Discrete Block Copolymers with Diverse Architectures: Resolving Complex Spherical Phases with One Monomer Resolution

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ABSTRACT: This work describes the first rigorous example of a single-component block copolymer system forming unconventional spherical phases. A library of discrete block polymers with uniform chain length and diverse architectures were modularly prepared through a combination of a step-growth approach and highly efficient coupling reactions. The precise chemical structure eliminates all the molecular defects associated with molar weight, dispersity, and compositional ratio. Complex spherical phases, including the Frank−Kasper phase (A15 and σ phase) and quasicrystalline phase, were experimentally captured by meticulously tuning the composition and architectures. A phase portrait with unprecedented accuracy was mapped out (up to one monomer resolution), unraveling intriguing details of phase behaviors that have long been compromised by inherent molecular weight distribution. This study serves as a delicate model system to bridge the existing gaps between experimental observations and theoretical assessments and to provide insights into the formation and evolution of the unconventional spherical phases in soft matter systems.

INTRODUCTION

Block copolymers with chemically distinct components continue to fascinate the scientific community for their capability to spontaneously form exquisitely ordered structures at the nanometer scale, offering a broad and expanding range of practical applications. The recent discovery of intriguing unconventional spherical packing lattices, e.g., Frank−Kasper phases and quasicrystalline phases, in block copolymer system disrupts the long-standing principles of block copolymer phase behaviors, representing significant advances in fundamental polymer science and opening up numerous possibilities for designing materials with unique properties. Despite interesting and unusual structures, detailed mechanisms of the formation and evolution of these complex lattices have yet to be fully established. Two existing obstacles must be addressed to gain deeper insights into underlying principles: (i) their exceptionally rare occurrence and (ii) the multicomponent nature associated with synthetic polymers due to inherent chain length heterogeneity.

The Frank−Kasper phases (e.g., A15 and σ phase) are a family of low symmetry spherical structures with large unit cells consisting of multiple nonequivalent lattice sites, observed originally in metals and alloys, and recently in soft matter systems. Different from common periodic packing of identical spherical motifs (i.e., body/face centered cubic), the A15 phase is built up by a cubic lattice containing eight distorted spherical supramolecular motifs partitioned into two dissimilar groups with different sizes and shapes, while the σ phase is featured by a more complicated tetragonal unit cell with 30 spheres adopting five different coordination environments (see Scheme 1, indicated by the different colored particles). On the other hand, the dodecagonal quasicrystalline

Scheme 1. Oblique View (Upper) and Top View (Lower) of Typical Spherical Packing Lattices

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phase (DQC) is generally recognized as an aperiodic structure that is closely related to the σ phase with 12-fold rotational symmetry (Scheme 1).

These low-symmetry spherical phases, however, are only sporadically identified. To date, there are merely a limited number of examples reported in the pure block copolymer system. The lack of sufficient and diversified case studies makes it very challenging to reach general and comprehensive understandings. Rational molecular design principles and high-resolution phase diagrams are highly desired to provide predictable access to these complex lattices.

It has been recently recognized that the formation of the unconventional phases is surprisingly sensitive to the chain length heterogeneity, due to delicate molecular packing schemes. Synthetic polymer is virtually a mixture of macromolecules with the same repeat unit and consecutive degree of polymerization (known as molecular weight distribution, and described by dispersity, D). Even minor fluctuations in molecular weight distribution can significantly shift the constitution of the sample, which may result in substantial differences in their structure and properties. Take a polymer with $M_n = 5000$ Da as an example. Only 17% of the chains have an exact molecular weight of 5000 Da when $D = 1.01$ (assuming a Gaussian distribution); this content further drops to 5% at $D = 1.10$. Therefore, even a generally considered “narrow-distributed” polymer will have an appreciable distribution of chain length. While most of the theoretical studies on block copolymers describe the packing of perfect and uniform chains, experimental explorations always employ materials with a certain distribution on their molecular weights. While the batch-to-batch variation would be sufficient to result in completely different assemblies. Modulation of dispersity through deconstruction (i.e., fractionation) or reconstruction (i.e., blending) strategies indeed generates dramatically distinct structures. The inherent chain length heterogeneity of synthetic polymers thus blurs the fundamental concepts, generating a substantial discrepancy between experiment and theories.

Discrete polymers with precise chemical structures and uniform chain lengths (i.e., $D = 1$) are ideal candidates to bridge the existing gaps. Recent advances in synthetic techniques enable the preparation of these exquisite macromolecules, which exhibit unique phase behaviors as compared to their dispersed analogues, revealing profound sensitivity of nanostructures to chain length heterogeneity. There are, however, only a very limited number of examples, most of which focus on simple linear diblock copolymers with symmetric composition and could only cover a small portion of the overall phase diagram. The synthetic challenges to reach a higher degree of polymerization (N) through existing stepwise approaches bring in several severe barriers for unifying experimental observations with theoretical advances, including insufficient immiscibility between two blocks (generally characterized by $\chi N$, where $\chi$ is the Flory–Huggins interaction parameter) and limited access to phase structures with large interfacial curvatures, especially complex spherical phases.

Introducing variations in molecular architecture offers unparalleled opportunities for expanding the spectrum of accessible nanostructures. As a close approximation of linear–linear diblock copolymer (AB), linear-branched block polymers (AB$_n$) with multiple short chains (B block) attached onto the same junction point could circumvent the synthetic difficulties for reaching exceedingly asymmetric composition, leading to the formation of diverse assembled structures. Meanwhile, it has been proposed that large conformational asymmetry in linear-branched block copolymers could stabilize the Frank–Kasper and quasicrystalline phases. In this study, we extend and expand the scope of the precision macromolecules by modularly constructing a library of discrete block copolymers with diverse architectures based on discrete oligo dimethylsiloxane (oDMS) and oligo lactic acid (oLA). Strong chemical incompatibility between oDMS and oLA blocks leads to the formation of a rich collection of ordered nanostructures at relatively low $N$. Classical phases, as well as unconventional spherical lattices (including A15, σ, and DQC), are identified through judicious regulation of the composition and architecture. The phase portrait is quantitatively depicted with unprecedented accuracy (up to one monomer resolution). The precise chemical structure eliminates all the inherent molecular “defects” associated with molar weight, dispersity, branching number, and compositional ratio, providing the first rigorous example of a single-component block copolymer system forming unconventional spherical phases. This study would serve as a delicate model system to correlate the experimental observations with the theoretical assessments and to provide insight into the formation of complex spherical phases in soft matter systems.

**RESULTS AND DISCUSSION**

Discrete amphiphilic block copolymers (labeled as $xS_L_{m/n}$, where S and L refer to oDMS and oLA block, $n$ and $m$ are the exact degree of polymerization, respectively) with linear–linear ($x = 1$) and linear-branched ($x = 2, 4$) architectures were modularly constructed by installing discrete oDMS and oLA chains onto specifically designed molecular adaptors with corresponding reactive handles (Figure 1). A dozen of discrete

![Figure 1. Schematic illustration and chemical structure of oLA and oDMS homopolymers (left), adaptors (middle), and discrete block copolymers (right).](https://dx.doi.org/10.1021/acscentsci.0c00798)
composition and architectures were prepared. The detailed characterizations are summarized in Table 1.

Table 1. Molecular and Structural Characterization of Discrete Block Copolymers

| Sample | MW (Da) | \( f_{LA} \) | Phase | \( a' \) | \( D' \) | \( N' \) |
|--------|--------|-------------|-------|------|------|-----|
| 2S13L38 | 5173.57 | 0.49 | DG | 22.62 | 3 | 9.81 | 74 |
| 2S13L34 | 4885.49 | 0.46 | DG | 20.72 | 3 | 9.43 | 66 |
| 2S13L32 | 4741.45 | 0.45 | HEX | 10.89 | 3 | 7.98 | 58 |
| 2S13L30 | 4597.41 | 0.44 | HEX | 10.23 | 3 | 7.53 | 51 |
| 2S13L28 | 4453.37 | 0.42 | HEX | 9.43 | 3 | 6.54 | 44 |
| 2S13L26 | 4319.33 | 0.41 | HEX | 8.64 | 3 | 5.72 | 37 |
| 2S13L24 | 4185.30 | 0.40 | HEX | 7.89 | 3 | 4.92 | 31 |
| 2S13L22 | 4051.27 | 0.39 | HEX | 7.09 | 3 | 4.12 | 24 |
| 2S13L20 | 3917.24 | 0.38 | HEX | 6.36 | 3 | 3.32 | 18 |
| S17L18 | 2730.88 | 0.44 | Dis | 15.83 | 3 | 9.54 | 56 |
| S17L17 | 2614.87 | 0.43 | Dis | 15.19 | 3 | 8.87 | 49 |
| S17L16 | 2498.86 | 0.42 | Dis | 14.51 | 3 | 8.17 | 42 |
| S17L15 | 2382.85 | 0.41 | Dis | 13.83 | 3 | 7.47 | 35 |
| S17L14 | 2266.84 | 0.40 | Dis | 13.15 | 3 | 6.77 | 28 |
| S17L13 | 2150.83 | 0.39 | Dis | 12.47 | 3 | 6.07 | 21 |
| S17L12 | 2034.82 | 0.38 | Dis | 11.79 | 3 | 5.37 | 14 |
| 2S17L40 | 4387.34 | 0.65 | LAM | 8.27 | 3 | 6.72 | 44 |
| 2S17L38 | 4261.33 | 0.64 | LAM | 7.57 | 3 | 6.02 | 37 |
| 2S17L36 | 4135.32 | 0.63 | LAM | 6.88 | 3 | 5.33 | 30 |
| 2S17L34 | 4009.31 | 0.62 | LAM | 6.19 | 3 | 4.63 | 23 |
| 2S17L32 | 3883.30 | 0.61 | LAM | 5.50 | 3 | 3.94 | 16 |

Notes: a) Overall exact molecular weight (Da). b) Volume fraction of \( \sigma_{LA} \) block. c) Phase structure, determined by SAXS. d) Evolving from the initial DQC phase after annealing at room temperature for 35 days. e) Lattice dimensions (nm): periodicities of LAM, intercolumn distances of HEX, interplanar spacing along the \( z \) direction for DQC, or lattice parameters of DG, A15, and \( \sigma \) phases. f) Average diameter of the spherical motifs of A15 and \( \sigma \) phases (nm). g) Number of molecules within one spherical motif. See Supporting Information for detailed calculations.

The discrete block copolymers and related intermediates/precursors were fully characterized by nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS). Representative examples of each category of molecules (\( x = 1, 2, \) and 4) are shown in Figure 2. For each case, MALDI-ToF MS displays a single peak with molecular mass in excellent accordance with the calculated value, confirming the chemical identity and discrete feature (Figure 2d–f). The SEC elution profiles show narrow and unimodal traces (with inevitable instrumental spread due to sample diffusion; Figure 2a–c). The purity is further validated by \(^1\)H NMR. Characteristic resonances from both oDMS and oLA blocks can be clearly identified, and all the rest of the signals can be properly assigned, with the integration agreeing well with the proposed structures (Figures S4–S8). Comprehensive characterizations are shown in Figure 3 and Figure S9. All of these complementary assessments substantiate the successful preparation of the discrete block copolymers with designed molecular architectures.

Benefitting from low glass transition temperature (typically around or below 0 °C, Figure S10) and absence of chain entanglement, diverse ordered nanostructures readily developed in the bulk state with a brief thermal treatment (80 °C for 10 min, further annealed at room temperature, ca. 25 °C), which were then characterized by small-angle X-ray scattering (SAXS). Sharp and intense scatterings were recorded, providing unambiguous evidence for structure identification (Figure 4). By meticulously tuning the composition, a plethora of classical and unconventional phases can be experimentally captured (Figures S11–S13).

The linear—linear discrete block copolymers (\( n = 17 \), i.e., S17-L17; Table 1) with \( m \) between 23 and 40 (corresponding to an oLA volume fraction \( 0.65 \geq f_{\text{LA}} \geq 0.52 \)) fall into the lamellae phase (LAM) at room temperature, while no long-range ordered structure could be identified below this limit (\( m < 23 \)). For example, the SAXS profile of the compound S17-L40 (\( f_{\text{LA}} = 0.65 \)) with the longest oLA block in this series shows an intense principal scattering peak at 4\( ^\circ = 0.76 \text{ nm}^{-1} \), together with high order peaks with equal \( q \) interval, corresponding to an LAM structure consisting of alternating oDMS and oLA layers with a periodicity (\( a \)) of 8.27 nm (Figure S11). Similar patterns were repeatedly observed in this series of discrete block copolymers due to relatively symmetric composition, with a continuous decrease of \( a \) as oLA chain shortens (Table 1). For those with \( m < 23 \), no ordered structure was identified, as the order–disorder transition temperature (\( T_{\text{ODT}} \)) dropped below room temperature. This boundary can be shifted to lower \( f_{\text{LA}} \) by increasing the overall chain length (\( N \)).

To open up a broader compositional window and further elucidate the effects of molecular architecture, we extend our investigation to linear–branched copolymers (\( x = 2 \) and 4). By attaching multiple oDMS chains, diverse phases with a curved interface can now be accessed. We first start with the 2S13-L16 series with a constant oDMS block (\( n = 13 \)). LAM packing was identified in sample 2S13-L40 with the highest oLA volume fraction in this category (\( f_{\text{LA}} = 0.56 \); Figure 4d, \( a = 8.78 \text{ nm} \)). Decreasing the chain length of the oLA block (\( 38 \geq m \geq 36 \)) triggers a phase transition to bicontinuous double gyroids (DG) with the oDMS component as the matrix, as indicated by the characteristic scattering peaks with a \( q/q^* \) ratio of \( \sqrt{6}: \sqrt{8} \): \( \sqrt{14} \): \( \sqrt{16} \) (take 2S13-L38 for instance, Figure 4c; space group \( Ia3d \), lattice parameter \( a = 22.62 \text{ nm} \)). Further reducing \( f_{\text{LA}} \) enters the neighboring cylindrical packing region (HEX). As a typical example, the SAXS profile of sample 2S13-L28 shows a \( q/q^* \) ratio of 1: \( \sqrt{3}: 2 \), indicating a HEX structure with hexagonally packed oLA cylinders embedded in the oDMS matrix (Figure 4b; intercolumn distance \( a = 9.43 \text{ nm} \)). Similar patterns were observed for other samples with \( m \) between 16 and 32 (Figure S12, Table 1). To reach an excessively asymmetric composition, the 2S13-L16 series with a longer oDMS block (\( n = 17 \)) were parallely synthesized (Table 1). Interestingly, for 2S17-L16 samples with \( m = 18 \), 17, and 16, multiple peaks with a \( q/q^* \) ratio of \( \sqrt{2}: \sqrt{4}: \sqrt{5}: \sqrt{6}: \sqrt{8} \).
√10: √17: √21 were indexed, which can be assigned as a highly ordered Frank–Kasper A15 phase with a cubic unit cell (space group Pm3n, Figures 4a and S12). Further shortening the chain length of oLA block finally enters the disordered region. For linear-branched block copolymers with the largest branching number in this study (4S13Lm), multiple complex supramolecular structures were identified across a substantial range of composition. We set the length of oDMS block to be constant (n = 13), while varying the length of the oLA block (m between 16 and 50, Table 1). In general, the phase transition with a sequence of HEX (50 ≥ m ≥ 44), A15 (40 ≥ m ≥ 28), DQC (27 ≥ m ≥ 24), σ (m = 22), and finally disordered phase (m ≤ 20), was clearly recorded as FA decreases (Figures 4 and S11). As representative examples, sample 4S13Lm (fLA = 0.40) adopts HEX packing with oLA cylinders embedded inside a continuous oDMS matrix (Figure 4h; a = 12.16 nm); sample 4S13L27 forms a highly ordered A15 lattice (Figure 4g; a = 19.22 nm); a DQC phase is identified in sample 4S13L27, which shows the characteristic features as reported (Figure 4f); signature diffraction with a dozen peaks was observed in sample 4S13L22 (Figure 4e), which perfectly matches the pattern of a σ lattice with a tetragonal unit cell (space group P42/mnm, a = b = 29.56 nm, c = 15.58 nm; see section 4.5 in Supporting Information and Figure S14 for detailed indexing). Other samples in each phase region show essentially the same pattern but with varied lattice parameters (Figure S13, Table 1).

To construct these complex phases, the block copolymers first aggregate into spherical micelles with an oLA core surrounded by an oDMS corona, which further organize into ordered supramolecular lattices. Each micellar motif has a diameter of around 10 nm and contains tens to hundreds of molecules (Table 1; see section 4 in Supporting Information for detailed calculation). Under an undiluted condition, the incompressibility of the melt mandates the spherical micelles to deform into various Wigner-Seitz polyhedra, mediated by mass exchange among different motifs, which leads to the diverse spherical packing phases with different symmetries. On the other hand, the DQC phase has been generally considered as a metastable state, which would eventually transform to the equilibrium σ phase (Scheme 1). Their occurrence is critically related to the processing method. Interestingly, quite a few samples in this study (4S13Lm, m = 24, 25, 26, and 27) adopt DQC packing under the thermal treatment described above (Figure S13). The followed up in situ SAXS scan indicates an order-to-order transition from the DQC to the σ phase for these samples before entering the disordered region (Figure S15, TDTTs are below 80 °C; see also the DSC thermograms in Figure S9). To determine the relative metastability of the two competing packing schemes, these DQC forming samples were subjected to different annealing protocols. On the one hand, annealing these samples at elevated temperatures (40 °C) for 24 h prompts the
formation of the $\sigma$ phase (Figure S16); on the other hand, a transition to the $\sigma$ phase was also recorded after keeping these samples at room temperature for a prolonged period of time (35 days, Figure S17). These results clearly confirm that the $\sigma$ phase is more stable than the DQC phase, and the latter is a long-live metastable phase at room temperature.

Even a minor dispersity would distort the predicted equilibrium phase behaviors and/or trigger phase transition.\textsuperscript{31–33} In order to fully understand the contribution of individual molecular parameters, it is of critical importance to rule out the interference from chain length heterogeneity. The precise chemical structure eliminates all the inherent molecular uncertainties, while the step growth approach improves the compositional resolution up to one monomer difference. Moreover, as mandated by the Gibbs phase rule, coexistence of multiple equilibrium phases is not allowed in a single-component system at constant temperature and pressure. In this study, pure and definite structures are unambiguously identified even near the phase boundaries (Figures S11–S13), in which mixed lattices usually coexist in the disperse counterparts.\textsuperscript{10} Discrete block copolymers thus provide an ideal and elegant model system for fundamental inquiries into the phase formation and evolution.

A phase portrait with exceptionally high resolution and accuracy was mapped out to depict the phase formation and transition sequences (Figure 5). Three distinct features can be immediately captured from the phase diagram with an increasing number of branches. First, the boundaries of neighboring phases progressively shift to higher $f_{LA}$. A similar phenomenon has also been reported in previous studies, which can be attributed to the increasing interfacial curvature due to the presence of multiple chains at the junction point.\textsuperscript{23} Second, the spherical packing window significantly expands, and multiple complex phases emerge in the linear-branched block copolymers. For example, in the 4S$_n$L$_m$ series, A15, DQC, and $\sigma$ phases were observed in sequence with $f_{LA}$ decreases from 0.35 to 0.23. Last and most interestingly, only the A15 phase could be identified in the case of $x = 2$, and it exists in a much broader phase window than expected in the case of $x = 4$. This observation is in stark contrast to the current theoretical knowledge that the $\sigma$ phase should be the dominating equilibrium phase, while the A15 phase is stable only within a narrow compositional zone at sufficiently higher conformational asymmetry and relatively larger immiscibility (i.e., $\chiN$).\textsuperscript{9,54} The absence of the BCC phase, on the other hand, is probably due to the insufficient segregation strength, as its formation requires exceedingly high compositional asymmetry. It has been widely accepted for decades that flexible diblock copolymers follow a simple and universal behavior, in which the spherical packing region is mainly occupied by the BCC phase.\textsuperscript{12–14} The organization of diblock copolymer is mainly determined by two thermodynamic parameters: composition ($f$) and immiscibility between two blocks ($\chiN$).\textsuperscript{15} Experimental observation of the Frank–Kasper and DQC phases has disrupted this common and simplified understanding. The conformational asymmetry has been generally recognized as
another critical factor.\textsuperscript{53,54,56,57} For AB linear block copolymer, the conformational asymmetry originates from the difference of the pervaded volume of each block, while introducing branches in AB, block copolymers further generates architectural asymmetry. Both contributions can be unified into a conformational parameter ($\epsilon$),\textsuperscript{54,58}

$$\epsilon = \frac{x_{b_A}}{b_b}$$

where $b$ refers to statistical segment length at 25 °C normalized with a reference volume ($v_0$) of 118 Å\textsuperscript{3}. At room temperature, $b$ of dDMS ($b_b$) is 0.54 nm,\textsuperscript{59} while that of DLA ($b_b$) is 0.79 nm.\textsuperscript{60,61} The conformational parameters of discrete block copolymers are thus calculated to be 1.46, 2.92, and 5.84 for $x = 1, 2$, and 4, respectively.

A delicate balance between the interfacial tension, which prefers to form spherical particles in order to minimize the interfacial contact, and the chain stretching necessitated to uniformly fill the space dictates how the molecules organize within the lattices. From a perspective of thermodynamics, a larger $\epsilon$ favors a higher curvature at the interface (toward minority A blocks) for a given composition, since A blocks are easier to stretch as compared with B blocks, allowing the latter to relax at the expense of the former. As a consequence, larger spheres, instead of cylinders, form at a relative higher $f_b$, which shifts the phase boundary and expands the spherical packing region on the B-rich side.\textsuperscript{53,54} Compared with the BCC packing, the A15 and $\sigma$ phases have smaller overall interfacial areas among neighboring micelles, as the motifs better approximate spherical symmetry on average.\textsuperscript{52} A transition to Frank–Kasper lattices will reduce the interfacial energy, at the expense of the entropic penalty due to unfavorable chain stretching. It has been predicted within the framework of mean-field theory that $\sigma$ and A15 phases become thermodynamically stable at sufficiently large values of $\epsilon$.\textsuperscript{54} A close comparison on a group of specifically designed linear AB diblock copolymers consisting of blocks with varying statistic segmental lengths,\textsuperscript{62} as well as a recent work on miktoarm star block copolymers,\textsuperscript{60} confirms experimentally that the complex phase window indeed expands as the conformational asymmetry increases. It is worth noting that the chain length heterogeneity also contributes to release the unfavored chain stretching, with the long blocks distributing to the further space, while the short ones occupying the nearby region.\textsuperscript{5} The discrete block copolymers with precise and uniform chain length could eliminate this disturbing interference, highlighting the profound contribution of the conformational parameter.

The origin of the unexpectedly broad A15 phase region observed in the phase portrait is still unclear. Although theoretical calculations indicate that the $\sigma$ phase possesses relatively lower Gibbs free energy than that of the A15 phase under most of the conditions, the differences turn out to be extremely small (on the order of $10^{-4}$ $k_B T$ per chain),\textsuperscript{63} and even a slight fluctuation would be sufficient to disrupt the local close packing and prompt a phase transition.\textsuperscript{63} We argue that under this circumstance the thermodynamic driving forces might no longer be the only dominating factor. Other uncertain factors, such as nucleation and/or growth kinetics, might be responsible for the preferential formation of the A15 phase. It could also be possible that additional considerations should be taken into account in the theoretical calculations. The origin of this inconsistency is still an open question, deserving more attention and investigations. The precise block copolymers with exact molecular parameters (e.g., $N$, $\chi$, $f$, and $\epsilon$) presented in this study would serve as a calibration to justify results from computations, substantiating the underlying theoretical concepts.

**CONCLUSION**

In this work, we systematically explored the phase behaviors of block copolymer using a single-component system with a precise chemical structure and uniform chain length. A library of discrete block copolymers with diverse architectures were modularly prepared, which self-organize into complex spherical lattices including A15, $\sigma$, and DQC phases. A phase portrait with remarkable compositional resolution was constructed. The profound impact of the conformational parameter on self-assembly was quantitatively highlighted. In general, the experimental observations are in good agreement with theoretical assessments, yet with interesting discrepancies that are worth further investigations. This study reveals intriguing details of phase behaviors that have long been blurred due to the inherent molecular defects, providing deeper insight into the formation and evolution of unconventional spherical phases in soft matter systems. It could also serve as a reference for quantitative explorations on the critical contribution of chain length heterogeneity, bridging the existing gaps between experiments and theories of block copolymers.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c00798.

Detailed syntheses and characterizations (PDF)

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Notes
The authors declare no competing financial interest.

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