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## Directional Self-Sorting with Cucurbit[8]uril Controlled by Allosteric $\pi$ - $\pi$ and Metal-Metal Interactions

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Abstract: To maximize Coulombic interactions, cucurbit[8]uril (CB[8]) typically forms ternary complexes that distribute the positive charges of the pair of guests (if any) over both carbonylated portals of the macrocycle. We present here the first exception to this recognition pattern. Platinum(II) acetylides flanked by 4'-substituted terpyridyl ligands (tpy) form 2:1 complexes with CB[8] in an exclusively stacked head-tohead orientation in a water/acetonitrile mixture. The host encapsulates the pair of tpy substituents, and both positive Pt centers sit on top of each other at the same CB[8] rim,

Introduction

Cucurbit[8]uril (CB[8]) has been used since 2000<sup>[1]</sup> to dynamically connect two units via ternary complex formation. A wellknown and early<sup>[2]</sup> example is the formation of a ternary complex between CB[8], electron-deficient methylviologen and electron-rich 2,6-dihydroxynaphthalene and 1,4-dihydroxybenzene, which is accompanied by a new absorption band at approximately 580 nm due to charge transfer between both guests. This recognition pattern has been applied on numerous occasions to the design of stimulus-responsive materials.[3-12]

CB[8] typically assembles with guest pairs in a conformation that distributes positive charges, if present, over both portals of the macrocycle. For example, two berberine guests (1) undergo concomitant encapsulation into CB[8], with each isoquinolinium nitrogen interacting with one CB[8] carbonylated rim. A similar behavior has been observed on multiple occasions with benzyl,<sup>[13]</sup> naphthen-2-ylmethyl<sup>[13-15]</sup> and anthracen-2-ylmethyl<sup>[16, 17]</sup> units bearing positive substituents (see Figure 1). CB[8] also distributes positive charges evenly when forming homoternary complexes with phenylalanine residues, either as part of a small peptide<sup>[18, 19]</sup> or as the N-terminal residue of a protein.<sup>[4,19-21]</sup> We recently showed that CB[8] can connect metal-terpyridine complexes into dynamic oligomers upon ter-

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leaving the other rim free of any interaction with the guests. This dramatic charge imbalance between the CB[8] rims would be electrostatically penalizing, were it not for allosteric  $\pi$ - $\pi$  interactions between the stacked tpy ligands, and possible metal-metal interactions between both Pt centers. When both tpy and acetylides are substituted with aryl units, the metal-ligand complexes form 2:2 assemblies with CB[8] in aqueous medium, and the directionality of the assembly (head-to-head or head-to-tail) can be controlled, both kinetically and thermodynamically.



Figure 1. Structures of berberine (1), dynamic oligomers (2·CB[8]·3·CB[8])<sub>n</sub> electron-rich diarylviologens 4a and azobenzene 4b.

nary complex formation with their 4'-substituents (see Figure 1).<sup>[22]</sup> Fe<sup>II</sup> and Ir<sup>III</sup> complexes 2 and 3 could thus be assembled into an alternate  $(Fe-Ir-)_n$  sequence, due to favorable quadrupole-quadrupole interactions between the 4-tolyl and tetrafluorophenyl substituents of the terpyridyl ligands. Here again, on average, every positive metal center interacts with one CB[8] portal, and the ligands act as areas of low dielectric that promote the interaction.

In 2010, Kim and co-workers showed a first exception to this recognition pattern in the binary complex of CB[8] and the 1,12-dodecane diammonium cation.<sup>[23]</sup> Both ammonium heads

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were found to sit at the same CB[8] portal, in solution and in the solid state. In the latter case, a water molecule separated the cationic heads at the portal. The authors concluded that enhanced interactions between the U-shaped guest and the inner wall of CB[8], as well as limited exposure of the alkyl chain to water, advantageously compensate conformational strain and Coulombic repulsion between the ammonium groups.<sup>[23]</sup> Very recently, Scherman and co-workers showed that electron-rich diarylviologens 4a (X = H, CH<sub>3</sub>, OCH<sub>3</sub>, SCH<sub>3</sub>, and N(CH<sub>3</sub>)<sub>2</sub>, NHCOCH<sub>3</sub>) form discrete 2:2 complexes with CB[8] instead of the expected dynamic oligomers (see Figure 1).<sup>[24]</sup> The balance of positive charges between the carbonylated rims is again drastically uneven, with two pyridinium units interacting with one pair of portals, and none with the other pair. The authors justify the 2:2 binding motif by proposing (1) favorable Coulombic interactions between the electron-rich aryl substituents of one quest with the electron-deficient pyridinium unit of the other, and (2) a reduced electrostatic repulsion between both positive methylviologen groups as the positive charges are weakened by the neighboring electron-rich units. A similar 2:2 complexation had been unequivocally identified a year earlier by the same group with CB[8] and azobenzene 4b.[25] In this study, we show that both guests do not even need to interact favorably inside the cavity of CB[8] or benefit from charge annihilation to adopt this 2:2 arrangement, and that allosteric  $\pi$ - $\pi$  and possibly metal-metal interactions between two positive guests outside the macrocycle can be significant enough to promote its formation. More surprisingly, we also show that these interactions promote the formation of ternary CB[8]/guest<sub>2</sub> complexes with the positive centers of both quests residing at the same CB[8] portal. To the best of our knowledge, the orientation of the guests, as well as the charge imbalance between both CB[8] rims, are unprecedented in ternary CB[n] complexes.

#### **Results and Discussion**

The guests presented in this study are square-planar d<sup>8</sup> Pt<sup>II</sup> terpyridyl (tpy) acetylides **5–7** (see Figure 2). Most bear potentially CB[*n*]-binding units at the 4'-position of the tpy ligand and at the acetylide unit (see supporting information section for details on their preparation). CB[8] was initially expected to assemble complexes **6** and **7** into dynamic oligomers (**6**-CB[8])<sub>*n*</sub> and (**7**-CB[8])<sub>*n*</sub> upon encapsulation of both binding sites, similarly to Fe<sup>II</sup> and Ir<sup>III</sup> complexes **2** and **3**. However, the sharpness of their <sup>1</sup>H nuclear magnetic resonance (NMR) signals and the inability for complexes **5b** and **5c** to undergo encapsulation, made us suspect a radically different arrangement.

While  $Pt^{II}$  complexes **6** and **7 b** were poorly soluble in deuterium oxide (<0.10 mM), addition of CB[8] aliquots allowed their gradual dissolution, which was completed after addition of 1.0 equivalent CB[8] at 1.0 mM. <sup>1</sup>H NMR experiments revealed that the composition of the assemblies in solution remains steady, regardless of CB[8] concentration, even when the latter is added in excess. In the case of complexes **6a**, **6b**, **6c** and **7b**, the Pt/CB[8] ratio after encapsulation is unequivocally 1:1, and in the case of complex **6d**, 2:1. For Pt acetylides



**Figure 2.** Complexes **5–7**. ONIOM-optimized structures ( $\omega$ B97x-D/def2-SVP:PM6) of assemblies (**6** $\mathbf{b}_2$ -CB[8]<sub>2</sub>)<sup>HT</sup> and (**6** $\mathbf{b}_2$ -CB[8]<sub>2</sub>)<sup>HH</sup>. <sup>1</sup>H–<sup>1</sup>H NOESY spectrum of complex (**6** $\mathbf{b}_2$ -CB[8]<sub>2</sub>)<sup>HT</sup> in a deuterium oxide buffer (5.0 mm Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 50 mm H<sub>3</sub>BO<sub>3</sub>); key correlations are highlighted with green rectangles. Chemical shifts in ppm.

**6a**, **6b** and **7b**, the CB[8] methylene signals present two pairs of doublets (5.88, 5.79, 4.18 and 4.12 ppm in the case of complex **6b**, see Figure 2), a characteristic feature for CB[*n*] hosts with non-equivalent rims. A dynamic oligomer of the type  $(\mathbf{6} \cdot \text{CB}[8])_n$  or  $(\mathbf{7} \cdot \text{CB}[8])_n$  would have resulted in a wide broadening of all <sup>1</sup>H NMR signals,<sup>[22]</sup> and formation of a binary complex is implausible, as neither the geometry nor the size of the 4'-aryl substituents of the terpyridyl ligands are suitable for CB[8] binding as sole guests. We thus considered the formation of 2:2 complexes of the type  $\mathbf{6}_2 \cdot \text{CB}[8]_2$ . This quaternary assembly

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was first confirmed by diffusion-ordered NMR spectroscopy (DOSY). Logarithms of diffusion coefficients for complexes **6**<sub>2</sub>·CB[8]<sub>2</sub> (**6a**-**6c**) and **7b**<sub>2</sub>·CB[8]<sub>2</sub> all ranged between -9.76 and -9.70. A similar diffusion coefficient (log D = -9.69) was measured for ternary complex **6d**·CB[7]<sub>2</sub>, which occupies a slightly smaller volume, but retains the same general shape. An analogue of Fe<sup>II</sup> complex **2**, with a tolyl group attached to the 4'-position of the tpy unit instead of a 2-naphthyl unit, also returned a diffusion constant log D of -9.72 after encapsulation of both tolyl substituents with CB[7].<sup>[22]</sup> To the contrary, dynamic oligomers (**2**·CB[8])<sub>n</sub> and (**3**·CB[8])<sub>n</sub> (n = 11 and 15, respectively) had average log D coefficients of -10.15 and -10.28.<sup>[22]</sup>

Two arrangements are possible for 2:2 complexes: "head-tohead" (HH), with CB[8] macrocycles forming two different homo-ternary complexes with a pair of tpy 4'-substituents and a pair of acetylides, or "head-to-tail" (HT), with CB[8] forming two identical hetero-ternary complexes with the tpy substituents and the acetylides (see Figure 2). The CB[8] methylene signals, which reveal two non-equivalent CB[8] rims, would only support a HT conformation, as four non-equivalent rims would be expected in a HH arrangement. The HT conformation was confirmed by two-dimensional nuclear Overhauser effect spectroscopy (NOESY). Correlations between the para-methyl groups of the 4'-tolyl tpy substituents, the para-methyl groups of the tolylacetylide units and the meta-hydrogens of each unit were observed in complex  $(\mathbf{6} \mathbf{b}_2 \cdot CB[8]_2)^{HT}$  (see signals labeled 7, 8, 10 and 11 in Figure 2). For a better depiction of the assembly, we optimized complexes  $(\mathbf{6} \mathbf{b}_2 \cdot CB[\mathbf{8}]_2)^{HH}$  and  $(\textbf{6} \, \textbf{b}_2 \cdot \text{CB}[8]_2)^{\text{HT}}$  using the ONIOM two-layer model,  $^{[26,\,27]}$  with the high layer being Pt complexes optimized using density functional theory, the  $\omega$ B97x-D functional and def2-SVP basis sets, and the low layer being the whole 2:2 assembly treated with the semi-empirical PM6 method (see Figure 2).

The case of complex **6c** is not as straightforward, and twodimensional NMR experiments are consistent with a 59:41 mixture of assemblies (**6c**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HH</sup> and (**6c**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup> that exchange slowly on the NMR time scale. <sup>1</sup>H-<sup>1</sup>H NOESY correlations between the nuclei of the 4'-tpy substituent and of the biaryl unit (see cross-peaks 8<sup>HT</sup>-13<sup>HT</sup>, 7<sup>HT</sup>-10<sup>HT</sup>, 7<sup>HT</sup>-9<sup>HT</sup>, 6<sup>HT</sup>-9<sup>HT</sup>, 6<sup>HT</sup>-10<sup>HT</sup>, 5<sup>HT</sup>-12<sup>HT</sup> and 5<sup>HT</sup>-11<sup>HT</sup> in Figure 3) are evidence for some HT arrangement. The lack of correlation between hydrogens 8<sup>HH</sup> and 13<sup>HH</sup> is consistent with concomitant HH orientation (see insert in Figure 3). Correlation spectroscopy experiments (COSY; see Supporting Information) allowed the unequivocal assignment of all signals in both HH and HT arrangements.

Complex **6d** (R=tolyl, R'=adamantyl) forms a unique 2:1 assembly in the presence of CB[8]. As two adamantyl units are too bulky to undergo ternary complex formation inside CB[8], only two arrangements can be considered. Both are HH assemblies with CB[8] encapsulating two 4'-tolyl terpyridyl substituents, one with both platinum centers near the same rim, and the other with a platinum center at each rim. Yet the two non-equivalent CB[8] portals can only support the first scenario (see Figure 4). To the best of our knowledge, this represents the first case of a severely unbalanced charge distribution between both CB[8] portals (+2 and 0) in a 2:1 guest/CB com-





**Figure 3.** <sup>1</sup>H–<sup>1</sup>H NOESY spectrum of a 59:41 mixture of complexes  $(\mathbf{6c}_2 \cdot \text{CB[8]}_2)^{\text{HH}}$  and  $(\mathbf{6c}_2 \cdot \text{CB[8]}_2)^{\text{HT}}$  in a deuterium oxide buffer. Key correlations are highlighted in green. Chemical shifts in ppm.



Figure 4. <sup>1</sup>H NMR spectrum of complex (6d<sub>2</sub>-CB[8])<sup>HH</sup>. Signals labeled "\*" refer to excess CB[8] present in the mixture.

plex. The imbalance seems to be driven by allosteric  $\pi$ - $\pi$  stacking between the extensively planar complexes, and even metal-metal interactions. Such interactions have been identified on numerous occasions in Pt<sup>II</sup> terpyridyl complexes, both in the solid state and in solution.<sup>[28-37]</sup> Square-planar d<sup>8</sup> metals bear filled d<sub>z<sup>2</sup></sub> orbitals, which can overlap into d $\sigma$  and d $\sigma$ \* bonding and antibonding molecular orbitals with the d<sub>z<sup>2</sup></sub> orbital of a stacked neighbor.<sup>[38-40]</sup> The strength of the isolated Pt– Pt interaction is significant, and reaches 4.2 kcalmol<sup>-1</sup> in the case of the [Pt(tpy)Cl]<sub>2</sub><sup>2+</sup> dimer (unsubstituted tpy).<sup>[41]</sup> Repercussions of such d<sub>z<sup>2</sup></sub> – d<sub>z<sup>2</sup></sub> interactions on the photophysics of our Pt<sup>II</sup> complexes are discussed below.

To test the strength of the extended  $\pi$ - $\pi$  (and Pt–Pt) interactions in assembly **6d**<sub>2</sub>·CB[8], we combined it with a solution of homoternary complex **8**<sub>2</sub>.CB[8], and monitored the scrambling process, if any. Remarkably, even after heating to 40 °C for 20 h, self-sorting remained exclusively narcissistic,<sup>[42,43]</sup> that is, only homoternary complexes **6d**<sub>2</sub>·CB[8] and **8**<sub>2</sub>·CB[8] were detected in solution, without any trace of heteroternary complex **6d**·**8**·CB[8].  $\pi$ - $\pi$  (and Pt-Pt) interactions are thus strong enough to compensate favorable quadrupole-quadrupole interactions between tolyl and 3,5-difluorophenyl units inside CB[8].

In a second attempt at testing the limits of the  $\pi$ - $\pi$ /Pt-Pt interactions in ternary complex **6d**<sub>2</sub>·CB[8], we combined it with 2.0 equiv CB[7]. As CB[7] does show significant affinity for ada-

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mantyl units,<sup>[44,45]</sup> but cannot encapsulate any of the two adamantyl substituents in ternary complex 6d<sub>2</sub>·CB[8] due to their proximity, only three scenarios are possible: (1) CB[7] remains a free host in solution; (2) CB[7] competes advantageously with CB[8], ejects it, and forms complex 6d·CB[7]<sub>2</sub>; or (3) CB[7] disrupts the dimer and converts the assembly into unstacked [5]pseudorotaxane CB[7]·6d·CB[8]·6d·CB[7]. <sup>1</sup>H NMR experiments showed unambiguously that the third option is preferred; а 75:18:7 mixture of complexes CB[7]·6 d·CB[8]·6 d·CB[7], 6 d·CB[7]<sub>2</sub> and 6 d<sub>2</sub>·CB[8] was obtained (see Figure 5).



**Figure 5.** <sup>1</sup>H NMR spectra of (a) complex ( $\mathbf{6d}_2$ ·CB[8])<sup>HH</sup>, (b) assembly CB[7]·**6d**·CB[8]·**6d**·CB[7], and (c) complex **6d**·CB[7]<sub>2</sub>. Blue and green dots indicate residual signals of complexes **6d**·CB[7]<sub>2</sub> and (**6d**<sub>2</sub>·CB[8])<sup>HH</sup>, respectively, in spectrum b.

As mentioned above, HH and HT assemblies exchange slowly on the NMR time scale. However, we questioned whether the exchange could also be slow on the experiment time scale (i.e. within hours instead of ms). In other terms, are these assemblies just kinetically favored, or has the system reached thermodynamic equilibrium? To answer this question, the 2:2 complexes were heated to 40  $^\circ\text{C},$  and the ratios of HH vs. HT orientations were monitored by <sup>1</sup>H NMR spectroscopy as a function of time. Complexes  $(\mathbf{6} \mathbf{a}_2 \cdot CB[8]_2)^{HT}$  and  $(\mathbf{6} \mathbf{b}_2 \cdot CB[8]_2)^{HT}$ both saw their partial conversion to HH assemblies, up to 17 and 31%, respectively, once equilibrium was reached after 6 and 30 days at 40 °C (see Figure 6, spectra a and b, and Figure 2 for numbering). Surprisingly, the 59:41 mixture of assemblies  $(\mathbf{6c}_2 \cdot CB[8]_2)^{HH}$  and  $(\mathbf{6c}_2 \cdot CB[8]_2)^{HT}$  underwent quantitative conversion to the HT arrangement in 30 h at 40 °C (see spectra c and d in Figure 6). Finally, assembly  $(7 b_2 \cdot CB[8]_2)^{HT}$ consistently retained its HT orientation.

Rationalizing the stabilities would be highly speculative, except perhaps for assembly  $(7 b_2 \cdot CB[8]_2)^{HT}$ , where quadrupolequadrupole interactions between 4-tolyl and 3,5-difluorophenyl units are arguably more favorable than the geometric mean of the corresponding interactions in the homodimers. Howev-



**Figure 6.** <sup>1</sup>H NMR spectra of (a) complex (**6b**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup>, (b) a 31:69 mixture of complexes (**6b**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HH</sup> and (**6b**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup> after a 30 day heating period at 40 °C, (c) a 59:41 kinetic mixture of complexes (**6c**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HH</sup> and (**6c**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup>, (d) complex (**6c**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup> obtained after heating the mixture of HH and HT assemblies for 30 h at 40 °C.

er, one can certainly try to decipher the mechanism of the assembly process. Assuming that free, monomeric platinum acetylides are present in solution before addition of CB[8] (an hypothesis that we will refine later), the first encapsulation event with a non-negligible activation barrier is the formation of a 1:1 inclusion complex between one of the two binding sites and CB[8] (see assembly labeled "1:1" in Figure 7). The second



**Figure 7.** Proposed mechanism for the formation and switching of HH and HT quaternary assemblies.

Pt complex guest may then (1) ingress the 1:1 complex to form a ternary complex (labeled "2:1" in Figure 7; rate constants  $k_{\text{HH}}$  and  $k_{\text{HT}}$ ), or (2) enter a free CB[8] unit via one of its binding sites (rate constants  $k'_{\text{HH}}$  and  $k'_{\text{HT}}$ , see complex labeled "(1:1)<sub>2</sub>"). The last step is either the dimerization of the (1:1)<sub>2</sub> complex or the capping of the 2:1 complex with a free CB[8], both affording the desired 2:2 assembly.

The sequence from free ditopic guests and CB[8] hosts to the 2:2 complexes is cascade-like, with each intermediate assembly being more stable than its precursor, and with low activation barriers connecting each step. Under kinetic control, the HH vs. HT selectivity is thus governed by the rates of 2:1 or  $(1:1)_2$  complex formation from the 1:1 assembly (rate constants  $k_{\text{HH}}$ ,  $k'_{\text{HH}}$ ,  $k_{\text{HT}}$  and  $k'_{\text{HF}}$  see Figure 7). Under thermodynamic control, the stabilities of HH and HT 2:2 complexes determine their ratios in solution.

To test the validity of the proposed mechanism, we measured apparent rate constants, and extracted free energies of activation for the partial conversion of complexes  $(6a_2:CB[8]_2)^{HT}$ 

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and  $(\mathbf{6}\mathbf{b}_2 \cdot CB[8]_2)^{HT}$  into their HH analogues. The apparent rate constants are  $3.2(\pm 0.5) \times 10^{-6}$  and  $7.1(\pm 0.2) \times 10^{-7} \text{ s}^{-1}$ , respectively (see Supporting Information for details). Blending the  $HT \rightarrow HH$  conversion into a single step, and applying the Eyring equation, returns free activation energies of  $26.2(\pm 0.1)$  and 27.2( $\pm$ 0.1) kcal mol<sup>-1</sup>. Using emission titration experiments (and a series of approximations and limitations, see Supporting Information), we determined a binding constant of  $1.6(\pm 0.1) \times$  $10^{13} \text{ m}^{-3}$  for two complexes **6a** forming a 2:2 assembly with two CB[8] hosts (i.e. an 18 kcal mol<sup>-1</sup> free binding energy). As alluded above, at least 4-5 kcalmol<sup>-1</sup> must be added to account for favorable  $\pi - \pi / Pt-Pt$  interations between both guests, bringing the total stabilization upon double CB[8] encapsulation of guests **6a** to at least 22–23 kcalmol<sup>-1</sup>. These interactions are likely significant, as the emission titration could also be fitted reasonably well with a 2:1 binding model that uses dimer **6a**<sub>2</sub> as the "free guest" (see Supporting Information). Biczók and co-workers determined that the rate constant for berberine (1) ingression into free CB[8] is  $6.4 \times 10^7 \,\mathrm{m^{-1} \, s^{-1}}$ , and  $5.0 \times 10^6 \,\mathrm{m^{-1} \, s^{-1}}$  for ingression into binary complex 1·CB[8]; the corresponding free energies of activation are thus 6.8 and 8.3 kcal mol<sup>-1</sup>, respectively. Assuming that complex **6a** suffers from the same penalty upon entering CB[8] (approximately 7 kcal mol<sup>-1</sup>), the free energy of activation for the HT $\rightarrow$ HH process should thus be lower than 29–30  $kcal\,mol^{-1}$  unless the conversion proceeds through a fully dissociative mechanism. As the barrier we measured is indeed lower (26.2 kcal mol<sup>-1</sup>), we propose the following mechanism for the  $HT \rightarrow HH$  conversion: complex (2:2)<sup>HT</sup> proceeds energetically uphill to complex (1:1)<sup>HT</sup>; the free guest, which may form an exclusion complex with the CB[8] rim, would then flip towards assembly (1:1)<sup>HH</sup> (see Figure 7), before undergoing reassembly to the  $(2:2)^{HH}$ complex. The free energy of activation for the overall process is lower than 29-30 kcal mol<sup>-1</sup>, as one CB[8]-binding unit remains encapsulated throughout the process.

We finally note that a different mechanism for the kinetically controlled self-sorting process can be envisioned. As the solubility of all Pt acetylides is very poor in water, and extensive  $\pi$ - $\pi$  and Pt–Pt interactions promote the formation of stacked aggregates in the solid state, one could argue that the rate-limiting step of the assembly process is the detachment of a stacked pair of Pt complexes from the aggregate, followed by rapid CB[8] encapsulation. Complex **6a** crystallizes in a HT arrangement,<sup>[46]</sup> in agreement with the structure of the kinetically favored quaternary assembly in solution. The arrangement could not be confirmed for the other complexes, and the 59:41 kinetic mixture of (**6c**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HH</sup> and (**6c**<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup> assemblies either invalidates this mechanism or suggests a poorly organized aggregate.

The self-sorting properties of the Pt acetylides and CB[8] do not stop here, however. We found that adding aliquots of  $[D_3]$  acetonitrile to deuterium oxide solutions of assemblies  $\mathbf{6}_2 \cdot \text{CB}[8]_2$  ( $\mathbf{6a} - \mathbf{6c}$ ) and  $\mathbf{7b}_2 \cdot \text{CB}[8]_2$  triggers the ejection of one CB[8] macrocycle and the reshuffling of the guests into 2:1 HH complexes ( $\mathbf{6}_2 \cdot \text{CB}[8]$ )<sup>HH</sup> and ( $\mathbf{7b}_2 \cdot \text{CB}[8]$ )<sup>HH</sup>. The 2:1 assemblies are quantitatively formed after addition of 40% (v/v) [ $D_3$ ] acetonitrile (see Figure 8). In the case of complex  $\mathbf{6b}$ , the



**Figure 8.** <sup>1</sup>H NMR spectra of (a) quaternary assembly  $(\mathbf{6} \mathbf{b}_2 \cdot \text{CB[8]}_2)^{\text{HT}}$  in D<sub>2</sub>O buffer (0.50 mL); (b) a mixture of assemblies  $(\mathbf{6} \mathbf{b}_2 \cdot \text{CB[8]}_2)^{\text{HT}}$  and  $(\mathbf{6} \mathbf{b}_2 \cdot \text{CB[8]})^{\text{HH}}$  upon addition of CD<sub>3</sub>CN (80  $\mu$ L); (c) ternary complex  $(\mathbf{6} \mathbf{b}_2 \cdot \text{CB[8]})^{\text{HH}}$  obtained after further addition of CD<sub>3</sub>CN (total volume 0.20 mL).

switch is accompanied by dramatic downfield shifts for the methyl and meta-hydrogens at the tolylacetylide moiety (0.95 and 1.21 ppm, respectively), due to their release from CB[8]. Adding an organic co-solvent to an aqueous solution of a CB[n]/quest complex has been shown to lower the interaction between the CB[n] and their guests,<sup>[47]</sup> as (1) the suboptimal arrangement of "high-energy" water inside the cavity compared to bulk water, whose release is the major driving force for guest encapsulation, is not as stark when the bulk is contaminated with a co-solvent; and (2) free guests may be better solvated in the presence of a co-solvent than in pure water. Both tpy substituents and acetylides are thus expected to display reduced binding affinities towards CB[8] in the presence of a cosolvent, but the loss of affinity is clearly greater at the acetylides. Again, the remarkable stacked arrangement, with short Pt-Pt distances, a biased charge distribution between both CB[8] rims, and extensive  $\pi$ - $\pi$  interactions between both guests is quantitatively preferred over a typical ternary complex assembly with two equivalent CB[8] rims.

We also note that CB[7] binds Pt acetylides **6** and **7** b (except complex **6** c, which remains aggregated in aqueous solution even after heating and sonication). Remarkably, CB[7] exclusively encapsulates the 4'-substituent of the tpy ligand even in the presence of an excess amount of the macrocycle, except in complex **6d**; the latter undergoes concomitant encapsulation at both binding sites, due to the excellent shape complementary between the adamantyl group and the cavity of CB[7] (see Figure 5). We attribute this selectivity to the more positive electrostatic potential surrounding the terpyridyl ligand compared to the acetylide. Also, the acetylide moiety may retain some carboanionic character at the terminal alkynyl carbon, which may then hamper ligand/CB[7] interactions. The CB[7] and CB[8] preference for the tpy binding site in water and water/acetonitrile mixtures, respectively, may suggest that the

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favored complexation pathway towards 2:2 assemblies under kinetically controlled conditions is the formation of 1:1 complexes between the tpy substituent and CB[8] (rate constant  $k'_{\rm HT}$  see Figure 7), followed by exclusion complex (1:1)<sub>2</sub> and (2:2)<sup>HT</sup> assembly. In the case of Pt complex **6***c*, extensive  $\pi$ - $\pi$ -stacking caused by the longer biphenyl substituent may promote competitive 2:1 HH complex formation (rate constant  $k_{\rm HH}$ , see Figure 7). The other two pathways ( $k_{\rm HT}$  and  $k'_{\rm HH}$ ) are certainly less likely.

As studied in detail by Castellano,<sup>[48–52]</sup> Yam<sup>[29–37, 53–58]</sup> and Che,<sup>[59–61]</sup> among others, Pt acetylides have a rich photochemistry. Absorption bands at  $\lambda < 400$  nm are intraligand  $\pi \rightarrow \pi^*$  transitions, and bands at lower energies correspond to <sup>1</sup>[d $\pi$ (Pt) $\rightarrow \pi^*$ (tpy)] metal-to-ligand charge transfers (<sup>1</sup>MLCT) and a combination of overlapping <sup>1</sup>MLCT and <sup>1</sup>[ $\pi$ (C $\equiv$ CR) $\rightarrow \pi^*$ (tpy)] ligand-to-ligand (<sup>1</sup>LLCT) transitions. In the solid state or in dinuclear complexes, short Pt–Pt distances (< 3.5 Å,<sup>[40]</sup> and as short as 2.8 Å<sup>[62]</sup>) destabilize the filled d<sub>z<sup>2</sup></sub> orbitals, resulting in lower energy <sup>1</sup>[d $\sigma^* \rightarrow \pi^*$ (tpy)] metal-metal-to-ligand charge transfer transitions (<sup>1</sup>MMLCT). Emissions typically originate from the <sup>3</sup>[ $\pi$ (C $\equiv$ CR) $\rightarrow \pi^*$ (tpy)] and <sup>3</sup>[d $\pi$ (Pt) $\rightarrow \pi^*$ (tpy)] transitions. Extensive stacking may also result in emission at lower energies (typically > 800 nm) corresponding to <sup>3</sup>MMLCT excited states.<sup>[52,56,57,62–71]</sup>

The impact of CB[n] encapsulation on transition energies varies greatly, with bathochromic shifts being typically more common than hypsochromic ones.[72-77] Shifts result from a combination of competitive factors: (1) as shown by Nau and co-workers in the case of 2,3-diazabicyclo-[2.2.2]oct-2-ene and its  $n \rightarrow \pi^*$  transitions,<sup>[78]</sup> a decrease in the environment polarizability from the solvent to the cavity of CB[7] causes hypsochromic shifts;<sup>[79]</sup> (2) as shown by Biczók and co-workers in the case of berberine (1),<sup>[77]</sup> a decrease in the orientation polarizability parameter of the environment (that has both a polarity and a polarizability term) causes bathochromic shifts from water to CB[7]. One should also note that while the CB[7] cavity has low polarities and polarizabilities, Kaifer and co-workers recently showed that the polarity of the environment surrounding the carbonyl rims of CB[7] is in fact more polar than water,<sup>[80]</sup> the impact of this specific environment on the optical properties of chromophores is not known.

Pt complex 6a presents its lowest energy transition at 441 nm, likely as a mixture of <sup>1</sup>MLCT/<sup>1</sup>LLCT (see spectrum in black in Figure 9a). As mentioned above, addition of CB[7] triggers the formation of binary complex 6a·CB[7], with CB[7] interacting exclusively with the 4'-tolyl substituent of the tpy ligand. This complexation is accompanied by a significant hypsochromic shift (33 nm; spectrum in blue). To the contrary, complexation with CB[8], which affords complex ( $6a_2$ ·CB[8])<sup>HT</sup>, triggers a bathochromic shift (32 nm; solid green spectrum). Complex  $(\mathbf{6a}_2 \cdot CB[8])^{HH}$  only sees a 7 nm hypsochromic shift compared to the free guest (dotted green spectrum in Figure 9a). Similar effects are observed with Pt complex 6b. In the case of complex 6d, a pair of bands is observed at 448 and 468 nm (see spectrum in black in Figure 9b). Those have been reported on several occasions for Pt acetylides, and may correspond to  ${}^{1}[d_{xz}(Pt) \rightarrow \pi^{*}(tpy)]$  and  ${}^{1}[d_{vz}(Pt) \rightarrow \pi^{*}(tpy)]$  transi-



**Figure 9.** UV/Vis spectra of (a) free guest **6a** (black line), complex **6a**-CB[7] (blue line), assembly (**6a**<sub>2</sub>-CB[8]<sub>2</sub>)<sup>HT</sup> (green line), a 17:83 mixture of assemblies (**6a**<sub>2</sub>-CB[8]<sub>2</sub>)<sup>HH</sup> and (**6a**<sub>2</sub>-CB[8]<sub>2</sub>)<sup>HT</sup> (dashed green line), complex (**6a**<sub>2</sub>-CB[8])<sup>HH</sup> (dotted green line; 5:2 aqueous borate buffer/acetonitrile solvent mixture); (b) free guest **6d** (black line), ternary complex **6d**-CB[7]<sub>2</sub> (blue line), ternary complex (**6d**<sub>2</sub>-CB[8])<sup>HH</sup> (dotted green line). Emission spectra of (c) free guest **6a** (black line), complex **6d**-CB[7] (blue line), assembly (**6a**<sub>2</sub>-CB[8])<sup>HH</sup> (green line); (d) free guest **6d** (black line), ternary complex **6d**-CB[7]<sub>2</sub> (blue line), ternary complex (**6d**<sub>2</sub>-CB[8])<sup>HH</sup> (dotted green line). Excitation wavelengths are chosen to match absorption maxima. The solvent is an aqueous borate buffer unless noted otherwise; Pt concentration for both absorption and emission experiments is 50 μM.

tions, possibly with a <sup>1</sup>LLCT component.<sup>[81]</sup> 1:2 Complexation with CB[7] at both its tpy and acetylide units again triggers a blueshift and the emergence of a single band at 424 nm (spectrum in blue). A very clear hypsochromic shift (16 nm) is also observed for the intra-ligand  $\pi \rightarrow \pi^*$  transitions. Surprisingly, the 2:1 HH complex  $(\mathbf{6d}_2 \cdot CB[8])^{HH}$  shows comparable bands in addition to significant hyperchromicity in the 350-420 nm range (dotted green spectrum). In the whole series, bathochromic shifts are only observed with 2:2 assemblies, while redshifts are obtained in all other configurations. Intriguingly, partial conversion of assembly (6a<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup> to its HH analogue (HH/HT ratio 17:83) alters those bands significantly, with an enhanced absorption between 380 and 440 nm, and a very significant hypochromicity at the 470 nm band (see solid and dashed green spectra in Figure 9a). The pattern may in fact be caused by an hypsochromic shift of the lowest energy transition, from 473 nm to approximately 450 nm. We cannot justify this trend at the moment.

As far as emissions are concerned, blueshifts, reduced Stokes shifts and fluorescence enhancements are frequently observed upon guest encapsulation by CB[*n*], as the polarity and polarizability of the macrocycles are low, and encapsulation limits nonradiative decay from the excited state through solvent relaxation.<sup>[82]</sup> To the best of our knowledge, we report here for

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the first time the effect of CB[n] encapsulation on the phosphorescence of a chromophore. Pt acetylide 6a shows very weak emission at 693 nm upon excitation at 460 nm (see Figure 9c). CB[7] complexation increases phosphorescence by 24fold and triggers an extremely large blueshift (131 nm;  $\lambda_{max}$  = 562 nm). CB[8] complexation towards assembly  $(6a_2 \cdot CB[8]_2)^{HT}$ enhances phosphorescence by a factor of 240, and causes a 86 nm blueshift ( $\lambda_{max} = 607$  nm), relative to the free metalligand complex (see Figure 9c). Such shifts are unprecedented in the literature; to the best of our knowledge, the longest shift measured until now was 51 nm, for the fluorescence of berberine (1) and CB[7].<sup>[77]</sup> In the case of Pt acetylide 6d, complexation by CB[7] and CB[8] towards assemblies 6 d CB[7]<sub>2</sub> and 6d<sub>2</sub>·CB[8] also results in very large blueshifts (from 673 nm to 559 and 568 nm, respectively, see Figure 9d). In this case, phosphorescence enhancement is greater in the presence of CB[7] (27-fold, similar to that of complex 6a·CB[7]); upon ternary complex formation with CB[8], phosphorescence is only increased by a factor of 6.4. Both  $\pi$ - $\pi$  stacking and double CB[8] encapsulation are thus needed to maximize emissions.

We finally note that despite short Pt-Pt distances (3.94 and 3.89 Å in ONIOM-optimized assemblies (6b<sub>2</sub>·CB[8]<sub>2</sub>)<sup>HT</sup> and  $(\mathbf{6} \mathbf{b}_2 \cdot CB[8]_2)^{HH}$ ; see Figure 2), we cannot unequivocally identify MMLCT transitions in both absorption and emission spectra. Yam and co-workers<sup>[54]</sup> showed that two Pt acetylide-functionalized calixarenes **9a** and **9b** undergo extensive  $\pi$ - $\pi$  and Pt-Pt stacking in the solid state, with extremely short Pt-Pt distances at least in the case of complex 9b (3.27 Å, shorter than the sum of both approximate van der Waals radii, 3.4 Å). Complex 9a could not be crystallized, however it was found to be emissive above 820 nm as a solid, at both room temperature and 77 K. Based on ample literature precedent,<sup>[83-85]</sup> the authors assigned this emission to <sup>3</sup>MMLCT transitions caused by the proximity of both Pt centers. In agreement with our results, MMLCT transitions were not observed in acetonitrile solution, where complexes 9a and 9b emitted between 640 and 740 nm; the origin of the emission was attributed to <sup>3</sup>MLCT/ <sup>3</sup>LLCT combinations, as discussed above. Similarly to complex 9b that does not present any MMLCT emission even in the solid state, our results further underline that MMLCT transitions are not a de facto consequence of  $\pi$ - $\pi$  and Pt-Pt interactions in stacked Pt acetylides, and are highly geometry and distance dependent.[86]

#### Conclusions

We showed that Pt<sup>II</sup> acetylides **6** and **7** engage in multiple selfsorting behaviors depending on the nature of the imposed external stimuli. Pt complexes **6a**, **6b** and **7b**, which carry aryl substituents at both tpy and acetylide ligands, form exclusive quaternary HT assemblies under kinetic control (i.e. at room temperature), but complexes **6a** and **6b** partially reshuffle to HH assemblies at higher temperature under equilibrium conditions. Complex **6c** adopts both HH and HT arrangements under kinetic control, but resolves into a pure HT orientation under thermodynamic control. We propose a partially dissociative mechanism for the conversion between both HH and HT arrangements, with one Pt guest leaving the CB[8] hosts to allow the reshuffling (see Figure 7). Adding acetonitrile to the aqueous solution of the quaternary assemblies (either as pure HT conformers or a mixture of HH and HT assemblies) triggers the ejection of one CB[8] host, and the reshuffling into ternary complexes in an exclusive HH arrangement, with the remaining CB[8] macrocycle forming a homoternary complex with the pair of tpy substituents. A similar 2:1 HH arrangement is obtained with complex 6d, even in the absence of organic co-solvent, as the cavity of CB[8] is too small to form ternary complexes with one of the guests being an adamantyl unit. To the best of our knowledge, this specific host-guest arrangement, with both positive centers sitting at the same CB[8] rim, and leaving the other rim free of any interaction with guests, is unprecedented in ternary CB[n] complexes. In all cases we surveyed, charged substituents are distributed between both CB[8] rims as evenly as possible. While Scherman's guests 4a<sup>[24]</sup> and our Pt complexes 6a-6c and 7b form quaternary complexes with uneven charge distributions at the CB[8] rims, one can argue that stacked 2:2 assemblies are typically more stable than unstacked ones (see Figure 10a), as long as encapsulating



Figure 10. Equilibria between stacked and unstacked (a) 2:2 assemblies, and (b) 2:1 assemblies.

the free moiety of one of the ditopic guests (labeled G in Figure 10a) into the water-filled cavity of the binary complex (labeled H) is more favorable than switching from an even to an uneven distribution of charges. An interaction between a positive group and a CB[n] rim corresponds to an approximate 4 kcal mol<sup>-1</sup> gain in total free energy (at least in the case of CB[7]),<sup>[45,87]</sup> and the free binding energy of a guest such as berberine (1) into binary complex 1.CB[8] is approximately 8-9 kcal mol<sup>-1.[73]</sup> Therefore, a stacked 2:2 assembly will remain favorable over an unstacked arrangement even if a CB[8] rim can only stabilize one positive charge, as long as the repulsion between both charged units does not exceed 4–5 kcalmol<sup>-1</sup>. A 2:2 assembly will also be entropically favored over a dynamic n:n oligomer, unless obvious steric hindrance prevents the formation of the quaternary assembly (like in the case of oligomers  $(2 \cdot CB[8])_n$  and  $(3 \cdot CB[8])_n$ , for example).<sup>[22]</sup>

The formation of ternary HH assemblies is much more surprising (see Figure 10 b). In this case, the allosteric interaction between both guests (i.e. outside CB[8]) *must* be favorable to compensate for (1) the loss of proper charge/rim interaction ( $\approx$ 4 kcalmol<sup>-1</sup>), and (2) Coulombic repulsion between both positive charges, even as those are weakened by their interactions with the CB[8] rim<sup>[87]</sup> and by solvation. We have shown

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here for the first time that extensive  $\pi$ - $\pi$  stacking between the guests, and possibly metal-metal interactions, can provide such a significant stabilization.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** cucurbituril • macrocycles • metal-metal interactions • Pi interactions • self-sorting

- J. Kim, I.-S. Jung, S.-Y. Kim, E. Lee, J.-K. Kang, S. Sakamoto, K. Yamaguchi, K. Kim, J. Am. Chem. Soc. 2000, 122, 540–541.
- H.-J. Kim, J. Heo, W. S. Jeon, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi,
  K. Kim, Angew. Chem. Int. Ed. 2001, 40, 1526–1529; Angew. Chem. 2001, 113, 1574–1577.
- [3] D. Wu, Y. Li, J. Yang, J. Shen, J. Zhou, Q. Hu, G. Yu, G. Tang, X. Chen, ACS Appl. Mater. Interfaces 2017, 9, 44392–44401.
- [4] P. J. de Vink, J. M. Briels, T. Schrader, L.-G. Milroy, L. Brunsveld, C. Ottmann, Angew. Chem. Int. Ed. 2017, 56, 8998–9002; Angew. Chem. 2017, 129, 9126–9130.
- [5] J. Liu, C. Soo Yun Tan, Y. Lan, O. A. Scherman, J. Polym. Sci. Part A 2017, 55, 3105–3109.
- [6] S. K. Samanta, J. Quigley, B. Vinciguerra, V. Briken, L. Isaacs, J. Am. Chem. Soc. 2017, 139, 9066–9074.
- [7] S. Sankaran, E. Cavatorta, J. Huskens, P. Jonkheijm, *Langmuir* 2017, 33, 8813–8820.
- [8] J. Liu, C. S. Y. Tan, Z. Yu, N. Li, C. Abell, O. A. Scherman, Adv. Mater. 2017, 29, 1605325.
- [9] W. Xu, Q. Song, J.-F. Xu, M. J. Serpe, X. Zhang, ACS Appl. Mater. Interfaces 2017, 9, 11368–11372.
- [10] S. Sankaran, L. Jaatinen, J. Brinkmann, T. Zambelli, J. Voeroes, P. Jonkheijm, ACS Nano 2017, 11, 3867–3874.
- [11] T. Wang, Y. Tang, X. He, J. Yan, C. Wang, X. Feng, ACS Appl. Mater. Interfaces 2017, 9, 6902–6907.
- [12] C. Hu, N. Ma, F. Li, Y. Fang, Y. Liu, L. Zhao, S. Qiao, X. Li, X. Jiang, T. Li, F. Shen, Y. Huang, Q. Luo, J. Liu, ACS Appl. Mater. Interfaces 2018, 10, 4603–4613.
- [13] D. Jiao, F. Biedermann, F. Tian, O. A. Scherman, J. Am. Chem. Soc. 2010, 132, 15734–15743.
- [14] Y. Liu, R. Fang, X. Tan, Z. Wang, X. Zhang, Chem. Eur. J. 2012, 18, 15650– 15654.
- [15] Y. H. Ko, K. Kim, J.-K. Kang, H. Chun, J. W. Lee, S. Sakamoto, K. Yamaguchi, J. C. Fettinger, K. Kim, J. Am. Chem. Soc. 2004, 126, 1932–1933.
- [16] Y. Liu, Y. Yu, J. Gao, Z. Wang, X. Zhang, Angew. Chem. Int. Ed. 2010, 49, 6576–6579; Angew. Chem. 2010, 122, 6726–6729.
- [17] Y.-L. Liu, K. Liu, Z.-Q. Wang, X. Zhang, Chem. Eur. J. 2011, 17, 9930– 9935.
- [18] S. Sonzini, S. T. Ryan, O. A. Scherman, *Chem. Commun.* **2013**, *49*, 8779–8781.
- Chem. Eur. J. 2018, 24, 1 10 www.chemeurj.org

[19] M. Ramaekers, S. P. W. Wijnands, J. L. J. van Dongen, L. Brunsveld, P. Y. W. Dankers, *Chem. Commun.* **2015**, *51*, 3147 – 3150.

- [20] H. D. Nguyen, D. T. Dang, J. L. J. van Dongen, L. Brunsveld, Angew. Chem. Int. Ed. 2010, 49, 895–898; Angew. Chem. 2010, 122, 907–910.
- [21] D. T. Dang, H. D. Nguyen, M. Merkx, L. Brunsveld, Angew. Chem. Int. Ed. 2013, 52, 2915–2919; Angew. Chem. 2013, 125, 2987–2991.
- [22] R. Joseph, A. Nkrumah, R. J. Clark, E. Masson, J. Am. Chem. Soc. 2014, 136, 6602-6607.
- [23] K. Baek, Y. Kim, H. Kim, M. Yoon, I. Hwang, Y. H. Ko, K. Kim, Chem. Commun. 2010, 46, 4091 – 4093.
- [24] G. Wu, M. Olesinska, Y. Wu, D. Matak-Vinkovic, O. A. Scherman, J. Am. Chem. Soc. 2017, 139, 3202–3208.
- [25] J. del Barrio, S. T. J. Ryan, P. G. Jambrina, E. Rosta, O. A. Scherman, J. Am. Chem. Soc. 2016, 138, 5745-5748.
- [26] S. Dapprich, I. Komiromi, K. S. Byun, K. Morokuma, M. J. Frisch, *THEO-CHEM* **1999**, 461–462, 1–21.
- [27] T. Vreven, K. S. Byun, I. Komaromi, S. Dapprich, J. A. Montgomery, Jr., K. Morokuma, M. J. Frisch, J. Chem. Theory Comput. 2006, 2, 815–826.
- [28] A. Aliprandi, D. Genovese, M. Mauro, L. De Cola, Chem. Lett. 2015, 44, 1152-1169.
- [29] H.-L. Au-Yeung, S. Y.-L. Leung, A. Y.-Y. Tam, V. W.-W. Yam, J. Am. Chem. Soc. 2014, 136, 17910–17913.
- [30] H.-L. Au-Yeung, A. Y.-Y. Tam, S. Y.-L. Leung, V. W.-W. Yam, Chem. Sci. 2017, 8, 2267 – 2276.
- [31] S. Chatterjee, A. E. Norton, M. K. Edwards, J. M. Peterson, S. D. Taylor, S. A. Bryan, A. Andersen, N. Govind, T. E. Albrecht-Schmitt, W. B. Connick, T. G. Levitskaia, *Inorg. Chem.* 2015, *54*, 9914–9923.
- [32] H.-K. Cheng, C. Y.-S. Chung, K. Zhang, V. W.-W. Yam, Chem. Asian J. 2017, 12, 1509–1516.
- [33] H.-K. Cheng, M. C.-L. Yeung, V. W.-W. Yam, ACS Appl. Mater. Interfaces 2017, 9, 36220–36228.
- [34] S. Y.-L. Leung, S. Evariste, C. Lescop, M. Hissler, V. W.-W. Yam, Chem. Sci. 2017, 8, 4264–4273.
- [35] S. Y.-L. Leung, W. H. Lam, V. W.-W. Yam, Proc. Natl. Acad. Sci. USA 2013, 110, 7986-7991.
- [36] S. Y.-L. Leung, A. Y.-Y. Tam, C.-H. Tao, H. S. Chow, V. W.-W. Yam, J. Am. Chem. Soc. 2012, 134, 1047–1056.
- [37] S. Yu-Lut Leung, V. Wing-Wah Yam, Chem. Sci. 2013, 4, 4228-4234.
- [38] I. Eryazici, C. N. Moorefield, G. R. Newkome, Chem. Rev. 2008, 108, 1834–1895.
- [39] J. A. G. Williams, Top. Curr. Chem. 2007, 281, 205-268.
- [40] M. Mauro, A. Aliprandi, D. Septiadi, N. S. Kehr, L. De Cola, Chem. Soc. Rev. 2014, 43, 4144–4166.
- [41] J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer, H. B. Gray, Inorg. Chem. 1995, 34, 4591–4599.
- [42] A. Shivanyuk, J. Rebek, Jr., J. Am. Chem. Soc. 2002, 124, 12074-12075.
- [43] P. N. Taylor, H. L. Anderson, J. Am. Chem. Soc. 1999, 121, 11538-11545.
- [44] S. Liu, C. Ruspic, P. Mukhopadhyay, S. Chakrabarti, P. Y. Zavalij, L. Isaacs, J. Am. Chem. Soc. 2005, 127, 15959–15967.
- [45] S. Moghaddam, C. Yang, M. Rekharsky, Y. H. Ko, K. Kim, Y. Inoue, M. K. Gilson, J. Am. Chem. Soc. 2011, 133, 3570-3581.
- [46] J. Schneider, P. Du, P. Jarosz, T. Lazarides, X. Wang, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* 2009, 48, 4306–4316.
- [47] S. Senler, B. Cheng, A. E. Kaifer, Org. Lett. 2014, 16, 5834-5837.
- [48] F. N. Castellano, I. E. Pomestchenko, E. Shikhova, F. Hua, M. L. Muro, N. Rajapakse, *Coord. Chem. Rev.* 2006, 250, 1819–1828.
- [49] M. L. Muro, A. A. Rachford, X. Wang, F. N. Castellano, Top. Organomet. Chem. 2010, 29, 159–191.
- [50] E. Shikhova, E. O. Danilov, S. Kinayyigit, I. E. Pomestchenko, A. D. Tregubov, F. Camerel, P. Retailleau, R. Ziessel, F. N. Castellano, *Inorg. Chem.* 2007, 46, 3038-3048.
- [51] X. Wang, S. Goeb, Z. Ji, F. N. Castellano, J. Phys. Chem. B 2010, 114, 14440–14449.
- [52] C. E. McCusker, A. Chakraborty, F. N. Castellano, J. Phys. Chem. A 2014, 118, 10391–10399.
- [53] H.-S. Lo, S.-K. Yip, K. M.-C. Wong, N. Zhu, V. W.-W. Yam, Organometallics 2006, 25, 3537 – 3540.
- [54] H.-S. Lo, S.-K. Yip, N. Zhu, V. W.-W. Yam, Dalton Trans. 2007, 4386-4389.
- [55] K. M.-C. Wong, V. W.-W. Yam, Coord. Chem. Rev. 2007, 251, 2477-2488.
- [56] C. Po, A. Y.-Y. Tam, V. W.-W. Yam, Chem. Sci. 2014, 5, 2688-2695.
  - © 2018 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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- [57] C. Yu, K. H.-Y. Chan, K. M.-C. Wong, V. W.-W. Yam, Chem. Commun. 2009, 3756–3758.
- [58] H. Sesolis, C. K.-M. Chan, G. Gontard, H. L.-K. Fu, V. W.-W. Yam, H. Amouri, Organometallics 2017, 36, 4794–4801.
- [59] S. C. F. Kui, Y.-C. Law, G. S. M. Tong, W. Lu, M.-Y. Yuen, C.-M. Che, Chem. Sci. 2011, 2, 221–228.
- [60] G. S. M. Tong, Y.-C. Law, S. C. F. Kui, N. Zhu, K. H. Leung, D. L. Phillips, C.-M. Che, Chem. Eur. J. 2010, 16, 6540–6554.
- [61] M.-X. Zhu, W. Lu, N. Zhu, C.-M. Che, Chem. Eur. J. 2008, 14, 9736-9746.
- [62] A. Chakraborty, J. E. Yarnell, R. D. Sommer, S. Roy, F. N. Castellano, *Inorg. Chem.* 2018, *57*, 1298–1310.
- [63] R. Buchner, C. T. Cunningham, J. S. Field, R. J. Haines, D. R. McMillin, G. C. Summerton, J. Chem. Soc. Dalton Trans. 1999, 711–718.
- [64] J. Forniés, S. Fuertes, J. A. Lopez, A. Martin, V. Sicilia, *Inorg. Chem.* 2008, 47, 7166–7176.
- [65] I. Mathew, W. Sun, Dalton Trans. 2010, 39, 5885-5898.
- [66] D. Schilter, J. K. Clegg, M. M. Harding, L. M. Rendina, Dalton Trans. 2010, 39, 239–247.
- [67] C. Cuerva, J. A. Campo, P. Ovejero, M. R. Torres, E. Oliveira, S. M. Santos, C. Lodeiro, M. Cano, J. Mater. Chem. C 2014, 2, 9167–9181.
- [68] A. Díez, J. Forniés, C. Larraz, E. Lalinde, J. A. Lopez, A. Martin, M. T. Moreno, V. Sicilia, *Inorg. Chem.* 2010, 49, 3239–3251.
- [69] J. Kang, X. Zhang, H. Zhou, X. Gai, T. Jia, L. Xu, J. Zhang, Y. Li, J. Ni, *Inorg. Chem.* 2016, 55, 10208–10217.
- [70] M. Martis, K. Mori, K. Kato, G. Sankar, H. Yamashita, ChemPhysChem 2013, 14, 1122-1125.
- [71] T. J. Wadas, Q.-M. Wang, Y.-J. Kim, C. Flaschenreim, T. N. Blanton, R. Eisenberg, J. Am. Chem. Soc. 2004, 126, 16841 – 16849.
- [72] N. Barooah, M. Sundararajan, J. Mohanty, A. C. Bhasikuttan, J. Phys. Chem. B 2014, 118, 7136-7146.
- [73] Z. Miskolczy, L. Biczok, Phys. Chem. Chem. Phys. 2014, 16, 20147-20156.

- [74] W. Lei, Q. Zhou, G. Jiang, Y. Hou, B. Zhang, X. Cheng, X. Wang, Chem-PhysChem 2011, 12, 2933–2940.
- [75] M. Gupta, D. K. Maity, M. K. Singh, S. K. Nayak, A. K. Ray, J. Phys. Chem. B 2012, 116, 5551–5558.
- [76] N. Barooah, J. Mohanty, H. Pal, A. C. Bhasikuttan, Phys. Chem. Chem. Phys. 2011, 13, 13117-13126.
- [77] M. Megyesi, L. Biczók, I. Jablonkai, J. Phys. Chem. C 2008, 112, 3410– 3416.
- [78] C. Marquez, W. M. Nau, Angew. Chem. Int. Ed. 2001, 40, 4387; Angew. Chem. 2001, 113, 4515.
- [79] R. N. Dsouza, U. Pischel, W. M. Nau, Chem. Rev. 2011, 111, 7941-7980.
- [80] S. Senler, W. Li, M. H. Tootoonchi, S. Yi, A. E. Kaifer, Supramol. Chem. 2014, 26, 677–683.
- [81] F. Guo, W. Sun, Y. Liu, K. Schanze, Inorg. Chem. 2005, 44, 4055-4065.
- [82] E. Masson, M. Raeisi, K. Kotturi, Isr. J. Chem. 2018, 58, 413-434.
- [83] C. Yu, K. H.-Y. Chan, K. M.-C. Wong, V. W.-W. Yam, Proc. Natl. Acad. Sci. USA 2006, 103, 19652.
- [84] C. Yu, K. M.-C. Wong, K. H.-Y. Chan, V. W.-W. Yam, Angew. Chem. Int. Ed. 2005, 44, 791 – 794; Angew. Chem. 2005, 117, 801 – 804.
- [85] A. Y.-Y. Tam, K. M.-C. Wong, G. Wang, V. W.-W. Yam, Chem. Commun. 2007, 2028–2030.
- [86] F.-W. Liu, L.-Y. Niu, Y. Chen, V. Ramamurthy, L.-Z. Wu, C.-H. Tung, Y.-Z. Chen, Q.-Z. Yang, *Chem. Eur. J.* 2016, 22, 18132 – 18139.
- [87] X. Ling, S. Saretz, L. Xiao, J. Francescon, E. Masson, Chem. Sci. 2016, 7, 3569–3573.

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## FULL PAPER

### Macrocycles

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Directional Self-Sorting with Cucurbit[8]uril Controlled by Allosteric π-π and Metal-Metal Interactions



# A novel recognition pattern between a pair of positively charged guests and cucurbit[8]uril is presented.