{ M}^{-1}$ for **3** were obtained at low concentrations of picric

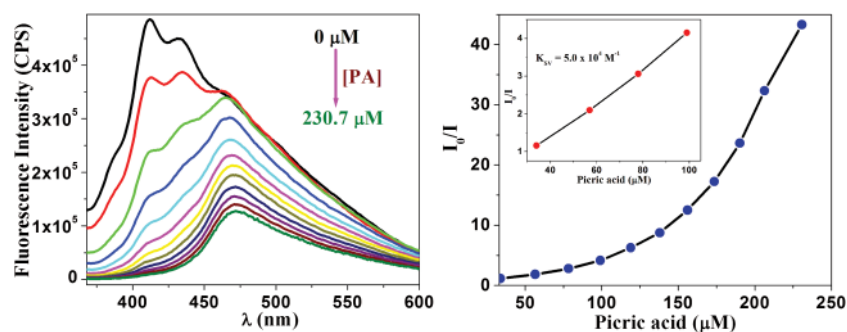


Fig. 8 Fluorescence quenching (left) of **3** (1.0×10^{-6} M) with picric acid (1.0×10^{-3} M) in DMF–methanol solution (excited at $\lambda_{\text{ex}} = 324$ nm and corresponding emission monitored from $\lambda_{\text{em}} = 368$ nm; excitation and emission slit width = 5 nm) and obtained Stern–Volmer plot (right). Inset: Stern–Volmer plot obtained at lower concentration of picric acid (right).

acid. According to the Stern–Volmer equation (see experimental section), for the static or dynamic quenching a linear Stern–Volmer plot is expected from the plot of I_0/I and picric acid concentration $[Q]$. However, the obtained non-linear plot suggests that the fluorescence quenching of macrocycles follows both static as well as dynamic quenching pathways through the ground state complex formation.¹⁸

We also have investigated the effect of other electron deficient aromatic compounds on the initial fluorescence intensity of the macrocycles (**2** and **3**) in order to check the selectivity of macrocycles towards nitroaromatic explosives. The obtained results are shown in Fig. 9, which indicates that both the macrocycles (**2** and **3**) show quite high quenching response towards nitroaromatic compounds over other analytes like anthraquinone (AQ), 4-methoxybenzoic acid (4-MeO-BA) and benzoic acid (BA). Since the reduction potential of these analytes are not significantly different from the nitro-substituted aromatic quenchers, we think that the observed quenching response of nitroaromatic compounds is due to the strong dipolar or electrostatic interactions of electron-poor quenchers with π -electron rich macrocycles. Among the tested nitroaromatics, picric acid exhibits the largest quenching response, which is attributed to its higher electron deficient in nature because of the strong electron withdrawing tendency of the substituted $-\text{NO}_2$ groups.

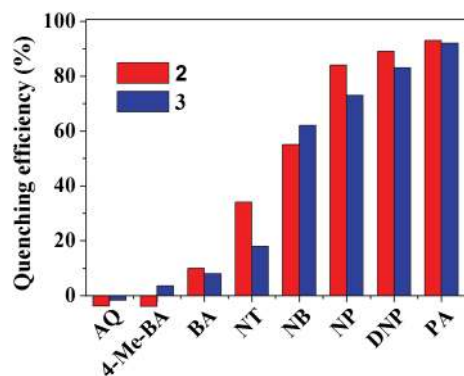


Fig. 9 Extent of fluorescence quenching of the macrocycles (**2** and **3**) observed upon the addition of various analytes. AQ = anthraquinone, 4-MeBA = 4-methoxybenzoic acid, BA = benzoic acid, NT = nitrotoluene, NB = nitrobenzene, NP = nitrophenol, DNP = dinitrophenol, PA = picric acid.

To further verify the formation of charge-transfer (CT) complex between macrocyclic squares and nitroaromatic quenchers, we carried out the electronic absorption study of macrocycle **3** with picric acid. A significant change in the initial absorption profile of macrocycle **3** was noticed upon the gradual addition of picric acid in methanol (1.0×10^{-3} M) to a DMF solution of (1.0×10^{-6} M) of **3** at room temperature. The initial strong absorption band of macrocycle **3** at $\lambda = 288$ nm and $\lambda = 324$ nm disappeared gradually, while a new sharp low-energy absorption band appeared at $\lambda = 378$ nm upon increasing the concentration of picric acid till the maximum picric acid concentration at $69.8 \mu\text{M}$ (Fig. 10). The appearance of a sharp absorption band along with the disappearance of original peaks of macrocycle is consistent with the formation of ground state charge-transfer (CT) complex between macrocycle **3** and nitroaromatic quenchers. The binding constant for the charge-transfer complex formation was evaluated using Benesi–Hilderbrand relationship. A reciprocal plot of changes in the initial absorption intensity of **3** with change in the concentration of the picric acid yields a linear correlation and the binding constant $K_a = 5.5 \times 10^3 \text{ M}^{-1}$ was obtained from the slope and intercept of the plot.

Conclusions

We report here the use of a shape-selective Pt^{II}_2 -organometallic 90° acceptor (**1**) to construct two $[4 + 4]$ self-assembled octanuclear molecular squares (**2** and **3**) and a $[2 + 2]$ self-sorted tetranuclear molecular rhomboid (**4a**) in good yields. Despite the possibility of formation of open chain oligomers, we demonstrate that discrete macrocycles incorporating carbazole ethynyl functionality are preferred. Most notably, the self-assembly reaction of **1** and linear rigid ditopic donors (L_{a-b}) favors the exclusive formation of $[4 + 4]$ molecular squares (**2** and **3**), whereas the use of semi-flexible amide based ditopic donor (L_c) resulted a $[2 + 2]$ self-sorted molecular rhomboid (**4a**). In spite of the possibility of several linkage isomeric macrocycles formation, exclusive formation of a symmetrical $[2 + 2]$ self-sorted rhomboid is attributed to the flexibility of the amide group of the linker. Though large numbers of molecular squares using a *cis*-blocked 90° acceptor in combination with linear ditopic donors are known, the present paper reports unusual homometallic octanuclear molecular squares from a dimetallic 90° acceptor. Because of their strong electron donating ability and the luminescence behavior in solution due to the presence of

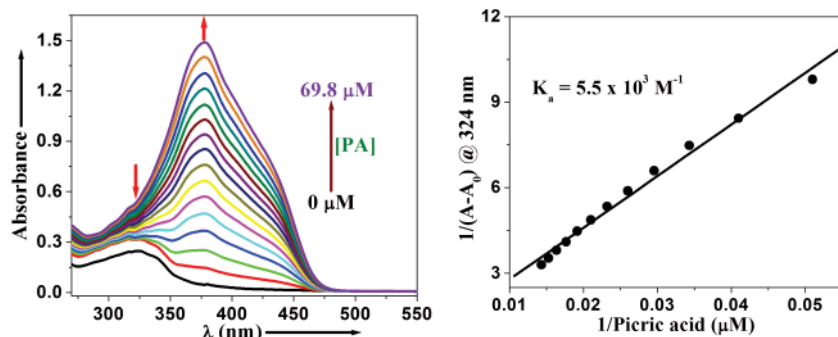


Fig. 10 Absorption spectral changes (left) of **3** in DMF (1.0×10^{-6} M) upon titrating with picric acid in methanol (0 – 69.8×10^{-6} M) at 25°C and its corresponding Benesi–Hilderbrand plot monitored at 324 nm (right).

Pt-ethynyl functionality and conjugated π -electrons, macrocycles **2** and **3** showed fluorescence sensing towards nitroaromatics. The solution phase emission intensity of the macrocycles was quenched rapidly and selectively in presence of electron deficient nitroaromatics, which are the common chemical constituents of many commercially available explosives.

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