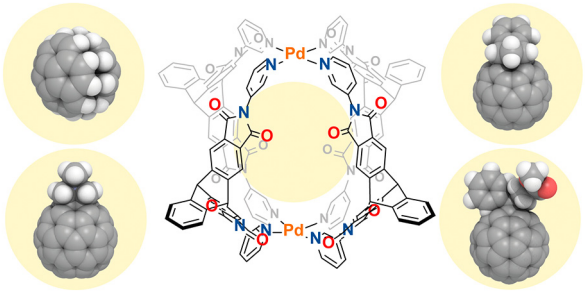
Accepted Manuscript online: 2022-09-29 Article published online: 2022-10-28



# Guest Encapsulation Scope of a Triptycene-Based $Pd_2L_4$ Coordination Cage

**Shota Hasegawa**[a]
**Ananya Baksi**[a]
**Bin Chen**[a,b]
**Guido H. Clever***[a]

[a] Department of Chemistry and Chemical Biology, TU Dortmund University, Otto-Hahn Str. 6, 44227 Dortmund, Germany
[b] State Key Laboratory of Radiation Medicine and Protection, Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, Soochow University, Suzhou, P. R. of China
* guido.clever@tu-dortmund.de



Aromatic and fullerene-based guests are encapsulated inside a triptycene-based coordination cage

Received: 16.08.2022
Accepted after revision: 16.09.2022
DOI: 10.1055/a-1953-0155; Art ID: OM-2022-08-0033-SC



**Abstract** The scope of a lantern-shaped, triptycene-based $Pd_2L_4$ coordination cage to encapsulate various carbon-rich guests was investigated. The cage was found to bind two molecules of corannulene and a variety of $C_{60}$ derivatives in moderate to quantitative yields. Non-disruptive extraction of encapsulated fullerene derivative $PC_{61}BM$ from the cage was demonstrated by the simple addition of $CS_2$ into an acetonitrile solution of the host–guest complex. This process can be accomplished in a layer-to-layer fashion, and thus, the recovered cage can be further utilized in a recycling process. As this self-assembled host is readily synthesized and able to transfer fullerenes and a range of its derivatives into polar organic solvents, it allows facilitating purification, chemical modification and solid-state processing of fullerenes for a range of materials applications.

**Key words:** supramolecular chemistry, host–guest complexes, fullerenes

## Introduction

Fullerene $C_{60}$ is a spherical molecular allotrope of carbon with plenty of applications.[1] For instance, the carbonaceous ball is a widely used electron-accepting material in photovoltaics.[2] Tuning of the molecular orbital energies of $C_{60}$ (and its derivatives) is a critical factor to tune the efficiency of exciton and electron transfer processes in materials for molecular electronics and photovoltaics.[3] Chemical modification of $C_{60}$ can be employed to tune both its electronic structure as well as its solubility and mode of embedding into composite materials, thus, many reactions to chemically modify $C_{60}$ have been developed.[4,5] For instance, $PC_{61}BM$ (**4**) is one of the most utilized $C_{60}$ derivatives as an electron-accepting material.[6] While covalent modification is a straightforward way to tune the electronic properties of $C_{60}$, chemical reactions that produce stereochemically defined products are often difficult to control due to a comparable reactivity of carbon positions on pure $C_{60}$ and its derivatives, causing the formation of multi-adduct isomers.[6,7] To achieve regio-controlled modification, various strategies have been developed such as tether-directed syntheses and supramolecular masking methods.[8–16] Furthermore, examples of $C_{60}$ derivative encapsulation inside coordination cages have been reported.[17–19] Among them, especially the coordination cages reported by Ribas and Yoshizawa were examined for their propensity to encapsulate and release $C_{60}$ derivatives.[17,19]

Tailored purification methods for $C_{60}$ derivatives are still scarce, and thus, there is demand for further strategies to be explored. Recently, our group has reported a new family of coordination cages based on organic ligands having a curved π-surface.[20–23] These self-assembled hosts provide a cavity of suitable size and shape to strongly bind $C_{60}/C_{70}$ via convex–concave π-interactions. Tight encapsulation of fullerenes inside these cages allows for a multitude of applications. For example, the generation and long-term stabilization of the $C_{60}^{\bullet-}$ radical anion by nano-confinement inside triptycene-based cage $Pd_2\mathbf{1}_4$ in organic solvents has been demonstrated.[23]

For some reported coordination cages composed of ligands with curved π-surfaces, binding of carbon-rich guests has been demonstrated in the past[24]; however, the encapsulation capability of $Pd_2\mathbf{1}_4$ has only been investigated for $C_{60}$ so far. We envisaged that this coordination cage should be able to accommodate not only pristine $C_{60}$, but also other carbon-rich guest compounds including $C_{60}$ derivatives. Stimulated by the idea of widening the scope of guest uptake, the encapsulation capability of $Pd_2\mathbf{1}_4$ has been further investigated in the herein-described study (Figure 1). In the course of this study, $Pd_2\mathbf{1}_4$ was found to be capable of encap-

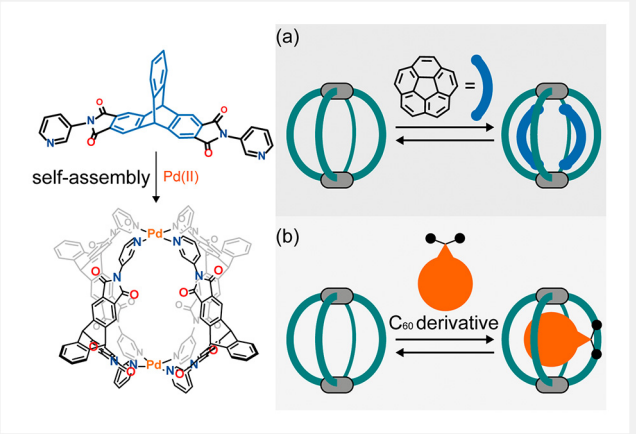



**Figure 1** Encapsulation of (a) two molecules of corannulene and (b) a $C_{60}$ derivative inside $Pd_2\mathbf{1}_4$.

sulating two molecules of corannulene (Figure 1a). Furthermore, $Pd_2\mathbf{1}_4$ displayed high to quantitative affinity towards a variety of $C_{60}$ derivatives such as $PC_{61}BM$ (Figure 1b). Stimulated by the fact that $Pd_2\mathbf{1}_4$ can encapsulate $PC_{61}BM$ but not $PC_{62}BM$, which is a bis-adduct analogue of $PC_{61}BM$, we explored a facile method to purify $PC_{61}BM$ by selective uptake and extraction from the cavity. We herein report that addition of $CS_2$ is able to liberate encapsulated $PC_{61}BM$ from the cage in a recycling, yet non-disruptive, manner.

## Results and Discussion

The triptycene-based $Pd_2L_4$ coordination cage was prepared following our previous work.[23] We started investigating the guest scope of $Pd_2\mathbf{1}_4$ with a selection of rather small neutral polyaromatic hydrocarbons (for details, see Figures S24 and S25). Among these, only corannulene, representing a substructure of $C_{60}$, was found to be encapsulated within the cavity (Figure 2a). In detail, an excess amount of powdered corannulene was added into an acetonitrile solution of $Pd_2\mathbf{1}_4$ and heated at 70 °C for 24 h.[25] In the $^1$H NMR spectrum, a new set of peaks which could be assigned to $(Cor)_2@Pd_2\mathbf{1}_4$ was observed besides parental $Pd_2\mathbf{1}_4$, which means that encapsulation of corannulene occurs pairwise in a cooperative fashion with exchange kinetics slower than the NMR time scale (Figure 2b). Two molecules of corannulene were found to be incorporated inside $Pd_2\mathbf{1}_4$ according to the $^1$H NMR signal integration ratio between host and guest signals and the results of an NOESY experiment (Figures S28 and S30). Noteworthy, the signals assigned to the $Pd_2\mathbf{1}_4$ host not containing the corannulene pair showed slightly different chemical shifts as compared to the cage sample in the absence of corannulene. We assume that this is caused by loose encapsulation of a single corannulene in fast exchange for this fraction of species in the equilibrium.

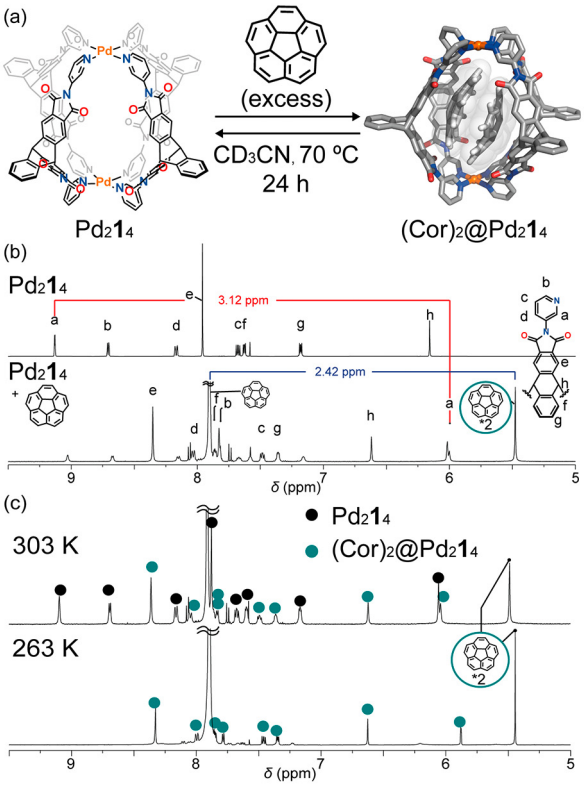



**Figure 2** (a) Encapsulation of corannulenes inside $Pd_2\mathbf{1}_4$. An optimized geometry is shown for $(Cor)_2@Pd_2\mathbf{1}_4$. (b) $^1$H NMR spectra ($CD_3CN$, 0.7 mM, 500 MHz, 298 K) of $Pd_2\mathbf{1}_4$ (top) and $Pd_2\mathbf{1}_4$ with excess amount of corannulene (bottom). (c) $^1$H NMR spectra ($CD_3CN$, 500 MHz) of $(Cor)_2@Pd_2\mathbf{1}_4$ at 303 K (top) and at 263 K (bottom).

The protons of the encapsulated corannulene guests display an upfield shift by 2.42 ppm compared to the free corannulene existing in the solution, comparable to what was observed with other hosts.[24,26] In addition, the $H^a$ signal of the pyridine donors, pointing inward the cavity, also undergoes an upfield shift by 3.12 ppm, probably due to direct interactions between corannulene and these hydrogen substituents, further supporting the encapsulation of corannulene within the cavity.[23] Furthermore, diffusion-ordered spectroscopy (DOSY) analysis revealed that the encapsulated corannulenes show a smaller diffusion coefficient compared to free corannulene in the same acetonitrile solution (Figure S31). Further, encapsulation was found to be strongly temperature-dependent. Upon cooling, the ratio of $(Cor)_2@Pd_2\mathbf{1}_4$ increased from 39% (303 K) up to 77% (253 K, both at 0.70 mM cage concentration and excess of powdered corannulene). Intriguingly, during the VT-$^1$H NMR experiment, a host–guest complex of $Pd_2\mathbf{1}_4$ and single corannulene, namely $Cor@Pd_2\mathbf{1}_4$, was not observed as a distinguishable species (Figure 2c). To elucidate the dynamic behavior

of guest exchange, a $^1$H NMR titration experiment was performed (Figure S37). Aliquots of an acetonitrile solution of corannulene were titrated into an acetonitrile solution of $Pd_2\mathbf{1}_4$. As a result, peaks assigned to the host–guest complex $(Cor)_2@Pd_2\mathbf{1}_4$ appeared over the addition of 7 equiv of corannulene, alongside with all remaining peaks of $Pd_2\mathbf{1}_4$ showing slight shifts ($\Delta\delta_{max} = -0.02$ ppm), probably indicating a fast equilibrium of the empty host with a labile mono-guest adduct.

To gain a further insight into this process, density functional theory (DFT) calculations at the M06-2X/Lanl2dz level of theory were performed. As a result, encapsulation of two corannulene molecules was found to lead to a more than two times higher gain in stabilization energy than encapsulation of only a single corannulene inside the host (Table S2). In the calculated geometry, convex–concave interactions between the encapsulated corannulenes and the ligands are clearly visible.

Next, we investigated the encapsulation of various $C_{60}$ derivatives inside $Pd_2\mathbf{1}_4$. Therefore, $C_{60}$ derivatives were dispersed in an acetonitrile solution of $Pd_2\mathbf{1}_4$ at 70 °C for 48 h, after which the residual powdered $C_{60}$ derivative remains were removed. Compounds **2**–**4**, comprising different $C_{60}$ mono-adducts, were bound in 87 – 100% yield, determined by $^1$H NMR analyses measured at 298 K (Figure 3a, b).[27] In the $^1$H NMR spectra of the resulting solutions, a new set of signals was found besides empty $Pd_2\mathbf{1}_4$. As shown in Figure 3a, the cage should be desymmetrized due to the encapsulation of these $C_{60}$ derivatives, containing a rather bulky substituent. Indeed, in the $^1$H NMR spectra of **2**–**4**$@Pd_2\mathbf{1}_4$, two sets and four sets of signals were observed for the pyridine and triptycene-backbone protons, respectively, which indicates the encapsulation of the $C_{60}$ derivatives with slow exchange dynamics (see Figure 3c and Figures S2, S8 and S16 for complete NMR assignments). In addition, DOSY $^1$H NMR shows that all of the newly appearing signals belong to a single species, having a similar hydrodynamic radius to $C_{60}@Pd_2\mathbf{1}_4$ (Figures S5, S13, and S21).[23] The formation of the host–guest complexes was further confirmed by ESI-MS measurements (Figure 3d). The encapsulation yield of **4** was 87% under the chosen conditions, while quantitative encapsulation of **2** was achieved. In addition, the small apertures found in the densely packed, modelled geometry of **4**$@Pd_2\mathbf{1}_4$ suggested that encapsulation of bulkier derivatives such as $PC_{62}BM$, which can be found as side-products in the course of the synthesis of **4**, should not be possible (Figure 4a, b).[6] To test this hypothesis, an excess amount of $PC_{62}BM$, available as a mixture of regio-isomers, was dispersed in an acetonitrile solution of $Pd_2\mathbf{1}_4$ for 24 h at 70 °C. In the resulting $^1$H NMR spectrum, only one set of signals for empty $Pd_2\mathbf{1}_4$ was observed (Figure S45). Hence, for steric reasons the bis-adduct does not seem to be able to bind. This result implies that $Pd_2\mathbf{1}_4$ is able to recognize $C_{60}$ mono-adducts over corresponding bis-adducts. In fact,

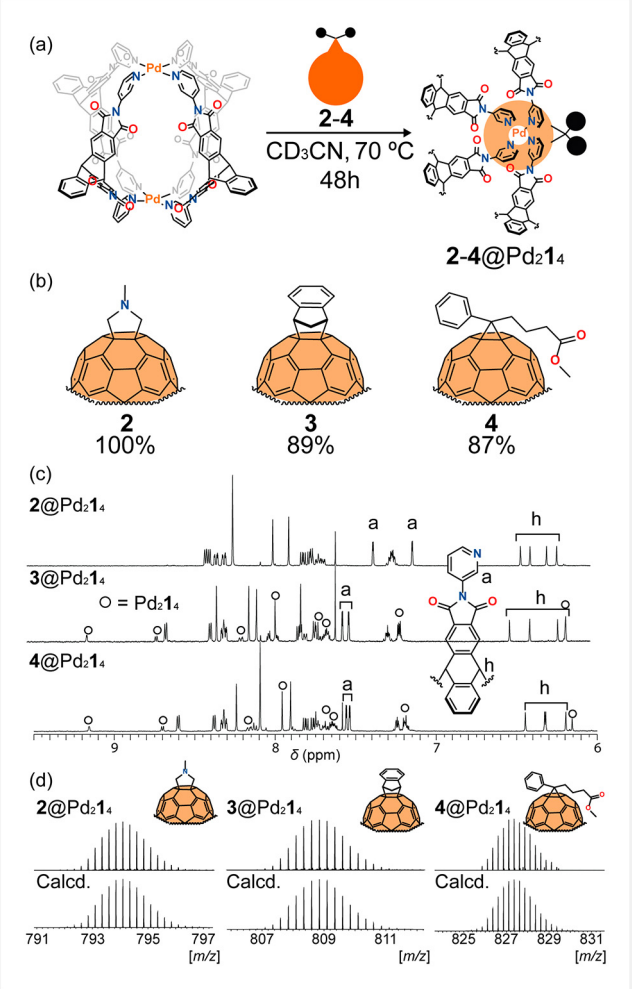



**Figure 3** (a) Encapsulation of **2**–**4** in $Pd_2\mathbf{1}_4$. (b) Chemical structures of **2**–**4** with encapsulation ratio indicated below each structure. (c) $^1$H NMR spectra ($CD_3CN$, 500 MHz, 298 K) of **2**$@Pd_2\mathbf{1}_4$ (top), **3**$@Pd_2\mathbf{1}_4$ (middle) and **4**$@Pd_2\mathbf{1}_4$ (bottom). (d) Excerpts of ESI-MS spectra (positive mode) of **2**$@Pd_2\mathbf{1}_4$ (left), **3**$@Pd_2\mathbf{1}_4$ (middle) and **4**$@Pd_2\mathbf{1}_4$ (right) with a calculated isotopic pattern for each species.

when the same equimolar amount of **4** and $PC_{62}BM$ were dispersed in an acetonitrile solution of $Pd_2\mathbf{1}_4$ (with minute amounts of $CS_2$ as an additive to accelerate guest uptake in the heterogeneous system) at room temperature for 24 h, **4**$@Pd_2\mathbf{1}_4$ was obtained as a major species (66% encapsulation yield), but again no host–guest complex with $PC_{62}BM$ was formed. As can be seen in the molecular model of **4**$@Pd_2\mathbf{1}_4$ calculated by DFT, the four ligands are forced close together to leave an enough space for accommodating the single appendix of **4** (Figure 4a, b). We assume that this structural detail then precludes encapsulation of bulkier $PC_{62}BM$. Often, encapsulation of lipophilic guest molecules such as fullerenes within a coordination cage dissolved in a very polar solvent is governed by solvophobic interactions,

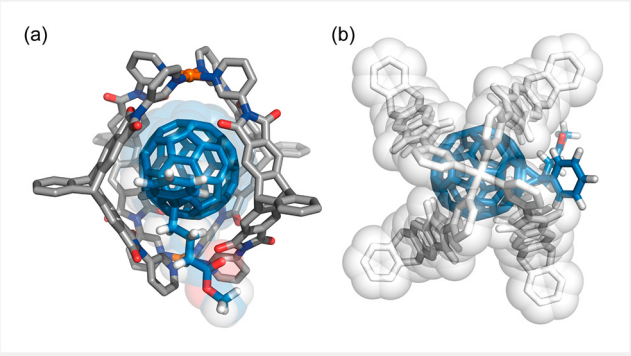



**Figure 4** Optimized geometry of **4**@$Pd_2$**1**$_4$ obtained by gas-phase DFT calculations at the B3LYP/Lanl2dz level of theory for Pd atoms and 6–31 G(d,p) for all other atoms; (a) front and (b) top views.

as these guests prefer a rather non-polar cavity environment.[28] Therefore, addition of a better solvent for $C_{60}$ to the host–guest complex solution was envisaged to shift the equilibrium between confined guest and free guest towards releasing of the guest molecule into the solvent.

Based on this assumption, we tested a variety of solvents which are commonly utilized to solubilize $C_{60}$. Indeed, addition of $CS_2$ was found to liberate encapsulated guest **4**. Once 33 vol% of $CS_2$ was added to an acetonitrile solution of **4**@$Pd_2$**1**$_4$, the mixture was shaken and was left to stand for a few minutes. After this period of resting time, two layers were obtained, where the upper layer is a transparent acetonitrile solution of the empty coordination cage and the bottom layer is a reddish $CS_2$ solution containing the liberated compound **4** (Figure 5). The purity of the extracted guest molecule was confirmed by $^1$H NMR measurement (Figure S44). Note that this method is non-disruptive with respect to the host system, as can be seen in the $^1$H NMR spectrum of intact $Pd_2$**1**$_4$ recovered from the upper layer (Figure S43). Finally, we challenged the repetitive encapsulation and release of **4** over 4 cycles (Table S3). After extracting **4** from **4**@$Pd_2$**1**$_4$, the mixture was cooled to −78 °C (to conveniently freeze the acetonitrile) and the $CS_2$ layer was removed by decanting. The recovered acetonitrile solution containing $Pd_2$**1**$_4$ was further utilized for the next extraction experiment. Although a decline of the encapsulation yield was observed over repetitive cycles, $Pd_2$**1**$_4$ was proven to accommodate and liberate **4** in a recycling yet non-disruptive manner (Figure 5). We presume that the observed decrease of the encapsulation yield can be attributed to losing some host by a slight miscibility of $CS_2$ in the acetonitrile solution.

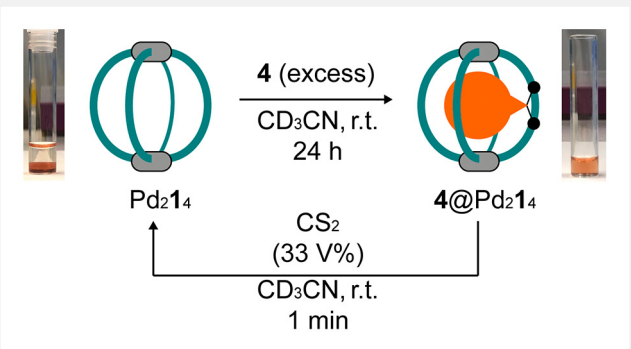



**Figure 5** Recycling encapsulation and release of **4** using $Pd_2$**1**$_4$; **4**@$Pd_2$**1**$_4$ was obtained in 80.5%, 80.3%, 62.9%, and 52.2% yields after the 1st to 4th cycle, respectively. The yields were determined by $^1$H NMR.

## Conclusions

We have investigated the encapsulation capability of coordination cage $Pd_2$**1**$_4$ towards corannulene and several $C_{60}$-derivatives. Owing to the curved π-surface of the triptycene backbone of **1**, $Pd_2$**1**$_4$ can encapsulate such non-planar aromatic compounds in high to quantitative yields. $Pd_2$**1**$_4$ binds two molecules of corannulene in solution. Furthermore, $Pd_2$**1**$_4$ incarcerates $C_{60}$ derivatives **2**–**4**, all mono-adducts of $C_{60}$, in a way that the guests' substituents point outside the cavity through the space between the ligands, leading to a breaking of the fourfold symmetry of the cage. Encapsulation and liberation of **4** utilizing $Pd_2$**1**$_4$ were demonstrated in a recycling manner. The recycling process can be accomplished in a layer-to-layer fashion, using two different solvents. In addition, $Pd_2$**1**$_4$ does not encapsulate bulkier bis-adducts of fullerene derivatives, which should make $Pd_2$**1**$_4$ a candidate for potent and sustainable fullerene derivative purification systems.

## Funding Information

This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), under Germany's Excellence Strategy EXC 2033 – Project No. 390677874 – RESOLV and GRK2376 "Confinement-controlled Chemistry" – Project No. 331085229.

## Acknowledgements

S. H. thanks the DAAD for a Ph.D. fellowship. We thank Prof. W. G. Hiller for assistance with NMR measurements.

## Supporting Information

Supporting Information for this article is available online at https://doi.org/10.1055/a-1953-0155.

## Conflict of Interest

The authors declare no conflict of interest.

## References and Notes

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.
(2) Brabec, C. J.; Gowrisanker, S.; Halls, J. J. M.; Laird, D.; Jia, S.; Williams, S. P. *Adv. Mater.* **2010**, *22*, 3839.
(3) Umeyama, T.; Imahori, H. *Acc. Chem. Res.* **2019**, *52*, 2046.
(4) Nierengarten, J.-F. *New J. Chem.* **2004**, *28*, 1177.
(5) Itami, K. *Chem. Rec.* **2011**, *11*, 226.
(6) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532.
(7) Puplovskis, A.; Kacens, J.; Neilands, O. *Tetrahedron Lett.* **1997**, *38*, 285.
(8) Isaacs, L.; Haldimann, R. F.; Diederich, F. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2339.
(9) Thilgen, C.; Diederich, F. *Chem. Rev.* **2006**, *106*, 5049.
(10) Maxouti, K. L.; Hirsch, A. *Eur. J. Org. Chem.* **2018**, *2018*, 2579.
(11) Fuertes-Espinosa, C.; García-Simón, C.; Pujals, M.; Garcia-Borràs, M.; Gómez, L.; Parella, T.; Juanhuix, J.; Imaz, I.; Maspoch, D.; Costas, M.; Ribas, X. *Chem* **2019**, *6*, 169.
(12) Leonhardt, V.; Fimmel, S.; Krause, A.-M.; Beuerle, F. *Chem. Sci.* **2020**, *11*, 8409.
(13) Hasegawa, S.; Clever, G. H. *Chem* **2020**, *6*, 5.
(14) Ubasart, E.; Borodin, O.; Fuertes-Espinosa, C.; Xu, Y.; García-Simón, C.; Gómez, L.; Juanhuix, J.; Gándara, F.; Imaz, I.; Maspoch, D.; von Delius, M.; Ribas, X. *Nat. Chem.* **2021**, *13*, 420.
(15) Wachter, M.; Jurkiewicz, L.; Hirsch, A. *Chem. Eur. J.* **2021**, *27*, 7677.
(16) Pujals, M.; Pèlachs, T.; Fuertes-Espinosa, C.; Parella, T.; Garcia-Borràs, M.; Ribas, X. *Cell Rep. Phys. Sci.* **2022**, *3*, 100992.
(17) Kishi, N.; Akita, M.; Kamiya, M.; Hayashi, S.; Hsu, H. F.; Yoshizawa, M. *J. Am. Chem. Soc.* **2013**, *135*, 12976.
(18) Yamashina, M.; Yuki, T.; Sei, Y.; Akita, M.; Yoshizawa, M. *Chem. Eur. J.* **2015**, *21*, 4200.
(19) García-Simón, C.; Monferrer, A.; Garcia-Borràs, M.; Imaz, I.; Maspoch, D.; Costas, M.; Ribas, X. *Chem. Commun.* **2019**, *55*, 798.
(20) Chen, B.; Holstein, J. J.; Horiuchi, S.; Hiller, W. G.; Clever, G. H. *J. Am. Chem. Soc.* **2019**, *141*, 8907.
(21) Chen, B.; Horiuchi, S.; Holstein, J. J.; Jacopo, T.; Clever, G. H. *Chem. Eur. J.* **2019**, *25*, 14921.
(22) Chen, B.; Holstein, J. J.; Platzek, A.; Schneider, L.; Wu, K.; Clever, G. H. *Chem. Sci.* **2022**, *13*, 1829.
(23) Hasegawa, S.; Meichsner, S. L.; Holstein, J. J.; Baksi, A.; Kasanmascheff, M.; Clever, G. H. *J. Am. Chem. Soc.* **2021**, *143*, 9718.
(24) Yang, Y.; Ronson, T. K.; Lu, Z.; Zheng, J.; Vanthuyne, N.; Martinez, A.; Nitschke, J. R. *Nat. Commun.* **2021**, *12*, 4079.
(25) To the NMR tube where an acetonitrile solution of $Pd_2\mathbf{1}_4$ (0.70 mM, 0.600 mL, 0.42 µmol) was placed, excess solid corannulene was added and heated at 70 °C for 24 h. **$^1$H NMR** (500 MHz, $CD_3CN$, 298 K): δ (ppm) **e** 8.35 (s, 16 H), **d** 8.03 (d, $J$ = 8.8 Hz, 8H), **f** 7.86 (m, 8 H), **b** 7.82 (m, 8 H), **c** 7.48 (dd, $J$ = 8.8, 5.7 Hz, 8 H), **g** 7.36 (dd, $J$ = 5.3, 3.3 Hz, 8 H), **h** 6.61 (s, 8 H), **a** 6.00 (s, 8H), **encapsulated corannulenes** 5.47 (s, 20 H). **$^{13}$C NMR** (125 MHz, $CD_3CN$, 298 K): δ (ppm) 166.12, 165.70, 154.15, 152.99, 151.33, 150.30, 148.64, 147.74, 142.88, 142.40, 139.94, 138.09, 133.29, 132.40, 131.49, 130.95, 130.35, 130.16, 128.66, 127.49, 126.89, 126.27, 125.91, 121.68, 120.64, 54.94, 54.54 (12 signals out of 13 signals from empty $Pd_2\mathbf{1}_4$). **DOSY:** Diffusion coefficient $D$ of corannulenes inside $Pd_2\mathbf{1}_4$ and free corannulene in the same solution were estimated to be $6.69 \times 10^{-10}$ and $18.58 \times 10^{-10}$ m$^2 \cdot$s$^{-1}$, respectively. **ESI MS** (positive): found: 724.6237; calculated for $[(C_{34}H_{18}N_4O_4)_4Pd_2(C_{20}H_{10})_2]^{4+}$ to be 724.6248
(26) Schmidt, B. M.; Osuga, T.; Sawada, T.; Hoshino, M.; Fujita, M. *Angew. Chem. Int. Ed.* **2015**, *55*, 1561.
(27) **General procedure:** To an acetonitrile solution of $Pd_2\mathbf{1}_4$ (0.35 mM, 1.0 mL, 0.35 µmol) in a vial was added an excess amount of solid guest. The heterogeneous mixture was stirred under heating at 70 °C for 24 h. After the reaction, the residual solid guest was removed by filtration. The yields were estimated from the $^1$H NMR integral ratio.
**2**@$Pd_2\mathbf{1}_4$: **$^1$H NMR** (500 MHz, $CD_3CN$, 298 K): δ (ppm) **b** 8.38 (d, $J$ = 5.2 Hz, 4 H), **b** 8.37 (d, $J$ = 5.2 Hz, 4 H), **d** 8.32 (ddd, $J$ = 8.5, 2.2, 1.2 Hz, 4 H), **d** 8.27 (ddd, $J$ = 8.5, 2.2, 1.2 Hz, 4 H), **e*2** 8.22 (s, 8 H), **e** 7.97 (s, 4 H), **e** 7.87 (s, 4 H), **c** 7.78 (dd, $J$ = 8.5, 5.6 Hz, 4 H), **c** 7.74 (dd, $J$ = 8.5, 5.6 Hz, 4 H), **f*4** 7.73 – 7.64 (m, 8 H), **a** 7.34 (d, $J$ = 2.1 Hz, 4 H), **g*4** 7.26 – 7.20 (m, 8 H), **a** 7.10 (d, $J$ = 2.1 Hz, 4 H), **h** 6.43 (s, 2 H), **h** 6.37 (s, 2 H), **h** 6.27 (s, 2 H), **h** 6.20 (s, 2 H), **i** 4.06 (s, 4 H), **j** 3.57 (s, 3 H). **$^{13}$C NMR** (150 MHz, $CD_3CN$, 298 K): δ (ppm) 166.15, 166.00, 165.71, 165.60, 154.38, 153.71, 153.49, 153.44, 153.30, 152.23, 152.15, 147.56, 147.45, 146.51, 146.10, 145.73, 145.18, 144.80, 144.15, 144.02, 143.35, 143.01, 142.99, 142.83, 142.81, 142.27, 142.13, 142.03, 141.02, 140.74, 140.28, 140.16, 138.79, 135.51, 132.62, 132.13, 131.09, 131.06, 130.96, 130.61, 129.45, 129.04, 127.76, 127.74, 127.70, 127.69, 126.24, 126.20, 126.16, 126.01, 121.91, 121.76, 121.58, 121.55, 71.41, 69.57, 54.77, 54.70, 54.58, 42.11. **DOSY:** Diffusion coefficient $D = 5.26 \times 10^{-10}$ m$^2 \cdot$s$^{-1}$, and hydrodynamic radius $r_H$ was calculated to be 12.4 Å. **ESI MS** (positive): found: 794.0999 and 1087.7986; calculated for $[(C_{34}H_{18}N_4O_4)_4Pd_2(C_{63}NH_7)]^{4+}$ and $[(C_{34}H_{18}N_4O_4)_4Pd_2(C_{63}NH_7)(BF_4)]^{3+}$ to be 794.1005 and 1087.8021, respectively.
**3**@$Pd_2\mathbf{1}_4$: **$^1$H NMR** (500 MHz, $CD_3CN$, 298 K): δ (ppm) **b** 8.63 (d, $J$ = 5.2 Hz, 4 H), **b** 8.36 (d, $J$ = 5.2 Hz, 4 H), **e** 8.32 (s, 4 H), **d** 8.28 (ddd, $J$ = 8.5, 2.2, 1.2 Hz, 4 H), **d** 8.26 (ddd, $J$ = 8.5, 2.2, 1.2 Hz, 4 H), **e** 8.12 (s, 4 H), **e** 8.07 (s, 4 H), **k**/**l** 7.99 (m, 2 H), **k**/**l** 7.94 (m, 2 H), **c** 7.80 (dd, $J$ = 8.5, 5.6 Hz, 4 H), **e** 7.79 (s, 4 H), **c** 7.70 (dd, $J$ = 8.5, 5.6 Hz, 4 H), **f*4** 7.70 – 7.61 (m, 8 H), **a** 7.54 (d, $J$ = 2.1 Hz, 4 H), **a** 7.50 (d, $J$ = 2.1 Hz, 4 H), **g*4** 7.26 – 7.17 (m, 8 H), **h** 6.50 (s, 2 H), **h** 6.37 (s, 2 H), **h** 6.20 (s, 2 H), **h** 6.15 (s, 2 H), **i** 4.44 (s, 2 H), **j** 3.04 (m, 1 H), **j** 2.71 (m, 1 H). **$^{13}$C NMR** (150 MHz, $CD_3CN$, 298 K): δ (ppm) 166.16, 166.13, 165.96, 165.68, 165.51, 156.20, 155.44, 153.78, 153.51, 153.36, 153.09, 153.01, 152.48, 151.80, 150.25, 148.66, 148.26, 147.15, 146.57, 146.51, 146.10, 145.71, 145.64, 145.52, 145.26, 145.01, 144.96, 144.76, 144.71, 144.19, 143.85, 143.84, 143.16, 143.11, 143.04, 143.02, 142.97, 142.85, 142.83, 142.61, 142.40, 142.34, 142.13, 142.03, 141.97, 141.13, 140.99, 140.72, 140.48, 140.47, 139.29, 138.21, 138.04, 137.23, 136.41, 132.94, 132.63, 132.48, 131.07, 131.03, 130.90, 130.68, 130.37, 129.42, 129.26, 129.23, 128.37, 127.70, 127.66, 127.53, 126.24, 126.22, 126.02, 125.96, 125.19, 121.83, 121.63, 121.59, 121.30, 120.71, 76.22, 58.71, 54.85, 54.79, 54.64, 54.48 (13 signals from empty $Pd_2\mathbf{1}_4$). **DOSY:** Diffusion coefficient $D = 5.47 \times 10^{-10}$ m$^2 \cdot$s$^{-1}$, and hydrodynamic radius $r_H$ was calculated to be 12.0 Å. **ESI MS** (positive): found: 808.8505 and 1107.4664; calculated for $[(C_{34}H_{18}N_4O_4)_4Pd_2(C_{69}H_8)]^{4+}$ and $[(C_{34}H_{18}N_4O_4)_4Pd_2(C_{69}H_8)(BF_4)]^{3+}$ to be 808.8518 and 1107.4704, respectively.

**4**@$Pd_2$**1**$_4$: **$^1$H NMR** (500 MHz, $CD_3CN$, 298 K): $\delta$ (ppm) **b** 8.60 (d, $J$ = 5.2 Hz, 4 H), **b** 8.38 (d, $J$ = 5.2 Hz, 4 H), **d** 8.33 (ddd, $J$ = 8.5, 2.2, 1.2 Hz, 4 H), **d** 8.31 (ddd, $J$ = 8.5, 2.2, 1.2 Hz, 4 H), **e** 8.24 (s, 4 H), **n** 8.12 (m, 2 H), **e*2** 8.09 (s, 8 H), **e** 7.90 (s, 4 H), **o** 7.89 (m, 1 H) **c** 7.81 (dd, $J$ = 8.5, 5.6 Hz, 4 H), **c** 7.76 (dd, $J$ = 8.5, 5.6 Hz, 4 H), **f*4&m** 7.74 – 7.61(m, 10 H), **a** 7.56 (d, $J$ = 2.1 Hz, 4 H), **a** 7.54 (d, $J$ = 2.1 Hz, 4 H), **g*4** 7.26 – 7.18 (m, 8 H), **h** 6.45(s, 2 H), **h** 6.33 (s, 2 H), **h** 6.32 (s, 2 H), **h** 6.19 (s, 2 H), **i** 3.68 (s, 3 H), **j** 2.52 (m, 2 H), **l** 2.31 (m, 2 H), **k** 2.00 (m, 2 H). **$^{13}$C NMR** (176 MHz, $CD_3CN$, 298 K): $\delta$ (ppm) 174.35, 166.17, 166.01, 165.96, 165.68, 165.57, 153.66, 153.65, 153.52, 153.45, 153.11, 152.61, 151.93, 150.26, 149.26, 148.70, 148.12, 147.44, 145.07, 144.91, 144.79, 144.33, 144.12, 144.09, 144.07, 143.96, 143.86, 143.48, 143.24, 143.18, 143.09, 142.99, 142.93, 142.82, 142.80, 142.72, 142.68, 142.62, 142.52, 142.21, 142.05, 141.86, 141.71, 141.59, 140.86, 140.72, 140.70, 140.54, 140.47, 140.41, 139.70, 138.05, 136.80, 136.62, 135.72, 132.88, 132.71, 132.63, 132.51, 131.11, 131.07, 131.03, 130.73, 130.39, 130.33, 130.11, 129.61, 129.24, 128.39, 127.76, 127.73, 127.55, 126.35, 126.25, 126.20, 125.98, 121.73, 121.59, 120.77, 120.72, 81.63, 54.81, 54.72, 54.66, 54.52, 54.50, 54.35, 52.21, 34.41, 33.80, 23.42 (13 signals from empty $Pd_2$**1**$_4$). **DOSY:** Diffusion coefficient $D = 5.38 \times 10^{-10}$ m$^2 \cdot$s$^{-1}$, and hydrodynamic radius $r_H$ was calculated to be 12.1 Å. **ESI MS** (positive): found: 827.3594 and 1132.1460; calculated for $[(C_{34}H_{18}N_4O_4)_4Pd_2(C_{72}H_{14}O_2)]^{4+}$ and $[(C_{34}H_{18}N_4O_4)_4Pd_2(C_{72}H_{14}O_2)(BF_4)]^{3+}$ to be 827.3610 and 1132.1494, respectively.

(28) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 3418.