Control of Heterometallic Three-Dimensional Macrocycles with Aromatic Stacks in Tunable Host Cavities

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ABSTRACT Using coinage metal (Cu(II), Ag(I)) hinges, two sets of heterometallic molecular capsules with analogous open-ended cavities were prepared based on the half-sandwich rhodium fragments. In the case of [Rh₄Cu₄] cages, up to six-fold-stacked host-guest structures were formed by varying the cavity's dimensions. Moreover, the series of capsules were demonstrated to self-fine-tune to form multi-heteroguest arrays via favourable donor-acceptor π interactions, as evidenced from single-crystal X-ray analysis.

KEYWORDS host-guest chemistry, open-ended cavity, heterometallic capsule, half-sandwich rhodium fragments

Introduction

Natural spontaneous and precise self-assembly of functional superstructures inspires the mimicking of analogues. Enzymes, nature's masterpiece, provide molecular-sized and specific-shaped pockets capable of selectively binding substrates and effectively catalysing unique reactions. Alternatively, so-called host-guest catalysis is regarded as a conventional route to produce artificial molecular flasks.^[1] Molecular capsules constructed by non-covalent interactions could offer well-defined local microenvironment trapping the guests within the cavities. Well-matched geometries of cavity and guest, as well as well-defined host-guest interactions, are both crucial to bind substrates in a predictable array or aggregation manner.^[2,3]

The pre-programming of smaller building blocks to come together to form more advanced assemblies has been extensively used^[4,5] in the construction of artificial molecular flasks to encapsulate small molecules. Thereby, strategic selection of rigid organic ligands and exploitation of the specific coordination geometries of metal centres are regarded as the basic design principles of stable confined cavities, resulting in closed box-shaped molecular capsules, which lack "windows" for guest release and catalysis turnover. This property contrasts with the structures of most natural vehicles, for which selected release and capture phenomena are frequently observed, restricting its further application.

Herein, a series of heterometallic supramolecular coordination capsules capable of anchoring aromatic guests in open-ended cavities by coinage metals centres Cu(II) and Ag(I) are presented. The assemblies have similar geometries but bind the aromatic guest molecules through completely different approaches. The dicopper building block $Cu_2(bddp)_2$ (H₂bddp=3,5-bis(1,3-dioxo-4,4-dimethylpentyl)pyridine) shown in Scheme 1, known to act as an electron-deficient metalloligand,^[6] was used to construct a series of heterometallic cages in a stepwise manner. Discrete sextet-stacking host-guest structures were formed by utilizing favourable donor-acceptor (D-A) π interactions. Furthermore, inspired by the geometry of the cages with embedded copper(II) centres, silver-containing heterometallic molecular containers were constructed in good yields, templated by stacks of multiple coronene units. The aromatic guests were found to be anchored in the open-ended cavity by Ag- π interactions, which was demonstrated by single-crystal X-ray analysis.

Results and Discussion

The [Rh₄Cu₆] heterometallic macrocage 1 was constructed in a

Scheme 1 Two multidentate ligands with distinct coordination modes and binuclear metalloligands $Cu_2(dppd)_2$, $[Ag_2(Hdmppd)_2][OTf]_2$



stepwise manner from binuclear macrocyclic metalloligand $[Cu_2(bddp)_2]$, as shown in Scheme 2. A solution of $[Cp*RhCl_2]_2$ ($Cp*=\eta^5$ -pentamethylcyclopentadienyl, 1.0 equiv.) was treated with AgOTf (Tf= O_2SCF_3) (4.0 equiv.), followed by the addition of bidentate ligand Na₂[Cu(opba)] [opba=1,2-phenylenebis(oxamate)] (1.0 equiv.) in methanol. The resulting solution was then treated with Cu₂(bddp)₂ (1.0 equiv.) to form the capsule complex **1** in a yield of 75.4%.

Slow vapor diffusion of diethyl ether into a methanol/tetrahydrofuran solution of **1** yielded single crystals suitable for X-ray diffraction analysis, confirming the open-ended cage-like framework of **1** in the solid state (Figure 1a). As expected, a pair of planar dicopper building blocks were bridged by rigid linear metalloligand $Cu(opba)^{2-}$ in a 1 : 1 molar ratio, whereby the four Cp*Rh fragments occupy the vertices, forming a [Rh₄Cu₆] heterometallic cage with an open-ended cavity. It was observed that one of the originally unsaturated copper cations from each dicopper plane was found to be coordinated to one tetrahydrofuran molecule inside the cavity, while another copper centre was coordinated by a molecule of methanol on the outside of the assembly.

Owing to the utilization of the dicopper(II)-containing platform, known to act as an electron-deficient surface, the cavity of cage **1** was initially investigated as an aromatic guest receptor, which was expected to interact with the aromatic moieties through aromatic donor-acceptor π interactions. In order to verify the guest-binding ability, a slight excess of electron-rich aromatic coronene (**G**₁) was introduced to the solution of cage **1**. The

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obtained UV-Vis spectra showed only minimal changes upon guest binding, and the fluorescence of the coronene moieties was largely quenched by the Cp*Rh fragments in the cages; hence, these techniques were not used to investigate guest binding in solution. However, the solid-state structure of the host-guest adduct was unambiguously demonstrated by X-ray diffraction analysis (Figure 1b). The capsule framework was observed to dilate to accommodate the double-stacked coronene molecules, whereupon the distance between two opposite copper centres increased to 9.95 Å from 7.37 Å. The duplex aromatic staking array was established by a π - π interaction with an average separation of 3.4 Å (Figure S10, Table S1 in the Supporting Information). Moreover, the stronger intermolecular binding of the aromatic coronene molecules and the electron deficient surface of the capsule resulted in complete displacement of the coordinated tetrahydrofuran in favour of the stacked coronene molecules.

To reach the full potential of the aromatic donor-acceptor π interactions between cavity and guest molecules, an attempt was made to wedge a π -electron acceptor guest, *N*,*N'*-dimethyl-1,4,5,8-naphthalene-tetracarboxylic diimide (**G**₂), in between the two aromatic molecules, in order to form a larger multiply-stacked inclusion complex. As expected, the cages, given their adaptable void volumes via strategic selection of different bridging ligands, were found to be capable of encapsulating heteroguest quintet and sextet stacks inside perfectly size-matched cavities, as unambiguously determined by single-crystal X-ray diffraction analysis.

As shown in Figure 2a, one electron-deficient G_2 guest was found to be sandwiched between two coronene molecules, which were further encapsulated in the cavity of the cage, forming the well-defined quintet stacking complex **2**. The two dicopper planes bridged by 1,4-bis(dipyrromethan-5-yl)benzene (bdpmb) ligands were found to be 13.44 Å apart (Cu…Cu non-bonding distance),



Figure 1 X-ray crystal structures of cationic parts of (a) the tetrahydrofuran adduct of heterometallic cage **1**; (b) coronene-encapsulated cage **1**. Hydrogen atoms, OTf⁻ anions and coordinated methanol molecules are omitted for clarity (N, blue; O, red; C, gray; Rh, pink; Cu, turquoise).

allowing quintet stacking with a favourable average distance of 3.36 Å.

In light of the encouraging synthesis of quintet stacking complexes, larger stacks were predicted to arise from analogous encapsulation in cavities of appropriately increased size. The longer bidentate ligand 4,4'-bis(dipyrromethan-5-yl)biphenyl (bdpmbp) was chosen to bridge two electron-deficient surfaces with a distance of 17.06 Å (Rh…Rh non-bonding distance). Gratifyingly, the results of single-crystal X-ray analysis revealed that a four-layer guest array was captured inside the open-ended cavity, as shown in Figure 2b. The distance between two opposite copper centres increased to 16.87 Å from 13.44 Å in the case of guest adduct 2, resulting in an average interplanar distances of 3.4 Å. This indicated a very close packing of the π -donor and -acceptor units in the A-D-A-A-D-A sextet inclusion complex **3** (Figure S11, Table S2 in the Supporting Information).



Figure 2 X-ray crystal structures of cationic parts of (a) quintet stacking complex 2; (b) sextet stacking host-guest adduct **3**. Hydrogen atoms and OTf⁻ anions are omitted for clarity (N, blue; O, red; C, gray; Rh, pink; Cu, turquoise).

Inspired by the encapsulation of multiple guests in the large cavity of heterometallic cage **3**, another coinage metal, silver(I), was selected to serve as an anchor to bind aromatic guests inside similar molecular capsules, which would possess analogous nano-cavities to the copper(II)-containing cages described above. Such an assembly would take advantage of metal– π interactions, a well-known class of bonding between metal centres and aromatic systems, and has been utilized to facilitate the formation of a wide range of metal-arene complexes.^[3a,7]

Scheme 3 Construction of $[Rh_4Ag_4]$ heterometallic adducts 4 and 5 from metalloligand $[Ag_2(Hdmppd)_2][OTf]_2$



The ligand 1,3-di(3-pyridyl)propane-1,3-dionato (Hdmppd, Scheme 1) was utilized to coordinate with one equivalent of silver cations to form a binuclear macrocycle,^[8] which could be used as a building block to construct silver(I)-containing molecular capsules with open-ended cavities as shown in Scheme 3. The reaction of macrocyclic building block [Ag₂(Hdmppd)₂][OTf]₂, 4,4'-bipyridine-bridged binuclear Cp*Rh fragments and coronene in methanol led to a light-yellow precipitate (**4**). Although initial attempts to reveal the structure of **4** in solution by detailed NMR studies were fruitless due to its extremely poor solubility, the solid-state structure of complex **4** was unambiguously confirmed by X-ray crystallographic analysis.

Single crystals suitable for X-ray analysis were grown by a heterogeneous layer diffusion method in the dark, where a CH_3OH solution of $[Ag_2(Hdmppd)_2][OTf]_2$ and the Cp*Rh-containing frag-

ments were placed at the bottom of a culture tube, followed by careful layering of a diethyl ether and hexane solution of coronene. The crystallographic analysis confirmed the host-guest structure of **4** as shown in Figure 3.



Figure 3 X-ray crystal structure of cationic parts of (a) **4**; (b) **5**. Hydrogen atoms and OTf⁻ anions are omitted for clarity (N, blue; O, red; C, gray; Rh, pink; Ag, orange).

In the resulting structure, two coronene molecules were included in the cavity *via* relatively weak Ag- π interactions with an average distance of 3.2 Å between the silver(I) centres and the coronene plane (Figure S12 in the Supporting Information), resulting in a Ag- π - π -Ag arrangement. Two N — Ag — N angles in the same disilver plane were found to be *ca*. 170.0 ° and 174.7 °, respectively. Moreover, multipoint CH- π interactions between the coronene and the lateral bridging ligands appear to stabilize the complex, with CH- π distances of around 2.75 Å.

Subsequently, we explored the ability of the capsule to encapsulate larger multi-aromatic arrays. For instance, the silvercontaining binuclear building block reacts with one equivalent of dinuclear Cp*Rh fragments bridged by trans-1,2-bis(4-pyridyl)ethene in the presence of a slight excess of coronene, affording a light-yellow precipitate of 5 in the dark. Structural authentication of ${\bf 5}$ confirmed its expected $[Rh_4Ag_4]$ structure. As shown in Figure 3b, each Cp*Rh(III) vertex is coordinated by one nitrogen atom from a trans-1,2-bis(4-pyridyl)ethene linker and one (O,O') chelating site of the deprotonated [Ag₂(Hdmppd)₂][OTf]₂ plane, whereby four monovalent silver cations serve as hinges, thus forming a cage framework with an open-ended cavity. In the resulting structure, a triplet stack of aromatic coronene molecules was found to reside in the cavity of capsule **5** via η^2 -type Ag- π interaction at the edge of the benzene ring, as shown in Figure S12 in the Supporting Information. Although the separation of opposite Ag... Ag atoms is 14.6 Å, which is a little large for the encapsulation of three aromatic planes, the capsule structure is somewhat distorted and the distance between the two disilver planes is decreased to ca. 13.1 Å. Interestingly, the opposite occurs in the aforementioned complex $(G_1)_2 \subset 1$, where the distance between opposite copper centres increases to satisfy the triplet stacking requirements. The change of the cavity size in the process of accommodating guest molecules indicates that the flexibility of both sets of capsules, provided by the metal (Cu(II), Ag(I)) hinges in the bridge positions, allows the capsule to fine-tune the size of the cavity to maximize its interaction with the multiple stacking arrays inside its nanocavity. In addition, the silver-hinged heterometallic adduct 5 was found to further connect in an intermolecular fashion via argentophilic interactions,^[8,9] forming a one-dimensional network as shown in Figure S13 in the Supporting Information.

Conclusions

In summary, we present herein two sets of heterometallic molecular capsules with similar open-ended cavities, which are demonstrated to be suitable hosts for the encapsulation of aromatic heteroguests. Remarkably, incorporation of coinage metal [Cu(II), Ag(I)] hinges enable the capsules to self-fine-tune to capture multiple heteroguests inside their nanocavity, leading to stable multi-stacked arrays. Furthermore, in the case of [Rh₄Cu₄] cages, up to six-fold-stacked host-guest structures were formed by utilizing favourable D-A π interactions. Our results thus present a simple model of the creation and control of supramolecular architectures with open-ended cavities, which can further accommodate multiply-stacked arrays through various interactions. We predict that these results will have an impact on the strategies used in the design of future molecular containers and functional nanovehicles.

Experimental

Preparation of 1. AgOTf (51.4 mg, 0.2 mmol) was added to a solution of $[Cp*RhCl_2]_2$ (31 mg, 0.05 mmol) in CH₃OH (10 mL) at room temperature. The reaction mixture was stirred in the dark for 6 h and then filtered, followed by addition of a solution of Na₂[Cu(opba)] (17.9 mg, 0.05 mmol) in CH₃OH (5 mL), and the suspension was kept stirring at room temperature for 6 h and then $[Cu_2(bddp)_2]$ (39.3 mg, 0.05 mmol) in CH₃OH (5 mL) was added to the mixture. After stirring for another 12 h at room temperature, the solvent was concentrated to about 3 mL and diethyl ether was added, to give **1** as green solid (yield 70.6 mg, 75.4%). IR (KBr) *v*: 3499, 2960, 1617, 1589, 1454, 1414, 1374, 1259, 1226, 1163, 1032, 786, 757, 640, 574, 519 cm⁻¹. Analysis calcd for C₁₄₀Cu₆F₁₂S₄O₄₀Rh₄N₈H₁₆₀: C 44.91, H 4.31, N 2.99; found C 44.72, H 4.26, N 2.85.

Preparation of $(G_1)_2$ ⊂1. Coronene (G_1) (18.0 mg, 0.06 mmol) was added to a solution of the complex 1 (93.6 mg, 0.025 mmol) in CH₃OH (10 mL) and the mixture was stirred at room temperature for 6 h. After filtration, the solution was concentrated (3 mL) and diethyl ether was added to precipitate the solid (yield 91.2 mg, 83.9 %). IR (KBr) ν : 3482, 1601, 1560, 1497, 1434, 1388, 1373, 1256, 1225, 1160, 1031, 758, 639, 574, 517 cm⁻¹. Analysis calcd for C₁₈₈Cu₆F₁₂S₄O₄₀Rh₄N₈H₁₈₄: C 51.97, H 4.27, N 2.58; found C 51.72, H 4.38, N 2.41.

Preparation of 2. AgOTf (30.6 mg, 0.12 mmol) was added to a solution of $[Cp*Rh]_2$ (bdpmb)Cl₂ (45.4 mg, 0.05 mmol) in CH₃OH (10 mL) at room temperature and stirred in dark for 6 h, followed by filtration and $[Cu_2(bddp)_2]$ (39.3 mg, 0.05 mmol) was added, and the mixture was stirred for another 12 h. Coronene (**G**₁) (15 mg, 0.06 mmol) and **G**₂ (7.4 mg, 0.025 mmol) were added to the above solution and the mixture was stirred at room temperature for 6 h. After filtration, the solution was concentrated (3 mL) and diethyl ether was added to precipitate the green solid (yield 108.2 mg, 83.2%). IR (KBr) v: 3443, 2958, 2917, 2848, 1663, 1603, 1552, 1499, 1407, 1376, 1304, 1249, 1158, 1030, 993, 858, 637, 518 cm⁻¹. Analysis calcd for C₂₃₂Cu₄F₁₂S₄O₃₂Rh₄N₁₄H₂₁₈: C 58.83, H 4.64, N 4.14; found C 58.65, H 4.56, N 4.02.

Preparation of 3. AgOTf (30.6 mg, 0.12 mmol) was added to a solution of $[Cp*Rh]_2$ (bdpmbp)Cl₂ (49.1 mg, 0.05 mmol) in CH₃OH (10 mL) at room temperature and stirred in dark for 6 h, followed by filtration and $[Cu_2(bddp)_2]$ (39.3 mg, 0.05 mmol) was added, and the mixture was stirred for another 12 h. Coronene (**G**₁) (33 mg, 0.11 mmol) and **G**₂ (32 mg, 0.11 mmol) were added to the above solution and the mixture was stirred at room temperature for 6 h. After filtration, the solution was concentrated (3 mL) and diethyl ether was added to precipitate the green solid (yield 115.1 mg, 81.5%). IR (KBr) v: 3444, 2922, 1702, 1666, 1549, 1447, 1403, 1374, 1340, 1282, 1248, 1154, 1029, 992, 887, 761, 717, 637, 571, 547 cm⁻¹. Analysis calcd for C₂₆₀Cu₄F₁₂S₄O₃₆Rh₄N₁₆H₂₃₆: C 60.25, H 4.59, N 4.32; found C 60.36, H 4.47, N 4.22.

Preparation of 4. AgOTf (51.4 mg, 0.2 mmol) was added to a solution of $[Cp*RhCl_2]_2$ (31 mg, 0.05 mmol) in CH₃OH (10 mL) at room temperature. The reaction mixture was stirred in the dark

for 6 h and then filtered, followed by addition of 4,4'-bipyridine (7.8 mg, 0.05 mmol). $[Ag_2(Hdmppd)_2][OTf]_2$ (48 mg, 0.05 mmol) and coronene (**G**₁) (30 mg, 0.1 mmol) were added to the above solution and the mixture was stirred at room temperature for 24 h. The light yellow precipitate was washed by diethyl ether and hexane. (yield 96.1 mg, 89.6%). Elemental analysis calcd for C₁₆₈H₁₄₈Ag₄F₂₄N₁₂O₂₅Rh₄S₈: C 47.03, H 3.48, N 3.92; found C 47.17, H 3.54, N 3.79.

Preparation of 5. AgOTf (51.4 mg, 0.2 mmol) was added to a solution of $[Cp*RhCl_2]_2$ (31 mg, 0.05 mmol) in CH₃OH (10 mL) at room temperature. The reaction mixture was stirred in the dark for 6 h and then filtered, followed by addition of *trans*-1,2-bis(4-pyridyl)ethene (9.1 mg, 0.05 mmol). $[Ag_2(Hdmppd)_2][OTf]_2$ (48 mg, 0.05 mmol) and coronene (**G**₁) (45 mg, 0.15 mmol) were added to the above solution and the mixture was stirred at room temperature for 24 h. The light yellow precipitate was washed by diethyl ether and hexane (yield 101.5 mg, 87.3%). Elemental analysis calcd (%) for C₁₉₆H₁₇₀Ag₄F₂₄N₁₂O₂₅Rh₄S₈: C 50.64, H 3.69, N 3.62; found C 50. 47, H 3.66, N 3.42.

Crystallographic details. Single crystals of 1, $(G_1)_2$ ⊂1, 2, 3, 4 and 5 suitable for X-ray diffraction study were obtained at room temperature. X-ray intensity data of 1, $(G_1)_2$ ⊂1 and 2, 3 were collected on a Bruker D8 VENTURE system at 150 K and 173 K, respectively, data of 4 was collected on a CCD-Bruker SMART APEX system at 173 K, data of 5 was collected on a Bruker D8 VENTURE system at 173 K. In these data, the disordered solvent molecules which could not be restrained properly were removed using the SQUEEZE route. The single-crystal X-ray diffraction data of 1, $(G_1)_2$ ⊂1, 2, 3, 4 and 5 have been deposited in the Cambridge Crystallographic Data Centre under accession number CCDC: 1825020 (1), 1825022 ($(G_1)_2$ ⊂1), 1825023 (2), 1825021 (3), 1825018 (4), 1825019 (5).

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.201800121.

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References

- (a) Han, M.; Engelhard, D. M.; Clever, G. H. Chem. Soc. Rev. 2014, 43, 1848; (b) Cook, T. R.; Stang, P. J. Chem. Rev. 2015, 115, 7001; (c) McConnell, A. J.; Wood, C. S.; Neelakandan, P. P.; Nitschke, J. R. Chem. Rev. 2015, 115, 7729; (d) Chen, L.-J.; Yang, H.-B.; Shionoya, M. Chem. Soc. Rev. 2017, 46, 2555; (e) Zhang, Y.-Y.; Gao, W.-X.; Lin, L.; Jin, G.-X. Coor. Chem. Rev. 2017, 344, 323.
- [2] (a) Chapin, J. C.; Kvasnica, M.; Purse, B. W. J. Am. Chem. Soc. 2012, 134, 15000; (b) Ronson, T. K.; Meng, W.; Nitschke, J. R. J. Am. Chem. Soc. 2017, 139, 9698; (c) Zhao, L.; Jing, X.; Li, X.; Guo, X.; Zeng, L.; He, C.; Duan, C. Coord. Chem. Rev. 2017, doi: 10.1016/j.ccr.2017.11.005; (d) Mirtschin, S.; Turski, A. S.; Scopelliti, R.; Velders, A. H.; Severin, K. J. Am. Chem. Soc. 2010, 132, 14004; (e) Schmidt, B. M.; Osuga, T.; Sawada, T.; Hoshino, M.; Fujita, M. Angew. Chem. Int. Ed. 2016, 55, 1561; (f) Ozores, H. L.; Amorín, M.; Granja, J. R. J. Am. Chem. Soc. 2017, 139, 776.
- [3] (a) Zhang, W.-Y.; Lin, Y.-J.; Han, Y.-F.; Jin, G.-X. J. Am. Chem. Soc. 2016, 138, 10700; (b) Zhang, Y.-Y.; Zhang, L.; Lin, Y.-J.; Jin, G.-X. Chem.-Eur. J. 2015, 21, 14893; (c) Zhang, L.; Lin, L.; Liu, D.; Lin, Y.-J.; Li, Z.-H.; Jin, G.-X. J. Am. Chem. Soc. 2017, 139, 1653; (d) Han, Y.-F.; Jin, G.-X. Acc.

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Chem. Res. 2014, 47, 3571; (e) Zhang, H.-N.; Gao, W.-X.; Deng, Y.-X.; Lin, Y.-J.; Jin, G.-X. Chem. Commun. 2018, 54, 1559; (f) Lang, J.-P.; Xu, Q.-F.; Yuan, R.-X.; Abrahams, B. F. Angew. Chem. Int. Ed. 2004, 43, 4741; (g) Liu, D.; Lang, J.-P.; Abrahams, B. F. J. Am. Chem. Soc. 2011, 133, 11042.

- [4] (a) Fujita, D.; Ueda, Y.; Sato, S.; Mizuno, N.; Kumasaka, T.; Fujita, M. *Nature* 2016, *540*, 563; (b) Ueda, Y.; Ito, H.; Fujita, D.; Fujita, M. *J. Am. Chem. Soc.* 2017, *139*, 6090; (c) Mal, P.; Breiner, B.; Rissanen, K.; Nitschke, J. R. *Science* 2009, *324*, 1697; (d) Jansze, S. M.; Cecot, G.; Wise, M. D.; Zhurov, K. O.; Ronson, T. K.; Castilla, A. M.; Finelli, A.; Pattison, P.; Solari, E.; Scopelliti, R.; Zelinskii, G. E.; Vologzhanina, A. V.; Voloshin, Y. Z.; Nitschke, J. R.; Severin, K. *J. Am. Chem. Soc.* 2016, *138*, 2046; (e) Brenner, W.; Ronson, T. K.; Nitschke, J. R. *J. Am. Chem. Soc.* 2017, *139*, 75; (f) Ronson, T. K.; Pilgrim, B. S.; Nitschke, J. R. *J. Am. Chem. Soc.* 2016, *138*, 10417; (g) Zhang, W.-H.; Ren, Z.-G.; Lang, J.-P. *Chem. Soc. Rev.* 2016, *45*, 4995; (h) Liu, Q.; Zhang, W.-H.; Lang, J.-P. *Coor. Chem. Rev.* 2017, *350*, 248.
- [5] (a) Yamauchi, Y.; Yoshizawa, M.; Akita, M.; Fujita, M. J. Am. Chem. Soc. 2010, 132, 960; (b) Murase, T.; Otsuka, K.; Fujita, M. J. Am. Chem. Soc. 2010, 132, 7864; (c) Singh, N.; Jo, J.-H.; Song, Y. H.; Kim, H.; Kim, D.; Lahc, M. S.; Chi, K.-W. Chem. Commun. 2015, 51, 4492; (d) Lu, Y.; Lin, Y.-J.; Li, Z.-H.; Jin, G.-X. Chin. J. Chem. 2018, 36, 106; (e) Lu, Y.; Deng, Y.-X.; Lin, Y.-J.; Han, Y.-F.; Weng, L.-H.; Li, Z.-H.; Jin, G.-X. Chem 2017, 3,

110; (f) Jiang, B.; Zhang, J.; Ma, J.-Q.; Zheng, W.; Chen, L.-J.; Sun, B.; Li, C.; Hu, B.-W.; Tan, H.; Li, X.; Yang, H.-B. *J. Am. Chem. Soc.* **2016**, *138*, 738; (g) Huang, C.-B.; Xu, L.; Zhu, J.-L.; Wang, Y.-X.; Sun, B.; Li, X.; Yang, H.-B. *J. Am. Chem. Soc.* **2017**, *139*, 9459; (h) Zheng, W.; Yang, G.; Shao, N.; Chen, L.-J.; Ou, B.; Jiang, S.-T.; Chen, G.; Yang, H.-B. *J. Am. Chem. Soc.* **2017**, *139*, 13811.

- [6] Fan, Q.-J.; Lin, Y.-J.; Hahn, F. E.; Jin, G.-X. Dalton Trans. 2018, 47, 2240.
- [7] (a) Omoto, K.; Tashiro, S.; Kuritani, M.; Shionoya, M. J. Am. Chem. Soc.
 2014, 136, 17946; (b) Shimada, M.; Yamanoi, Y.; Ohto, T.; Pham, S.-T.;
 Yamada, R.; Tada, H.; Omoto, K.; Tashiro, S.; Shionoya, M.; Hattori, M.;
 Jimura, K.; Hayashi, S.; Koike, H.; Iwamura, M.; Nozaki, K.; Nishihara,
 H. J. Am. Chem. Soc. 2017, 139, 11214; (c) Lindeman, S. V.; Rathore,
 R.; Kochi, J. K. Inorg. Chem. 2000, 39, 5707.
- [8] Banerjee, K.; Biradha, K. New J. Chem. 2016, 40, 1997.
- [9] Schmidbaur, H.; Schier, A. Angew. Chem. Int. Ed. 2015, 54, 746.

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