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Novel platinum–acetylide metallocycles constructed *via* a stepwise fragment coupling approach and their aggregation behaviour†

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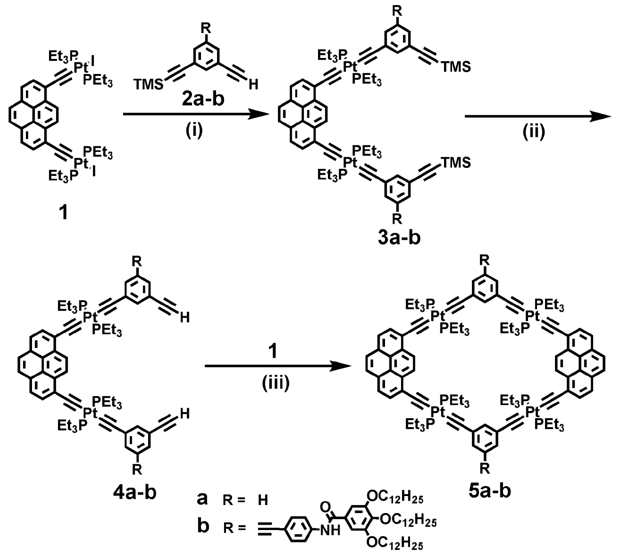
Through a stepwise fragment coupling approach, a family of novel platinum–acetylide metallocycles with well-defined shape and size were successfully constructed. Their aggregation behavior was investigated.

Macrocyclic host molecules have played important roles in the development of supramolecular chemistry.[1] The milestone research progress in crown ethers,[2a] cryptands,[2b] and spherands[2c] has laid the solid foundation of supramolecular chemistry as an independent discipline. With the development of supramolecular chemistry, a series of novel macrocyclic host molecules such as heteracalixaromatics,[3a,b] pillar[*n*]arenes,[3c] and [*n*]cycloparaphenylenes[3d] have been well investigated and new energy has been instilled into macrocyclic chemistry. Thus the design and construction of novel macrocyclic molecules has always been one of the driving forces to stimulate the development of supramolecular chemistry.

Recently, the design and self-assembly of nanostructured aggregates from macrocyclic molecules *via* a "bottom-up" strategy have attracted considerable attention. A great number of nano/micro-structured materials that form vesicle, fiber, microtube and microsphere structures through the supramolecular self-assembly of macrocycles have been reported. Some of these materials have presented wide applications in diverse fields such as supramolecular amphiphiles,[4a,b] supramolecular polymers,[4c] drug delivery,[4d] fluorescent sensors,[4e] organogels,[4f] *etc.* As an important functional linker, platinum(II) acetylide has been extensively explored in the areas of organometallic gels,[5a] solar cells,[5b,c] functional oligomers,[5d,e] and luminescent materials[5f] because of its unique π-conjugated character. For instance, we have prepared a series of novel platinum–acetylide complexes, which exhibited potential applications as luminescent organometallic gels.[6] However, compared to the considerable work on the supramolecular self-assembly of platinum–acetylide oligomers, very few studies have explored the aggregation of platinum–acetylide metallocycles, which might be due to the difficulties in their synthesis.

It should be noted that some previous methods employed to construct the covalent macrocycles often suffer from low yields. With the aim of constructing well-defined platinum–acetylide metallocycles with high efficiency, in this study, a stepwise fragment coupling strategy was explored to build well-defined organometallic macrocycles from predesigned platinum acetylide building blocks with appropriate geometrical structures. Moreover, by using the functionalized building blocks, a new metallocycle decorated with a hydrophobic long chain was obtained. Its aggregation behaviour has been well investigated.

Two novel metallocycles **5a-b** were prepared *via* a stepwise fragment coupling approach as shown in Scheme 1. According to the geometry of rhomboidal macrocycles, 60° fragment **1** and 120° linker **2a-b** were employed to build such metallocycles. The [2+1] fragment **3a** with a strictly geometric angle was prepared *via* a coupling



Scheme 1 Preparation of metallocycle **5a** and *exo*-functional metallocycle **5b**. *Reagents and conditions*: (i) CuI, THF, Et_2NH, rt; (ii) K_2CO_3, THF, MeOH, rt; and (iii) CuI, THF, Et_2NH, rt.

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reaction[7] of **1** and **2a** by using CuI as the catalyst. Then the deprotection reaction[7] of **3a** with K_2CO_3 in a mixture of methanol and THF led to the formation of the key intermediate oligomer **4a** with terminal alkynes. The final novel metallocycle **5a** was prepared through the [3+1] coupling of oligomer **4a** with fragment **1**, and isolated as a yellow solid in 55.6% yield. Through a similar method, another metallocycle **5b** decorated with a hydrophobic long chain was obtained in 63.8% yield.

The molecular structures of platinum–acetylide metallocycles **5a-b** were characterized using multiple nuclear NMR (^1H, ^{31}P, and ^{13}C), infrared spectroscopy, mass spectrometry, and elemental analysis. The ^1H NMR spectrum of **5a-b** showed only one set of signals, respectively, which indicated the formation of highly symmetrical structures. For instance, the ^1H NMR spectrum of metallocycle **5a** displayed two singlets at 7.88 and 8.74 ppm, respectively, which were assigned to the protons on 4-, 5- and 9-, 10-substituted location of pyrene, respectively. The doublet–doublet at 7.91–7.96 ppm attributed to the protons on 2-, 3-, 6-, 7-substituted location of pyrene was found as well. Moreover, the $^{31}P\{^1H\}$ NMR spectra of **5a-b** displayed a sharp singlet (*ca.* 11.97 ppm for **5a** and 12.53 ppm for **5b**) with two ^{195}Pt satellites ($J_{Pt–P}$, *ca.* 2371.8 Hz for **5a** and 2358.9 Hz for **5b**), respectively, which supported the existence of symmetrical metallocycles. Additionally, the investigation of MALDI-TOF mass provided further strong support for the formation of metallocycles **5a-b**. For instance, in the mass spectra, the peaks at m/z = 2469.75 for **5a** (0.03 Da deviation) and m/z = 4013.09 (0.08 Da deviation) for **5b**, attributed to the $[M + H]^+$ ion, were observed, respectively. These peaks were isotopically resolved and their isotopic resolution is in excellent agreement with the theoretical distribution (ESI†).

X-ray crystallographic analysis unambiguously established the structure of metallocycle **5a** as a discrete platinum–acetylide rhomboid (Fig. 1). Pale-yellow crystals suitable for single-crystal X-ray analysis were grown by slow diffusion of ethyl acetate into a chloroform solution of **5a** at room temperature. X-ray crystallographic analysis showed that the platinum–acetylide macrocycles featured a rhomboidal ring with a size of 1.40 × 1.43 nm. The ORTEP representation of the crystal structure showed that all atoms (except for the triethylphosphine ligands) lay approximately in the same plane. The platinum atoms in the complexes were found to adopt a slightly distorted *trans*-square-planar geometry with C–Pt–P in the range of 87.2° and 92.1°, which might be caused by the steric demand of the bulky triethylphosphine ligands (ESI†).

The investigation of UV-visible absorption and emission spectra of the platinum–acetylide macrocycles **5a-b** in diluted dichloromethane solutions was carried out at 298 K (Fig. 2). The absorption spectra of macrocycles **5a-b** exhibited similar patterns. For example, the absorption spectrum of **5b** showed two intense absorption bands in the range of 307–325 nm and 407–433 nm. According to the previous spectroscopic investigation on *trans*-[Pt(PEt$_3$)$_2$(C≡CR)$_2$] and its derivatives,[8a] the low energy absorption bands are described as an admixture of intraligand (IL) [π–π*(C≡CR)] and metal-to-ligand charge transfer (MLCT) [d(Pt) π–π*(C≡CR)] transition with predominant IL character. The higher energy absorption bands are likely attributed to an admixture of π–π* and n–π* transitions localized on the alkoxyphenyl fragments with MLCT (dπ(Pt) → π*(C≡CR)) transition.[8] Upon being excited at 358 nm, macrocycles **5a-b** displayed strong emission at *ca.* 457 nm with a shoulder at 455 nm in a dilute dichloromethane solution (*ca.* 10^{-5} M, Fig. 2b).

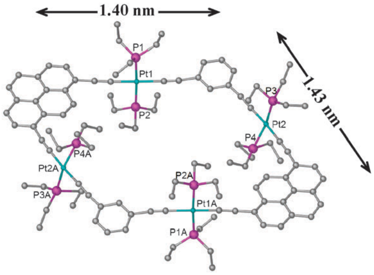

Fig. 1 Ball-and-stick model of the X-ray crystal structure of metallocycle **5a**.

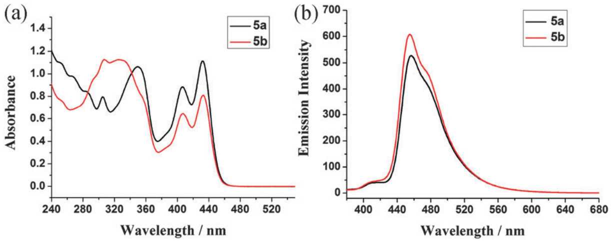

Fig. 2 (a) UV-vis absorption spectra and (b) emission spectra of metallocycles **5a-b** in dichloromethane at 298 K (concentration: **5a** = 5.79 × 10^{-6} M; **5b** = 5.16 × 10^{-6} M).

It is well known that the hydrophobic interaction of alkyl chains and the hydrogen bonding between amide groups enables the orientation and ordered aggregation of the molecules. The morphologies of aggregates oligomer **4b** and macrocycles **5a-b** were examined using scanning electron microscopy (SEM). SEM samples were prepared by depositing the solution of complexes onto a SiO_2/Si substrate (1 × 1 cm^2). Interestingly, it was found that the oligomer **4b** and macrocycles **5a-b** displayed obviously different morphologies even under the same conditions. The morphologies of these platinum–acetylide complexes were heavily dependent on the molecular shapes as shown in Fig. 3 and ESI.† For example, upon exposure to the solvent mixture of dichloromethane–methanol (v/v, 1 : 1), the morphologies of oligomer **4b** featured twining agglomerates while ordered fibers with a flake-like appearance were found in the case of **5b**. Notably, **5a** could not form any ordered aggregation under the same conditions (ESI†). This difference might be caused by the structural difference among oligomer **4b**, macrocycle **5a**, and **5b**. In the case of **5a**, due to the lack of alkyl chains, the solubility of **5a** turned out to be very poor, which led to the absence of ordered aggregation. Macrocycle **5b** preferred the face to face mode because of the existence of the rigid rhomboidal ring, allowing for the formation of well-organized aggregates.

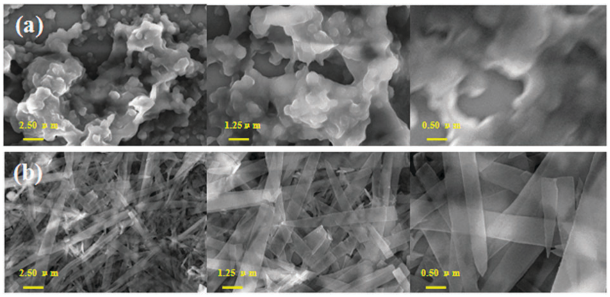

Fig. 3 SEM images of (a) oligomer **4b** and (b) macrocycle **5b** prepared in dichloromethane–methanol (v/v, 1 : 1).

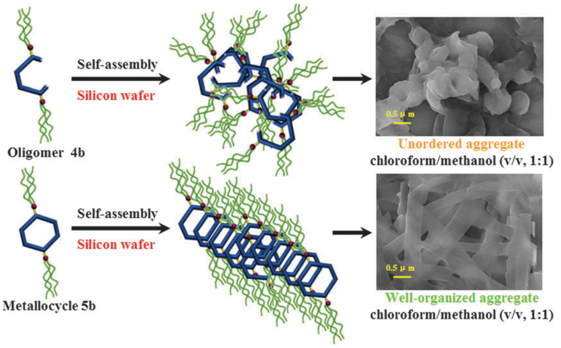

Fig. 4 Schematic representation of the supposed patterns of the formation of different supramolecular aggregates.

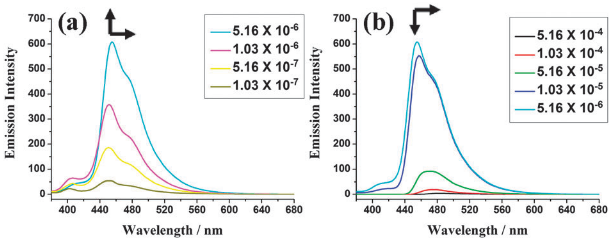

Fig. 5 Emission spectra of **5b** in dichloromethane at different concentrations at 298 K (λ_{ex} = 358 nm). (a) Concentration-dependent: 1.03×10^{-7}–5.16×10^{-6} M; (b) concentration-dependent: 5.16×10^{-6}–5.16×10^{-4} M.

The structure of oligomer **4b** was more flexible than metallocycle **5b**, so these oligomer molecules were ready to intertwine and form unordered aggregates (Fig. 4).

To obtain insights into the aggregation behaviour of **5b**, further spectroscopic investigation was carried out. Detailed concentration-dependent and variable-temperature UV-vis and emission spectroscopy of **5b** were performed in dichloromethane (ESI†). Although no significant changes were observed in UV-vis absorption spectra, macrocycle **5b** exhibited concentration-dependent emission properties in dichloromethane solution. As shown in Fig. 5a, it was found that the increase in the concentration of **5b** from 1.03×10^{-7} to 5.16×10^{-6} M at 298 K led to a significant increase in the intensity of the emission band at 402 nm with a slight red-shift (4.0 nm). This observation is consistent with the formation of the excimer during the aggregation process as illustrated in previous reports.[9] Moreover, upon increasing the concentration from 5.16×10^{-6} to 5.16×10^{-4} M (Fig. 5b), the emission band was found to drop dramatically in intensity with an obvious red-shift (*ca.* 28 nm), which indicated that the main aggregation pattern of **5b** was changed into some complicated manner from the dimer in the higher concentration range.[10] Furthermore, the concentration-dependent ^{1}H NMR spectroscopic studies of **5b** in CD_2Cl_2 were performed to probe the driving forces for the aggregation process (ESI†). It was found that the NH resonance displayed an obvious downfield shift upon the increase of concentration (δ = 7.817 ppm at 1.45 mg mL^{-1} and δ = 7.856 ppm at 25.02 mg mL^{-1}), which was indicative of the existence of hydrogen-bonding interactions during the formation of supramolecular aggregates.[6]

In conclusion, through a stepwise fragment coupling approach, a family of novel platinum–acetylide metallocycles with a well-defined shape and size were successfully constructed in modest yields. By employing a functionalized precursor, a metallocycle decorated with a hydrophobic long chain was obtained *via* this strategy as well. The sharp NMR signals in both ^{31}P {^{1}H} and ^{1}H NMR spectra along with the solubility of these species ruled out the formation of oligomers. Moreover, X-ray crystallographic analysis of **5a** provided further evidence for the unambiguous determination of rhomboidal metallocycles. These newly designed platinum–acetylide metallocycles are air- and humidity-stable at room temperature. The supramolecular aggregation of metallocycle **5b** was studied through concentration- and temperature-dependent absorption and emission spectra. Furthermore, the concentration-dependent ^{1}H NMR spectroscopic studies were performed as well. All results indicated that the hydrophobic interaction between alkyl chains and the hydrogen-bonding between amides are the driven forces during the formation of ordered aggregates. Moreover, the morphologies of these platinum–acetylide complexes were dependent on the molecular shape. These findings obviously enrich the library of novel macrocyclic host molecules and provide a new platform to design potential functional nanostructured aggregates.

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