

Efficient Route to Organometallic Cage Formation via C–H Activation-Directed Multicomponent Assembly Accompanying Aromatic Guest Encapsulation

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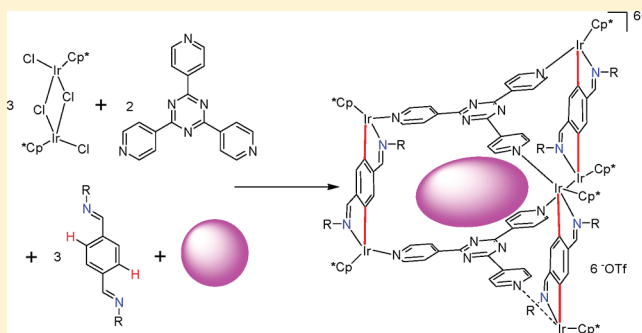
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Supporting Information

ABSTRACT: Driven by C–H activation-directed self-assembly, a series of organometallic cages, **4a–4e**, was obtained from the reaction of $[\text{Cp}^*\text{IrCl}_2]_2$ (**1**) and 2,4,6-tri(4-pyridyl)-1,3,5-triazine (tpt) (**2**) with terephthal-bis-aromatic imine ligands **3a–3e** in the presence of AgOTf (Tf = O_2SCF_3). The ^1H NMR spectra of **4a–4d** revealed that two isomers of the organometallic cages (symmetrical isomer **SI-4** and asymmetrical isomer **ASI-4**) are formed. Pure isomer can be isolated from their chloroform solution of the product mixture by crystallization at low temperature. In the resulting supramolecular assemblies, the two central triazine units are very close, and the centroid...centroid distance between the two triazine moieties is only 3.3 Å. These discrete cages can form complexes with a wide variety of π -donor substrates, including $\text{Pt}(\text{acac})_2$, pyrene, and coronene. The transannular separation between the centers of the triazine rings in the host–guest complex is now enlarged to about 6.66 Å. The preparation of host–guest systems in a one-pot procedure was accomplished. The 1:1 complexation between the guest and host was confirmed by ^1H NMR, elemental analyses and single-crystal X-ray diffraction analyses (**6CSI-4b**, **7CSI-4b**, and **6CSI-4c**).



INTRODUCTION

Discrete three dimensional (3-D) coordination cages are an exciting class of structures with utility in host–guest chemistry, in catalysis, and as microreaction vessels.^{1–4} For example, metal-hinged and organic-pillared caged structures with a large cavity can be self-assembled through stacking interactions. These frameworks can accommodate one, two, or more large π -conjugated molecules. The host–guest system leads to the exhibition of unique chemical and physical properties.^{1,5} Therefore, in order to generate an efficient host–guest system, the design and construction of sufficient cavity size and portal size of the host is very important. Equally, the investigation of the host–guest process to take place is also significant.

In contrast to a vast number of discrete 3-D coordination cages that have been explored through a two-component coordination-driven self-assembly method,^{1,5–8} construction of discrete 3-D coordination cages through a multicomponent coordination-driven self-assembly method remains tedious.^{9–11} Recently, we have developed an efficient procedure for the construction of a series of metallosupramolecules via C–H activation-directed multicomponent self-assembly. This method has been successful in the synthesis of 2-D structures.¹² Self-

assembled 3-D structures are more prevalent and important in nature and biology. One example of the construction of flexible 3-D organometallic cage **4a** via C–H activation-directed multicomponent self-assembly has been reported.¹³ The resulting three-dimensional assembled cages have different cavity sizes, from being “closed” (without internal cavity) to “open” (accommodating one appropriate aromatic guest molecule).

In an extension to this work we have prepared a series of new cationic hexanuclear organometallic cages, **4b–4e**, which incorporate half-sandwich cyclometalated iridium corners. This method connects two panel-like tpt subunits **2** with three double-Schiff-base ligands **3**. Three guest molecules, $\text{Pt}(\text{acac})_2$, pyrene, and coronene, were encapsulated into the cavities of these organometallic prisms and, in contrast to our previous work, the formation of host–guest systems was accomplished in a one-pot procedure.

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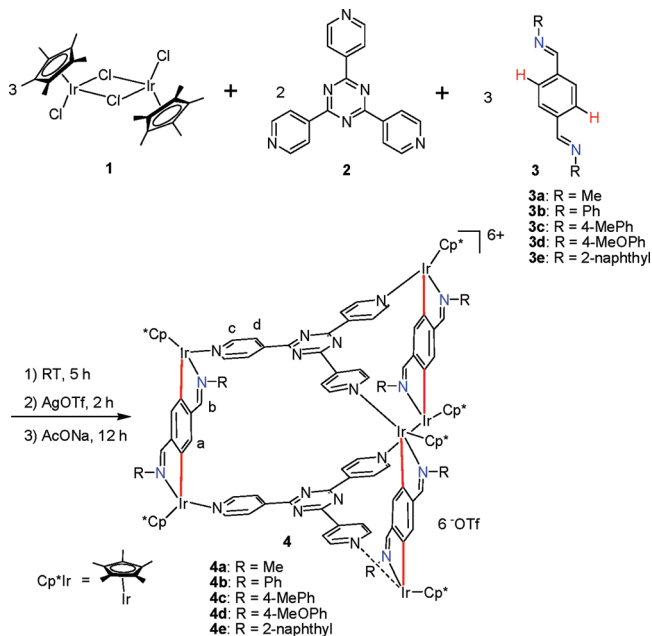
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RESULTS AND DISCUSSION

Synthesis of Organometallic Cages. We have described hexanuclear prism **4a**, which was obtained by C–H activation-directed multicomponent self-assembly of *N,N'*-dimethylterephthal-bis-imine ligand **3a**, tpt, and Cp^*Ir . The formation of half-sandwich cyclometalated iridium corners was confirmed by its X-ray structural analysis.¹³ In the solid state, complex **4a** presented a “closed” form, in which the centroid⋯centroid distance between the two triazine moieties is only 3.3 Å. In order to investigate whether other substituted terephthal-bis-imine ligands can be employed to build polynuclear organometallic cages, we have examined the reaction of $[\text{Cp}^*\text{IrCl}_2]_2$ (**1**) and tpt (**2**) with terephthal-bis-aromatic imine ligand **3b–3e** in the presence of AgOTf (Tf = O_2SCF_3). In all cases hexanuclear cages (**4b–4e**) were obtained in medium to good yields. The elemental analyses of the isolated products were indicative of a 3:1 ratio of Cp^*Ir and the tpt ligand. The ^1H NMR spectra of **4b**, **4c**, and **4d** revealed that two isomers of the organometallic cages (symmetrical isomer **SI-4** and asymmetrical isomer **ASI-4**)¹³ are formed. However, pure **ASI-4** can be isolated from the chloroform solution of the product mixture by crystallization at low temperature. When the double-Schiff-base ligand was changed to (naphthalen-1-ylimino)-methylbenzylidene-naphthalen-1-amine **3e**, only symmetrical isomer **SI-4e** was obtained, as suggested by its NMR spectrum. The synthesis of **4b–4e** demonstrates that organometallic cages can be obtained with various Schiff-base ligands. This flexibility is important for modifying the solubility and isomer selectivity of the cages.

Scheme 1. C–H Bond Activation-Directed Multicomponent Assembly of Organometallic Cages 4



Host–Guest Properties. The cage **4a** has turned out to be an extremely potent container for aromatic molecules. The transformation of host **4a** from the “closed” form to the “open” one was realized by an encapsulated guest. Thus, the preparation of host–guest systems in a one-pot procedure seems feasible. When $\text{Pt}(\text{acac})_2$ (**5**), sodium acetate, and terephthal-bis-imine ligand **3b** were added to the light yellow

solution, which originated from **1**, **2**, and AgOTf , the formation of **5C4b** was accomplished after stirring for 12 h at room temperature.

The ^1H NMR spectrum of the reaction mixture showed distinct signals suggesting the selective formation of two different host–guest systems (Figure 1). The two products

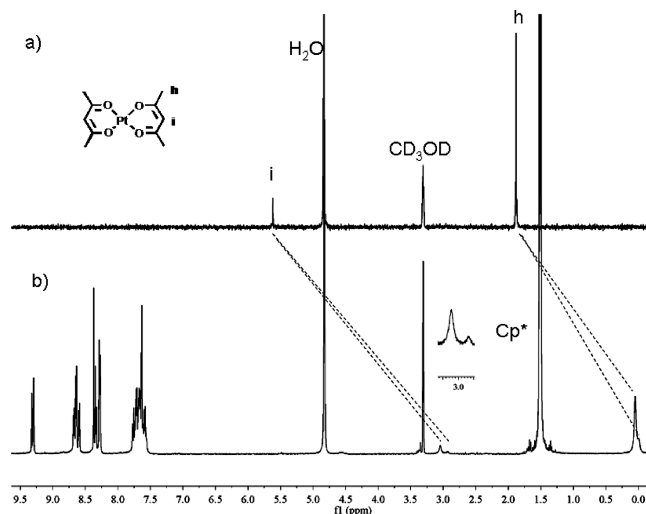


Figure 1. ^1H NMR (500 MHz, CD_3OD , RT) spectra of (a) free **5** and (b) **5C4b**.

were assigned as different intercalating structures between the host and the guest. The following observations are fully consistent with the hypothesis. (i) $\text{Pt}(\text{acac})_2$ (**5**) is placed in two different positions in a 3:1 ratio, where highly upfield-shifted signals of **5** were observed at 3.04 (2.94) and 0.05 (0.01) ppm (compared with those of 5.62 and 1.88 ppm of free **5**), because of the shielding effect by the host. (ii) The host **4b** is located in two different positions in a 1:3 ratio, which indicated that there are two isomers (symmetrical isomer **SI-4b** and asymmetrical isomer **ASI-4b**). (iii) The stoichiometry of host and guest is 1:1.

Because X-ray-quality single crystals of **5C4b** could not be obtained, we resorted to increasing the available π -surface area of the guest, as this would provide a possible method of enhancing the binding strength through an increase of atom–atom contacts. We hence turned to pyrene **6** (four fused rings) and coronene **7** (six fused rings) as potential substrates to obtain more structural information on these host–guest systems. Pyrene **6** and coronene **7** are known to form crystalline donor–acceptor complexes with an electron-deficient triazine core (because of the electron-withdrawing effect of the pyridyl groups).¹³ Computational modeling indicated that pyrene **6** and coronene **7** would fit comfortably in the cavities of **4b**. Indeed, as one equivalent of pyrene **6** or **7** was added to the reaction mixture of **1**, **2**, and **3**, the self-assembly of **6C4b** or **7C4b** can be achieved. For example, pyrene **6** was effectively trapped inside the cage. As shown in Figure 2b, the ^1H NMR spectrum of the resultant solution in CD_3OD showed very large $\Delta\delta$ values for both the host and the substrate. Similar to that in **5C4b**, two series of signals of **4b** in a 3:1 ratio were observed, which suggests there are two different environments of host–guest systems. The integral ratio of **6** and **4b** in the ^1H NMR spectra and elemental analysis confirmed the formation of the 1:1 host–guest complex **6C4b**.

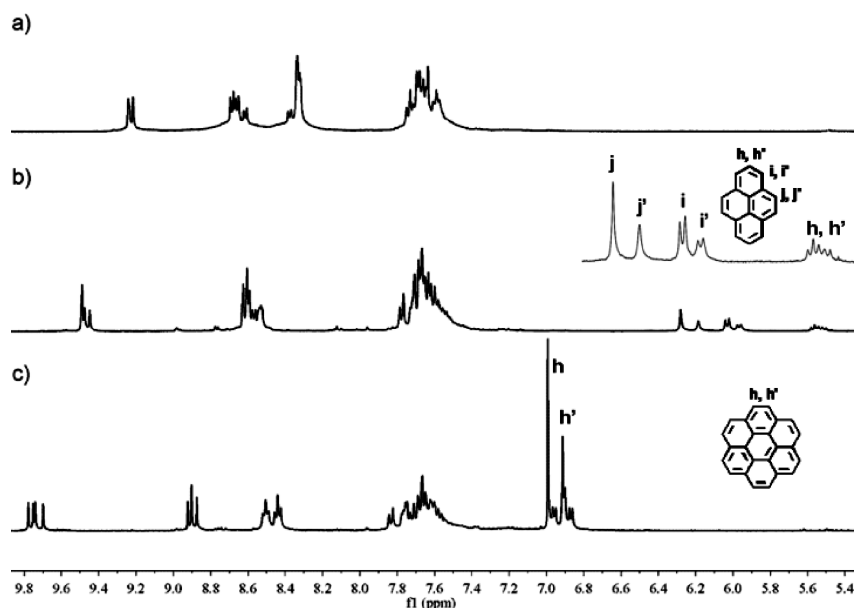


Figure 2. ^1H NMR (400 MHz, CD_3OD , RT) spectra of (a) **4b**, (b) **6C4b**, and (c) **7C4b**.

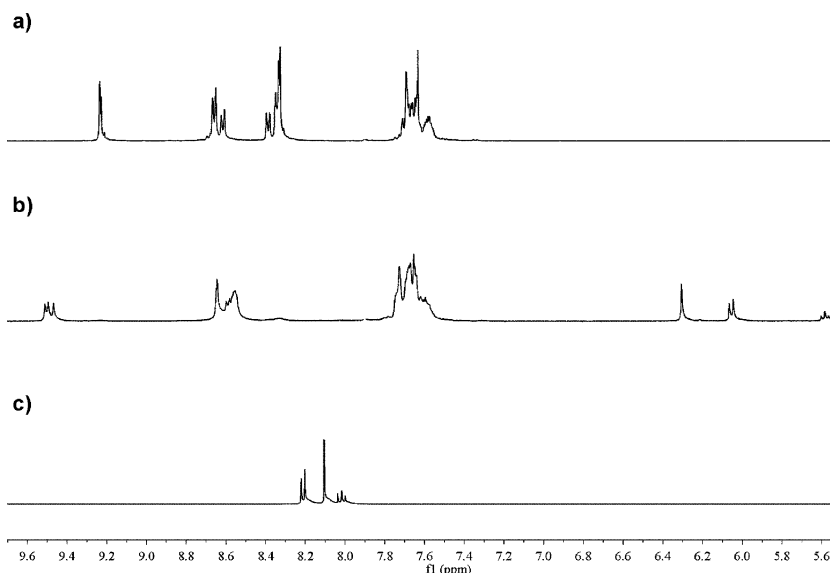


Figure 3. ^1H NMR (400 MHz, CD_3OD , RT) spectra of (a) **ASI-4b**, (b) **6CASI-4b**, and (c) free **6**.

Formation of a donor–acceptor complex between **6** and **4b** was confirmed by single-crystal X-ray analysis. Red crystals of the isomer **6CSI-4b** were obtained from vapor diffusion of diethyl ether into a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ solution of the product mixture for several days. As shown in Figure 4, the pyrene molecule is trapped in the cavity, with distances between the centroid of the pyrene unit and the centroids of the triazine system of 3.33 Å. The pure isomer **6CASI-4b** can also be separated, as determined by ^1H NMR (Figure 3b). However, its X-ray analysis is still elusive despite intense efforts in growing single crystals of this complex.

Characteristic high-field resonances and two signals of coronene **7** suggest the formation of different host–guest systems between **7** and the designed cage. Large complexation shifts ($\Delta\delta > 1$ ppm) were observed in the ^1H NMR spectra of **7** in the presence of cage **4b** (Figure 2c). The guest proton encapsulated by the symmetrical isomer is shifted much more upfield than that of its asymmetrical isomer. This result clearly

demonstrated different intercalations between the host and the guest.

We have established the formation of relatively flexible organometallic cages with a facile “breathing” distortion. Depending on the rotation of the rigid pillars, the distance between the “roof” and “floor” of the cage (the distance between the trigonal planes) can vary. In the “closed” form, the guest molecule is unable to contact both binding surfaces of the triazine rings. In the guest-encapsulation processes, the modulation of cavity size (“closed” form to “open” form conversion) is influenced by “conformational selection”. The transannular separation between the centers of the triazine rings in the complex **7CSI-4b** is now enlarged to about 6.66 Å. But this is slightly shorter (ca. 4.4%) than the estimated Ir–Ir separation of related clips (ca. 6.97 Å).^{12a} It is thus consistent with the presence of strong face-to-face $\pi\cdots\pi$ interactions between the host and the guest molecule. Moreover, cage **SI-4b**

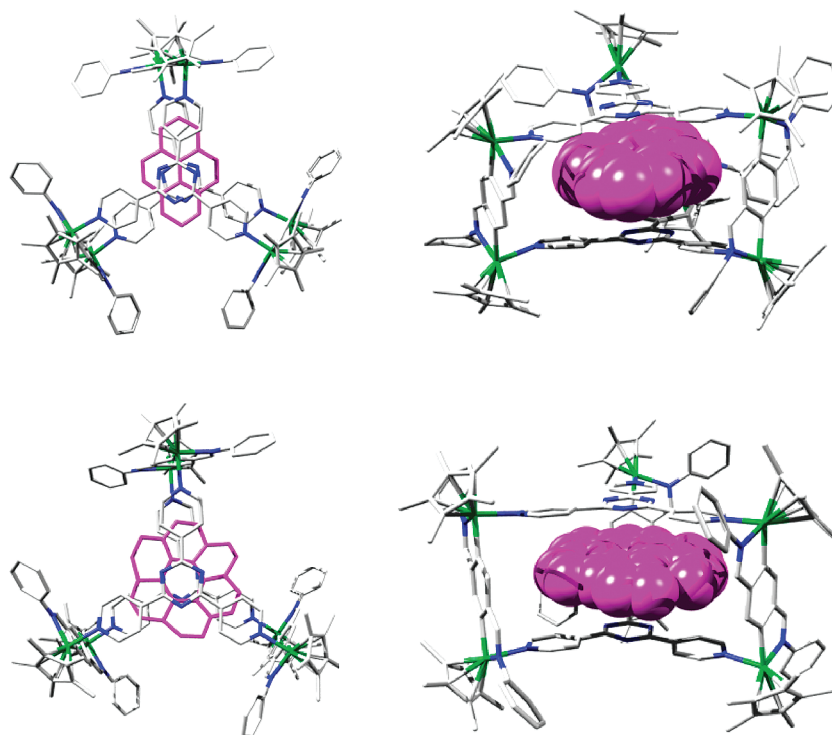


Figure 4. Left: Top views of crystal structures of **6CSI-4b** and **7CSI-4b** in stick mode. Right: Side views of crystal structures of **6CSI-4b** and **7CSI-4b** in stick mode. Guest molecules in space-filling mode. Hydrogen atoms, solvents, and counterions have been omitted for clarity. Color labels: Ir green, N blue, C gray or purple.

itself is twisted by 13° in order to maximize the host–guest interaction.

In the self-assembly process, the successful formation of cyclometalated half-sandwich corners is a key step in the construction of metallosupramolecules.^{14,15} As shown in Figure 4, each imine moiety is coordinated to the corresponding Cp^*Ir fragments by transmetalation to form six Cp^*Ir -based five-membered metallacyclic corners. In these systems, the most important driving force for complexation is clearly the donor–acceptor $\pi\cdots\pi$ -stacking interaction.

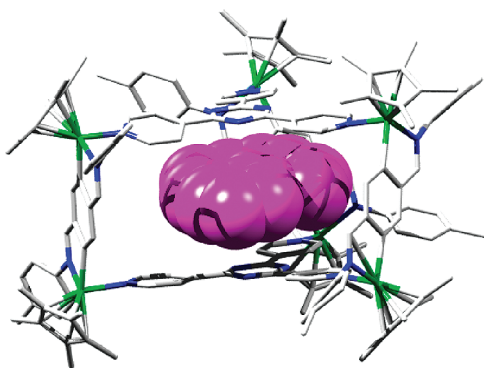


Figure 5. Side views of crystal structures of **6CSI-4c** in stick mode. Guest molecule **6** in space-filling mode. Hydrogen atoms, solvents, and counterions have been omitted for clarity. Color labels: Ir green, N blue, C gray or purple.

CONCLUSION

In conclusion, we present a facile and versatile strategy for the synthesis of host–guest complexes in which a C–H activation-

directed self-assembly allows precise control over cage formation. Using this approach, new chemical phenomena can be better manipulated at the molecular level based on specific host–guest interactions. The strong interaction found between cages **4** and π -conjugated molecule **5**, **6**, or **7** suggests that more complex supramolecular assemblies might be achieved through the interactions of these cages with guests. Current efforts are directed to develop this design strategy into the synthesis of an organic-pillared framework with a large box-shaped hydrophobic cavity, which is ideal for binding two or more planar molecules.

EXPERIMENTAL SECTION

General Data. All reactions and manipulations were performed under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were purified by standard methods prior to use. $[\text{Cp}^*\text{IrCl}_2]_2$ ¹⁶ and **4a**¹³ were prepared according to the reported procedure. The ^1H NMR spectra were measured on a VAVCE-DMX 400 or 500 spectrometer in CDCl_3 or CD_3OD . Elemental analysis was performed on an Elementar Vario EL III analyzer. IR (KBr) spectra were recorded on a Nicolet FT-IR spectrophotometer.

Synthesis of Organometallic Cage 4b. 2,4,6-Tri(4-pyridyl)-1,3,5-triazine (tpt) (**2**) (31 mg, 0.10 mmol) was added to a solution of $[\text{Cp}^*\text{IrCl}_2]_2$ (**1**) (120 mg, 0.15 mmol) in CH_2Cl_2 at room temperature and stirred for 5 h. AgOTf (154 mg, 0.6 mmol) was added to the resulting yellow precipitate and stirred for 2 h. NaOAc (72 mg, 0.9 mmol) and ligand **3** (0.15 mmol) were added, and the mixture was kept stirring for an additional 12 h. The solvent was removed, and the residue was extracted with CH_2Cl_2 , followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL, and diethyl ether was added, to give cage **4b**. Complex **4b** was dissolved in warm CHCl_3 and crystallized at 0°C over 6 h three times. Pure **ASI-4b** was isolated as prismatic crystals, and pure **SI-4b** was isolated from the mother liquor.

SI-4b. Anal. Calcd (%) for $C_{162}H_{156}F_{18}Ir_6N_{18}O_{18}S_6$: C 44.93, H 3.63, N 5.82. Found: C 44.96, H 3.46, N 5.61. 1H NMR (400 MHz, $CDCl_3$, ppm, 25 °C): δ 9.317 (HC=N, Hb); 8.497 (d, Ar-H, Hc); 8.367 (s, Ar-H, Ha); 8.027 (d, Ar-H, Hd); 7.602 (m, Ar-H); 7.498 (m, Ar-H); 1.440 (s, Cp*). IR (KBr): $\nu(C=N)$, 1562 cm^{-1} .

Synthesis of Organometallic Cage 4c. This complex (83% yield) was obtained from **1**, **2**, and **3c** by a procedure similar to that described for **4b**. Pure **SI-4c** was isolated from the mother liquor. Anal. Calcd (%) for $C_{168}H_{168}F_{18}Ir_6N_{18}O_{18}S_6$: C 45.70, H 3.84, N 5.71. Found: C 45.52, H 3.75, N 5.49. 1H NMR (400 MHz, $CDCl_3$, ppm, 25 °C): δ 9.308 (HC=N, Hb); 8.472 (d, Ar-H, Hc); 8.350 (s, Ar-H, Ha); 7.980 (d, Ar-H, Hd); 7.406 (s, Ar-H); 2.496 (s, Me); 1.458 (s, Cp*). IR (KBr): $\nu(C=N)$, 1562 cm^{-1} .

Synthesis of Organometallic Cage 4d. This complex (85% yield) was obtained from **1**, **2**, and **3d** by a procedure similar to that described for **4b**. Pure **SI-4d** was isolated from the mother liquor. Anal. Calcd (%) for $C_{168}H_{168}F_{18}Ir_6N_{18}O_{24}S_6$: C 44.73, H 3.75, N 5.59. Found: C 44.53, H 3.72, N 5.62. 1H NMR (400 MHz, $CDCl_3$, ppm, 25 °C): δ 9.188 (HC=N, Hb); 8.472 (d, Ar-H, Hc); 8.290 (s, Ar-H, Ha); 7.502 (d, Ar-H, Hd); 7.082 (d, Ar-H); 3.906 (s, Me); 1.463 (s, Cp*).

Synthesis of Organometallic Cage 4e. This complex (76% yield) was obtained from **1**, **2**, and **3e** by a procedure similar to that described for **4b**. Anal. Calcd (%) for $C_{186}H_{168}F_{18}Ir_6N_{18}O_{18}S_6$: C 48.24, H 3.66, N 5.44. Found: C 48.19, H 3.37, N 5.14. 1H NMR (400 MHz, $CDCl_3$, ppm, 25 °C): δ 9.375 (HC=N, Hb); 8.756 (d, Ar-H, Hc); 8.521 (s, Ar-H, Ha); 8.350 (d, Ar-H, Hd); 8.070 (d, Ar-H); 7.983 (d, Ar-H); 7.793 (m, Ar-H); 7.629 (d, Ar-H); 7.603 (d, Ar-H); 1.226 (s, Cp*).

General Procedure for the Synthesis of Host–Guest Systems. Typically, tpt (**2**) (31 mg, 0.10 mmol) was added to a solution of $[Cp^*IrCl_2]_2$ (**1**) (120 mg, 0.15 mmol) in CH_2Cl_2 at room temperature and stirred for 5 h. AgOTf (154 mg, 0.6 mmol) was added to the resulting yellow precipitate and stirred for 2 h. NaOAc (72 mg, 0.9 mmol), Pt(acac)₂ (**5**) or pyrene (**6**), or coronene (**7**) (0.05 mmol), and ligand **3b** or **3c** (0.15 mmol) were added, and the mixture was kept stirring for an additional 12 h. The solvent was removed and the residue was extracted with CH_2Cl_2 , followed by filtration through a glass filter (G5) to remove insoluble compounds. The filtrate was concentrated to about 3 mL, and diethyl ether was added, to give the host–guest complex as a red solid.

5C4b: 236 mg, 72% yield. Anal. Calcd (%) for $C_{172}H_{170}F_{18}Ir_6N_{18}O_{22}PtS_6$: C 43.73, H 3.63, N 5.34. Found: C 43.54, H 3.48, N 5.20. 1H NMR (500 MHz, CD_3OD , ppm, 25 °C): δ 9.292, 9.297, 9.302, 9.325 (HC=N, Hb and Hb'); 8.588–8.685 (m, Ar-H, Ha,a' and Hc,c'); 8.269–8.372 (m, Ar-H, Hc,c' Hd,d'); 7.578–7.775 (m, Ar-H); 3.044 (s, acac-H, Hi'), 2.935 (s, acac-H, Hi), 1.497, 1.512, 1.527 (s, Cp* and Cp*'); 0.051 (s, acac-H, Hh'), 0.005 (s, acac-H, Hh).

6C4b: 226 mg, 86% yield. Anal. Calcd (%) for $C_{178}H_{166}F_{18}Ir_6N_{18}O_{18}S_6$: C 47.16, H 3.69, N 5.56. Found: C 47.23, H 3.42, N 5.33. 1H NMR (400 MHz, CD_3OD , ppm, 25 °C): δ 9.469, 9.497, 9.510 (s, HC=N, Hb and Hb'); 8.545–8.652 (m, Ar-H, Ha,a', Hc,c', and Hd,d'); 7.557–7.808 (m, Ar-H); 6.302 (s, pyrene, Hj'); 6.207 (s, pyrene, Hj); 6.052 (d, pyrene, Hi'); 5.985 (d, pyrene, Hi); 5.584 (m, pyrene, Hh'); 5.541 (m, pyrene, Hh); 1.506, 1.521, 1.531 (s, Cp*); 1.500 (s, Cp*). IR (KBr): $\nu(C=N)$, 1561 cm^{-1} .

7C4b: 231 mg, 89% yield. Anal. Calcd (%) for $C_{186}H_{168}F_{18}Ir_6N_{18}O_{18}S_6$: C 48.24, H 3.66, N 5.44. Found: C 48.06, H 3.28, N 5.48. 1H NMR (400 MHz, CD_3OD , ppm, 25 °C): 9.799 (s, HC=N, Hb); 9.720, 9.762, 9.774 (s, HC=N, Hb'); 8.895 (s, Ha); 8.944, 8.942 (s, Ar-H, Ha'); 8.511–8.541, m, Hc and Hc'); 8.445–8.478 (m, Hc'); 7.855 (d, $J = 6.4$ Hz, Hd); 7.569–7.797 (m, Ar-H and Hd'); 7.014 (s, corone, Hh'); 6.979 (d, $J = 6.4$ Hz, Hd'); 6.934 (s, corone, Hh); 6.926 (d, $J = 6.4$ Hz, Hd'); 6.890 (d, $J = 6.4$ Hz, Hd'); 1.513, 1.534, 1.541 (s, Cp*); 1.509 (s, Cp*). IR (KBr): $\nu(C=N)$, 1573 cm^{-1} .

6CASI-4b. Pyrene **6** (0.1 mmol) was added a methanol solution of **ASI-4b** (0.1 mmol), and the reaction mixture was stirred for 2 h at room temperature. The solution was concentrated by evaporation to

about 3 mL, and diethyl ether was added, to give the product **6CASI-4b** as a dark red solid. Anal. Calcd (%) for $C_{178}H_{166}F_{18}Ir_6N_{18}O_{18}S_6$: C 47.16, H 3.69, N 5.56. Found: C 47.23, H 3.42, N 5.33. 1H NMR (400 MHz, CD_3OD , ppm, 25 °C): δ 9.469, 9.495, 9.512 (s, HC=N, Hb'); 8.555–8.645 (m, Ar-H, Ha' and Hc'); 7.596–7.727 (m, Ar-H and Hd'); 6.307 (s, pyrene, Hj'); 6.056 (d, pyrene, Hi'); 5.584 (m, pyrene, Hh'); 1.508, 1.521, 1.531 (s, Cp*').

7CASI-4b. Coronene **7** (0.1 mmol) was added to a methanol solution of **ASI-4b** (0.1 mmol), and the reaction mixture was stirred for 2 h at room temperature. The solution was concentrated by evaporation to about 3 mL, and diethyl ether was added, to give the product **7CASI-4b** as a dark red solid. 1H NMR (400 MHz, CD_3OD , ppm, 25 °C): δ 9.719, 9.762, 9.773 (s, HC=N, Hb'); 8.943, 8.942 (s, Ar-H, Ha'); 8.519 (d, $J = 6.4$ Hz, Hc'); 8.446–8.479 (m, 9H, Hc'); 7.587–7.795 (m, Ar-H); 7.014 (s, corone, Hh'); 6.978 (d, $J = 6.4$ Hz, Hd'); 6.928 (d, $J = 6.4$ Hz, Hd'); 6.890 (d, $J = 6.4$ Hz, Hd'); 1.513, 1.534, 1.541 (s, Cp*').

Crystal Structure Determinations. All the determinations of unit cell and intensity data of **6CASI-4b** were collected using a Bruker APEX DUO diffractometer and using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) monochromatized by a Triumph Mo monochromator at 173 K. Data of **7CASI-4b** were collected on a CCD-Bruker SMART APEX system using Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) monochromatized by a Triumph Mo monochromator at 203 K.

The structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL). SADABS absorption corrections were applied to the data.^{17,18} In complex **6CASI-4b** there are several disordered chloroform molecules in the asymmetric unit which cannot be refined or restrained properly. One of six triflate anions is also strongly disordered, so the SQUEEZE¹⁹ algorithm had to be used to omit them. Atoms O4–12, S2, S3, F4–12, C31, C38, C39, C78, C101, C113, C119–121, C157–161, C170, C171, and C179 were refined isotropically, and other non-hydrogen atoms were refined anisotropically. Hydrogen atoms that could be found were placed in the geometrically calculated positions with fixed isotropic thermal parameters. However, hydrogen atoms of water molecules could not be found. In the asymmetric unit of complex **7CASI-4b**, one triflate anion and several solvent molecules were disordered and could not be refined or restrained properly. Therefore, the SQUEEZE¹⁹ program had to be used to remove them. Atoms F1–6, C79–96, C98, and O12 were refined isotropically because of nonpositive definition, and other non-hydrogen atoms were refined anisotropically. Hydrogen atoms of methanol molecules could not be found, and other hydrogen atoms were put in calculated positions. Further crystallographic details can be found in the CIF files. In complex **6CASI-4c**, there are several disordered chloroform molecules in the asymmetric unit that cannot be refined or restrained properly. Two of six triflate anions are also strongly disordered, so the SQUEEZE¹⁹ algorithm had to be used to omit them. One 4'-methylphenyl fragment is disordered, and it was refined to two positions (50:50). Atoms O2, O7–9, S3, F1–12, C12, C56, C58, C64, C141, C148, C163–166, C168–170, C172, C173, C175–178, C181, and C182 were refined isotropically, and other non-hydrogen atoms were refined anisotropically. In all complexes, hydrogen atoms that could be found were placed in the geometrically calculated positions with fixed isotropic thermal parameters.

Crystal data for **6CASI-4b**: $C_{178}H_{166}F_{18}Ir_6N_{18}O_{18}S_6 \cdot 2CHCl_3 \cdot H_2O$, $M_r = 4789.60$, $T = 173(2)$ K, monoclinic space group $C2/c$, $a = 54.785(4)$ Å, $b = 25.759(2)$ Å, $c = 38.850(5)$ Å, $\beta = 131.3530(10)^\circ$, $V = 41155(7)$ Å³, $Z = 8$, $\rho_{calcd} = 1.546$ g cm^{-3} . A total of 97 391 reflections, of which 35 300 were independent ($R_{int} = 0.1095$). The structure was refined to final $R_1 = 0.0878$ [$I > 2\sigma(I)$], $wR_2 = 0.2524$ for all data, GOF = 0.828, and residual electron density max./min. = 2.964 and -1.731 e Å⁻³. Crystal data for **7CASI-4b**: $C_{186}H_{168}F_{18}Ir_6N_{18}O_{18}S_6 \cdot 4MeOH \cdot 2Et_2O$, $M_r = 4907.35$, $T = 203(2)$ K, monoclinic space group $C2/c$, $a = 37.877(8)$ Å, $b = 20.798(5)$ Å, $c = 30.783(12)$ Å, $\beta = 116.856(2)^\circ$, $V = 21634(10)$ Å³, $Z = 4$, $\rho_{calcd} = 1.507$ g cm^{-3} . A total of 52 558 reflections, of which 19 032 were independent ($R_{int} = 0.0668$). The structure was refined to final $R_1 = 0.0851$ [$I > 2\sigma(I)$], $wR_2 = 0.2533$ for all data, GOF = 1.041, and residual electron density max./min. = 5.609 and -2.648 e Å⁻³.

Crystal data for **6CSI-4c**: $C_{184}H_{178}F_{18}Ir_6N_{18}O_{18}S_6$, $M_r = 4617.00$, $T = 173(2)$ K, monoclinic space group $C2/c$, $a = 56.022(4)$ Å, $b = 25.982(2)$ Å, $c = 38.976(3)$ Å, $\beta = 131.8910(10)^\circ$, $V = 42233(6)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.452$ g cm⁻³. A total of 12 6737 reflections, of which 37 110 were independent ($R_{\text{int}} = 0.0876$). The structure was refined to final $R_1 = 0.0792$ [$I > 2\sigma(I)$], $wR_2 = 0.2297$ for all data, GOF = 0.878, and residual electron density max./min. = 3.681 and -1.516 e Å⁻³.

■ ASSOCIATED CONTENT

Supporting Information

Crystallographic data for **6CSI-4b**, **7CSI-4b**, and **6CSI-4c** are available free of charge via the Internet at <http://pubs.acs.org>.

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