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Defective Nanographenes Containing Seven-Five-Seven (7–5–7)-Membered Rings

Yiyang Fei, Yubin Fu, Xueqin Bai, Lili Du, Zichao Li, Hartmut Komber, Kam-Hung Low, Shengqiang Zhou, David Lee Phillips, Xinliang Feng, and Junzhi Liu*

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ABSTRACT: Defects have been observed in graphene and are expected to play a key role in its optical, electronic, and magnetic properties. However, because most of the studies focused on the structural characterization, the implications of topological defects on the physicochemical properties of graphene remain poorly understood. Here, we demonstrate a bottom-up synthesis of three novel nanographenes (1–3) with well-defined defects in which seven-five-seven (7– 5–7)-membered rings were introduced to their sp² carbon frameworks. From the X-ray crystallographic analysis, compound 1 adopts a nearly planar structure. Compound 2, with an additional five-membered ring compared to 1, possesses a slightly saddle-shaped geometry. Compound 3, which can be regarded as the "head-to-head" fusion of 1 with two bonds, features two saddles connected together. The resultant defective nanographenes 1-3 were well-investigated by



UV-vis absorption, cyclic voltammetry, and time-resolved absorption spectra and further corroborated by density functional theory (DFT) calculations. Detailed experimental and theoretical investigations elucidate that these three nanographenes 1-3 exhibit an anti-aromatic character in their ground states and display a high stability under ambient conditions, which contrast with the reported unstable biradicaloid nanographenes that contain heptagons. Our work reported herein offers insights into the understanding of structure-related properties and enables the control of the electronic structures of expanded nanographenes with atomically precise defects.

■ INTRODUCTION

Graphene is an atomically thick sheet composed of a hexagonal network of sp²-hybridized carbon atoms with exceptional electronic and optical properties and is also a credible starting point of materials for new disruptive technologies across a wide range of fields.¹⁻⁴ However, graphene is a semimetal without a bandgap and cannot be directly used for electronics. This makes finding a way to open the bandgap for graphene-based nanoelectronics crucial.⁵ The most prominent way is to locally confine the electrons in what renders stripes of graphene, socalled graphene nanoribbons (GNRs), as semiconducting materials.⁶⁻⁹ Another pathway to influence the electronic structure of graphene is the introduction of imperfections or defects in the basal plane of the graphene.¹⁰ Theoretical calculations have described that the topological defects in graphene significantly affect its optical, electronic, and magnetic properties.¹¹ The typical stable graphene defects, including atom dislocation (pentagon-heptagon pair, Figure 1a), Stone-Wales (SW) defects (point defects, Figure 1b), vacancies (single and multiple), and one-dimensional defects (line defects), have been predicted and also experimentally observed.¹⁰ From the viewpoint of energetic stability, the pentagon-heptagon pair (5-7 rings) is one of the reasonable defect models that can be generated in a graphene layer due to



Figure 1. (a) Azulene unit. (b) Stone–Wales defect. (c) Recent examples of nanographenes with an open-shell character containing 5-7-membered rings.^{17,20} (d) The defective nanographenes with 7-5-7-membered rings reported in this work.

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Scheme 1. Schematic Illustration of the Synthesis of 1, 2, and 3



Figure 2. X-ray crystallographic molecular structures of (a) 1 and (b) 2. The hydrogen atoms are omitted for clarity. Side view of (c) 1 and (d) 2 as well as the bond lengths of the embedded 7-5-7-membered rings (the substituents in 1 and 2 are removed for clarity). (e and f) Crystal packing of 1 and 2, respectively. Orange represents the *M*-enantiomer, and light green represents the *P*-enantiomer.

an atom dislocation (Figure 1a).^{12,13} Generally, the topological defects either can be introduced to graphene or related 2D materials by electron irradiation or are formed during a high-temperature growth.^{14,15} Despite the growing number of experimental observations, the defects in graphene are still not well understood, especially in regard to evaluating and studying the effect of topological defects on the optical, electronic, and magnetic properties.¹⁶ Therefore, the investigation of the chemical and physical properties that arise from the defined defects plays an important role in the defect engineering of the structure–property relationship of graphene.

Recently, processes embedding pentagon-heptagon pairs (an azulene unit) into nanographenes (also called polycyclic aromatic hydrocarbons, PAHs) have been developed. For instance, we reported the synthesis of open-shell nanographenes containing a pair of azulene units both in a solution and on a surface (Figure 1c).¹⁷ Contorted PAHs embedding two azulene cores were synthesized by Mastalerz et al. through cyclopent- and cycloheptannulations.¹⁸ A nonbenzenoid PAH with two pentagons and two heptagons with high hole-mobility was reported by Zhang and coauthors.¹⁹ Konishi and Yasuda et al. reported an open-shell nonalternant isomer of bisanthene that contained a heptalene structure (Figure 1c).²⁰ Chi et al. demonstrated the synthesis of an azulene-embedded nanographene due to the unexpected naphthalene-to-azulene rearrangement during the Scholl reaction.²¹ Very recently, helical nanographenes containing azulene units were successfully and independently synthesized by us²² and Takasu et al.²³. Despite this achieved progress, the synthesis of a nonalternant topology in graphene nanostructures,²⁴⁻²⁶ such as with the seven-five-seven (7-5-7)-membered ring motifs (Figure 1d), remains elusive due to the lack of a facile synthetic approach²⁷⁻³⁰ and the unexpected rearrangements.^{21,31,32}

Herein, for the first time we demonstrate an efficient synthetic strategy toward three unprecedented defective nanographenes containing 7-5-7-membered ring motifs (1-3, Figure 1d and Scheme 1). Compared with 1, there is an additional five-membered ring in 2, and compound 3 with two pairs of 7-5-7-membered rings can be regarded as a "head-to-head" fusion of 1 at the zigzag edge. Single-crystal Xray analysis unequivocally reveals the unique nonalternant topologies embedded in 1-3. Compound 1 adopts a nearly planar structure, while 2 possesses a slightly saddle-shaped geometry, with torsion angles of 20.6° and 21.4°, respectively (Figure 2). Compound 3 adopts a different geometry compared to its monomer 1 in which the subunits "1" feature the saddle-shaped geometry, resulting in two saddles connected together (Figure 3). Interestingly, ring A in 1 (Figure 2a) possesses a pronounced bond alternation for the *p*quinodimethane framework²⁸ (Figure 2c), leading to its antiaromatic character in contrast to the aromatic dibenzocorannulene with 6-5-6-membered rings (Figure 1d). However, ring A in 2 (Figure 2b) does not feature the bond alternation of the *p*-quinodimethane unit as exhibited in 1, suggesting its open-shell biradical character (Scheme S1).³³⁻³⁵ Indeed, from the density functional theory (DFT) calculations compounds 1 and 3 display a closed-shell (antiaromatic) feature (see below), while 2 has a moderate singlet biradical character ($y_0 = 0.29$, UHF method) with a large singlet-triplet energy gap ($\Delta E_{\text{S-T}} = -15.1 \text{ kcal/mol}$, UCAM-B3LYP/6-31G(d)). However, all the experimental results, including temperature-dependent NMR, electron paramagnetic reso-



Figure 3. X-ray crystallographic molecular structure of 3. The hydrogen atoms are omitted for clarity. (a) Top view and (b) side view of 3 (the substituents are removed for clarity). (c) The bond lengths of the embedded 7-5-7-membered rings. (d) Crystal packing of 3.

nance (EPR), and superconducting quantum interfering device (SQUID) measurements, suggest that it is more reasonable to describe **2** as a closed-shell antiaromatic compound in its ground state. Therefore, the resultant antiaromatic nanographenes **1**–**3** exhibit high stabilities over months; this feature stands in contrast with the reported unstable open-shell nanographenes containing 5–7-membered rings (Figure 1c).^{17,20} Our work reported herein provides a new line to the synthesis of air-stable antiaromatic nanographenes with nonalternant topologies and enables the control of their electronic structures.

RESULTS AND DISCUSSION

Synthesis of 1, 2, and 3. The synthetic routes toward compounds 1-3 are descried in Scheme 1. First, the key building block 1,6-dibromo-3,4-dichloro-7,10-dimethylfluoranthene (8) was synthesized from the starting material 1,2-dihydroacenaphthylene (4) in four steps through chlorination, bromination, oxidation, and a Diels–Alder reaction.³⁶ Then, compound 9 was obtained via the Suzuki coupling of 8 and (4-(tert-butyl)phenyl)boronic acid in a 23% yield. The methyl groups in 9 were transformed into dialdehydes by bromination, esterification, hydrolysis, and oxidation to afford compound 10 with a yield of 47%. Dihydro-precursor 11 was synthesized by the treatment of 10 with mesitylmagnesium bromide (MesMgBr), followed by Friedel–Crafts cyclization. The dehydrogenation of 11 using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) provided the dark yellow compound



Figure 4. Calculated isomerization process of (a) 1, (b) 2, and (c) 3. The relative Gibbs free energy (kcal/mol) was calculated at the B3LYP/6-31G(d) level. All calculations were corrected for dispersion (D3BJ).

1 with a yield of 90% in three steps. On the other hand, compounds 12 and 16 were achieved through the selective Suzuki coupling of 8 and (4-(tert-butyl)phenyl)boronic acid. Subsequently, the Pd-involved Heck reaction of 12 gave 13 (quantitative). Following a similar synthetic strategy, compound 2 was successfully synthesized as dark red solid with a yield of 92% in three steps. In addition, the key precursor dialdehyde 17 was synthesized in a 33% yield from compound 16. Finally, dark red compound 3 containing two pairs of 7–5–7-membered rings was achieved through the Yamamoto coupling of 19 in a 73% yield. The chemical structures of 1, 2 and 3 were confirmed by high-resolution mass spectrometry (HR-MS), NMR analysis (both see the Supporting Information), and X-ray single-crystal analysis (vide infra).

Structural Characterization. The single crystals of 1 and 2 were each grown by slow evaporation from an *n*-hexane/ dichloromethane solution, which could distinctly unveil their structural uniqueness with the presence of 7-5-7-motifs through the X-ray single-crystal analysis. Compound 1 adopts a nearly geometric plane surface (Figure 2a) in which the heptagonal ring B induces the adjacent benzene ring out of planarity with a dihedral angle of 21.9° (Figure 2c), whereas the other seven-membered ring C features a planar structure. Accordingly, there are two different conformations in the solid state of 1, that is, enantiomers M and P coexist with a ratio of 1:1 in the crystal (Figure 2e). In comparison to 1, compound 2 with an additional five-membered ring displays a slightly saddle-shaped geometry, where the heptagonal rings B and C arise from the steric hindrance between their adjacent benzene rings E and F and G and H with the dihedral angles of 21.6° and 20.4°, respectively (Figure 2b and d). In the packing pattern, compound 2 crystallizes along the *c*-axis of the unit cell with a pair of enantiomers (M and P) to establish columnar superstructures with a minimum interplanar space of 3.28 Å (Figure 2f).

Moreover, the single crystals of 3 were obtained from an *n*-hexane/dichloroethane solution. Compound 3, which can be regarded as a "head-to-head" fusion of 1 at the rings F and G with two bonds (Figure 3a), adopts a different geometry than

its monomer 1. The subunits "1" in 3 feature the saddle-shaped geometries, resulting in two saddles connected together in 3 (Figure 3b). Accordingly, the dihedral angles of rings E and F and G and H in 3 are 23.0° and 28.4° (Figure 3a), respectively, which are larger than those in 2. Due to the presence of the sterically hindered mesityl and tert-butyl groups in 3, no intermolecular $\pi - \pi$ stacking interaction can be formed between the adjacent molecules (Figure 3d). In addition, the X-ray analysis discloses the detailed bonding information on 1, 2, and 3 (Figures 2c and d and 3c). The bond lengths in 1 reveal that the six-membered ring A (Figure 2c) has two short C-C bonds (1.346(4) and 1.376(3) Å) and four long C-C bonds (1.437(3)-1.463(3) Å), manifesting a pronounced bond alternation for the *p*-quinodimethane skeleton in $1^{28,29}$ as indicated by the antiaromaticity that appeared in the B-A-C framework (7-6-7 rings, Figure 2). For 2, the intermediate value (1.407(8) Å, Figure 2d) of bond *a* is substantially longer than that of 1 (1.370(3) Å), indicating the contribution of the open-shell resonance structure in the ground state of 2(2-1) in Scheme S1);³⁷⁻⁴⁰ nevertheless, the bond length of a in 2 is shorter than that of the open-shell indeno [2,1-b] fluorene⁴¹ (1.437 Å, $y_0 = 0.68$, Figure S64), coinciding with the relatively smaller open-shell character of 2 ($y_0 = 0.29$). However, the temperature-dependent NMR (Figure S18), EPR, and SQUID (Figure S63) measurements suggest that it is more reasonable to describe 2 as a closed-shell antiaromatic compound in its ground state. Interestingly, the bond length of b at the junction (ring I) in 3 is 1.462(4) Å, suggesting its single-bond character (Figure 3a). The bond lengths of the six-membered ring A in 3 are comparable with those in 1 (Figure 3c).

Theoretical Characterization. Since there are different conformations in the solid state, DFT calculations for the relative energies of 1, 2, and 3 as well as the transition states (TS), were performed at the B3LYP/6-31G(d) level of theory to evaluate the isomerization process of the different enantiomers (Figure 4). The dispersion correction was conducted using Grimme's D3 version with the BJ damping function.⁴² The thermodynamic stabilities of the *M*- and *P*-enantiomers for 1 are similar in terms of their Gibbs free

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Figure 5. NICS(1)_{zz-avg} values (calculated at the GIAO-B3LYP/6-31+G(2d,p) level of theory) and calculated ACID plots of (a and b) 1, (c and d) 2, (e and f) 3, and (g and h) dibenzo-corannulene. The isovalue is 0.05, and the diamagnetic (clockwise) and paramagnetic (counterclockwise) ring currents under the magnetic field parallel to the *z*-axis are highlighted by red and blue arrows, respectively.

energies (ΔG). DFT calculations show that compound 1 can undergo an M-to-P conversion through a flat transition state (Figure 4a). The free-activation energy of 1 was estimated to be 3.08 kcal/mol, which is significantly higher than that without a dispersion correction (2.82 kcal/mol, Figure S72) and substantially smaller than that of dibenzocorannulene with a 6-5-6-membered ring (8.10 kcal/mol, Figure S73), indicating a fast isomerization process even at room temperature. This result is also in line with the variable-temperature NMR measurements (Figure S6) and the fact that both *M*- and P-enantiomers were experimentally observed in the solid state of 1 (Figure 2e). Therefore, two enantiomers of racemic 1 always exist together, and it is not possible to separate them for further investigations. Similar to compound 1, the thermodynamical stabilities of the M- and P-isomers for 2 are almost the same (Figure 4b). The energy barrier for the isomerization process in 2 was calculated to be 2.69 kcal/mol based on the dispersion-corrected model. This is comparable to that without a dispersion correction (2.76 kcal/mol, Figure S72) and lower than that of 1 (3.08 kcal/mol). For 3, DFT calculations with the dispersion-corrected model predict the activation energies of 1.17 and 2.97 kcal/mol for the M,M-to-P,M and P,M-to-P,P isomerization processes (Figure 4c), respectively, which are lower than that of compound 1 (3.08 kcal/mol).

Furthermore, to evaluate the aromaticity of each of the rings in these three defective nanographenes 1-3, nucleusindependent chemical shift (NICS) calculations were performed at the GIAO-B3LYP/6-311+G(2d,p) level of theory. The obtained NICS(1)_{zz} values of 1 are 13.5 and 9.4 for the heptagonal rings (B, C) and hexagonal ring A (Figure 5a), respectively, which is consistent with the X-ray structural analysis and demonstrates their antiaromatic feature; meanwhile, large negative values were found at the peripheral benzene rings E (-15.7) and F (-20.7). Accordingly, the paratropic character on ring A and the heptagons in 1 magnetically suppresses the aromatic character of the peripheral hexagons E and F. Therefore, the 7-5-7 ringembedded nanographene 1 exhibits an antiaromatic nature compared to the aromatic dibenzo-corannulene with a 6-5-6motif (Figure 5g). Compound 3 containing dual 7-5-7 ring motifs features a similar behavior to that of 1 (Figure 5e). For instance, the values of rings A and B in 3 are comparable with those of 1, while the ring G in 3 displays a large positive value (21.4). Moreover, the values of rings A and B in 2 are similar to those of 1 (Figure 5c); however, the central five-membered ring D (-1.2) in 2 seems to behave as a nonaromatic ring in which the value is noticeably higher than that of in 1 (-14.1) (Figure 5a). This difference in 1 and 2 also suggests the possibility of an open-shell character for 2. To further support the local aromaticity of the 7-5-7 embedded nanographenes 1-3, the anisotropy of the induced current density (ACID) analysis was evaluated (Figure 5b, d, and f, respectively). Continuous counterclockwise paratropic ring currents appear around the 7–6–7 units (rings B-A-C) in the ACID plots of 1, 2, and 3. However, diamagnetic ring currents are found in other six-membered rings. These results indicate that the 7-6-7 rings (rings B-A-C) in 1-3 display an antiaromatic character, which is consistent with the results of the NICS calculations.

Optical and Electrochemical Properties. Compounds 1, 2, and 3 have excellent solubilities in common organic solvents such as dichloromethane (DCM), tetrahydrofuran (THF), toluene, etc. The UV-vis absorption spectra of 1-3 in DCM solutions are shown in Figure 6a. Compounds 1 and 2 display similarly shaped UV-vis absorption patterns. For instance, there is one major absorption peak at 310 nm and another absorption peak centered at 520 nm with two shoulder peaks at 490 and 455 nm for 1. Compound 2 exhibits a bathochromic shift by 49 nm relative to that of 1, with an absorption maximum at 569 nm and two shoulder peaks at 530



Figure 6. (a) UV–vis absorption spectra of 1, 2, and 3 in DCM (1 × 10^{-5} mol/L). The insert shows photos of their solutions. (b) Cyclic voltammetry of 1, 2, and 3 in THF containing 0.1 M *n*Bu₄NPF₆ at a scan rate of 50 mV/s.

and 492 nm. The maximum absorption peak of 3, which can be regarded as the dimerization of 1 with a "head-to-head" fusion, displays a red-shift by 10 nm, with a broad absorption shoulder at 582 nm compared to 1 due to the π -expanded conjugation. The calculated UV-vis spectra of compounds 1-3 are also displayed in Figures S74-S76 and Tables S1-S3, respectively, which are consistent with the experimental results. Accordingly, the optical energy gaps for 1, 2, and 3 were determined to be 2.21, 2.06, and 1.96 eV, respectively, from the onset of their UV-vis absorption spectra. Interestingly, the DCM solutions of compounds 1-3 were nonemissive when excited with UV light, which is also in agreement with their antiaromatic character. Furthermore, time-dependent UV-vis measurements were performed under ambient conditions to investigate the stability of 1, 2, and 3. There were no significant changes in the absorption curves for 1-3 within two months (Figure S39). The electrochemical behaviors of 1, 2, and 3 were investigated by cyclic voltammetry (CV) in THF (Figure 6b). Compound 1 shows one reversible oxidation wave with a half-wave potential $(E_{1/2}^{ox})$ at 0.92 V (vs Fc⁺/Fc) and one reversible reduction wave with a half-wave potential $(E_{1/2}^{re})$ at -1.32 V (vs Fc⁺/Fc). However, compound 2 manifests two reversible oxidation waves with half-wave potentials $(E_{1/2}^{ox})$ at 0.76 and 1.15 V and one reversible reduction wave with a halfwave potential $(E_{1/2}^{re})$ at -1.10 V (vs Fc⁺/Fc). For compound 3, there are two reversible oxidation waves $(E_{1/2}^{ox})$ and two reversible reduction waves $(E_{1/2}^{re})$ with half-wave potentials at 0.98 and 1.01 and -0.68 and - 0.91 V, respectively. Thus, the HOMO/LUMO energy levels were estimated to be -5.61/-3.37, -5.45/-3.59, and -5.67/-4.01 eV for compounds 1, 2, and 3, respectively, based on the first reversible oxidation/

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reduction waves. The corresponding electrochemical energy gaps for **1**, **2**, and **3** were calculated to be 2.24, 1.86, and 1.66 eV, respectively.

Time-Resolved Absorption Spectroscopy. Femtosecond transient absorption spectra with 400 nm excitation were recorded in THF to study the excited-state photophysical dynamics of defective nanographenes **1**, **2**, and **3**. As shown in Figure 7, the ground-state bleaching (GSB) signals were



Figure 7. Femtosecond time-resolved absorption (fs-TA) spectra of compounds (a) 1, (b) 2, and (c) 3 in THF at a 400 nm laser pulse excitation.

observed for compounds 1-3, which is consistent with their UV-vis spectra. Unlike the GSB, the excited-state absorption (ESA) spectra were explicitly different for compounds 1-3. As shown in Figure 7a, the compound 1 exhibits two main ESA bands at 440 and 630 nm with a shoulder at 690 nm, which can be assigned to the singlet excited states of compound 1 due to its short lifetime (15 ps, Figure S62a) and nonfluorescent behavior. Unlike compound 1, only one ESA band at 450 nm with an absorption tail band extending up to 700 nm was

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observed for compound 2, as shown in Figure 7b. This band can also be assigned to the singlet excited states of compound 2 with a lifetime of 12 ps (Figure S62b). Considering the different ESA pattern, one is able to conclude that the ESA spectra for both compounds 1 and 2 have contributions from the different electronic configurations of their singlet excited states. Furthermore, the fs-TA spectra of compound 3 in Figure 7c exhibit only one broad ESA band at 680 nm, which is red-shifted by 50 nm compared to that of compound 1 and suggests that an extended conjugation contributes to the overall singlet-states stabilization in compound 3. A short lifetime within 10 ps was also observed for the singlet excited states of compound 3 in Figure S62c. Therefore, those differences in the fs-TA spectra for compounds 1-3 are likely due to their different molecular topologies, suggesting that their singlet excited states have different electronic configurations.

CONCLUSIONS

In summary, we have demonstrated the synthesis of three unprecedented nanographenes with seven-five-seven (7-5-7)-membered rings. The crystallographic characterizations unambiguously show that 1 adopts a nearly planar structure, while compound 2, with an additional five-membered ring compared to 1, manifests a slightly saddle-shaped geometry. Interestingly, the subunits "1" in compound 3, which can be regarded as the "head-to-head" fusion of 1 with two bonds, feature the saddle-shaped geometries. The structural analyses combined with the DFT calculations demonstrated that compounds 1, 2, and 3 represent a new type of air-stable and fully conjugated antiaromatic nanographenes containing 7-5-7-membered rings. More importantly, the synthetic strategy in regard to the defect engineering in nanographenes by building 7-5-7-membered rings can be applied to the construction of other air-stable and π -expanded nanographenes with antiaromatic or open-shell structures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c12116.

Synthetic procedures and characterization data for all new compounds, general experimental methods, additional NMR and HR-MS spectroscopic data and spectra, DFT calculation details, and crystallographic data (PDF)

Accession Codes

CCDC 2033693 for compound 1, CCDC 2010758 for compound 2, and CCDC 2042159 for compound 3 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Junzhi Liu – Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, 999077 Hong Kong, P. R. China; orcid.org/0000-0001-7146-0942; Email: juliu@hku.hk

Authors

- Yiyang Fei Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, 999077 Hong Kong, P. R. China
- Yubin Fu Centre for Advancing Electronics Dresden (CFAED), Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany;
 orcid.org/0000-0002-2613-394X
- Xueqin Bai Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, 999077 Hong Kong, P. R. China
- Lili Du Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, 999077 Hong Kong, P. R. China
- **Zichao Li** Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, 01328 Dresden, Germany
- Hartmut Komber Leibniz-Institut für Polymerforschung Dresden e. V., 01069 Dresden, Germany; orcid.org/0000-0001-6176-6737
- Kam-Hung Low Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, 999077 Hong Kong, P. R. China; Orcid.org/0000-0003-3292-8893
- Shengqiang Zhou Helmholtz-Zentrum Dresden-Rossendorf, Institute of Ion Beam Physics and Materials Research, 01328 Dresden, Germany; © orcid.org/0000-0002-4885-799X
- **David Lee Phillips** Department of Chemistry and State Key Laboratory of Synthetic Chemistry, The University of Hong Kong, 999077 Hong Kong, P. R. China
- Xinliang Feng Centre for Advancing Electronics Dresden (CFAED), Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, 01062 Dresden, Germany; orcid.org/0000-0003-3885-2703

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c12116

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