

A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

Accepted Article

Title: Spherical Supramolecular Structures Constructed via Chemically Symmetric Perylene Bisimides: Beyond Columnar Assembly

Authors: Jiahao Huang, Zebin Su, Mingjun Huang, Rongchun Zhang, Jian Wang, Xueyan Feng, Rui Zhang, Ruimeng Zhang, Wenpeng Shan, Xiao-Yun Yan, Qing-Yun Guo, Tong Liu, Yuchu Liu, Yunpeng Cui, Xiaopeng Li, An-Chang Shi, and Stephen Z. D. Cheng

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.201914889

Link to VoR: https://doi.org/10.1002/anie.201914889

WILEY-VCH

RESEARCH ARTICLE

Spherical Supramolecular Structures Constructed via Chemically Symmetric Perylene Bisimides: Beyond Columnar Assembly

Jiahao Huang, [†] ^[a] ^[b] Zebin Su[†] ^[b], Mingjun Huang^[a], Rongchun Zhang^[a], Jian Wang^[d], Xueyan Feng^[b], Rui Zhang^[a], Ruimeng Zhang^[b], Wenpeng Shan^[b], Xiao-Yun Yan^[b], Qing-Yun Guo^[b], Tong Liu^[b], Yuchu Liu^[b], Yunpeng Cui^[e], Xiaopeng Li^[e], An-Chang Shi^{*[c]}, and Stephen Z. D. Cheng^{*[a][b]}

Abstract: Like other discotic molecules, self-assembled supramolecular structures of perylene bisimides (PBIs) are commonly limited to columnar or lamellar structures due to their distinct π conjugated scaffolds and unique rectangular shape of perylene cores. The discovery of PBIs with supramolecular structures beyond layers and columns may expand the scope of PBI-based materials. Herein, we report a series of unconventional spherical packing phases in PBIs including A15 phase, σ phase, dodecagonal quasicrystalline (DQC) phase, and body-centered cubic (BCC) phase. By the functionalization of perylene core with several polyhedral oligomeric silsesquioxane (POSS) cages, our strategy successfully achieves spherical assemblies of PBIs, instead of columnar assemblies, due to the significantly increased steric hindrance at the periphery. This strategy may also be employed for the discovery of unconventional spherical assemblies in other related discotic molecules by the introduction of similar bulky functional groups at their periphery. In addition, an unusual inverse phase transition sequence from BCC phase to σ phase by increasing annealing temperature is observed.

Introduction

In the past decades, perylene bisimides (PBIs) have attracted much research attention due to their self-assembled π -conjugated scaffolds with outstanding stability as well as conveniently tuned absorption/fluorescence properties.^[1] These features make PBI-based materials an ideal candidate for a wide range of applications including organic electronics,^[2] photovoltaic

| [a] | J. Huang, Prof. M. Huang, Prof. RC. Zhang, Prof. R. Zhang, Prof. S. Z. D. Chong |
|------|---|
| | S. Z. D. Olleng South China Advanced Institute for Soft Matter Science and |
| | Technology |
| | School of Molecular Science and Engineering |
| | South China University of Technology, Guangzhou 510640, China |
| [b] | J. Huang, Z. Su, X. Feng, RM. Zhang, W. Shan, XY. Yan, QY. |
| | Guo, T. Liu, Y. Liu, Prof. S. Z. D. Cheng |
| | Department of Polymer Science |
| | College of Polymer Science and Polymer Engineering |
| | The University of Akron, Akron, Ohio 44325-3909, USA |
| | E-mail: scheng@uakron.edu |
| [c] | Prof. AC. Shi |
| | Department of Physics and Astronomy |
| | McMaster University, Hamilton, Ontario L8S 4M1, Canada |
| | E-mail: shi@mcmaster.ca |
| [d] | Prof. J. Wang |
| | School of Life Science and Technology |
| | ShanghaiTech University, Shanghai 201210, China |
| [e] | Y. Cui, Prof. X. Li |
| | Department of Chemistry |
| | University of South Florida, Tampa, Florida 33620, USA |
| | J. Huang and Z. Su contribute equally to this work. |
| Supr | porting information for this article is given via a link at the and of the |
| docu | iment |

devices,^[3] photonics,^[4] and some biology related applications.^[5] It is well recognized that the properties of materials do not solely depend on their primary chemical structures, but also rely on how they are organized across multiple length scales.^[6] A simple example is that the optical properties of PBIs are largely affected by their different packing arrangements.^[7]Tailoring the properties of PBI-based materials with different hierarchical structures may help improve their performance and lead to new applications. From a physiochemical perspective, the most important factor affecting the molecular packing is the π - π stacking interaction between rigid polycyclic aromatic cores of PBIs. This relatively strong interaction usually favors the formation of columnar assemblies in solution,^[8] organo-gels,^[9] or liquid crystalline phases.^[10] In particular, Percec and co-workers have explored in great detail the supramolecular organization of dendronized PBIs and observed the formation of different columnar liquid-crystalline phases.[11] Discotic and guasi-discotic molecules have already employed in the design of spherical assemblies such as triphenylenes and cyclotriveratrylenes.^[12] However, observation of spherical assembly of PBIs based on π - π stacking interaction is scarce due presumably to the unique molecular geometry of PBIs.[13]

Periodically or quasiperiodically ordered structures generated from spherical motifs occur in many different classes of selfassembling soft matter systems. The last two decades have witnessed remarkable progresses in the discovery of a series of highly ordered and complex Frank-Kasper (F-K) phases composed of spherical motifs in soft matters, including liquid crystals,^[14] small-molecular surfactants,^[15] dendrimers,^[16] block copolymers,^[17] colloidal particles,^[18] giant molecules,^[19] and very recently, sugar-polyolefin conjugates.^[20] It should be mentioned that the Frank-Kasper phases refer to a family of topologically close-packed spherical packing phases originally observed in metal alloys.^[21] Furthermore, the dodecagonal guasicrystalline phase (DQC) with 12-fold rotational symmetry but no long-range translational periodicity has also been reported in soft matters.^[22] Aperiodic DQC phase is closely related to some Frank-Kasper phases due to their similar local tetrahedral sphere packing.^[22e, 23] The discovery of these complex spherical phases in PBI-based materials still remains a challenging topic.

Here, we present an experimental study of a series of rationally designed POSS-based PBIs constructed by attaching six cubic polyhedral oligomeric silsesquioxane (POSS) cages to the planar PBI core at its imide positions with tunable linkage lengths, exhibiting features of shape amphiphiles (Figure 1).^[24] These molecules are distinguished from previously reported PBIs by the introduction of the bulky and rigid peripheric BPOSS (POSS functionalized with seven isobutyl groups, Figure 1) cage building

RESEARCH ARTICLE



Figure 1. Molecular cartoon model and chemical structures of the PBI-Cn-6BP with linkage structure variations. For the naming of these molecules, PBI refers to perylene bisimides, Cn refers to the number of methylene group in each linkage part between triazole group and one POSS cage, BP refers to BPOSS, and ISO refers to isomer. (a) Simplified carton of POSS-based PBIs, exhibiting features of shape amphiphiles. Blue sphere represents BPOSS cages, red block represents aromatic rings, and detailed linkage chemical structures are shown in the blue dashed box. (b) Chemical structure and molecular model (shown in shadow, hydrogen atoms are omitted for clarity) of PBI-C1-6BP. Dimensions of perylene core (12.3 Å in length and 7.3 Å in width, including hydrogen atoms) and cross center distance (13 Å) of cubic BPOSS cage are indicated.

blocks. The self-assembly of these PBIs is dictated by the interplay between the planar PBI cores and the cubic POSS cages. On the one hand, the π - π stacking interaction between PBIs combined with relative short linkages inhibits the crystallization of BPOSS cages, which usually have strong tendency to crystallize.^[25] On the other hand, due to significant steric hindrance of the rigid and bulky BPOSS cages, the formation of columnar structures as commonly observed in PBI is impeded. The unique nanometer size and shape persistency of cubic POSS cages combined with flexible linkages provide significant and tunable steric hindrance during PBI stacking process, facilitating the spherical assemblies of PBIs and further the formation of various spherical packing phases. Surprisingly, diverse and highly ordered spherical supramolecular lattices, including BCC phase, A15 phase, σ phase, and DQC phase, are observed in the POSS-based PBIs. Moreover, an unusual inverse phase transition sequence from a BCC phase to a σ phase by increasing annealing temperature is observed.

Results and Discussion

Synthesis and characterization. The synthesis of $PBI-C_1-6BP$ is briefly shown in Scheme 1 as an example. In short, three BPOSS cages were first connected simultaneously via coppercatalyzed azide-alkyne [3+2] cycloaddition (CuAAC) "click" chemistry. The targeted POSS-based PBIs were then synthesized via an imidation reaction between perylene-3,4,9,10tetracarboxylic dianhydride (PTCDA) and aromatic amines attached with three BPOSS cages at elevated temperature. The lengths and chemical structures of the linkages could be precisely tuned, resulting in variations on the flexibility of the linkages, and, thus, the steric effect of the peripheric BPOSS cages. The detailed synthetic procedures of these PBIs are shown in the **Supporting Information (SI)**. Their precise chemical structures and high purity were confirmed by mass spectroscopy, gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR) spectroscopy (Figures S1, S2, and S3).

Typical thermal properties of these POSS-based PBIs were characterized by thermal gravimetric analysis (Figure S4) and differential scanning calorimetric experiments (Figure S5). The samples are thermally stable at temperatures higher than 250 °C (no weight loss up to 320 °C at a heating rate of 10 °C/min with N₂ flow). No crystallization peak of BPOSS cages was observed in the DSC curves, which indicates that crystallization of BPOSS cages is strongly suppressed. No visible phase transition peak was observed in the DSC curves, either. We speculate that π - π interaction between the PBI cores could induce stacking of the entire molecules and result in disordered yet dense packing of the BPOSS cages, which have relatively short linkages with the PBI cores. Optical properties of the POSS-based PBIs were investigated by ultraviolet-visible (UV-vis) and fluorescence

RESEARCH ARTICLE

Scheme 1. Synthesis of PBI-C1-6BP



Reagents and conditions: (i) CuBr, PMDETA, THF, 25 °C, 6h; (ii) DMAP, imidazole, ODCB, 125 °C, 6h

spectroscopy (Figure S6). Taking PBI-C1-6BP as an example, in dilute solution (10^{-5} **M**, monomeric state), the absorption bands between 410 and 550 nm for the S₀-S₁ transition of PBIs with wellresolved vibronic structure from the breathing vibrations of the perylene skeleton, was observed in the corresponding UV-vis spectrum (Figure S6a). In annealed thin film (aggregated state), a shift of absorption maximum about 30 nm was observed compared to in dilute solution, indicating the face-to-face stacking of perylenes in the aggregated state.^[10c] The fluorescence of the POSS-based PBIs was observed in monomeric and aggregated state by the fluorescence emission spectra in dilute solution and in annealed thin film (Figure S6c). The photoluminescence in the aggregated state suggests there is a relatively large rotational displacement between perylenes in the π -stacked aggregates.^[10e] It's worthy to note that previously reported tridodecyloxyphenylsubstituted PBIs are not photoluminescent despite comparative chemical structure to our POSS-based PBIs.[10b] The POSSbased PBIs were annealed in a series of temperatures with 5 °C interval for 12 h with N₂ flow. After the thermal annealing processes, a variety of complex supramolecular phases were obtained in the POSS-based PBIs. The formation of the highly ordered supramolecular structures was demonstrated by a combination of small angle X-ray scattering (SAXS) technique and bright field (BF) transmission electron microscopy (TEM) images.

Analysis of self-assembly behavior and phase transition. For PBI-C₀-6BP with the shortest and most rigid linkage, no ordered structures could be observed based on SAXS result (Figure S7), despite extensive thermal and solvent annealing efforts. As expected, the strong steric hindrance of the BPOSS cages prevents the common columnar assembly of the PBIs. However, the mobility of the BPOSS cages is also severely constrained by the rigid linkage, inducing significant steric hindrance from BPOSS cages, as well as inhibiting the formation of suitable supramolecular spheres and ordered phases in the bulk state.

Adding one methyl group between the phenyl group and the triazole group in the linkage (sample PBI-C1-6BP) slightly increases the flexibility of the linkage and results in a completely different self-assembly behavior. After annealing at 200 °C for 12 h, PBI-C1-6BP powder sample exhibited sharp diffraction peaks in the SAXS pattern with a set of scattering vector (q) ratios of $\sqrt{4}$: $\sqrt{5}$: $\sqrt{6}$: $\sqrt{8}$ (Figure 2a). These scattering peaks could be assigned as an F-K A15 cubic phase^[25a] (space group $Pm\overline{3}n$) with unit cell parameter a = 7.8 nm. This structural assignment was further confirmed by a representative 4⁴ tiling pattern along the [001] direction in the BF TEM images (Figures 2g and 2h after Fourier filtering) and the corresponding fast Fourier transformed (FFT) diffraction pattern (Figure 2g, inset).[16e] The formation of the spherical packing phases is also demonstrated by unit cell electron density reconstruction (Figure S10). Increasing the flexibility of this linkage enhances the mobility of the BPOSS cage shells, facilitating the formation of supramolecular spherical motifs and further assembling into an A15 phase. The cubic unit cell of this phase is composed of eight supramolecular spheres (two with coordination number (CN) = 12 and six with CN = 14).^[26] On the basis of the lattice parameter and experimentally measured density, the average diameter of the supramolecular spheres (<d_{sphere}>) and the average number of molecules in each supramolecular sphere ($\langle \mu \rangle$) can be estimated as 4.84 nm and 6.3, respectively (Table 1). The crystallization of BPOSS cages is inhibited in this A15 phase, demonstrated by the observation of one broad scattering peak corresponding to the average size of BPOSS cages in the wide-angle X-ray diffraction (WAXD) pattern (Figure S8a).

On the basis of **PBI-C₁-6BP**, we further tune the linkage structure by adding a short amide linkage with different methylene number between BPOSS cage and phenyl group (Figure 1a). After thermal treatment of **PBI-C₃-6BP** at 220 °C for 12 h, a complex SAXS pattern with multiple diffraction peaks was recorded (Figure 2b). We could assign this SAXS pattern as an F-K σ phase (space group $P4_2/mnm$) with a tetragonal unit cell and unit cell

RESEARCH ARTICLE



Figure 2. Self-assembled supramolecular structures of some POSS-based PBIs. **PBI-C₁-6BP** shows an A15 phase in the SAXS pattern (a) and BF TEM images (g and h after Fourier filtering). **PBI-C₃-6BP** shows a σ phase in the SAXS pattern (b) and BF TEM images (k and I after Fourier filtering). **PBI-C₄-6BP** and **PBI-C₅-6BP** exhibit BCC phases in the SAXS patterns (d and e) at 215 °C, and these BCC phases transfer to the σ phase in the SAXS pattern (d) and the DQC phase in the SAXS pattern (e) for **PBI-C₄-6BP** and **PBI-C₅-6BP** at 225 °C and 230 °C, respectively. And BF TEM images (m and n after Fourier filtering) further demonstrate the DQC phase of **PBI-C₄-6BP** at 230 °C. **PBI-C₆-6BP** shows a BCC phase in the SAXS pattern (c) and BF TEM images (i and j after Fourier filtering). TEM images are taken along the [001] direction of the A15 phase, the [001] direction of the DQC phase. The upper left insets of the TEM images are corresponding FFT diffraction patterns. The packing models of the A15 phase, the σ phase, the BCC phase are illustrated in f.

RESEARCH ARTICLE

parameters a = b = 16.85 nm and c = 8.87 nm.^[14b] The corresponding BF TEM images along the [001] direction (Figures 2k and 2l after Fourier filtering) display a typical 3².4.3.4 tiling pattern. The corresponding FFT diffraction pattern (Figure 2k, inset) suggests the tetragonal lattice of the σ phase.^[17a] A typical tetragonal unit cell in the σ phase consists of thirty supramolecular spheres in five different coordination environments. The average $< d_{sphere} >$ and $< \mu >$ values are derived as 5.43 nm and 8.4, respectively (Table 1). The self-assembled σ phase remains thermodynamically stable up to around 230 °C and then, this phase transfers to the disordered melts state at higher temperature (Figure S9a). It should be noted that here, hydrogen bonding could be observed by Fourier-transform infrared (FT-IR) spectroscopy due to the introduction of amide groups in the linkages (Figure S12), which may assist the stacking of the POSS-based PBIs and facilitate the phase formation process.

PBI-C₄-6BP and PBI-C₅-6BP contain longer and more flexible linkages, exhibiting distinct phase structures and transition behaviors in a relatively wide range of temperatures. Annealing these two molecules at 215 °C first, both molecules formed BCC phases (space group $Im\bar{3}m$), which were identified by two sharp peaks in their SAXS patterns with characteristic q ratios of 1: $\sqrt{2}$ (Figures 2d and 2e). The d_{sphere} and μ value (note that here these two values are not average) are 5.80 nm and 10, respectively, in the BCC phase of PBI-C₄-6BP. The d_{sphere} and μ value of PBI-C₅-6BP in the BCC phase are 5.99 nm and 11, respectively. As the annealing temperatures of the two molecules increase, two different SAXS patterns were recorded. The PBI-C4-6BP exhibits the formation of a σ phase with a tetragonal unit cell (a = b = 17.56nm, c = 9.24 nm) after thermal annealing at 225 °C for a few hours with average values of $\langle d_{sphere} \rangle$ and $\langle \mu \rangle$ of 5.66 nm and 9.4 in the σ phase (Figure 2d). These numbers change between two phases may imply the exchange and redistribution of the POSS-based PBIs among the supramolecular spheres during the phase transition from the BCC phase to the σ phase. A clearly indexed σ phase is shown in Figure S11 and Table S1.

On the other hand, for PBI-C5-6BP, the SAXS pattern at 230 °C is in good accordance with a DQC phase, exhibiting identical features and q ratios of the reported DQC phase (with typical diffraction peaks of 00002, 12100, 10102, and 12101 in Figure 2e).^[19d, 22a] From the BF TEM images along the [00001] direction (Figures 2m and 2n after Fourier filtering), representative mixed tiling patterns including 3².4.3.4, 3³.4², and 3⁶ can be identified, further supporting the formation of an aperiodic DQC phase. Although lacking long-range translational order in twodimensional (2D) plane, this morphology contains 12-fold rotational symmetry as demonstrated by the FFT pattern (Figure 2m, inset). The DQC phase was able to maintain after thermal annealing for prolonged time (3 days at 230 °C, Figure S9b). Annealing at higher temperature led to the disordered melts state (12 hours at 235 °C, Figure S9c). Finally, PBI-C6-6BP with the longest linkage forms a BCC phase after thermal annealing at 230 °C, as indicated by the q ratios of 1: $\sqrt{2}$: $\sqrt{3}$ in the SAXS pattern (a = 6.2 nm, Figure 2c) and the BF images with the FFT diffraction pattern (Figures 2i and 2j after Fourier filtering). No phase transition phenomenon has been observed after thermal annealing in a wide range of temperatures (Figure S9d).

Thermodynamic analysis of self-assembly behavior. To better illustrate the rich variety of spherical packing phases formed by our POSS-based PBIs, a simplified description of this selfassembly process is shown in Figure 3. The π - π stacking interaction between the PBI cores enables the segregation between the inner aromatic regions and the peripheric BPOSS cages. Without those BPOSS cages at the periphery, the PBI chromophores would stack to form a normal columnar structure. However, the significant steric hindrance of those BPOSS cages at the periphery breaks down the column and each broken fragment that contains a few PBIs forms a supramolecular spherical motif, in which the perylene cores are face-to-face π stacked together with rotational displacement (See additional discussion in the SI). The self-assembled supramolecular spheres sequentially pack into different superlattices. The thermodynamic principle governing the structure formation of selfassembled soft spheres is in generally dictated by maximizing entropy and minimizing surface area. From an energy perspective, the self-assembled soft spheres tend to keep their spherical shape thus minimizing the surface area. On the other hand, when packed to form an ordered crystalline phase, the supramolecular spherical motifs must deform their shapes to polyhedra, corresponding to the Winger-Seitz Cells or Voronoi Cells, so that the system would maintain a uniform space filling.^[27] The competition of these two opposing trends leads to the formation of complex spherical packing phases. Due to the bulky and rigid nature of those BPOSS cages, it is reasonable that the deformability of supramolecular spheres in our POSS-based PBIs system is mainly coordinated by the flexible linkages in those molecules. Therefore, the occurrence of different spherical packing phases could be regulated by varying the length of the linkage.

Deforming a spherical domain would break its spherical symmetry. The extent of spherical symmetry breaking of a deformed supramolecular sphere could be quantified by using the isoperimetric quotient ($IQ = 36\pi V^2/S^3$), where V and S represent the volume and surface area of deformed spheres, based on Voronoi cells).^[17b, 27c] For the superlattice consisting of more than one type of Voronoi cells, the average value of $IQ(\overline{IQ})$ of all Voronoi cells is used to quantify the average sphericity. The IQ of a perfect sphere is 1, whereas IQ < 1 for non-spherical domains. As reported in the literature, the \overline{IQ} values of an A15 phase, a σ phase, and a BCC phase are 0.7618, 0.7624, and 0.7534, respectively, and the sphericity of a DQC phase is expected to be similar to the σ phase.^[22e] The complex spherical packing phases, *i.e.* A15 phase, σ phase, and DQC phase, have a larger \overline{IQ} , thus they are less deformed away from sphericity than the domains in the BCC phase. When the spherical domains are with a higher deformation energy, the spherical motifs with higher \overline{IQ} , such as those in both A15 and σ phases, would be favored. On the other hand, when the spherical domains are easily deformable, the

RESEARCH ARTICLE



Figure 3. Schematic illustration of the hierarchical self-assembly mechanism of the POSS-based PBIs. The central red blocks represent perylene cores, the gray shell of the supramolecular sphere represent amorphous BPOSS cages.

BCC phase is favored because it could accommodate more deformed spherical motifs and realized more uniform space filling. For PBI-C1-6BP and PBI-C3-6BP, they have short and relatively rigid linkages, resulting in less deformed self-assembled supramolecular spheres. Therefore, the A15 phase and the σ phase would be favored for these samples. However, for PBI-C4-6BP and PBI-C5-6BP with longer linkage lengths, the relatively more flexible linkages induce higher degree of deformability in their self-assembled supramolecular spheres. Thus the BCC phase would become thermodynamically stable at lower temperature because it could accommodate more gauche conformation and better packing for the flexible linkages.^[28]. When the temperature is increased for **PBI-C₄-6BP**, the σ phase overtakes BCC phase and becomes stable at higher temperature. It's worthy to note that this phase transition sequence is inverse to that observed or predicted in the other soft matter systems including block copolymers and dendrimers,^[14b, 17b] where the BCC phase is more stable at higher temperature. In the diblock copolymer system, maximizing conformational entropy (minimizing the stretching energy) of soft polymer chains dominates over reducing interfacial tension during heating, leading to the phase transition from a σ phase to a BCC phase.^[29] However, in the POSS-based PBIs system, the effect of conformation entropy is relatively weak. Instead, we speculate that the orientational entropy (S_{or}) of the whole molecule would play a significant role in their self-assembly process. At lower temperature, the BCC phase is preferred due to better packing of flexible and deformable linkages. In addition, each spherical motif in the BCC phase contains more molecules than in the σ phase (Table 1). In other words, the BCC phase exhibits higher degree of π - π stacking than the σ phase, indicating a smaller enthalpy (H_{Di}) in the BCC phase. At high temperature, the degree of π - π stacking would become less due to thermal fluctuations. At the same time, the orientational entropy of the whole molecule becomes significant so that each molecule would tend to occupy larger area on the surface of the domain. This could be achieved by a more regular arrangement of the molecules, which in turn would drive the spherical motifs constructed by PBI-C4-6BP molecules to be even less deformed. Therefore, a transition from the BCC phase to the σ phase would occur as the temperature is increased. Similarly, for **PBI-C**₅-**6BP**, with the redistribution ability of the POSS-based PBIs among the spherical motifs, the BCC phase transfer to the DQC phase with higher sphericity at higher temperature. For **PBI-C**₆-**6BP** with the longest linkage length, the high degree of deformability is largely kept, and the BCC phase structure is retained in the entire temperature range studied.

Different self-assembly behaviors with subtle variations in chemical structures of linkages. To further elucidate the effects of linkage structure on the supramolecular self-assembly, we specifically designed and examined a set of constitutional isomers: PBI-C5-6BP, ISO1-PBI-C5-6BP, and ISO2-PBI-C5-6BP (Figure 4a). Their linkages are divided into two parts: the alkyl amide between the POSS cage and the phenyl group and the methylene between the phenyl group and the triazole group. With identical chemical composition and extended linkage chain length, different self-assembly behaviors are observed among these three isomers due to the subtle differences in their linkage structures. As described above, PBI-C5-6BP exhibits a phase transition from a BCC phase at low temperature to a DQC phase at high temperature. However, ISO1-PBI-C5-6BP only forms a BCC phase after thermal annealing in the entire temperature range studied (Figure 4b), while ISO2-PBI-C5-6BP shows a phase transition from a BCC phase to a σ phase at 230 °C (Figure 4c). A SAXS pattern with multiple sharp diffraction peaks illustrates the formation of the σ phase (a = b = 18.3 nm, c = 9.63 nm) in ISO2-PBI-C5-6BP at 230 °C, in contrast to the DQC phase observed in PBI-C5-6BP and the BCC phase in ISO1-PBI-C5-6BP. These results suggest that self-assembled supramolecular structures of POSS-based PBIs are highly sensitive to the chemical structures of the linkage. Detailed supramolecular structure analysis of all samples is summarized in Table 1.

We speculate that the length of alkyl amide linkage connecting the POSS cage and the phenyl group plays a major role in increasing the flexibility of the PBIs compared with the methylene

RESEARCH ARTICLE



Figure 4. Linkage chemical structures of the isomers are magnified in the blue dashed box (a). For the naming of these three isomers, prefix **ISO** refers to isomer. **ISO₁-PBI-C₅-6BP** shows BCC phase in a wide range of temperature in the SAXS pattern (b). **ISO₂-PBI-C₅-6BP** forms a BCC phase in low temperature and transfers to a σ phase at high temperature in the SAXS pattern (c). Solid-state ¹H NMR spectra of the annealed isomers under the 700 MHz magnetic field at a MAS rate of 100 kHz. The samples for Solid-state ¹H NMR were annealed at 230 °C for 12 h.

linkage connecting the phenyl group and the triazole group, considering the hydrogen bonding between amide groups. The increased flexibility of linkage would help reduce steric hindrance of the BPOSS cages and improve the extent of molecular aggregation. The extent of molecular aggregation could be qualitatively estimated by ¹H solid-state NMR spectroscopy. The 1D proton NMR spectra at 100 kHz magic angle spinning (MAS) for the three annealed samples (annealing at 230 °C for 12 h) are shown in Figure 4d. The chemical shifts of aromatic region between 7 and 10 ppm vary among these three samples. Such broad signals are resulted from the strong π - π stacking interaction between PBIs. In fact, stronger molecular aggregation will lead to stronger ¹H-¹H dipolar couplings as well as the increase of anisotropic bulk magnetic susceptibility (ABMS), both of which will lead to the broadening of aromatic proton peaks.^[30] Therefore, based on the comparison of the full width at half maximum (FWHM) of the aromatic peaks (around 1.8 kHz, 1.3 kHz and 1.2 kHz for ISO1-PBI-C5-6BP, PBI-C5-6BP, and ISO2-PBI-C5-6BP, respectively), it could be concluded that the highest extent of molecular aggregation occurs in ISO1-PBI-C5-6BP sample, and the PBI-C5-6BP has slightly higher extent of molecular aggregation than that of ISO₂-PBI-C₅-6BP. Therefore, we could deduce that ISO1-PBI-C5-6BP possesses the most flexible linkage among the isomers and thus the largest

deformability while ISO₂-PBI-C₅-6BP's linkage is relatively most rigid. The differences in the flexibility of linkages among isomers is in line with their different phase structures at high temperature, ranging from σ phase in ISO₂-PBI-C₅-6BP, DQC phase in PBI-C₅-6BP to BCC phase in ISO₁-PBI-C₅-6BP.

 Table 1. Summary of supramolecular structures of the POSS-based PBIs.

| Molecules | phase | a (nm) ^[a] | M wt ^[b] | d/ sphere [[] c] | µ ^[d] |
|-------------------------|----------|--------------------------|----------------------------|-------------------------------------|------------------|
| PBI-C₀-6BP | Disorder | - | 6474.4 | - | - |
| PBI-C ₁ -6BP | A15 | 7.8 | 6558.6 | 4.84 | 6.3 |
| PBI-C ₃ -6BP | σ | 16.85 ² ×8.87 | 6985.1 | 5.43 | 8.4 |
| PBI-C₄-6BP | BCC | 5.89 | 7000 0 | 5.8 | 10.1 (10) |
| | σ | 17.56 ² ×9.24 | 7069.2 | 5.66 | 9.4 |
| PBI-C₅-6BP | BCC | 6.08 | 7153.4 | 5.99 | 11 |
| | DQC | - | | - | - |
| ISO₁-PBI-C₅- 6BP | BCC | 6.23 | 7153.4 | 6.13 | 11.9 (12) |
| ISO₂-PBI-C₅- | BCC | 6.04 | 7153.4 | 5.95 | 10.8 (11) |
| 6BP | σ | 18.3 ² ×9.63 | | 5.9 | 10.5 |
| | | | | | |

RESEARCH ARTICLE

| PBI-C6-6BP | BCC | 6.2 | 7237.5 | 6.1 | 11.6 (12) | [2] |
|------------|-----|-----|--------|-----|-----------|-----|
| | | | | | | |

[a] Lattice parameters derived from corresponding SAXS results. [b] Average molecular weights of POSS-based PBIs. [c] Diameters of supramolecular spheres. [d] Number of molecules in each supramolecular sphere based on experimental measured density. The number of molecules in each supramolecular sphere in the BCC phase should be an integer, which is indicated in the parentheses.

Conclusion

In summary, we have designed and synthesized a series of precisely defined POSS-based PBIs by tuning the linkage structures. The incorporation of the peripheric BPOSS in our molecular design successfully achieved the unconventional spherical assemblies in PBIs instead of columnar assemblies due to significantly increased steric hindrance at the periphery. Furthermore, the deformability of the supramolecular spheres can be precisely regulated by carefully tuning linkage structures (linkage flexibility), resulting in diverse unconventional spherical packing phases in PBIs including BCC phase, A15 phase, σ phase, and DQC phase. By the introduction of similar bulky functional groups at the periphery, this strategy may also be employed for the achievement of unconventional spherical assemblies in other related discotic or rod-like molecules. The discovery of a series of spherical packing phases in PBIs may offer opportunities for understanding their packing-function relationships, expanding the scope of PBI-based materials.

Acknowledgements

This work was supported by National Science Foundation (DMR-1408872 to S.Z.D.C.) and the Program for Guangdong Introducing Innovative and Entrepreneurial Teams (no. 2016ZT06C322). Mingjun Huang thanks the support from the Fundamental Research Funds for the Central Universities (no. 2019JQ05). The research of A.-C.S. is supported by the Natural Science and Research Council (NSERC) of Canada. We thank technical support from Shanghai Synchrotron Radiation Facility (SSRF) and mass spectrometry characterization by Molecular Scale Lab (X. Li).

Keywords: supramolecular chemistry • nanostructures • perylene bisimides • discotic molecules • Frank-Kasper phases •quasicrystalline phase

Reference

 (a)F. Würthner, C. R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* 2016, *116*, 962-1052; (b)Z. Guo, X. Zhang, Y. Wang, Z. Li, *Langmuir* 2018, *35*, 342-358; (c)C. Huang, S. Barlow, S. R. Marder, *J. Org. Chem* 2011, *76*, 2386-2407.

- (a)A. Nowak-Król, K. Shoyama, M. Stolte, F. Würthner, *Chem. Commun.* 2018, *54*, 13763-13772; (b)R. Gupta,
 A. Sudhakar, *Langmuir* 2018, 2455-2479; (c)M.
 Gsänger, D. Bialas, L. Huang, M. Stolte, F. Würthner, *Adv. Mater.* 2016, *28*, 3615-3645; (d)X. Zhan, A.
 Facchetti, S. Barlow, T. J. Marks, M. A. Ratner, M. R.
 Wasielewski, S. R. Marder, *Adv. Mater.* 2011, *23*, 268-284; (e)J. E. Anthony, A. Facchetti, M. Heeney, S. R.
 Marder, X. Zhan, *Adv. Mater.* 2010, *22*, 3876-3892; (f)H.
 Bisoyi, Q. Li, *Prog. Mater Sci.* 2019, *104*, 1-52.
- (a)P. E. Hartnett, A. Timalsina, R. H. S. S. Matte, N. Zhou, X. Guo, W. Zhao, A. Facchetti, R. P. H. Chang, M. C. Hersam, M. R. Wasielewski, T. J. Marks, *J. Am. Chem. Soc.* 2014, 136, 16345-16356; (b)J. E. Anthony, *Chem. Mater.* 2011, 23, 583-590; (c)Y. Huo, H.-L. Zhang, X. Zhan, *ACS Energy Letters* 2019, 4, 1241-1250; (d)G. J. Hedley, A. Ruseckas, I. D. W. Samuel, *Chem. Rev.* 2016, *117*, 796-837; (e)C. Li, H. Wonneberger, *Adv. Mater.* 2012, 24, 613-636.

[3]

[4]

[5]

[6]

[7]

- (a)J. Xia, E. Busby, S. N. Sanders, C. Tung, A. Cacciuto,
 M. Y. Sfeir, L. M. Campos, ACS Nano 2017, 11, 4593-4598;
 (b)M. J. Ahrens, M. J. Fuller, M. R. Wasielewski, *Chem. Mater.* 2003, 15, 2684-2686;
 (c)C. Xue, O. Birel,
 M. Gao, S. Zhang, L. Dai, A. Urbas, Q. Li, J. Phys. Chem
 2012, 116, 10396-10404.
- (a)H. M. Ardoña, J. D. Tovar, *Bioconjugate Chem.* 2015, 26, 2290-2302; (b)K. Liu, Z. Xu, M. Yin, *Prog. Polym. Sci.* 2015, 46, 25-54; (c)S. Yang, X. Shi, S. Park, S. Doganay, T. Ha, S. C. Zimmerman, *J. Am. Chem. Soc.* 2011, 133, 9964-9967; (d)D. Görl, F. Würthner, *Angew. Chem. Int. Ed.* 2016, 55, 12094-12098; (e)D. Görl, X. Zhang, F. Würthner, *Angew. Chem. Int. Ed.* 2012, 51, 6328-6348.
- (a)G. M. Whitesides, B. Grzybowski, *Science* 2002, *295*, 2418-2421;
 (b)T. Aida, E. W. Meijer, S. I. Stupp, *Science* 2012, *335*, 813-817;
 (c)W.-B. Zhang, X. Yu, C.-L. Wang, H.-J. Sun, I. F. Hsieh, Y. Li, X.-H. Dong, K. Yue, R. Horn, S. Z. D. Cheng, *Macromolecules* 2014, *47*, 1221-1239;
 (d)W.-B. Zhang, S. Z. D. Cheng, *Chin. J. Polym. Sci.* 2015, *33*, 797-814.
- (a)P. Spenst, R. M. Young, B. T. Phelan, M. Keller, J. Dostál, T. Brixner, M. R. Wasielewski, F. Würthner, J. Am. Chem. Soc. 2017, 139, 2014-2021; (b)T. E. Kaiser, V. Stepanenko, F. Würthner, J. Am. Chem. Soc. 2009, 131, 6719-6732; (c)S. Yagai, T. Seki, T. Karatsu, A. Kitamura, F. Würthner, Angew. Chem. Int. Ed. 2008, 47, 3367-3371; (d)R. F. Fink, J. Seibt, V. Engel, M. Renz, M. Kaupp, S. Lochbrunner, H.-M. Zhao, J. Pfister, F. Würthner, B. Engels, J. Am. Chem. Soc. 2008, 130, 12858-12859.
- [8] (a)W. Wagner, M. Wehner, V. Stepanenko, S. Ogi, F. Würthner, *Angew. Chem. Int. Ed.* 2017, 56, 16008-16012; (b)C. Jarrett Wilkins, X. He, H. E. Symons, R. L. Harniman, C. F. J. Faul, I. Manners, *Chem. Eur. J* 2018, 24, 15556-15565; (c)S. Ogi, V. Stepanenko, K. Sugiyasu, M. Takeuchi, F. Würthner, *J. Am. Chem. Soc.* 2015, 137, 3300-3307; (d)D. Görl, X. Zhang, V. Stepanenko, F. Würthner, *Nat. Commun.* 2015, *6*, 7009.
 [9] (a)O. Simalou, X. Zhao, R. Lu, P. Xue, X. Yang, X.
 - (a)O. Simalou, X. Zhao, R. Lu, P. Xue, X. Yang, X. Zhang, *Langmuir* 2009, *25*, 11255-11260; (b)E. Krieg, E. Shirman, H. Weissman, E. Shimoni, S. G. Wolf, I. Pinkas, B. Rybtchinski, *J. Am. Chem. Soc.* 2009, *131*, 14365-14373; (c)K. Sugiyasu, N. Fujita, S. Shinkai, *Angew. Chem. Int. Ed.* 2004, *116*, 1249-1253.
- [10] (a)T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, *Chem. Rev.* 2016,

116, 1139-1241; (b)F. Würthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.* **2001**, *7*, 2245-2253; (c)F. Würthner, Z. Chen, V. Dehm, V. Stepanenko, *Chem. Commun.* **2006**, *0*, 1188-1190; (d)Z. Chen, U. Baumeister, C. Tschierske, F. Würthner, *Chem. Eur. J.* **2007**, *13*, 450-465; (e)Z. Chen, V. Stepanenko, V. Dehm, P. Prins, L. D. A. Siebbeles, J. Seibt, P. Marquetand, V. Engel, F. Würthner, *Chem. Eur. J.* **2007**, *13*, 436-449.

- [11] (a)M.-S. Ho, B. E. Partridge, H.-J. Sun, D. Sahoo, P. Leowanawat, M. Peterca, R. Graf, H. W. Spiess, X. Zeng, G. Ungar, P. A. Heiney, C.-S. Hsu, V. Percec, ACS Comb. Sci. 2016, 18, 723-739; (b)C. Roche, H.-J. Sun, P. Leowanawat, F. Araoka, B. E. Partridge, M. Peterca, D. A. Wilson, M. E. Prendergast, P. A. Heiney, R. Graf, H. W. Spiess, X. Zeng, G. Ungar, V. Percec, Nat. Chem. 2016, 8, 80-89; (c)B. E. Partridge, P. Leowanawat, E. Aqad, M. R. Imam, H.-J. Sun, M. Peterca, P. A. Heiney, R. Graf, H. W. Spiess, X. Zeng, G. Ungar, V. Percec, J. Am. Chem. Soc. 2015, 137, 5210-5224; (d)V. Percec, H.-J. Sun, P. Leowanawat, M. Peterca, R. Graf, H. W. Spiess, X. Zeng, G. Ungar, P. A. Heiney, J. Am. Chem. Soc. 2013, 135, 4129-4148; (e)V. Percec, M. Peterca, T. Tadjiev, X. Zeng, G. Ungar, P. Leowanawat, E. Aqad, M. R. Imam, B. M. Rosen, U. Akbey, R. Graf, S. Sekharan, D. Sebastiani, H. W. Spiess, P. A. Heiney, S. D. Hudson, J. Am. Chem. Soc. 2011, 133, 12197-12219; (f)V. Percec, S. D. Hudson, M. Peterca, P. Leowanawat, E. Agad, R. Graf, H. W. Spiess, X. Zeng, G. Ungar, P. A. Heiney, J. Am. Chem. Soc. 2011, 133, 18479-18494.
- [12] (a)V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, P. A. Heiney, J. Am. Chem. Soc. 2009, 131, 1294-1304;
 (b)V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, R. Graf, H. W. Spiess, V. S. Balagurusamy, P. A. Heiney, J. Am. Chem. Soc. 2009, 131, 7662-7677; (c)M. Peterca, M. R. Imam, S. D. Hudson, B. E. Partridge, D. Sahoo, P. A. Heiney, M. L. Klein, V. Percec, ACS Nano 2016, 10, 10480-10488.
- [13] (a)D. Sahoo, M. Peterca, E. Aqad, B. E. Partridge, P. A. Heiney, R. Graf, H. W. Spiess, X. Zeng, V. Percec, J. Am. Chem. Soc. 2016; (b)D. Sahoo, M. Peterca, E. Aqad, B. E. Partridge, P. A. Heiney, R. Graf, H. W. Spiess, X. Zeng, V. Percec, ACS Nano 2016, 11, 983-991; (c)D. Sahoo, M. Peterca, E. Aqad, B. E. Partridge, M. L. Klein, V. Percec, Polym. Chem. 2018, 9, 2370-2381.
- [14] (a)K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, Angew. Chem. Int. Ed. 1997, 36, 2087-2089; (b)G. Ungar, Y. Liu, X. Zeng, V. Percec, W.-D. Cho, Science 2003, 299, 1208-1211; (c)G. Ungar, X. Zeng, Soft Matter 2005, 1, 95-106.
- [15] (a)R. Vargas, P. Mariani, A. Gulik, V. Luzzati, *J. Mol. Biol.* **1992**, 225, 137-145; (b)Y. Sakamoto, M. Kaneda, O. Terasaki, D. Zhao, J. Kim, G. Stucky, H. Shin, R. Ryoo, *Nature* **2000**, 408, 449; (c)S. Che, A. E. Garcia-Bennett, T. Yokoi, K. Sakamoto, H. Kunieda, O. Terasaki, T. Tatsumi, *Nat. Mater.* **2003**, *2*, 801-805; (d)S. A. Kim, K.-J. Jeong, A. Yethiraj, M. K. Mahanthappa, *Proc. Natl. Acad. Sci. U.S.A.* **2017**, *114*, 4072-4077.
- [16] (a)B. M. Rosen, C. J. Wilson, D. A. Wilson, M. Peterca, M. R. Imam, V. Percec, *Chem. Rev.* 2009, *10*9, 6275-6540; (b)H.-J. Sun, S. Zhang, V. Percec, *Chem. Soc. Rev.* 2015, *44*; (c)V. Percec, M. R. Imam, M. Peterca, D. A. Wilson, R. Graf, H. W. Spiess, V. S. K. Balagurusamy, P. A. Heiney, *J. Am. Chem. Soc.* 2009, *131*, 7662-7677; (d)V. S. K. Balagurusamy, G. Ungar, V. Percec, G.

Johansson, *J. Am. Chem. Soc.* **1997**, *11*9, 1539-1555; (e)S. D. Hudson, H. T. Jung, V. Percec, W. D. Cho, G. Johansson, G. Ungar, V. S. K. Balagurusamy, *Science* **1997**, *278*, 449-452.

- (a)S. Lee, M. J. Bluemle, F. S. Bates, *Science* 2010, 330, 349-353; (b)S. Lee, C. Leighton, F. S. Bates, *Proc. Natl. Acad. Sci. U.S.A.* 2014, *111*, 17723-17731; (c)K. Kim, M. W. Schulze, A. Arora, R. M. Lewis, M. A. Hillmyer, K. D. Dorfman, F. S. Bates, *Science* 2017, *356*, 520-523.
- [18] (a)E. V. Shevchenko, D. V. Talapin, N. A. Kotov, S. O'Brien, C. B. Murray, *Nature* **2006**, *439*, 55; (b)R. J. Macfarlane, B. Lee, M. R. Jones, N. Harris, G. C. Schatz, C. A. Mirkin, *Science* **2011**, *334*, 204-208.
- (a)R. Zhang, X. Feng, R. Zhang, W. Shan, Z. Su, J. Mao, C. Wesdemiotis, J. Huang, X. Y. Yan, T. Liu, T. Li, M. Huang, Z. Lin, A. C. Shi, S. Z. D. Cheng, *Angew. Chem.* [19] Int. Ed. 2019, 58, 11879-11885; (b)X. Feng, G. Liu, D. Guo, K. Lang, R. Zhang, J. Huang, Z. Su, Y. Li, M. Huang, T. Li, S. Z. D. Cheng, ACS Macro Lett. 2019, 875-881; (c)X. Feng, R. Zhang, Y. Li, Y.-I. Hong, D. Guo, K. Lang, K.-Y. Wu, M. Huang, J. Mao, C. Wesdemiotis, Y. Nishiyama, W. Zhang, W. Zhang, T. Miyoshi, T. Li, S. Z. D. Cheng, ACS Cent. Sci. 2017, 3, 860-867; (d)K. Yue, M. Huang, R. L. Marson, J. He, J. Huang, Z. Zhou, J. Wang, C. Liu, X. Yan, K. Wu, Z. Guo, H. Liu, W. Zhang, P. Ni, C. Wesdemiotis, W.-B. Zhang, S. C. Glotzer, S. Z. D. Cheng, Proc. Natl. Acad. Sci. U.S.A. 2016, 113, 14195-14200; (e)Z. Su, C.-H. Hsu, Z. Gong, X. Feng, J. Huang, R. Zhang, Y. Wang, J. Mao, C. Wesdemiotis, T. Li, S. Seifert, W. Zhang, T. Aida, M. Huang, S. Z. D. Cheng, Nat. Chem. 2019, 11, 899-905; (f)W. Zhang, Y. Liu, J. Huang, T. Liu, W. Xu, S. Z. D. Cheng, X.-H. Dong, Soft Matter 2019, 15, 7108-7116.
- [20] (a)K. K. Lachmayr, C. M. Wentz, L. R. Sita, Angew. Chem. Int. Ed. 2020, 1521-1526; (b)K. K. K. Lachmayr, L. R. Sita, Angew. Chem. Int. Ed. 2020, 59, 3563-3567.
 [21] E. C. Frank, L. S. Kasper, Ang. Crystallographics 1959.
- [21] F. C. Frank, J. S. Kasper, *Acta Crystallographica* **1958**, *11*, 184-190.
- [22] (a)X. Zeng, G. Ungar, Y. Liu, V. Percec, A. E. Dulcey, J. K. Hobbs, *Nature* 2004, 428, 157; (b)G. Ungar, V. Percec, X. Zeng, P. Leowanawat, *Isr. J. Chem.* 2011, 1206-1215; (c)T. Dotera, *Isr. J. Chem.* 2011, 1197-1205; (d)J. Zhang, F. S. Bates, *J. Am. Chem. Soc.* 2012, 134, 7636-7639; (e)T. M. Gillard, S. Lee, F. S. Bates, *Proc. Natl. Acad. Sci. U.S.A.* 2016, 113, 5167-5172.
- [23] (a)A. S. Keys, S. C. Glotzer, *Phys. Rev. Lett.* 2007, 99, 235503; (b)C. R. lacovella, A. S. Keys, S. C. Glotzer, *Proc. Natl. Acad. Sci. U.S.A.* 2011, 108, 20935-20940.
- [24] (a)S. C. Glotzer, *Science* 2004, 306, 419-420; (b)R. W. Date, D. W. Bruce, *J. Am. Chem. Soc.* 2003, 125, 9012-9013.
- [25] (a)M. Huang, C.-H. Hsu, J. Wang, S. Mei, X. Dong, Y. Li, M. Li, H. Liu, W. Zhang, T. Aida, W.-B. Zhang, K. Yue, S. Z. D. Cheng, *Science* 2015, *348*, 424-428; (b)H. Liu, C.-H. Hsu, Z. Lin, W. Shan, J. Wang, J. Jiang, M. Huang, B. Lotz, X. Yu, W.-B. Zhang, K. Yue, S. Z. D. Cheng, *J. Am. Chem. Soc.* 2014, *136*, 10691-10699.
- [26] F. C. Frank, J. S. Kasper, *Acta Crystallographica* **1959**, *12*, 483-499.
- [27] (a)P. Ziherl, R. D. Kamien, J. Phys. Chem. B 2001, 105, 10147-10158; (b)P. Ziherl, R. D. Kamien, Phys. Rev. Lett. 2000, 85, 3528-3531; (c)W. Li, C. Duan, A.-C. Shi, ACS Macro Lett. 2017, 1257-1262.
- [28] Y. Li, S.-T. Lin, W. A. Goddard, *J. Am. Chem. Soc.* **2004**, *126*, 1872-1885.

RESEARCH ARTICLE

[29] (a)E. L. Thomas, D. J. Kinning, D. B. Alward, C. S. Henkee, *Macromolecules* 1987, 20, 2934-2939; (b)G. M. Grason, Physics Reports 2006, 433, 1-64. (a)R. Zhang, K. H. Mroue, A. Ramamoorthy, Acc. Chem. Res. 2017, 1105-1113; (b)Y. Nishiyama, Solid State [30] Nucl. Magn. Reson. 2016, 78, 24-36.

RESEARCH ARTICLE

RESEARCH ARTICLE

The unconventional spherical assembly of discotic PBIs were successfully achieved, instead of common columnar assembly, by the incorporation of bulky units at the periphery. The peripheric steric hindrance can be tuned by varying the linkage structures, resulting in diverse spherical supramolecular structures in PBIs.



Jiahao Huang, Zebin Su, Mingjun Huang, Rongchun Zhang, Jian Wang, Xueyan Feng, Rui Zhang, Ruimeng Zhang, Wenpeng Shan, Xiao-Yun Yan, Qing-Yun Guo, Tong Liu, Yuchu Liu, Yunpeng Cui, Xiaopeng Li, An-Chang Shi*, and Stephen Z. D. Cheng*

Page No. – Page No.

Spherical Supramolecular Structures Constructed *via* Chemically Symmetric Perylene Bisimides: Beyond Columnar Assembly