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Molecular Arrangement

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Simultaneous Arrangement of up to Three Different Molecules on the Pore Surface of a Metal–Macrocycle Framework: Cooperation and Competition**

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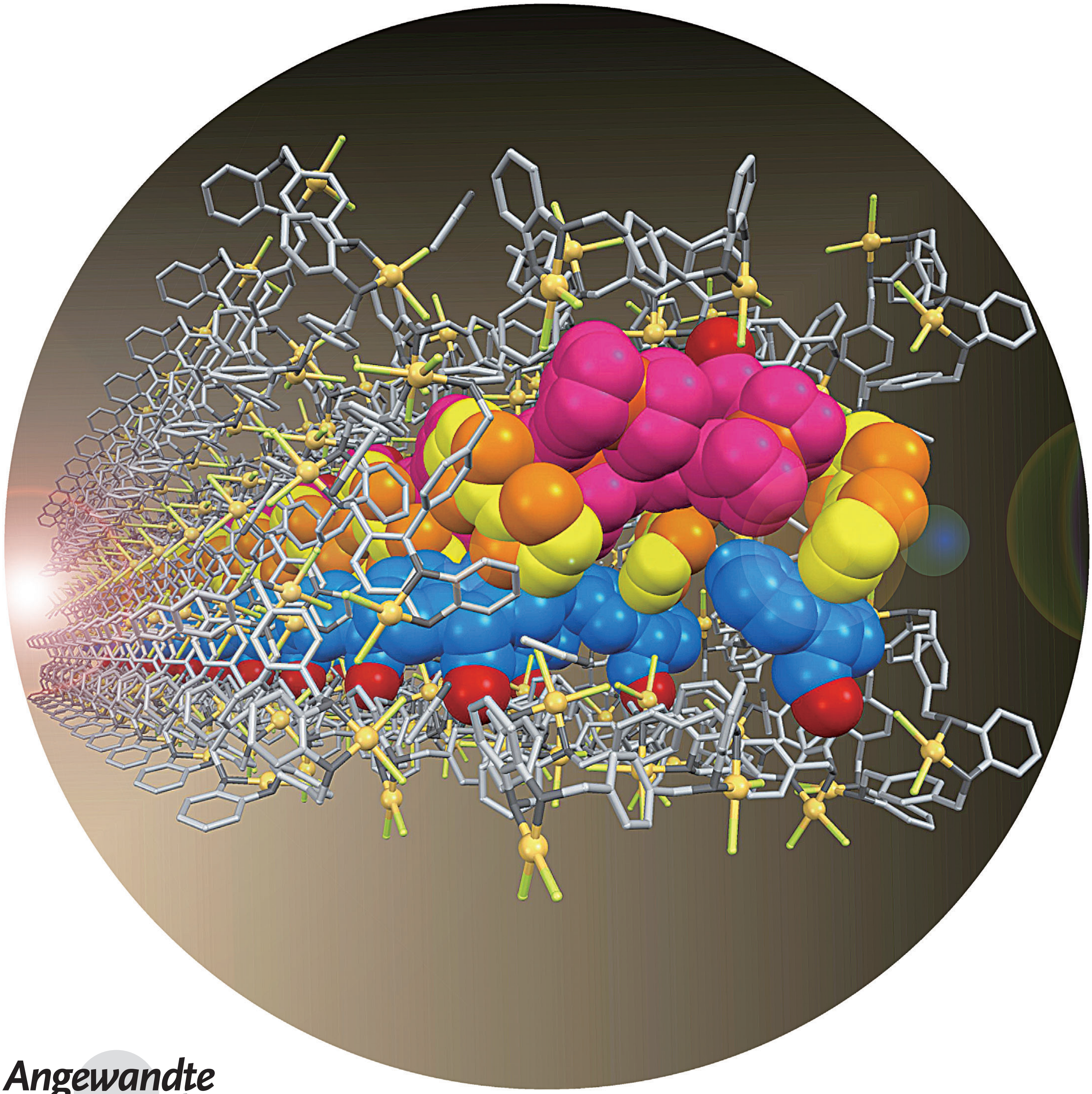


Abstract: *Porous crystals are excellent materials with potential spatial functions through molecular encapsulation within the pores. Co-encapsulation of multiple different molecules further expands their usability and designability. Herein we report the simultaneous arrangement of up to three different guest molecules, TTF (tetrathiafulvalene), ferrocene, and fluorene, on the pore surfaces of a porous crystalline metal–macrocycle framework (MMF). The position and orientation of adsorbed molecules arranged in the pore were determined by single-crystal X-ray diffraction analysis. The anchoring effect of hydrogen bonds between the hydroxy groups of the guest molecules and inter-guest cooperation and competition are significant factors in the adsorption behaviors of the guest molecules. This finding would serve as a design basis of multicomponent functionalized nanospaces for elaborate reactions that are realized in enzymes.*

Molecular recognition is one of the most fundamental chemical events. In particular, the simultaneous recognition of multiple different molecules in a confined space is important to achieve positional and orientational control of the assembled guest molecules. Such highly complex molecular systems are seen in multicomponent enzyme reactions with high affinity, efficiency, and selectivity.[1] In artificial systems, co-encapsulation of two different molecules has been extensively studied with synthetic molecular hosts which have relatively large binding cavities in solution.[2] Several groups have demonstrated co-encapsulation of two different substrates in a single binding pocket of a molecular host, in which specific and catalytic reactions have been achieved.[3] However, co-encapsulation of more than three different molecules in a single molecular host is still rare and therefore challenging.[4] In contrast to molecular hosts in solution, porous crystals, as typified by metal–organic frameworks, coordination polymers, and molecular crystals containing potential voids, exhibit an excellent ability for storage, separation, purification, and catalysis of gaseous molecules in the crystalline states.[5,6] To date, there are several excellent examples of porous crystals which can sort different molecules site-selectively into a crystal.[7] However, only a few examples have been reported on the simultaneous postsynthetic uptake of multiple guest molecules in a unit pore of crystal.[7b,8] A remarkable difference between solution and crystal states is the periodicity of the crystal, which allows the precise site-selective arrangement of different molecules which are co-encapsulated in a unit pore (Figure 1). This feature has been extensively utilized for copolymers,[9] heteronuclear metal wires or particles,[10] and photonic or conductive materials[11] based on the hybrid composites in a unit pore.

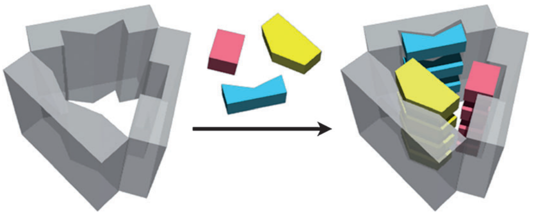
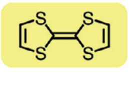


Figure 1. Schematic representation of the simultaneous arrangement of three different guest molecules in a single crystalline pore.

In this context, we have explored the possibility to simultaneously arrange multiple molecules in a single pore of a crystalline metal–macrocycle framework (MMF) that we first reported in 2012.[5h,12] This crystalline MMF (**1**) is formed by the cocrystallization of four stereoisomers of macrocyclic trinuclear palladium complexes (Figure 2), and its nanochannel pore provides six enantiopairs of binding pockets on the inner surface. For example, two isomers of *m*- and *p*-dibromobenzene molecules can be arranged site selectively, and moreover, chiral molecules preferentially bind to only one of the enantiopaired binding pockets on the pore surface. This situation indicates that MMF (**1**) is an excellent scaffold for precise molecular arrangement in the crystalline state.[12a,b] In this study, we aimed to simultaneously capture up to three different guest molecules in a site-selective manner on the pore surface, using ferrocene (**3**), fluorene (**4**), their hydroxymethylated derivatives (**5**) and (**6**), and tetrathiafulvalene (TTF; **2**).[13–15] As a result, the simultaneous arrangement of three different molecules was successfully achieved in two characteristic adsorption manners, guest-assisted cooperative co-adsorption and competitive adsorption. The structure of the ternary inclusion complex was determined by single-crystal X-ray diffraction (XRD) analysis. Moreover, hydrogen bonding between hydroxymethylated guest molecules and the functionalized inner surface was a key factor to control the molecular adsorption behaviors. To our knowledge, there are no reports on the postsynthetic site-selective arrangement of three different molecules in a single pore of porous crystals with structural determination by XRD analysis.



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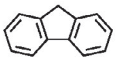

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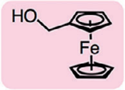

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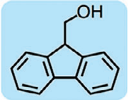

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The nanochannel crystal, MMF (**1**), is obtained by the self-assembly in CH_3CN of four structural isomers, (*P*)-*syn*, (*M*)-*syn*, (*P*)-*anti*, and (*M*)-*anti* forms, of trinuclear Pd^{II} complexes of the tris(*o*-phenylenediamine) macrocyclic ligand **L**, $[Pd_3\mathbf{L}Cl_6]$.[12] The resulting crystal, in which the molecules are held together by hydrogen bonds and Pd–Pd interactions, has large rectangular pores (1.9 × 1.4 nm) that are arranged mutually parallel within the crystal. By

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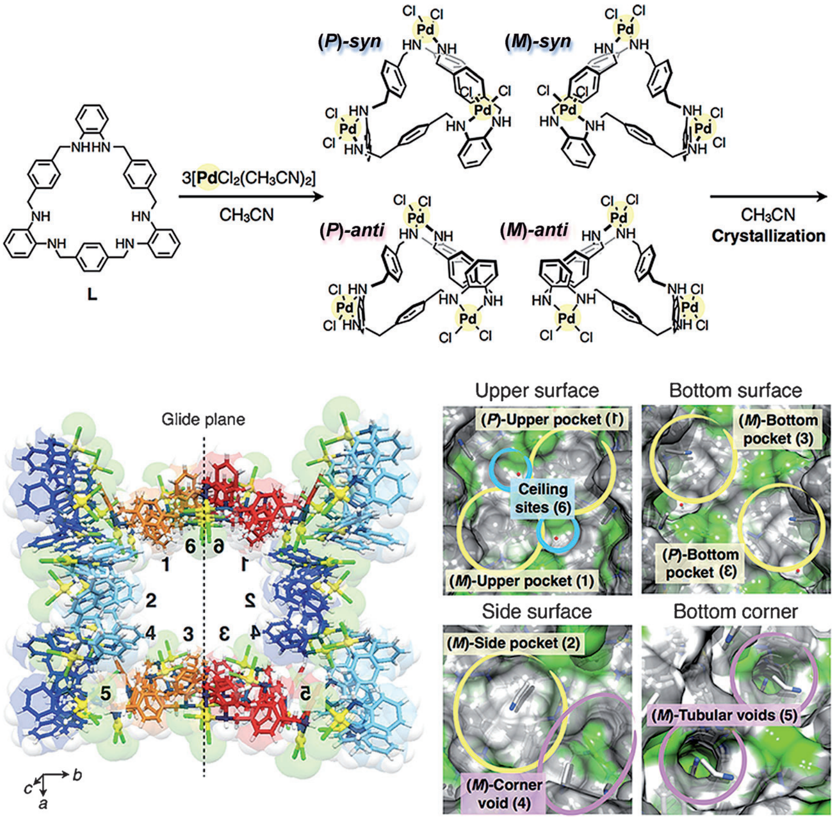

Figure 2. Top: Schematic representation of the formation of MMF (**1**) through cocrystallization of four stereoisomers of [Pd_3LCl_6], (*P*)-*syn*, (*M*)-*syn*, (*P*)-*anti*, and (*M*)-*anti* forms. Bottom: Each individual binding pocket, void, and site is numbered on the solvent-excluded molecular surfaces of the pore.

PLATON analysis, the solvent-accessible volume of the crystal was estimated to be approximately 44%. Note, the pore surface of MMF (**1**) provides six enantiopaired binding sites; specifically the (*P*/*M*)-enantiomers of the upper pocket (the head cavity with *anti* form), side pocket (the tail cavity with *syn* form), bottom pocket (the tail cavity with *anti* form), two interstitial voids (the corner and tubular voids), and one ceiling site with a glide plane (Figure 2). This unique combination and arrangement of the binding pockets allows the arrangement of two different guest molecules on the pore surface in a site-selective or a diastereoselective fashion.[12a,b]

We previously found that, without any advance preparation of the crystal, such as activation or solvent exchange of the pore, MMF (**1**) can readily accommodate guest molecules inside simply by soaking the crystal in a CH_3CN solution containing guest molecules. In most cases, crystal-to-crystal transformation to guest-inclusion complexes took place and the guest binding modes could be determined by single-crystal XRD analyses. We considered only conclusive structures of guest molecules on the inner surfaces of the crystal whose electrons were clearly observed in the electron-density maps. Ambiguous electrons in the center of pores caused by highly disordered guest and/or solvent molecules were removed by the SQUEEZE function.[16] The occupancies of guest molecules were refined based on electron densities in the XRD analyses. The reproducibility of each soaking experiment was confirmed by repeated experiments.

We conducted soaking experiments employing substituent-free guest molecules, TTF (**2**), ferrocene (**3**), or fluorene (**4**) according to our procedure ([**2**], [**3**], and [**4**] = 0.10, 0.12, and 0.40 M, respectively, in CH_3CN). For example, soaking crystals of MMF (**1**) in a saturated solution of **2** caused a color change of the crystals from yellow to brown. This suggests that TTF molecules were accommodated in the pore and a significant amount of oxidized TTF radical cations were generated.[17] For single guest soaking experiments, inclusion of guest molecules **2**–**4** in a pore of MMF (**1**) was suggested by ^1H NMR spectra of solutions obtained by dissolving the resulting soaked crystals in [D_6]dimethylsulfoxide with DCl. In contrast, guest molecules **2**–**4** were not detected at all in the XRD analyses. These observations suggest that the interactions between these guest molecules and the pore surfaces are not significant. After soaking of MMF (**1**) in a solution containing these three compounds, no guest molecules were detected on the pore surface by XRD analysis. Remarkably, however, upon introduction of a hydroxymethyl group to guests **3** and **4** to give **5** and **6**, simultaneous adsorption of guests **2**, **5**, and **6** became possible in a unit pore by both collaborative and competitive effects that are caused between different guest molecules.

Given that the inner surface of MMF (**1**) has a few types of functionalities for hydrogen bonding, that is, N−H and Pd−Cl moieties,[12b] we envisioned that the introduction of a hydroxymethyl group onto guests **3** and **4** would facilitate the adsorption of these guest molecules through hydrogen bonding. Hydroxymethylferrocene (**5**) was employed in a soaking experiment ([**5**] = 0.76 M in CH_3CN), which was followed by single-crystal XRD analysis (Figure 3a–c). Guest **5** was observed in two (*P*/*M*)-upper pockets (62% occupancy), although the position of the hydroxymethyl moiety of **5** could not be determined as a result of disorder. Moreover, guest **5** was also bound to two (*P*/*M*)-corner voids (37% occupancy) through two-point hydrogen bonding, H−O···H−N (O−N bond length 2.87 Å) and O−H···Cl−Pd (O−Cl bond length 3.47 Å). The ferrocene moieties were loosely captured in the cavities of MMF (**1**) through CH–π and van der Waals interactions. As a result, the ferrocene moieties were arranged in the channel direction with intervals of 14.3 Å, although some lattice defects should exist as a result of the moderate occupancies. When 9-fluorenylmethanol (**6**) was used in the soaking experiment ([**6**] = 0.49 M, saturated in CH_3CN), the fluorene moieties were arranged along the (*P*/*M*)-ceiling sites (83% occupancy) through two-point hydrogen bonding, H−O···H−N (O−N bond length 2.92 Å) and O−H···Cl−Pd (O−Cl bond length 3.19 Å) (Figure 3d–f). When the crystals incorporating fluorescent **6** in the pore were irradiated using ultraviolet light ($\lambda_{ex} = 365$ nm), no fluorescence was detected because of efficient quenching by the palladium(II)-containing framework of MMF (**1**). In addition to the XRD analysis, the inclusion of **5** or **6** within the pore of MMF (**1**) was qualitatively confirmed by diffuse reflectance UV/Vis-near-infrared spectra of the KCl-diluted powder samples prepared from the resulting crystals. The spectra obtained were a simple sum of absorption bands derived from MMF (**1**) and **5** (or **6**) as shown in Figure S9 and S13 in the Supporting Information. The inclusion of each guest was also supported by ^{1}H NMR spectroscopic measurements of the solutions obtained from dissolving the resulting crystals (see Tables S4 and S5 in the Supporting Information).

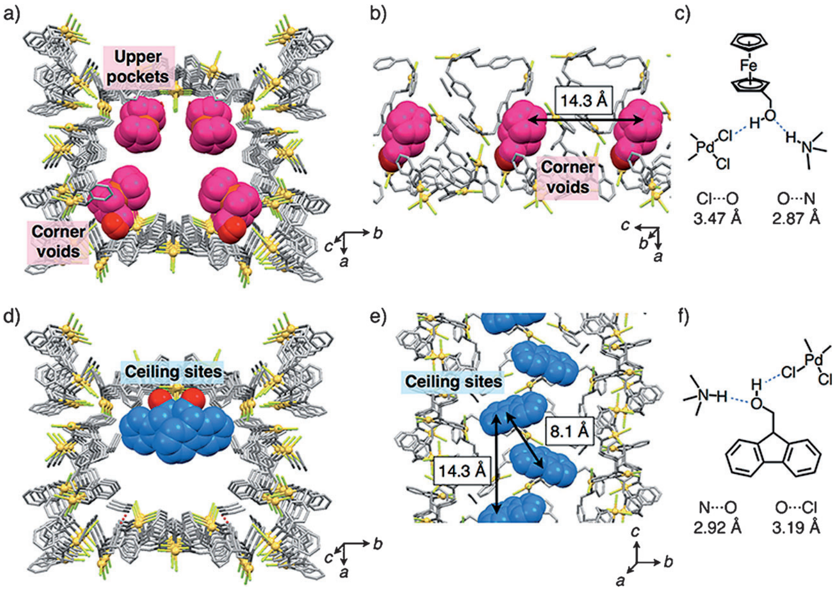

Figure 3. Crystal structures[19] of MMFs including a)–c) **5** (upper pockets and corner voids with 62% and 37% occupancies, respectively) or d)–f) **6** (ceiling sites with 83% occupancy) as the guests (MMF: stick model, each guest: CPK model). a) and d) The pore structures, b) and e) the side or upper surfaces of the MMFs including **5** or **6**, respectively, and c) and f) chemical structures of **5** or **6** forming hydrogen bonds with some functionalities of MMF.

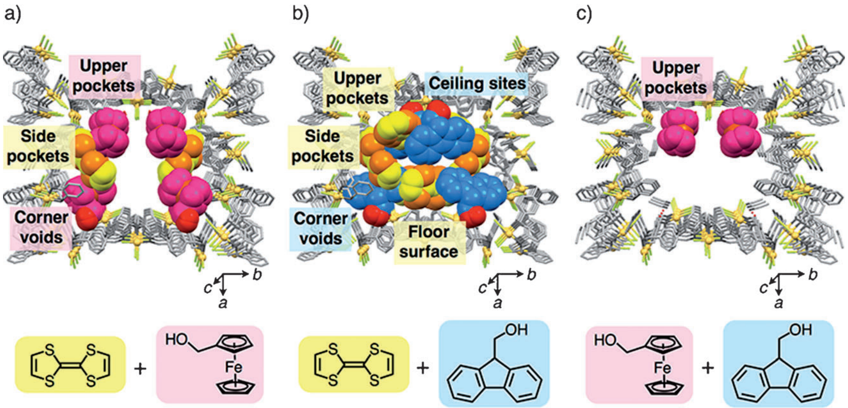

Figure 4. Crystal structures[19] of binary systems composed of a) **2** (side pockets with 43% occupancy) and **5** (upper pockets and corner voids with 55% and 26% occupancies, respectively); b) **2** (side and upper pockets, and floor surface with 28%, 29%, and 20% occupancies, respectively) and **6** (ceiling sites and corner voids with 55% and 40% occupancies, respectively), and c) **5** (upper pockets with 54% occupancy) and **6** (not detected). MMF: stick model, each guest: CPK model.

For double guest adsorption, we examined coadsorption of substituent-free TTF (**2**) and hydroxymethylated compound **5** or **6** in expectation of cooperative behaviors. Strikingly, when MMF (**1**) was soaked in a solution containing TTF (**2**) and the ferrocene derivative **5** ([**2**] and [**5**] = 0.098 and 0.70 M, respectively, in CH$_3$CN), both **2** and **5** were adsorbed on the pore surfaces as determined by single-crystal XRD analysis (Figure 4a). The adsorption sites of **5** were identical to the case with **5** alone as shown above ((*P*/*M*)-upper pockets and (*P*/*M*)-corner voids with 55 and 26% occupancies, respectively). Interestingly, molecules of **2** were also captured by two (*P*/*M*)-side pockets (43% occupancy). In the binding mode, **2** and the macrocyclic cavity in MMF (**1**) are likely to be sterically compatible. A similar effect was observed in the case of a solution containing TTF (**2**) and fluorenyl **6** ([**2**] and [**6**] = 0.098 and 0.40 M, respectively, in CH$_3$CN). In this case, **6** was found to bind to (*P*/*M*)-ceiling sites and (*P*/*M*)-corner voids (55 and 40% occupancies, respectively) and TTFs (**2**) were also captured by (*P*/*M*)-side pockets, (*P*/*M*)-upper pockets, and the floor surface (28, 29, and 20% occupancies, respectively; Figure 4b). As a result, a moderately packed structure composed of **2** and **6** was formed in the channel. It is not clear why the adsorption of **2** was enhanced and **6** was additionally bound at the corner voids. However, there may be some cooperative effects in the steric or electronic interactions between guest molecules, although the sum of their occupancies was less than 100%.

In contrast to this cooperative arrangement, a competitive adsorption was also observed for a solution containing both **5** and **6** ([**5**] and [**6**] = 0.72 and 0.40 M, respectively, in CH$_3$CN). In this case, only **5** was found to bind to (*P*/*M*)-upper pockets with 54% occupancy and no molecules of **6** were observed in the pore in the single-crystal XRD analysis (Figure 4c). This absence of binding of **6** contrasts to the result obtained for the single guest soaking experiment with **6**, in which **6** adsorbs to the ceiling site as shown in Figure 3d. This situation is a result of the competition between **5** and **6** around the upper surface, caused by the steric repulsion between **5** at the upper pocket and **6** at the ceiling site. Moreover, whereas both **5** and **6** are capable of binding to the corner void as mentioned above, no guest molecules could be detected here probably because of the significant competition between **5** and **6** with fairly low occupancies at the corner void.

Simultaneous arrangement of two different molecules, **2** and **5**, or **2** and **6**, was achieved by the effect of the hydroxy anchor group through both cooperative and competitive hydrogen bonding and guest–guest interactions. We then examined co-adsorption of three different molecules, **2**, **5**, and **6**. Upon soaking crystalline MMF (**1**) in a solution containing **2**, **5**, and **6** ([**2**], [**5**], and [**6**] = 0.098, 0.70, and 0.40 M, respectively, in CH_3CN), all three molecules were identified on the pore surface by single-crystal XRD analysis (Figure 5).[17] In this ternary complex, TTF (**2**) was captured at the (*P*/*M*)-side pocket with 56 % occupancy, as was observed with binary systems using **2** and **5** as guests, or **2** and **6**. Hydroxymethylferrocene (**5**) was observed only on the upper surface, the (*P*/*M*)-upper pockets and (*P*/*M*)-ceiling sites with 63 and 60 % occupancies, respectively (Figure 5 b), and 9-fluorenylmethanol (**6**) was adsorbed to the (*P*/*M*)-corner voids with 51 % occupancy. The hydroxymethyl groups of **5** and **6** served as anchors at the ceiling sites and the corner voids for the adsorption through two-point hydrogen bonding with the H–N and Cl–Pd moieties of the surface of MMF (**1**). In contrast to the cases in which **1** was soaked in solutions of **5** or **6** alone, the adsorption sites of **5** and **6** (ceiling sites and corner voids) were exchanged in the ternary system probably as a result of the competitive effect and/or the steric compatibility of the three molecules in the pore. Indeed, several guest–guest interactions were observed, such as a CH–π interaction between two molecules of **5** (C–C bond length 3.40 Å), a CH–π interaction between **5** and **2** (C–C bond length 3.51 Å), and an S–π interaction[18] between **2** and **6** (S–C bond length 3.65 Å), though each occupancy (50–60 %) was moderate. The ternary system composed of **2**, **5**, and **6** in MMF (**1**) was also characterized by diffuse reflectance UV/Vis-NIR analysis of a KCl-diluted powder sample of the resulting crystal (Figure S26 in the Supporting Information).

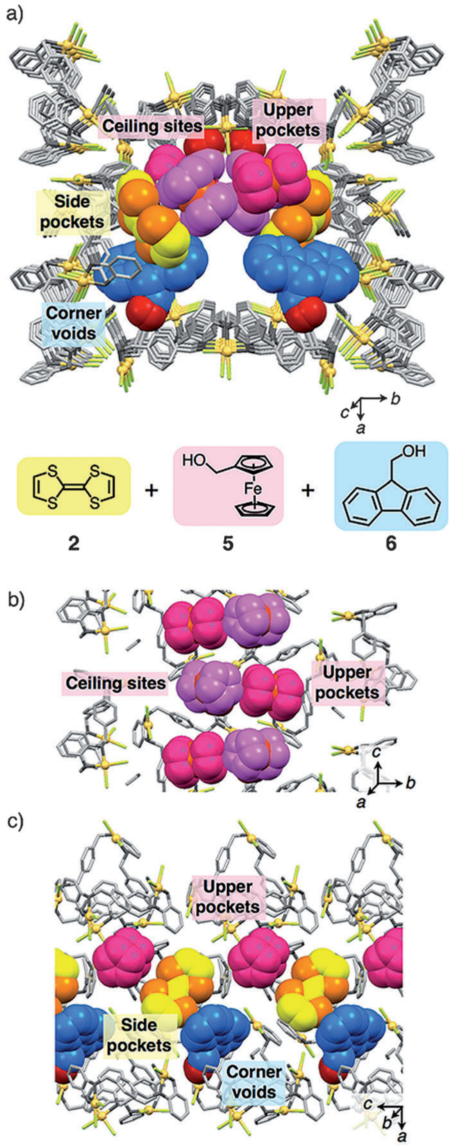

Figure 5. Crystal structure[19] of a ternary system composed of **2** (side pockets with 56 % occupancy), **5** (upper pockets and ceiling sites with 63 % and 60 % occupancies, respectively), and **6** (corner voids with 51 % occupancy) in MMF (**1**) (MMF: stick model, each guest: CPK model). a) The pore structure and b) the upper and c) the side surface structures of the ternary system.

In conclusion, simultaneous binding of three different guest molecules was achieved in a porous crystal, MMF (**1**), by the hydrogen-bonded binding of hydroxymethylferrocene (**5**) and 9-fluorenylmethanol (**6**) to the corner void or ceiling site, and the steric compatibility observed between TTF (**2**) and the side pocket. Thus, as the inner surface of MMF (**1**) has well-defined molecular binding sites, macrocyclic pockets, voids, and hydrogen donor and acceptor sites, it would be possible to predict how multiple different molecules can be arranged in a tailored space based on the adsorption behavior of each individual guest molecule. On the other hand, in addition to the anchoring effect of hydrogen bonding, cooperative and competitive behaviors of more than two different guest molecules are also critical control factors to determine the final position of each guest molecule at equilibrium. Such precise control of the relative position and orientation of multiple different molecules within a confined space would lead to specific or efficient catalytic reactions, such as concerted, multicomponent, or cascade reactions, with the aid of multiple functionalities arranged in the nanochannel.

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[19] CCDC 991585 (**5**-containing MMF), 991586 (**6**-containing MMF), 991587 (**2**,**5**-containing MMF), 991588 (**2**,**6**-containing MMF), 991589 (**5**,**6**-containing MMF), and 991590 (**2**,**5**,**6**-containing MMF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
