



CORNELL UNIVERSITY LIBRARY

Subscriber access provided by CORNELL UNIVERSITY LIBRARY

### Article

## Self-assembled Perylene Bisimide-cored Trigonal Prism as an Electrondeficient Host for C60 and C70 Driven by 'Like Dissolves Like'

Xingmao Chang, Simin Lin, Gang Wang, Congdi Shang, Zhaolong Wang, Kaiqiang Liu, Yu Fang, and Peter J. Stang

J. Am. Chem. Soc., Just Accepted Manuscript • Publication Date (Web): 26 Aug 2020 Downloaded from pubs.acs.org on August 26, 2020

### **Just Accepted**

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

# Self-assembled Perylene Bisimide-cored Trigonal Prism as an Electron-deficient Host for C<sub>60</sub> and C<sub>70</sub> Driven by 'Like Dissolves Like'

Xingmao Chang,<sup>1,2</sup> Simin Lin,<sup>1</sup> Gang Wang,<sup>1</sup> Congdi Shang,<sup>1</sup> Zhaolong Wang,<sup>1</sup> Kaiqiang Liu,<sup>1</sup> Yu Fang,<sup>1,\*</sup> and Peter J. Stang<sup>2,\*</sup>

<sup>1</sup>Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education), School of Chemistry and Chemical

Engineering, Shaanxi Normal University, Xi'an 710119, P. R. China

<sup>2</sup>Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, United States

**Abstract** Poor processability of fullerenes is a major remaining drawback for them to be studied monomolecularly and to find real-life applications. One of the strategies to tackle this problem is to encapsulate them within a host, which is however quite often, accompanied with significant alteration of their physical/chemical properties as encountered in chemical modification. To minimize the effect, an electron-deficient entities-based, dissolvable and fluorescence active supramolecular host was designed and constructed via coordination-driven self-assembly of ortho-tetrapyridyl perylene bisimide (PBI) with cis-(PEt<sub>3</sub>)<sub>2</sub>Pt(OTf)<sub>2</sub>. The trigonal prism 1 possesses a trigonal-prismatic inner cavity with 14.7 Å as the diameter of its inscribed circle. Host-guest chemistry investigations revealed that both  $C_{60}$  and  $C_{70}$  could be quantitatively encapsulated by the host in a 1:1 ratio. Further studies demonstrated that the produced host-guest complex  $1 \supset C_{70}$  is significantly more stable than  $1 \supset C_{60}$ , allowing complete transformation of the latter to the former and separation of C<sub>70</sub> from its mixture with C<sub>60</sub>. The fullerenes in the inclusion state could rotate freely within the cavity. Electrochemistry and spectroscopy studies disclosed that the encapsulation of the guests shows little effect upon the reduction of the host and its fluorescence properties. Thus, 'like dissolves like' is believed to be the main driving force for the formation of the host-guest complexes. Moreover, the host and host-guest complexes can be fabricated into monomolecular membranes, using conventional Langmuir-Blodgett technique. We propose that these unique host-guest complexes could be used as model ensembles for further studies of the physical/chemical properties of fullerenes in both single molecular and 2D membrane states. In addition, their reversible four-electron reduction property may allow them to find applications in photo-/electro-catalysis, organic electronics, etc.

#### Introduction

Coordination-driven self-assembly has been developed as a powerful tool for precise construction of Supramolecular Coordination Complexes (SCCs) with diverse sizes and shapes, including 2D metallacycles, 3D metallacages, and even more elegant and complex molecular assemblies.<sup>1-9</sup> Apart from building structures with special shape, large size or unique topology,<sup>10-13</sup> development of functional SCCs leading to important applications is also a hot topic of the research.<sup>14-21</sup> A noticeable strategy to achieve such a purpose is to embed selected functional moieties in the building blocks of SCCs.<sup>22-28</sup> Fluorescence is known to be sensitive and selective to micro-environment changes owing to its excited state nature, and thereby, incorporating fluorescent moieties will definitely extend the applications of SCCs.<sup>17,18</sup> In fact, emissive SCCs have already been utilized in multi-responsive (solvents, pressure, or temperature) materials, photodynamic therapy, film-based fluorescence sensors, etc.<sup>18, 20, 29-31</sup>

As known, perylene bisimides (PBIs) have received significant attention during the last few decades owing to their unique properties, such as large optical absorption range, superior photochemical and thermal stability, high fluorescence quantum yield, switchable emission between monomeric state and aggregated state.<sup>32-34</sup> Yet, they generally suffer from low solubility in common solvents due to strong intermolecular  $\pi$ - $\pi$  stacking originating from large conjugated structure of their perylene core, which limits the study of their properties and applications. Therefore, alkyl chains with different lengths or steric structures are often introduced into the imide or *bay* positions (3,4,9,10-positions) of PBIs to increase their solubility.<sup>35-37</sup> Recently, selective modification at the *ortho*-positions (2,5,8,11-positions) of PBIs is also used to improve the solubility.<sup>38-40</sup> Unlike being modified at the *bay* positions, structural modification at the *ortho*-positions to the planar structure of the perylene core, which is believed to bring less alteration to their electronic structures and the excited state properties.<sup>41, 42</sup>

As a family of zero-dimensional carbon materials, fullerenes exhibit superior semi-conducting properties, leading to versatile applications in solar cells, field effect transistors (FET), photo-detectors, etc.<sup>43-45</sup> These applications, however, greatly depend on their purity, crystalline structures, aggregated geometries, such as 1D fibers, 2D plates, etc. Additionally, well defined structures are also the basis for exploring their fundamental properties. However, the spherical or

#### 2 / 25

Page 3 of 25

ellipsoid shape and the unpolarized polyene surfaces greatly hinder their dissolution in common solvents, impeding their purification, crystallization and property studies in conventional ways. To tackle the challenge, various strategies, such as volatile diffusion, controlled precipitation, liquid-liquid interface precipitation, gel-assisted crystallization, etc., have been developed to grow the crystals or to purify the materials.<sup>46-52</sup> Among them, host-guest chemistry-based extraction was proposed recently, which brings new inclusion compounds with fullerenes as guests, leading to assisted dissolution as well as new structures. The key issue in the studies is the design and construction of supramolecular hosts. Till now, a large number of macrocycles and several 3D cages have been developed as the hosts.<sup>53-56</sup> Examination reveals that effective hosts generally possess two features, the first is size match of their cavities with the guests, fullerenes, and the second is electronic match of the hosts with the electron-poor guests, as evidenced by the fact that electron-rich moieties, such as porphyrins, pyrene, anthracenes, tetrathiafulvalenes and carbon belts/bowls, were adopted as their main components.<sup>57-79</sup> However, electronic communication between electron-rich host and electron-deficient guest is sure to alter the primary properties of the guest as well as the host, which could induce similar problems encountered as in the chemical modifications. Therefore, it would be of great interest to develop electron-poor hosts that include the guests via other driving forces.

Considering the electron-deficient property and the polyene surface feature of fullerenes, constructing the expected host-guest complexes via the development of electron-poor hosts with  $\pi$ -conjugated structures, such as PBI derivatives, as the main entities becomes feasible. This is due to the fact that 'like dissolves like' may function as the driving force, which originates from their common  $\pi$ -structure. In addition, incorporating such fluorescence active moieties in the hosts could offer the opportunity to monitor the coming host-guest interaction via their sensitivity to micro-environment of changes. As aforementioned, coordination-driven self-assembly is a powerful technique to build 3D metallacages with controllable sizes and changeable functional moieties. Thus, it may be adopted as a strategy to build the designed hosts. In fact, several (supra)molecular cycles or cages composed of PBI moieties have been synthesized via covalent linkage or noncovalent bonding,<sup>80-84</sup> where only one metallacage and one metallacycle have been built for the encapsulation of fullerenes.<sup>62, 78</sup> However, in the hosts, PBIs were modified at the

*bay*-positions, leading to distorted structure of the perylene core. To avoid this distortion, in the present study, an *ortho*-position modified PBI derivative is incorporated into a specially designed 3D metallacage, resulting in the trigonal prism 1. Encapsulation examination reveals effective formation of inclusion complexes of  $1\supset C_{60}$  and  $1\supset C_{70}$ . Further investigation depicts that  $1\supset C_{70}$  is more stable than  $1\supset C_{60}$ . Accordingly, selective extraction of  $C_{70}$  from its mixture with  $C_{60}$  and complex to complex transformation from  $1\supset C_{60}$  to  $1\supset C_{70}$  were realized. Weak electronic communication between the host and the guests is verified by little change of the host's electrochemical and spectroscopy properties after encapsulation.

Scheme 1 Formation of Trigonal Prism 1 via Coordination-Driven Self-Assembly



#### **Results and Discussion**

#### Synthesis of PBI-4Py

*Ortho*-tetrapyridiyl-containing PBI (**3**) was targeted to construct trigonal prism **1**, and the PBI derivative was synthesized by coupling of 4-ethynylpyridine with *ortho*-iodinated PBI (**2**), where **2** was obtained *via* carbonyl-directed ortho C-H halogenation of PBI.<sup>39</sup> Structural optimization of **3** was performed through DFT calculation. The results are depicted in Figure S21. As expected, the core of **3** adopts a perfect planar structure, allowing for the construction of well-defined and non-distorted architecture via coordination-driven self-assembly.

#### Self-assembly of Trigonal Prism

As shown in Scheme 1, reacting **3** with cis-(PEt<sub>3</sub>)<sub>2</sub>Pt(OTf)<sub>2</sub> in a molar radio of 2:4 in acetone for 5 h at 45 °C, and then precipitating by the addition of diethyl ether resulted in **1** with an

 excellent yield (98%). It is worthwhile to note that reacting of four-arm ligand (L) with Pt/Pd( $\mathbb{I}$ ) (M) could result in metallo-cages with a composition of M<sub>2n</sub>L<sub>n</sub>, where M<sub>6</sub>L<sub>3</sub>, M<sub>8</sub>L<sub>4</sub>, M<sub>10</sub>L<sub>5</sub>, and even M<sub>12</sub>L<sub>6</sub> have been documented.<sup>85-90</sup> In this work, the supramolecular ensemble is confirmed to be M<sub>6</sub>L<sub>3</sub>, for which the characterization details via multinuclear NMR (<sup>31</sup>P and <sup>1</sup>H), correlation spectroscopy NMR (COSY), diffusion-ordered spectroscopy NMR (DOSY), electrospray ionization time-of-flight mass spectroscopy (ESI-TOF-MS), etc. are provided below.



Figure 1 (a) Partial <sup>1</sup>H NMR spectra (600 MHz, Acetone- $d_6$ , 298 K) of 3 (black) and 1 (red). (b) <sup>31</sup>P NMR spectra (243 MHz, Acetone- $d_6$ , 298 K) of 4 (black) and 1 (red). (c) Experimental (black) and calculated (red) ESI-TOF-MS spectra of 1 [1 – 50Tf]<sup>5+</sup>.

As seen from Figure 1b, the <sup>31</sup>P {<sup>1</sup>H} NMR spectrum of **1** shifts considerably upfield comparing with that of 90° Pt(II) **4** and exhibits sharp singlet at -0.15 ppm with concomitant <sup>195</sup>Pt satellites  $(J_{Pt-P} = 3100.7 \text{ Hz})$ , corresponding to single chemical environments around the phosphorus center. For the <sup>1</sup>H NMR spectrum of **3**, it can be observed that it contains three sets of protons in the aromatic area, including two doubles for pyridinyl ( $\delta = 8.74$  and 7.65 ppm for H<sub>3a</sub> and H<sub>3b</sub>, respectively) and one singlet for PBI moiety ( $\delta = 8.79$  ppm for H<sub>3c</sub>) (Figure 1a). The <sup>1</sup>H NMR spectrum of **1** exhibits a simple set of proton signals, where the aromatic part is composed of four doublets and one singlet, which are ascribable to the protons of pyridinyl moiety and PBI unit, respectively (Figure S3). The COSY spectra shown in Figure S5 indicate that the 3a and 3b protons of the pyridinyl moiety exhibit a remarkable split and a significant shift in comparison with **3**. The shift of the proton signals is a result of the nitrogen coordination to Pt since it reduces the electron density of the pyridyl unit. The splitting of 3a and 3b might be because of restricted rotation of the pyridinyl moieties due to the formation of the trigonal prism that makes a difference between the magnetic environment of the two 3a (H<sub>1a</sub> and H<sub>1a</sub><sup>·</sup>) and the two 3b (H<sub>1b</sub> and H<sub>1b</sub><sup>·</sup>) protons of a pyridyl moiety. These observations tentatively reveal the formation of the expected discrete, highly symmetrical supramolecular cage.

The DOSY results are depicted in Figure S8. As seen, the sample displays a single vertical trace with a diffusion coefficient of  $4.0 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, suggesting the formation of a single supramolecular ensemble via self-assembly. With reference to the ESI-TOF-MS spectra shown in Figure 1c and Figure S7, six isotopically resolved peaks corresponding to a trigonal prism (M<sub>6</sub>L<sub>3</sub>) with the loss of several trifluoromethanesulfonate (OTf) anions were observed, including m/z = 1646.36 for [1–40Tf]<sup>4+</sup>, m/z = 1287.30 for [1–50Tf]<sup>5+</sup>, m/z = 1047.93 for [1–60Tf]<sup>6+</sup>, m/z = 876.94 for [1–70Tf]<sup>7+</sup>, m/z = 748.58 for [1–80Tf]<sup>8+</sup>, and m/z = 648.96 for [1–90Tf]<sup>9+</sup>. These peaks match very well with the calculated theoretical distributions, and confirm the stoichiometry of the trigonal prism as produced. Moreover, traces of other possible M<sub>2n</sub>L<sub>n</sub> structures are not observable.

#### Molecular Modeling and Langmuir-Blodgett Technique

The chemical formula of three ligands and six metals of the trigonal prism has been proved via NMR and mass spectroscopy measurements. However, as depicted in Scheme 1, **3** is a highly symmetrical and four-arm ligand, which determines that it could form two isomeric trigonal prisms when it reacts with 90° Pt in a molar ratio of 1:2. The two structures were simulated via PM6 semi-empirical calculations. As shown in Figure 2, the only difference between them is the orientation of the PBI moieties, which makes isomer **a** possess a larger triangular section. Specifically, the area of the section for **a** is 575 Å<sup>2</sup>, and that for **b** is 447 Å<sup>2</sup> (for calculation details, see Figure S22 in the SI). Energetically, **a** is much more stable that **b**, and the energy difference between them is 36 kcal/mol. The difference could be a result of the high distortion of

the PBI units in b and the crowding of the imide parts of the moieties in the isomer. Accordingly, the most likely structure of the cage as obtained should be **a**. To exam the exact structure of the cage, Langmuir–Blodgett (LB) measurements were performed as it could provide the information of molecular size, which helps to ascertain the structure.

Considering the good solubility in volatile organic solvents, and insolubility in water of the cage, it is possible to prepare a monomolecular layer via utilization of the classical LB technique. The experiments resulted in the  $\pi$ -A isotherms, which are the surface pressure *vs* molecular area plots that are presented in Figures 2c and Figure S23a.



**Figure 2** The PM6-simulated conformation of the trigonal prism of **1** in '**a**' state (a, c) and the PM6-simulated conformation of the trigonal prism in '**b**' state (b). The  $\pi$ -A isotherm of the trigonal prism of **1** in the air/water interface (d).

As depicted in Figure S23, three independent measurements (with the addition of different volumes of the stock solution of 1) resulted in highly repeatable  $\pi$ -A isotherms, indicating the reliability of the measurements. Examination of the  $\pi$ -A isotherms reveals that they all exhibit a

sharp rise of surface pressure when decreasing the surface area, it can also be seen that the liquid condensed (LC) phase appears from 2 to 33 mN<sup>-1</sup>, and the "liquid" to "solid" inflection appears at 33 mN m<sup>-1</sup>. Further increase of the surface pressure results in the collapse of the "solid" mono-molecular membrane as evidenced by the gradual appearance of a precipitation on the slider. (Figure S23b) From the inflection point, the area of cross-section (*A*) of **1** can be calculated using eq. 1, where *S* stands for the total surface area of the membrane, *C* the concentration of the solution, *V* the volume of the solution added, and  $N_A$  is Avogadro's number. The result is about 569 Å<sup>2</sup>/molecule, which matches well with the area of the triangle side of conformation **a** as shown in Figures 2c and S22.

$$A = \frac{S}{CVN_A} \tag{1}$$

**Fullerenes Host-Guest Encapsulation** 

(1⊃C<sub>70</sub>) c f С b е (1⊃C<sub>60</sub>) c а 1c d 0.5 9.5 9.3 7.9 7.7 0.0 -0.5 9.4 9.2 9.1 8.2 8.1 8.0 7.8

Figure 3 <sup>31</sup>P{<sup>1</sup>H} (a-c) and partial <sup>1</sup>H NMR spectra (d-f) of 1 (a and d),  $1 \supset C_{60}$  (b and e), and  $1 \supset C_{70}$  (c and f). (243 MHz for <sup>31</sup>P{<sup>1</sup>H}NMR and 600 MHz for <sup>1</sup>H NMR, Acetone- $d_{6}$ , 298 K)

The existence of large void and electron deficient PBI moieties in the trigonal prism could create two different environments, where one is inside and the other outside of the metallacage. Examination of the size of the cavity as shown in Figure 2 reveals that a sphere or cylinder of a maximum diameter of 14.7 Å could be embedded within the cavity, suggesting that the compound may be used as a host for encapsulation of  $C_{60}$  and  $C_{70}$  since the van der Waals diameter of the former is ~11 Å and the latter a little bit larger.<sup>70, 73, 76</sup> Encapsulation tests were conducted by adding a large excess of  $C_{60}$  or  $C_{70}$  (10 equiv) to a solution of **1** in acetone, followed by continuous

heating and stirring at 40 °C overnight. The solution was filtered to remove excess  $C_{60}$  or  $C_{70}$ , and then precipitated by adding ethyl ether. Acetone was chosen as it is a good solvent of the host but a poor solvent of the guests.<sup>91</sup> The precipitates (possibly  $1 \supset C_{60}$  or  $1 \supset C_{70}$ ) were collected by centrifugation, and characterized by NMR and ESI-TOF-MS measurements.



(c). *Note:* • stands for  ${}^{13}C$  signal of  $C_{60}$  or  $C_{70}$ .

As depicted in Figure 3, similar to that of the host, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of  $1 \supset C_{60}$  is also characterized by a sharp singlet, which shifted downfield to 0.30 ppm, indicating a change of the chemical environment of the phosphorus center. The <sup>31</sup>P{<sup>1</sup>H} NMR could be a result of the expected encapsulation, which is further supported by the results from <sup>1</sup>H NMR studies. As shown in the same figure, comparing the <sup>1</sup>H NMR spectrum of  $1 \supset C_{60}$  with that of 1, the proton signals of pyridinyl residues (H<sub>1a</sub>, H<sub>1a</sub>'; H<sub>1b</sub>', H<sub>1b</sub>) in the PBI structures show an upfield shift in support of the possible host-guest interaction. The protons of PBI (H<sub>1c</sub>) show a considerable downfield shift from 9.21 to 9.31, which is almost mixed with one of the pyridinyl signals (H<sub>1a</sub>). This observation could be ascribed to the  $\pi$ - $\pi$  interaction between PBI and C<sub>60</sub>, another evidence to support the host-guest interaction. The <sup>13</sup>C NMR spectra of  $1 \supset C_{60}$  and empty 1 were also recorded (Figure 4a, b). An intense extra resonance signal appears at 141.6 ppm, which belongs to C<sub>60</sub>, further confirming formation of the expected host-guest complex,  $1 \supset C_{60}$  are depicted in Figure 5c and Figure S13, displaying a series of prominent peaks at m/z = 1826.36, 1431.50, 1168.09, 979.50, 838.70, and 728.96, which correspond to the loss of several OTf units during ionization, including  $[1 \supset C_{60}-4OTf]^{4+}$ ,  $[1 \supset C_{60}-5OTf]^{5+}$ ,  $[1 \supset C_{60}-6OTf]^{6+}$ ,  $[1 \supset C_{60}-7OTf]^{7+}$ ,  $[1 \supset C_{60}-8OTf]^{8+}$ , and  $[1 \supset C_{60}-9OTf]^{9+}$ , respectively. These m/z results match very well with the theoretically simulated values, in support of the expected 1:1 composition of the host-guest complex. Further examination of the results depicted in Figure 5 reveals that there are weak signals of the empty trigonal prism in the sample of the host-guest complex, suggesting dissociation of  $1 \supset C_{60}$  during the ionization measurements.

 $C_{70}$  was also expected to form an inclusion complex  $1 \supset C_{70}$ . <sup>31</sup>P{<sup>1</sup>H} NMR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra exhibit the formation of the complex (Figure 3, Figure 4c), but the proton signal of PBI shifts obviously upfield rather than downfield as observed in the complexation of  $C_{60}$ . The reason behind is probably the different interaction with the hosts as the size and shape of the two guests are different from each other. The difference in the proton signal shift of PBI can be used to identify the two different fullerenes. Results from ESI-TOF-MS provide further support for possible inclusion. As shown in Figure 5 and Figure S18, six isotopically resolved peaks, which are 1856.61 ( $[1\supset C_{70}-4OTf]^{4+}$ ), 1455.50 ( $[1\supset C_{70}-5OTf]^{5+}$ ), 1187.93 ( $[1\supset C_{70}-6OTf]^{6+}$ ), 996.94 ( $[1\supset C_{70}-7OTf]^{7+}$ ), 853.71 ( $[1\supset C_{70}-8OTf]^{8+}$ ) and 742.31 ( $[1\supset C_{70}-9OTf]^{9+}$ ), respectively, corresponding to  $1\supset C_{70}$  after losing four to nine OTf units were detected, confirming the stoichiometry of the expected host-guest complex. Examination of the results depicted in Figure 5 reveals that unlike  $1\supset C_{60}$ , there is no empty trigonal prism in the sample, indicating effective encapsulation of  $C_{70}$ , which indicates no significant dissociation of  $1\supset C_{70}$  during the ionization measurements.



**Figure 5** Partial mass spectra monitoring the formation of host-guest complexes with loss of seven (a) and five (b) OTf. Experimental (black) and calculated (red) ESI-TOF-MS spectra of  $1 \supset C_{60}$  $[1 \supset C_{60} - 5 \text{OTf}]^{5+}$  (c) and  $1 \supset C_{70} [1 \supset C_{70} - 5 \text{OTf}]^{5+}$  (d).

DOSY studies of the two host-guest complexes in acetone- $d_6$  were also performed, and the results are shown in Figure S14 and Figure S20, respectively. As shown, the diffusion coefficients of  $1\supset C_{60}$  and  $1\supset C_{70}$  are all close to  $4.0 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, which are almost the same as that of empty 1, indicating that complexation shows little effect upon the size of the host, an evidence of internal inclusion rather than external association.

Further examination of the <sup>13</sup>C NMR spectra depicted in Figure 4 reveals that  $1 \supset C_{60}$  shows only one <sup>13</sup>C NMR signal (Figure 4b: 141.6 ppm), whereas  $1 \supset C_{70}$  shows five (Figure 4c: 149.43 ppm, 146.33 ppm, 145.86 ppm, 143.41 ppm and 128.83 ppm), which are consistent with the numbers of carbon types of the relevant fullerenes.<sup>57, 70</sup> These results may be taken as an indication that the guests are trapped within an isotropic electromagnetic field, which however is, not the case, due to complicated internal structure of the host. However, a possible rationalization of the results is to assume free rotation of the guests within the cavity of the host, due to the weak electronic communication between the guest and the host.

#### Competitive Encapsulation of C<sub>60</sub> and C<sub>70</sub>

To gain insight on the timescale of the exchange between host and host-guest complex, empty cage **1** was respectively added into the acetone- $d_6$  solution of **1** $\supset$ C<sub>60</sub> and **1** $\supset$ C<sub>70</sub> (in 10% and 30%), and then the solution was continuously stirred for 5 hours. As shown in Figure S24, both signals of free host and complexes exist in their <sup>1</sup>H NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra, indicating that the exchange is slow. Competitive encapsulation tests of C<sub>60</sub> and C<sub>70</sub> were also performed, which may provide information about the comparative affinities of the host to the guests.

The mixture of  $1 \supset C_{60}$  and large excess of  $C_{70}$  (10 equiv), and vice versa, the mixture of  $1 \supset C_{70}$ and large excess of  $C_{60}$  (10 equiv) in acetone- $d_6$  were mixed and stirred for 5 hours at 45 °C. Then, the <sup>1</sup>H NMR spectra of the two systems were recorded. The results are depicted in Figures 6a-c and S25, respectively. As seen, the introduction of  $C_{70}$  resulted in complete disappearance of the characteristic proton signal (9.31 ppm) of  $1 \supset C_{60}$  and the appearance of that (9.13 ppm) of  $1 \supset C_{70}$ , indicating full transformation of  $1 \supset C_{60}$  to  $1 \supset C_{70}$ . The result from the replacement test of  $C_{60}$  to  $1 \supset C_{70}$ , is in support of this conclusion as there is no observable change in the recorded <sup>1</sup>H NMR spectra, even though a large excess of  $C_{60}$  was added. Therefore, it might be concluded that the binding affinity of the trigonal prism toward  $C_{70}$  is much larger than that toward  $C_{60}$ .

#### 12 / 25



Figure 6 Cartoons for complex transformation from  $1 \supset C_{60}$  to  $1 \supset C_{70}$  (a) and selective extraction of  $C_{70}$  from its mixture with  $C_{60}$  (d), and the corresponding partial <sup>1</sup>H NMR spectra of the processes before (c) and after (b) the transformation, as well as before (f) and after (e) the separation.( 600 MHz, Acetone- $d_6$ , 298 K)

Given the different binding affinity of the host to  $C_{60}$  and  $C_{70}$ , its potential in their separation was briefly explored. A mixture of  $C_{60}$  and  $C_{70}$  was added to the acetone- $d_6$  solution of **1**, and then the mixture was stirred 5 hours at 40 °C. <sup>1</sup>H NMR spectrum of the supernatant solution was recorded (Figures 6d-f), and only **1** $\supset$  $C_{70}$  was observed as the H<sub>1c</sub> signal appears at 9.13 ppm, a beacon of the complex, suggesting potential application of the prepared host in separation of C<sub>70</sub> from its mixture with C<sub>60</sub>.

The <sup>1</sup>H NMR measurements of  $1 \supset C_{60}$  and  $1 \supset C_{70}$  in very low concentrations were also conducted to further check the stability of complexes (Figure S26). It is seen that the <sup>1</sup>H NMR spectra are still dominated by the signals of  $1 \supset C_{60}$  and  $1 \supset C_{70}$ , and there is no observable signals

of the free cage, indicating good stability of the host-guest complexes.

#### **Electrochemistry Study**

Both PBI and fullerenes ( $C_{60}$  and  $C_{70}$ ) are electron-deficient conjugated systems and could undergo reversible electrochemical oxidation and reduction.<sup>62, 68</sup> To understand the property of the host and the host-guest complex, cyclic voltammetry (CV) and square wave voltammetry (SWV) were performed on **1**, **1** $\supset$ **C**<sub>60</sub>, **1** $\supset$ **C**<sub>70</sub> and the relevant PBI derivative **3**. The specific parameters of the systems and the electrochemical traces are given in Table 1 and Figure S27. As seen, **3** exhibits two reversible reductions at -0.85 and -1.08 V, respectively, which could originate from successive reductions of the PBI core (PBI $\stackrel{e}{\rightarrow}$ PBI $\stackrel{e}{\rightarrow}$ PBI $^{2-}$ ).<sup>61</sup> As akin to other shoulder substituted PBI derivatives, oxidation is not found within the examined electrochemical widow.<sup>39</sup> For only **1**, two reversible reduction processes around -0.61 and -0.81 V are observed, which are from the reduction of the PBI core. However, compared to the reference, reduction of PBI in the host becomes easier, which could be a result of coordination to the platinum center.

Table 1 Redox potentials of 3, 1,  $1 \supset C_{60}$ , and  $1 \supset C_{70}^{a, b}$ 

Reduction Potentials	E <sub>1st</sub>	E <sub>2nd</sub>	E <sub>3rd</sub>	E <sub>4th</sub>
Ligand 3	-0.85	-1.08		
1	-0.61	-0.81		
1⊃C <sub>60</sub>	-0.59	-0.77	-1.05	-1.21
1⊃C <sub>70</sub>	-0.59	-0.78	-1.05	-1.23

<sup>a</sup> All measurements were performed in dry CH<sub>3</sub>CN except for 3 (CH<sub>2</sub>Cl<sub>2</sub>) with 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as electrolyte. <sup>b</sup> The data presented were obtained from square wave voltammetry measurements.

In the CV and SWV of  $1 \supset C_{60}$ , four reduction processes are found, where the initial two are associated with the PBI units (-0.59 and -0.77 V), and the third and fourth (-1.05 and -1.21 V) could be successive reductions of the guest ( $C_{60} \stackrel{e}{\rightarrow} C_{60} \stackrel{-e}{\rightarrow} C_{60}^{2-}$ ). As seen, encapsulation of the guest shows limited effect upon the reduction of the PBI units, confirming weak electronic communication between the guest and the host, as tentatively already concluded from the <sup>13</sup>C NMR studies. Similar results were obtained in the examination of  $1 \supset C_{70}$ . These results further

confirm the formation of the host-guest complexes.

#### **Optical Properties**



Figure 7 UV-Vis (a) and fluorescence (b) spectra of 1,  $1 \supset C_{60}$ , and  $1 \supset C_{70}$  in acetone, where the excitation wavelength adopted is 480 nm.

UV-Vis absorption, fluorescence, and fluorescence lifetimes of 1,  $1 \supset C_{60}$  and  $1 \supset C_{70}$  were also measured, and the results are provided in Figure 7 and Figure S28. In the UV-Vis absorption spectra, it is seen that the spectrum of 1 contains two characteristic monomeric absorption bands of the PBI unit, appearing at  $\sim$ 531 nm and  $\sim$ 495 nm, respectively, which are ascribable to the 0-0 and 0-1 absorptions of the S<sub>0</sub>-S<sub>1</sub> transition, respectively. The second is the vibronic progression of the main absorption band resulting from the coupling of the electronic transition to the C-C-stretching modes of the perylene core. The ratio of the intensities of the 0-0 and 0-1 absorption bands (A<sub>0-0</sub>/A<sub>0-1</sub>) is ~1.56, further suggesting a monomeric nature of PBI units in the host, which is commonly used to monitor the aggregation of the PBI moiety.<sup>32</sup> This result can be taken as an additional evidence to support the framework structure of the host, ruling out packing both inter- and intramolecularly. Inclusion of C<sub>60</sub> resulted in the red-shift of the spectrum with little change in the profile and the ratio of A<sub>0-0</sub>/A<sub>0-1</sub>, again confirming the weak interaction between the host and the guest, since little effect is observed for the coupling between the electronic transition and the PBI core. For  $1 \supset C_{70}$ , a similar result is observed. The only difference is more significant red-shift, which could be a result of a closer contact of C70 with the PBI moieties in the host due to its larger size. This result is in agreement with that aforementioned in the <sup>1</sup>H NMR, <sup>13</sup>C NMR and electrochemical studies.

To gain further insight into the electronic communication between the guests and the PBI 15 / 25

moieties in the host, their fluorescence spectra were also recorded in dilute condition in acetone  $(1.0 \times 10^{-5} \text{ mol/L})$  to minimize the reabsorption effect. The results are depicted in Figure 7b. Cage **1** shows a fluorescence spectrum characteristic for the PBI monomers with an emission maximum at ~541 nm and well-resolved vibronic fine structures, which is a mirror-image of the absorption of the PBI unit. In addition, a small Stokes shift of 10 nm and a relatively high fluorescence quantum yield of 0.20 were observed, which are in support that the PBI moieties exist in a monomeric state within the host.

In contrast, the fluorescence emission spectra of the two host-guest complexes, especially that of  $1 \supset C_{70}$ , show observable changes in the profiles as the relative intensity of the first band (short wavelength) to the second one decreases with the complexation, which is a result of re-absorption since the Stokes shifts are getting narrower from 1 to  $1 \supset C_{60}$  and then to  $1 \supset C_{70}$ . However, the monomeric feature of the PBI moieties in the complexes still remains, not only because of their slightly-changed UV-Vis absorptions, but also because of their similar emission profiles. These results further demonstrate that the inclusion of  $C_{60}$  or  $C_{70}$  shows limited effect upon the electronic nature of the host and, likewise, upon the guests, an expected result but different with that reported by Beer et al.<sup>77</sup> Fluorescence lifetime measurements further support these conclusions as the fluorescence decay curves of the PBIs moieties in the three systems are very similar to each other, and their lifetimes are almost the same (Figure S28, Table S1).

Combining the results from the electrochemical and optical studies with those from the encapsulation experiments, we can conclude that the examined host-guest interaction is mainly driven by the so called 'like dissolves like' principle. Size matching may further stabilize the complexes. In other words, the cavity property of the dissolved hosts could be very different from that of the bulk medium, acetone, as it is characterized by delocalized electrons due to the conjugated structures of the PBI moieties. It is exactly this property that makes the host function as microdomains in the solution, leading to preponderant affinity to fullerenes and, thus, resulting in the observed encapsulation.

#### Conclusion

In conclusion, a fluorescent SCC, trigonal prism **1**, was synthesized *via* coordination-driven self-assembly of tetrapyridinyl perylene bisimides and 90° organoplatinum(II) in a molar ratio of

1:2. The structure of **1** was confirmed by various techniques, including <sup>1</sup>H NMR, <sup>31</sup>P{<sup>1</sup>H} NMR, <sup>13</sup>C NMR, COSY, DOSY, and high-resolution mass spectrometry, and further studied by structural simulation and the Langmuir-Blodgett technique. As designed, **1** possesses a trigonal-prismatic cavity that makes it suitable for encapsulation of  $C_{60}$  and  $C_{70}$ , which may be owing to the 'like dissolves like' principle. The formation of the host-guest complexes of  $1 \supset C_{60}$ and  $1 \supset C_{70}$  was verified by using the same methods. Further studies revealed that **1** exhibits a greater binding affinity toward  $C_{70}$  than  $C_{60}$ , and the encapsulated  $C_{60}$  and  $C_{70}$  could rotate freely within the cavity of the host. Electrochemical studies demonstrated that  $1 \supset C_{60}$  and  $1 \supset C_{70}$  possess a four-electron accepting property. We suggest that the generated electron-deficient entities-based, dissolvable, fluorescence active host-guest complexes will not only allow detailed studies of the physical and chemical properties of the caged fullerenes in single molecular and 2D membrane states, but also further investigation of applications of these unique host-guest complexes in a variety of fields, such as photo-/electro-catalytic processes, organic electronics, etc.

#### **Author information**

#### **Corresponding Authors**

\*yfang@snnu.edu.cn

\*stang@chem.utah.edu

#### Notes

The authors declare no competing financial interest.

#### Acknowledgements

This work was supported by the Natural Science Foundation of China (21527802, 21673133, 21872091, 21820102005), 111 project (B14041), Program for Changjiang Scholars and Innovative Research Team in University (IRT-14R33). X. C. thanks Drs. Yan Sun, Zaiwen Yang and Yiliang Wang for extensive helpful discussions, Ms. Juan Fan for discussion on ESI-TOF-MS experiments, and Miss Xiaohua (Sophie) Fang for linguistic assistance during the preparation of this manuscript.

#### References

1. Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. Coordination assemblies from a Pd(II)-cornered square complex. *Acc. Chem. Res.* **2005**, *38*, 371-380.

- 2. Cook, T. R.; Zheng, Y. R.; Stang, P. J. Metal-organic frameworks and self-assembled supramolecular coordination complexes: comparing and contrasting the design, synthesis, and functionality of metal-organic materials. *Chem. Rev.* **2013**, *113*, 734-777.
- 3. Mukherjee, S.; Mukherjee, P. S. Template-free multicomponent coordination-driven self-assembly of Pd(II)/Pt(II) molecular cages. *Chem. Commun.* **2014**, *50*, 2239-2248.
- 4. Cook, T. R.; Stang, P. J. Recent developments in the preparation and chemistry of metallacycles and metallacages *via* coordination. *Chem. Rev.* **2015**, *115*, 7001-7045.
- 5. Newkome, G. R.; Moorefield, C. N. From 1→3 dendritic designs to fractal supramacromolecular constructs: understanding the pathway to the Sierpinski gasket. *Chem. Soc. Rev.* 2015, 44, 3954-3967.
- 6. Clever, G. H.; Punt, P. Cation-anion arrangement patterns in self-assembled Pd<sub>2</sub>L<sub>4</sub> and Pd<sub>4</sub>L<sub>8</sub> coordination cages. *Acc. Chem. Res.* **2017**, *50*, 2233-2243.
- Fielden, S. D. P.; Leigh, D. A.; Woltering, S. L. Molecular knots. *Angew. Chem. Int. Ed.* 2017, 56, 11166-11194.
- 8. Saha, S.; Regeni, I.; Clever, G. H. Structure relationships between bis-monodentate ligands and coordination driven self-assemblies. *Coordin. Chem. Rev.* **2018**, *374*, 1-14.
- 9. Sun, Y.; Chen, C.; Liu, J.; Stang, P. J. Recent developments in the construction and applications of platinum-based metallacycles and metallacages via coordination. *Chem. Soc. Rev.*, **2020**, *49*, 3889-3919.
- Danon, J. J.; Krüger, A.; Leigh, D. A.; Lemonnier, J.-F.; Stephens, A. J.; Vitorica-Yrezabal, I. J.; Woltering, S. L. Braiding a molecular knot with eight crossings. *Science*, 2017, 355, 159-162.
- 11. Fujita, D.; Ueda, Y.; Sato, S.; Mizuno, N.; Kumasaka, T.; Fujita, M. Self-assembly of tetravalent goldberg polyhedra from 144 small components. *Nature* **2016**, *540*, 563-566.
- Fujita, D.; Ueda, Y.; Sato, S.; Yokoyama, H.; Mizuno, N.; Kumasaka, T.; Fujita, M. Self-assembly of M<sub>30</sub>L<sub>60</sub> icosidodecahedron. *Chem* **2016**, *1*, 91-101.
- Wang, H.; Liu, C. H.; Wang, K.; Wang, M.; Yu, H.; Kandapal, S.; Brzozowski, R.; Xu, B.; Wang, M.; Lu, S.; Hao, X. Q.; Eswara, P.; Nieh, M. P.; Cai, J.; Li, X. Assembling pentatopic terpyridine ligands with three types of coordination moieties into a giant supramolecular hexagonal prism: synthesis, self-assembly, characterization, and antimicrobial study. *J. Am. Chem. Soc.* 2019, *141*, 16108-16116.
- Yoshizawa, M.; Klosterman, J. K.; Fujita, M. Functional molecular flasks: new properties and reactions within discrete, self-assembled hosts. *Angew. Chem. Int. Ed.* 2009, *48*, 3418-3438.
- 15. Brown, C. J.; Toste, F. D.; Bergman, R. G.; Raymond, K. N. Supramolecular catalysis in

2	
3	
4	
5	
7	
8	
9	
10	
12	
13	
14	
15	
10	
18	
19	
20	
21	
23	
24	
25 26	
20 27	
28	
29	
30 31	
32	
33	
34 25	
35 36	
37	
38	
39 40	
40 41	
42	
43	
44 45	
46	
47	
48 ⊿0	
+9 50	
51	
52	
53 54	
55	
56	
57	
эө 59	

metal-ligand cluster hosts. Chem. Rev. 2015, 115, 3012-3035.

- 16. Chen, K.; Shu, Q.; Schmittel, M. Design strategies for lab-on-a-molecule probes and orthogonal sensing. *Chem. Soc. Rev.* **2015**, *44*, 136-160.
- 17. Yam, V. W.-W.; Au, V. K.-M.; Leung, S. Y.-L. Light-emitting self-assembled materials based on d<sup>8</sup> and d<sup>8</sup> transition metal complexes. *Chem. Rev.* **2015**, *115*, 7589-7728.
- Saha, M. L.; Yan, X.; Stang, P. J. Photophysical properties of organoplatinum(II) compounds and derived self-assembled metallacycles and metallacages: fluorescence and its applications. *Acc. Chem. Res.* 2016, 49, 2527-2539.
- Roberts, D. A.; Pilgrim, B. S.; Nitschke, J. R. Covalent post-assembly modification in metallosupramolecular chemistry. *Chem. Soc. Rev.* 2018, 47, 626-644.
- 20. Sepehrpour, H.; Fu, W.; Sun, Y.; Stang, P. J. Biomedically relevant self-assembled metallacycles and metallacages. *J. Am. Chem. Soc.* **2019**, *141*, 14005-14020.
- 21. Sun, Y.; Chen, C.; Stang, P. J. Soft materials with diverse suprastructures *via* the self-assembly of metal-organic complexes. *Acc. Chem. Res.* **2019**, *52*, 802-817.
- Cao, L.; Wang, P.; Miao, X.; Dong, Y.; Wang, H.; Duan, H.; Yu, Y.; Li, X.; Stang, P. J. Diamondoid supramolecular coordination frameworks from discrete adamantanoid Platinum(II) cages. *J. Am. Chem. Soc.* 2018, *140*, 7005-7011.
- Sun, Y.; Li, S.; Zhou, Z.; Saha, M. L.; Datta, S.; Zhang, M.; Yan, X.; Tian, D.; Wang, H.; Wang, L.; Li, X.; Liu, M.; Li, H.; Stang, P. J. Alanine-based chiral metallogels via supramolecular coordination complex platforms: metallogelation induced chirality transfer. *J. Am. Chem. Soc.* 2018, *140*, 3257-3263.
- Shi, B.; Zhou, Z.; Vanderlinden, R. T.; Tang, J. H.; Yu, G.; Acharyya, K.; Sepehrpour, H.; Stang, P. J. Spontaneous supramolecular polymerization driven by discrete Platinum metallacycle-based host-guest complexation. *J. Am. Chem. Soc.* 2019. 141, 11837-11841.
- 25. Yan, X.; Cook, T. R.; Wang, P.; Huang, F.; Stang, P. J. Highly emissive Platinum(II) metallacages. *Nature Chem.* **2015**, *7*, 342-348.
- Zhou, Z.; Chen, D. G.; Saha, M. L.; Wang, H.; Li, X.; Chou, P. T.; Stang, P. J. Designed conformation and fluorescence properties of self-assembled phenazine-cored Platinum(II) metallacycles. *J. Am. Chem. Soc.* 2019, *141*, 5535-5543.
- 27. Li, G.; Zhou, Z.; Yuan, C.; Guo, Z.; Liu, Y.; Zhao, D.; Liu, K.; Zhao, J.; Tan, H.; Yan, X. Trackable supramolecular fusion: cage to cage transformation of tetraphenylethylene-based metalloassemblies. *Angew. Chem. Int. Ed.* **2020**, *59*, 10013-10017.
- Zhang, Z.; Zhao, Z.; Wu, L.; Lu, S.; Ling, S.; Li, G.; Xu, L.; Ma, L.; Hou, Y.; Wang, X.; Li, X.; He, G.; Wang, K.; Zou, B.; Zhang, M. Emissive Platinum(II) cages with reverse fluorescence resonance energy transfer for multiple sensing. *J. Am. Chem. Soc.* 2020, *142*, 2592-2600.
- 29. Tang, J. H.; Sun, Y.; Gong, Z. L.; Li, Z. Y.; Zhou, Z.; Wang, H.; Li, X.; Saha, M. L.; Zhong,

Y. W.; Stang, P. J. Temperature-responsive fluorescent organoplatinum(II) metallacycles. *J. Am. Chem. Soc.* **2018**, *140*, 7723-7729.

- Zhou, Z.; Liu, J.; Huang, J.; Rees, T. W.; Wang, Y.; Wang, H.; Li, X.; Chao, H.; Stang, P. J. A self-assembled Ru-Pt metallacage as a lysosome-targeting photosensitizer for 2-photon photodynamic therapy. Proc. Natl. Acad. Sci. U. S. A. **2019**, *116*, 20296-20302.
- Chang, X.; Zhou, Z.; Shang, C.; Wang, G.; Wang, Z.; Qi, Y.; Li, Z. Y.; Wang, H.; Cao, L.; Li, X.; Fang, Y.; Stang, P. J. Coordination-driven self-assembled metallacycles incorporating pyrene: fluorescence mutability, tunability, and aromatic amine sensing. *J. Am. Chem. Soc.* 2019, 141, 1757-1765.
- 32. Würthner, F.; Saha-Moller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D. Perylene bisimide dye assemblies as archetype functional supramolecular materials. *Chem. Rev.* **2016**, *116*, 962-1052.
- Chen, S.; Slattum, P.; Wang, C.; Zang, L. Self-assembly of perylene imide molecules into 1D nanostructures: methods, morphologies, and applications. *Chem. Rev.* 2015, *115*, 11967-11998.
- 34. Yang, Z.; Chen, X. Semiconducting perylene diimide nanostructure: multifunctional phototheranostic nanoplatform. *Acc. Chem. Res.* **2019**, *52*, 1245-1254.
- Kang, R.; Miao, R.; Qi, Y.; Chang, X.; Shang, C.; Wang, L.; Fang, Y. Tuning the formation of reductive species of perylene-bisimide derivatives in DMF *via* aggregation matter. *Chem. Commun.* 2017, *53*, 10018-10021.
- Liu, K.; Shang, C.; Wang, Z.; Qi, Y.; Miao, R.; Liu, K.; Liu, T.; Fang, Y. Non-contact identification and differentiation of illicit drugs using fluorescent films. *Nature Commun.* 2018, *9*, 1695.
- Wang, Z.; Wang, G.; Chang, X.; Liu, K.; Qi, Y.; Shang, C.; Huang, R.; Liu, T.; Fang, Y. A perylene bisimide-contained molecular dyad with high-efficient charge separation: switchability, tunability, and applicability in moisture detection. *Adv. Funct. Mater.* 2019, *29*, 1905295.
- Battagliarin, G.; Li, C.; Enkelmann, V.; Müllen, K. 2,5,8,11-Tetraboronic ester perylenediimides: a next generation building block for dye-stuff synthesis. *Org. Lett.* 2011, *13*, 3012-3015.
- Wu, J.; He, D.; Zhang, L.; Liu, Y.; Mo, X.; Lin, J.; Zhang, H. J. Direct synthesis of large-scale ortho-iodinated perylene diimides: key precursors for functional dyes. *Org. Lett.* 2017, 19, 5438-5441.
- 40. Nowak-Król, A.; Würthner, F. Progress in the synthesis of perylene bisimide dyes. *Org. Chem. Front.* **2019**, *6*, 1272-1318.
- 41. Yu, Z.; Wu, Y.; Liao, Q.; Zhang, H.; Bai, S.; Li, H.; Xu, Z.; Sun, C.; Wang, X.; Yao, J.; Fu, H. Self-assembled microdisk lasers of perylenediimides. *J. Am. Chem. Soc.* 2015, *137*, 15105-15111.

#### 20 / 25

1	
2	
4 5	
6	
7	
, 8	
9	
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	
20	
21	
22	
23	
24	
25	
26	
27	
28	
29	
30	
31	
32	
33 24	
24 25	
36	
37	
38	
39	
40	
41	
42	
43	
44	
45	
46	
47	
48	
49	
50	
51	
52	
53	
54	
55	
50 57	
57 50	
50 50	
60	
00	

- 42. Zeng, C.; Xiao, C.; Feng, X.; Zhang, L.; Jiang, W.; Wang, Z. Electron-transporting bis(heterotetracenes) with tunable helical packing. *Angew. Chem. Int. Ed.* **2018**, *57*, 10933-10937.
- 43. Park, S. K.; Kim, J. H.; Park, S. Y. Organic 2D optoelectronic crystals: charge transport, emerging functions, and their design perspective. *Adv. Mater.* **2018**, *30*, e1704759.
- Yang, F.; Cheng, S.; Zhang, X.; Ren, X.; Li, R.; Dong, H.; Hu, W. 2D organic materials for optoelectronic applications. *Adv. Mater.* 2018, *30*, 1702415.
- 45. Yang, Y.; Li, G. Progress in high-effcient solution process organic photovoltaic devices, Springer-Verlag, Berlin/Heidelberg, Germany **2015**.
- 46. Nair, V. S.; Mukhopadhyay, R. D.; Saeki, A.; Seki, S.; Ajayaghosh, A. A π-gel scaffold for assembling fullerene to photoconducting supramolecular rods. *Sci. Adv.* **2016**, *2*, e1600142.
- Geng J.; Zhou, W.; Skelton, P.; Yue, W.; Kinloch, I. A.; Windle, A. H.; Johnson, B. F. G. Crystal structure and growth mechanism of unusually long fullerene (C<sub>60</sub>) nanowires. *J. Am. Chem. Soc.* 2008, *130*, 2527-2534.
- Wu, K. Y.; Wu, T. Y.; Chang, S. T.; Hsu, C. S.; Wang, C. L. A facile PDMS-assisted crystallization for the crystal-engineering of C<sub>60</sub> single-crystal organic field-effect transistors. *Adv. Mater.* 2015, *27*, 4371-4376.
- Cui, D.; Ebrahimi, M.; Rosei, F.; Macleod, J. M. Control of fullerene crystallization from 2D to 3D through combined solvent and template effects. *J. Am. Chem. Soc.* 2017, *139*, 16732-16740.
- Yan, W.; Qu, Y.; Gupta, T. D.; Darga, A.; Nguyên, D. T.; Page, A. G.; Rossi, M.; Ceriotti, M.; Sorin, F. Semiconducting nanowire-based optoelectronic fibers. *Adv. Mater.* 2017, 29, 1700681.
- Lee, K.; Choi, B.; Plante, I. J.; Paley, M. V.; Zhong, X.; Crowther, A. C.; Owen, J. S.; Zhu, X.; Roy, X. Two-dimensional fullerene assembly from an exfoliated van der Waals template. *Angew. Chem. Int. Ed.* 2018, *57*, 6125-6129.
- Liu, K.; Gao, S.; Zheng, Z.; Deng, X.; Mukherjee, S.; Wang, S.; Xu, H.; Wang, J.; Liu, J.; Zhai, T.; Fang, Y. Spatially confined growth of fullerene to super-long crystalline fibers in supramolecular gels for high-performance photodetector. *Adv. Mater.* 2019, *31*, e1808254.
- 53. Tashiro, K.; Aida, T. Metalloporphyrin hosts for supramolecular chemistry of fullerenes. *Chem. Soc. Rev.* **2007**, *36*, 189-197.
- 54. Pérez, E. M.; Martín, N. Curves ahead: molecular receptors for fullerenes based on concave-convex complementarity. *Chem. Soc. Rev.* **2008**, *37*, 1512-1519.
- 55. Canevet, D.; Pérez, E. M.; Martín, N. Wraparound hosts for fullerenes: tailored macrocycles and cages. *Angew. Chem. Int. Ed.* **2011**, *50*, 9248-9259.
- 56. García-Simón, C.; Costas, M.; Ribas, X. Metallosupramolecular receptors for fullerene binding and release. *Chem. Soc. Rev.* **2016**, *45*, 40-62.

- 57. Yanagisawa, M.; Tashiro, K.; Yamasaki, M.; Aida, T. Hosting fullerenes by dynamic bond formation with an iridium porphyrin cyclic dimer: a "chemical friction" for rotary guest motions. *J. Am. Chem. Soc.* **2007**, *129*, 11912-11913.
- Suzuki, K.; Takao, K.; Sato, S.; Fujita, M. Coronene nanophase within coordination spheres: increased solubility of C<sub>60</sub>. J. Am. Chem. Soc. 2010, 132, 2544-2545.
- Huerta, E.; Isla, H.; Pérez, E. M.; Bo, C.; Martín, N.; de Mendoza, J. Tripodal exTTF-CTV hosts for fullerenes. J. Am. Chem. Soc. 2010, 132, 5351-5353.
- 60. Song, J.; Aratani, N.; Shinokubo, H.; Osuka, A. A porphyrin nanobarrel that encapsulates C<sub>60</sub>. *J. Am. Chem. Soc.* **2010**, *132*, 16356-16357.
- Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S. Size-selective encapsulation of C<sub>60</sub> by [10]cycloparaphenylene: formation of the shortest fullerene-peapod. *Angew. Chem. Int. Ed.* 2011, *50*, 8342-8344.
- Mahata, K.; Frischmann, P. D.; Würthner, F. Giant electroactive M<sub>4</sub>L<sub>6</sub> tetrahedral host self-assembled with Fe(II) vertices and perylene bisimide dye edges. *J. Am. Chem. Soc.* 2013, *135*, 15656-15661.
- Nakamura, T.; Ube, H.; Miyake, R.; Shionoya, M. A C<sub>60</sub>-templated tetrameric porphyrin barrel complex *via* zinc-mediated self-assembly utilizing labile capping ligands. *J. Am. Chem. Soc.* 2013, *135*, 18790-18793.
- 64. Kishi, N.; Akita, M.; Yoshizawa, M. Selective host-guest interactions of a transformable coordination capsule/tube with fullerenes. *Angew. Chem. Int. Ed.* **2014**, *53*, 3604-3607.
- Yokoi, H.; Hiraoka, Y.; Hiroto, S.; Sakamaki, D.; Seki, S.; Shinokubo, H. Nitrogen-embedded buckybowl and its assembly with C<sub>60</sub>. *Nature Commun.* 2015, *6*, 8215.
- Brenner, W.; Ronson, T. K.; Nitschke, J. R. Separation and selective formation of fullerene adducts within an M<sup>II</sup><sub>8</sub>L<sub>6</sub> cage. J. Am. Chem. Soc. 2017, 139, 75-78.
- Ke, X. S.; Kim, T.; Lynch, V. M.; Kim, D.; Sessler, J. L. Flattened calixarene-like cyclic BODIPY array: a new photosynthetic antenna model. *J. Am. Chem. Soc.* 2017, *139*, 13950-13956.
- 68. Rizzuto, F. J.; Wood, D. M.; Ronson, T. K.; Nitschke, J. R. Tuning the redox properties of fullerene clusters within a metal-organic capsule. *J. Am. Chem. Soc.* **2017**, *139*, 11008-11011.
- Kawano, S. I.; Fukushima, T.; Tanaka, K. Specific and oriented encapsulation of fullerene C<sub>70</sub> into a supramolecular double-decker cage composed of shape-persistent macrocycles. *Angew. Chem. Int. Ed.* **2018**, , 14827-14831.
- Shi, Y.; Cai, K.; Xiao, H.; Liu, Z.; Zhou, J.; Shen, D.; Qiu, Y.; Guo, Q. H.; Stern, C.; Wasielewski, M. R.; Diederich, F.; Goddard, W. A., III; Stoddart, J. F. Selective extraction of C<sub>70</sub> by a tetragonal prismatic porphyrin cage. *J. Am. Chem. Soc.* **2018**, *140*, 13835-13842.
- Takeda, M.; Hiroto, S.; Yokoi, H.; Lee, S.; Kim, D.; Shinokubo, H. Azabuckybowl-based molecular tweezers as C<sub>60</sub> and C<sub>70</sub> receptors. *J. Am. Chem. Soc.* **2018**, *140*, 6336-6342.

72.	Xu, Y.; Wang, B.; Kaur, R.; Minameyer, M. B.; Bothe, M.; Drewello, T.; Guldi, D. M.; von Delius, M. A Supramolecular [10]CPP junction enables efficient electron transfer in modular porphyrin-[10]CPP ⊃fullerene complexes. <i>Angew. Chem. Int. Ed.</i> <b>2018</b> , <i>57</i> , 11549-11553.
73.	Chen, B.; Holstein, J. J.; Horiuchi, S.; Hiller, W. G.; Clever, G. H. Pd(II) coordination sphere engineering: pyridine cages, quinoline bowls, and heteroleptic pills binding one or two fullerenes. <i>J. Am. Chem. Soc.</i> <b>2019</b> , <i>141</i> , 8907-8913.
74.	Huang, Q.; Zhuang, G.; Jia, H.; Qian, M.; Cui, S.; Yang, S.; Du, P. Photoconductive curved-nanographene/fullerene supramolecular heterojunctions. <i>Angew. Chem. Int. Ed.</i> <b>2019</b> , <i>58</i> , 6244-6249.
75.	Lu, X.; Gopalakrishna, T. Y.; Han, Y.; Ni, Y.; Zou, Y.; Wu, J. Bowl-shaped carbon nanobelts showing size-dependent properties and selective encapsulation of C <sub>70</sub> . <i>J. Am. Chem. Soc.</i> <b>2019</b> , <i>141</i> , 5934-5941.
76.	Martinez-Agramunt, V.; Eder, T.; Darmandeh, H.; Guisado-Barrios, G.; Peris, E. A size-flexible organometallic box for the encapsulation of fullerenes. <i>Angew. Chem. Int. Ed.</i> <b>2019</b> , <i>58</i> , 5682-5686.
77.	Nakamura, T.; Tsukuda, S.; Nabeshima, T. Double-circularly connected Saloph-belt macrocycles generated from a bis-armed bifunctional monomer. <i>J. Am. Chem. Soc.</i> <b>2019</b> , <i>141</i> , 6462-6467.
78.	Barendt, T. A.; Myers, W. K.; Cornes, S. P.; Lebedeva, M. A.; Porfyrakis, K.; Marques, I.; Félix, V.; Beer, P. D. The green box: an electronically versatile perylene diimide macrocyclic host for fullerenes. <i>J. Am. Chem. Soc.</i> <b>2020</b> , <i>142</i> , 349-364.
79.	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. Supramolecular fullerene sponges as catalytic masks for regioselective functionalization of C <sub>60</sub> . <i>Chem</i> <b>2020</b> , <i>6</i> , 169-186.
80.	Würthner, F.; Sautter, A. Highly fluorescent and electroactive molecular squares containing perylene bisimide ligands. <i>Chem. Commun.</i> <b>2000</b> , 445-446.
81.	You, C. C.; Hippius, C.; Grune, M.; Würthner, F. Light-harvesting metallosupramolecular squares composed of perylene bisimide walls and fluorescent antenna dyes. <i>Chem. Eur. J.</i> <b>2006</b> , <i>12</i> , 7510-7519.
82.	Frischmann, P. D.; Kunz, V.; Stepanenko, V.; Würthner, F. Subcomponent self-assembly of a 4 nm $M_4 L_6$ tetrahedron with Zn(II) vertices and perylene bisimide dye edges. <i>Chem. Eur. J.</i> <b>2015</b> , <i>21</i> , 2766-2769.
83.	Frischmann, P. D.; Kunz, V.; Würthner, F. Bright fluorescence and host-guest sensing with a nanoscale $M_4L_6$ tetrahedron accessed by self-assembly of Zinc-imine chelate vertices and perylene bisimide edges. <i>Angew. Chem. Int. Ed.</i> <b>2015</b> , <i>54</i> , 7285-7289.
84.	Sapotta, M.; Hofmann, A.; Bialas, D.; Würthner, F. A water-soluble perylene bisimide cyclophane as a molecular probe for the recognition of aromatic alkaloids. <i>Angew. Chem. Int.</i> <b>23</b> / <b>25</b>

Ed. 2019, 58, 3516-3520.

- Bhat, I. A.; Jain, R.; Siddiqui, M. M.; Saini, D. K.; Mukherjee P. S. Water-soluble Pd<sub>8</sub>L<sub>4</sub> self-assembled molecular barrel as an aqueous carrier for hydrophobic curcumin. *Inorg. Chem.* 2017, *56*, 5352-5360.
- Bivaud, S.; Balandier, J. -Y.; Chas, M.; Allain, M.; Goeb, S.; Sallé, M. A metal-directed self-assembled electroactive cage with bis(pyrrolo)tetrathiafulvalene (BPTTF) side walls. *J. Am. Chem. Soc.* 2012, *134*, 11968-11970.
- Cecot, G.; Marmier, M.; Geremia, S.; De Zorzi, R.; Vologzhanina, A. V.; Pattison, P.; Solari, E.; Fadaei, F. T.; Scopelliti, R.; Severin, K. The intricate structural chemistry of M<sup>II</sup><sub>2n</sub>L<sub>n</sub>-type assemblies. *J. Am. Chem. Soc.* 2017, *139*, 8371-8381.
- Cecot, G.; Alameddine, B.; Prior, S.; De Zorzi, R.; Geremia, S.; Scopelliti, R.; Fadaei, F. T.; Solari, E.; Severin, K. Large heterometallic coordination cages with gyrobifastigium-like geometry. *Chem. Commun.* 2016, *52*, 11243-11246.
- Bhat, I. A.; Devaraj A.; Zangrando E.; Mukherjee, P. S. A discrete self-assembled Pd<sub>12</sub> triangular orthobicupola cage and its use for intramolecular cycloaddition. *Chem. Eur. J.* 2018, *24*, 13938-13946.
- Yang, J.; Bhadbhade, M.; Donald, W. A.; Iranmanesh, H.; Moore, E. G.; Yan, H.; Beves, J. E. Self-assembled supramolecular cages containing Ruthenium(II) polypyridyl complexes. *Chem. Commun.* 2015, *51*, 4465-4468.
- Semenov, K. N.; Charykov, N. A.; Keskinov, V. A.; Piartman, A. K.; Blokhin, A. A.; Kopyrin, A. A. Solubility of light fullerenes in organic solvents. *J. Chem. Eng. Data* 2010, 55, 13-36.

# Self-assembled Perylene Bisimide-cored Trigonal Prism as an Electron-deficient Host for C<sub>60</sub> and C<sub>70</sub> Driven by 'Like Dissolves Like'

Xingmao Chang,<sup>1,2</sup> Simin Lin,<sup>1</sup> Gang Wang,<sup>1</sup> Congdi Shang,<sup>1</sup> Zhaolong Wang,<sup>1</sup> Kaiqiang Liu,<sup>1</sup> Yu Fang,<sup>1,\*</sup> and Peter J. Stang<sup>2,\*</sup>

<sup>1</sup>Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education), School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710119, P. R. China

<sup>2</sup>Department of Chemistry, University of Utah, 315 South 1400 East, Room 2020, Salt Lake City, Utah 84112, United States

## TOC







ACS Paragon Plus Environment