Self-Assembled Molecular Squares Containing Metal-Based Donor: Synthesis and Application in the Sensing of Nitro-aromatics†

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Abstract

Self-assemblies between a linear Pt-based donor and ferrocene-chelated metallic acceptors produce novel heterometallic squares 4 and 5, which show fluorescence quenching upon addition of nitro-aromatics.

Coordination-driven self-assembly is one of the most useful protocols in contemporary supramolecular research due to its simple, rapid and efficient approach for the construction of complex molecular topologies with tailor-made properties like molecular reactors and host-guest chemistry.[1,2] Metal-based acceptors are widely employed to provide an accessible range of angles and shapes for the ligand-metal-ligand subunits of supramolecular assemblies.[3–5] Although various combinations between organic donors and metal-based acceptors have been used to design self-assembled metallomacrocycles[6,7], little attention has

been paid on the preparation of heterometallic supramolecules assembled from metal-based donors.[8]

Subsequent to the early developments, we aimed to design novel heterometallic electron-rich molecular squares using a metal-based donor in combination with *cis*-blocked square planar metallic acceptors. As a tactics to accomplish this purpose, ferrocene-chelated metallic acceptors were chosen since they preferred to provide the sufficient rigidity at corners which help in producing discrete molecular squares. Also, the linear donor *trans*-[(4-pyridylethynyl)$_2$Pt(PEt$_3$)$_2$] (**3**) containing Pt-ethynyl groups was selected to introduce another metallic centers on the sides of the squares, and to make the final assemblies π electron-rich. This electron-rich system can be anticipated for the detection of electron-poor guests like nitro-aromatics, the common chemical component for many explosives.[9] Interestingly, the presence of Pt-ethynyl functionality endows the supramolecules with photo-luminescent properties[10] which have been exploited for sensing applications.[11] Herein, we report the first examples of [4 + 4] self-assembled heterometallic molecular squares **4** and **5** from 90° metallic acceptors *cis*-(dppf)M(OTf)$_2$ [where M = Pd (**1**) or Pt (**2**)] and the Pt-based donor **3**. These new macrocycles can be utilized as a molecular sensor for the detection of nitro-aromatic explosives.

The molecular square **4** (Scheme 1) was obtained upon equimolar reaction of *cis*-(dppf)Pd(OTf)$_2$ (**1**) with **3** in CH$_2$Cl$_2$ with continuous stirring for 3 h at room temperature. The final product was isolated as a dark-red solid in a high yield (95%) by adding diethyl ether. The molecular square **4** has been fully characterized by multi-nuclear NMR, ESI-MS and X-ray diffraction study.

The ^{31}P{^{1}H} NMR spectrum (Figure 1; left) of **4** shows two singlets at δ 32.9 and 12.3 ppm corresponding to the phosphorous peak of metallic acceptor and metallic donor, respectively.

The downfield shift of the latter peak compared to **3** indicates the coordination of **3** to Pd(II). Consistently, ^{1}H NMR spectrum also shows the expected downfield shifts of the pyridyl protons of **3** due to coordination (Supporting Information).

Likewise, the reaction of the acceptor **2** with the metal-based donor **3** in a 1:1 molar ratio in CH$_2$Cl$_2$ led to the molecular square **5** (97%). The ^{31}P NMR spectra of **5** exhibited two sharp singlets at δ 11.85 ppm and 3.74 ppm originated from Pt donor and acceptor, respectively, (Figure 1; right) with a significant shift and decrease in coupling of the ^{195}Pt satellites as compared to the starting precursors. Additionally, the proton resonances of the pyridine rings exhibited downfield shifts resulting from the loss of electron density upon coordination of the pyridyl N atom to the Pt(II) metal center. Electrospray ionization mass spectrometry (ESI-MS) provided further evidence for the formation of molecular squares. For example, the ESI mass spectrum of **5** showed peaks at *m/z* 2094, 1533, and 1197 corresponding to the consecutive loss of triflate anions, [M-3CF$_3$SO$_3$]$^{3+}$, [M-4CF$_3$SO$_3$]$^{4+}$ and [M-5CF$_3$SO$_3$]$^{5+}$. The [M-3CF$_3$SO$_3$]$^{3+}$ and [M-5CF$_3$SO$_3$]$^{5+}$ peaks were isotopically resolved and well matched with the corresponding theoretical distribution patterns (Supporting Information).

Finally, crystal structures of **4** and **5** were determined by X-ray crystallography. Needle-shaped single crystals of **4** and **5** suitable for X-ray analysis by a synchrotron radiation were obtained by vapor diffusion of ether into acetone and CH$_2$Cl$_2$ solution, respectively. The structural analysis provides an unequivocal evidence of the molecular squares (Figure 2). Interstitial sites of the crystal structures for **4** and **5** are occupied by triflate counter anions and solvent molecules. Pd(II) and Pt(II) corners in **4** and **5** adopt square planar geometry. The bite angles of bidentate phosphine (P–Pd–P and P–Pt–P) in **4** and **5** are 99.9° and 100.5°

with a bond distance of 2.30 Å and 2.29 Å on average, respectively. The ethyl groups of the four PEt$_3$ moieties in **4** and **5** are oriented towards the interior of the macrocycle, which makes the hydrophobic pocket of the macrocycle. Interestingly, the complex **4** and **5** have two different sizes of molecular cavities; the complex **4** with a bent geometry of **3** has a square cavity with 5.5 Å × 5.8 Å, while the complex **5** with a straight geometry of **3** shows an elongated cavity with 20 Å × 4 Å.

Next, the optical properties of complexes **4** and **5** were investigated with absorption and emission studies. The UV-vis absorption spectra of **4**, **5** and the linker **3** were recorded in THF at ambient temperature. The spectra of **4** and **5** show absorption bands centered at 342 nm mainly due to metal to ligand or intramolecular charge transfer (Supporting Information).[12] Upon excitation at 342 nm, the THF solutions (5×10^{-6} M) of **4** and **5** exhibited intense photo-luminescence at around 380 nm and 396 nm for **4** and **5** (Supporting Information). On comparing the emission spectra of **3**, **4** and **5** we can tentatively assign that the emissive property of these squares is originated from the electron-rich and photoluminescent Pt-ethynyl donor center.

Since the observed intense emission could be served as a basis for the sensing of guest molecules, we finally tested the complex **4** for the detection of small molecules, particularly aromatic compounds which can potentially induce π–π interactions with the π electron system of the metallic donor. Although it was reported that conjugated aromatic compounds, self-assembled cages and polymers can be used as efficient fluorescent sensing materials,[11,13] however, 2-D metallomacrocycles have not been explored much for this purpose. We have studied a variety of analytes ranging from electron-rich to electron-poor derivatives. As shown in Figure 3, no significant quenching was noticed with electron-rich molecules like benzene, xylene and 2,4,6-TMP even at a high quencher concentration (Supporting Information). The similar quenching pattern was observed with polar aromatics like benzoic acid and phloroglucinol. The weak quenching responce towards carboxylic acid and phenols also ruled out the possibility of simple acid-base reaction of the analytes with molecular square **4**. Further extending the investigation successively to nitro-aromatics known as electron-poor molecules like 4-NB and 1,3,5-TNB, apparent quenching of photoluminiscence is noticed. Particularly, high quenching reponse is observed for 1,3,5-TNB guest. This result indicates that the increased electron-withdrawing nature of nitro-aromatics may induce the enhanced π–π interactions with the π electron-rich molecular square **4**. Since the UV-vis and NMR studies did not provide any evidence for the direct binding between the molecular square **4** and electron-deficient analytes, the observed emission quenching could be ascribed to weak interactions such as π–π interactions.

Since the electron-deficient nitro-aromatic molecules are the core constituents for the explosive materials, we have carried out detailed investigations by using picric acid (known as explosive) as a quencher and established the high sensitivity of **4** (Figure 4) and **5** (Supporting Information) toward picric acid. As shown in Figure 3, picric acid exhibits the higher quenching response than 1,3,5-TNB. The high polarizability of the picric acid could be another factor along with π–π interactions contributing to the high sensitivity. According to the emission quenching titrations with picric acid (Figure 4), the quenching constants (Ksv) which describe the quenching efficiency of the receptor were estimated to be ca. 6.72 $\times 10^5$ M^{-1} for **4** and 7.00×10^5 M^{-1} for **5**, pointing to the high sensitivity of molecular squares toward picric acid. As we have stated earlier that photoluminescence in molecular squares is originated from π electron-rich donor center **3**, to defend this statement we have also checked the quenching phenomena with donor **3** and metal acceptor **1** alone. As expected, some emission quenching in the presence of picric acid was noticed (Supporting Information) with **3** and no quenching was observed in case of **1** respectively. This result validates the involvement of donor center in the quenching process and also supports the

enhanced response of the these squares for the sensing of picric acid. These results signify that the strong π–π interactions facilitate energy transfer from the electron-rich donor of these squares to the electron-deficient nitro-aromatics and thereby the enhanced emission quenching is noticed. The similar Ksv values for **4** and **5** also support that the metallic donor **3** is mainly associated to the π–π interactions leading to emission quenching.

In summary, we have synthesized and characterized a new class of heterometallic squares possesing a metal-based donor via the self-assembly approach. These new, electron-rich and photoluminescent molecular squares have been examined for emission quenching effects with various aromatic compounds and they show the high quenching selectivity and sensitivity towards nitro-aromatics particularly picric acid. Thus we demonstrate that our unique self-assembled squares can be used as a molecular sensor for the detection of picric acid. The host–guest chemisty and detailed photophysical studies with the relavent self-assembled metallomacrocycles are in progress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Notes and references

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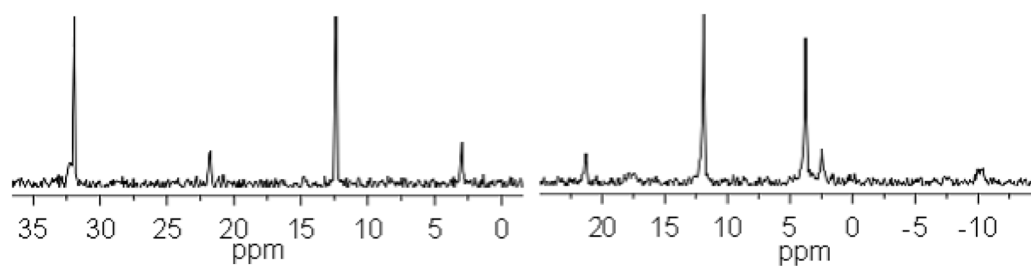
Fig. 1.
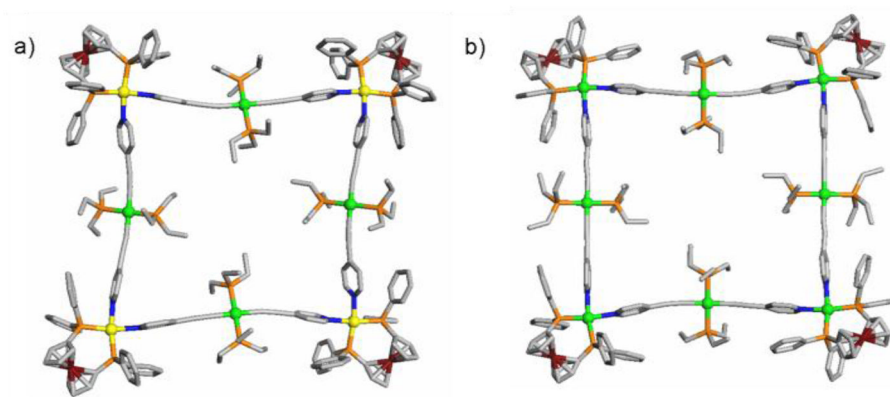^{31}P NMR spectra of the complexes **4** (left) and **5** (right).

Fig. 2.
X-ray crystal structure of **4** (left) and **5** (right). Color codes: yellow = Pd, green = Pt, brown = Fe, orange = P, gray = C. H-atoms are omitted for clarity and pertinent bond distances and angles are given in the text.
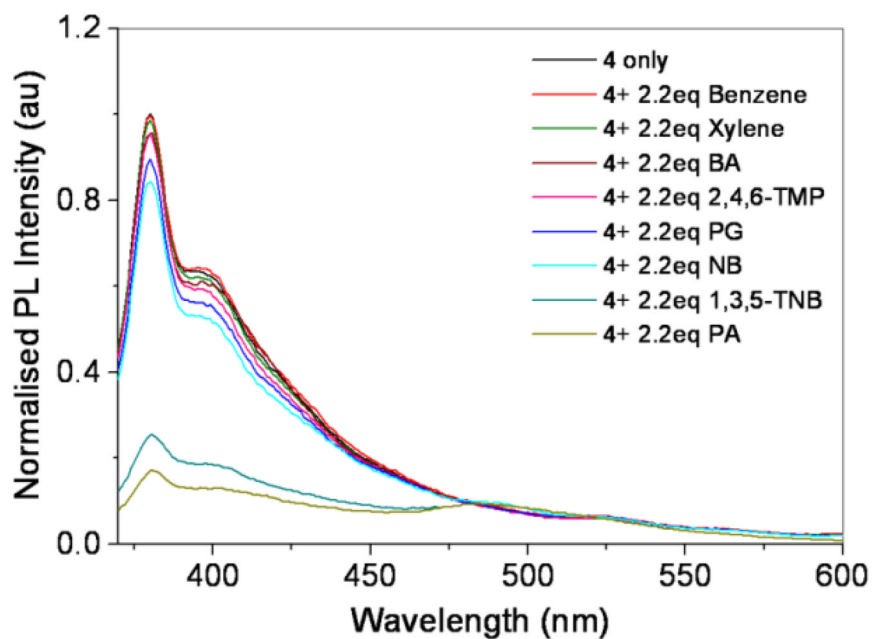
Fig. 3.
Emission quenching of **4** upon addition of the various guest molecules (1×10^{-4} M in THF). BA = benzoic acid, 2,4,6-TMP = 2,4,6-trimethylphenol, PG = phloroglucinol, 4-NB = 4-nitrobenzene, 1,3,5-TNB = 1,3,5-trinitrobenzene, PA = picric acid.
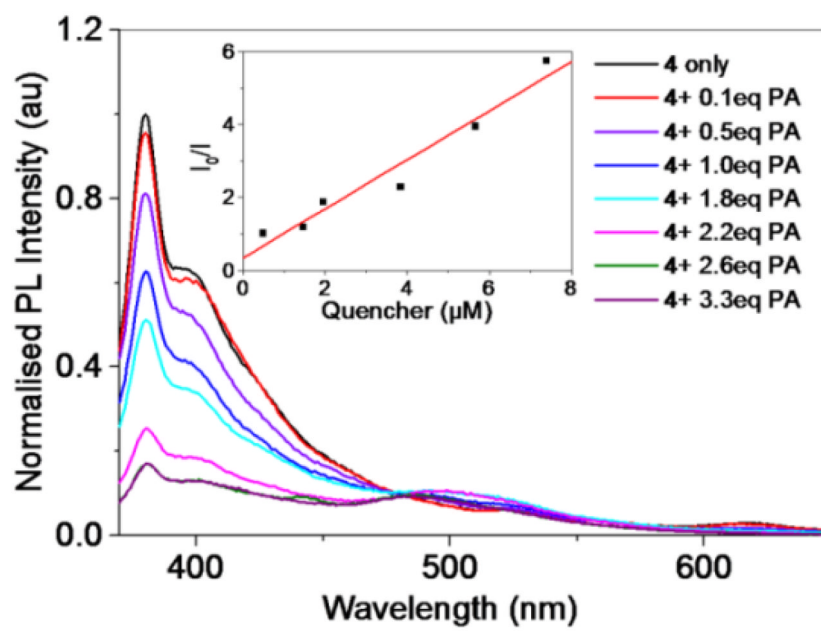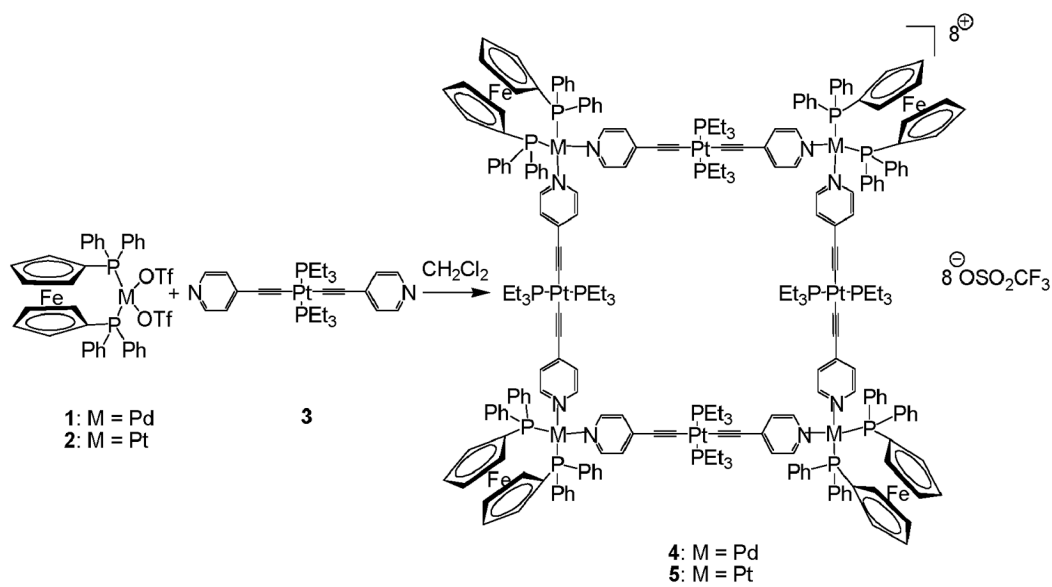
Fig.4.
Emission quenching of complex **4** by picric acid and Stern-Volmer plot (inset).

Scheme 1.
Self-assembly of the heterometallic squares **4** and **5**.