Funnel-shaped electronic structure and enhanced thermoelectric performance in ultralight $C_x(BN)_{1-x}$ biphenylene networks

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Carbon biphenylene has stimulated substantial research because of extraordinary properties introduced by the metallic character, e.g., the ultrahigh electron thermal transport. Here, inspired by the synthesis of carbon biphenylene [Fan et al., Science 372, 852 (2021)], we identify the stability of $C_x(BN)_{1-x}$ biphenylene as CBN and C₄BN semiconductors with four-, six-, and eight-membered periodic rings of irregularly sp²-hybridized atoms via structural searches. Unexpectedly, we confirm that CBN biphenylene exhibits a peculiar funnel-shaped band structure, which is a direct consequence of the delocalization /localization of π bonds formed by B-, N-, or C- p_{τ} electrons. The band structure greatly improves the thermoelectric performance by enhancing the power factor, although the lattice thermal conductivity is relatively large after including four-phonon scattering resistance because of low atomic masses. The similar behaviors are absent in C₄BN biphenylene because of the localization of π bonds formed by C-p_z electrons, although with a stronger anharmonicity and thus a lower lattice thermal conductivity. The anomalous power factor can be explained by the constant τ approximation: the *p*-type doping controls the carrier group velocities and thus realizes the tunability of tensor ratio K_1/K_0 . Our analysis suggests that the funnel-shaped electronic structure could be reproduced in two-dimensional semiconductor systems with the small electronegativity difference and the comparable stoichiometry. Our work realizes the thermoelectric improvement through controlling the shape of band structure, which provides insights for designing promising two-dimensional thermoelectric materials.

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I. INTRODUCTION

With the progress in material synthesis and characterization, two-dimensional (2D) nonhexagonal carbon allotropes are a current focus [1-4]. One major breakthrough is the syntheses of planar carbon biphenylene network, which comprises the four-, six-, and eight-membered periodic rings by the irregular sp^2 orbital hybridization [5–7]. Graphene is more favorable in energy [8,9]; however, carbon biphenylene is stabilized by the large kinetic barrier induced by the in-plane rotations of covalent bonds at the stress-free conditions [10,11]. To retain the planar configuration, the covalent bonds are symmetry allowed to distort in a special range to release the internal strains [12]. The hexagonalto-nonhexagonal evolution intrigues numerous interesting physical properties, e.g., metallic character, abnormal thermal transport, and topological superconductivity [13-17]. For instance, carbon biphenylene shares the ultrahigh electron thermal conductivity because of its metallic nature. This obviously contradicts with the established notion in 2D carbon-based materials that the thermal transport is usually dominated by the phonon modes and the electron-based conduction becomes essential only under *n* doping [18-21]. Since the thermal transport and the thermoelectric (TE) performance closely correlate with the electronic structure, our one focus is to elucidate how the band structure determines the lattice thermal conductivity κ_L , the electron thermal conductivity κ_e , and the figure of merit $ZT = S^2 \sigma T / (\kappa_L + \kappa_e)$ in $C_x(BN)_{1-x}$ biphenylene networks, where σ and S are the electrical conductivity and the Seebeck coefficient, respectively.

Further investigations reveal that biphenylene network can be either planar (e.g., BN, SiC, and AlN) or buckled (e.g., Si, Ge, BAs, and ZnSe) in IV-IV, III-V, and II-VI compounds [22,23]. The nonhexagonal configuration has a great impact on the electronic structures, compared to the conventional hexagonal structure. For example, C, Si, and Ge biphenylene networks are metallic and the others are semiconductors with direct band gap from 0.24 eV (BP) to 4.49 eV (BN) [23]. The band structure can be further tuned by controlling the alloy composition in $C_x(BN)_{1-x}$ biphenylene. Recently, 2D $C_x(BN)_{1-x}$ alloys have attracted extensive attention because of the diverse structures and the intriguing properties [4,24–32]; however, this alloy system in biphenylene configuration remains unexplored so far. Note that the biphenylene network can retain planar because the difference in atomic mass and radius is small enough in $C_x(BN)_{1-x}$ biphenylene.

In the quest for higher ZT, two strategies are based on either reducing the κ_L or enhancing the power factor ($PF = S^2\sigma$) [33–39]. The alloying is also a general strategy to reduce the κ_L through disorder in a large and complex unit cell [40,41]. In $C_x(BN)_{1-x}$ biphenylene, the complex configuration and the difference in atomic species favor the low κ_L

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by strengthening the anharmonicity and thus improving the ZT. Unfortunately, the TE properties of biphenylene, especially their relationships with the electronic band structure, are seldom mentioned so far. This is ascribed to the following aspects. (1) The κ_L is usually supposed to be high in the carbon-based systems because of the strong bonding, for example, in graphene [42]. (2) Heavy atom prefers high ZTbecause the small group velocity of low frequency phonon mode greatly reduces the κ_L [43,44]. However, it is not the case in the $C_x(BN)_{1-x}$ system because of very small atomic masses. In addition, the three-phonon scattering usually overestimates the κ_L [45,46]. As an example, the κ_L of zinc-blende BAs is predicted to be \sim 2200 W/mK, compared to the measured value of ~ 200 W/mK, and the κ_L drops by 60% at 1000 K after including the four-phonon picture [47-49]. The impact of four-phonon scattering on the κ_L of biphenylene remains unclear so far, which hinders the predictive power for applications such as thermal barrier coatings and room/hightemperature thermoelectrics.

In this work, we identify that 2D $C_x(BN)_{1-x}$ stabilizes as CBN and C₄BN biphenylene using the first-principles structural searches. Unexpectedly, the ultrahigh ZT is present at the reachable hole concentration in CBN not in C₄BN, although C₄BN shares a stronger anharmonicity and thus a lower κ_L . We demonstrate that the four-phonon scattering is more remarkable in C₄BN than in CBN because of the dominant role of C atom, as illustrated by the phonon density of states (DOS). We show that this anomalous ZT behavior in CBN biphenylene is attributed to the funnel-shaped band structure, where both dispersive and flat valence bands greatly augment the PF in the dependent momentum space. We unveil that the funnel-shaped band structure is caused by the delocalization/localization of π bonds formed by C-, B-, or N- p_z electrons in CBN biphenylene; however, the π bonds are much more localized because of the dominant contribution of $C-p_z$ electrons in C_4BN biphenylene. Finally, we point out that the bonding modes of π bond are eventually determined by the alloy composition in $C_x(BN)_{1-x}$ biphenylene, and can result in excellent TE behaviors by enlarging the σ and S simultaneously.

II. COMPUTATIONAL METHODS

Structural searches in this study are performed by the USPEX code [50,51], in combination with the structural relaxations and the total energy calculations based on the density functional theory (DFT) [52] within the generalized gradient approximation (GGA) parametrized by Perdew, Burke, and Ernzerhof (PBE) [53] as implemented in the VASP package [54-56]. A 500 eV plane-wave energy cutoff and the Γ -centered **K** meshes of $2\pi \times 0.05 \text{\AA}^{-1}$ resolution for Brillouin zone sampling are adopted to ensure the convergence within 10^{-8} eV and 0.005 eV/Å for energy and force, respectively. A vacuum region is set to 20 Å to avoid the layer-layer interactions in the periodic structure along the out-of-plane direction. Harmonic and anharmonic interatomic force constants (IFCs) are calculated within the $4 \times 4 \times 1$ supercells by the PHONOPY code [57]. Lattice thermal conductivity based on the three-phonon scattering is predicted by solving the phonon Boltzmann transport equation with $70 \times 70 \times 1$ Γ -centered **Q**

grids using the SHENGBTE code [58]. Furthermore, the impact of four-phonon scattering on the thermal transport is verified by the FOURPHONON package [59], which is very computationally expensive. Details on the phonon-phonon interactions within three- and four-phonon scattering are described in Sec. I in the Supplemental Material [60].

In this section, we focus on the shape of the valence band near the Fermi level as well as its relationship with the *PF* and the *ZT* in $C_x(BN)_{1-x}$ biphenylene networks. In Boltzmann's equation approach, the electronic transport properties including *S*, σ : and κ_e tensors are expressed as follows [61]:

$$S = \frac{1}{eT} \boldsymbol{K}_1 \boldsymbol{K}_0^{-1}, \qquad (1)$$

$$\sigma = e^2 K_0, \tag{2}$$

$$\kappa_e = L\sigma T,\tag{3}$$

where *L* is a constant of the Lorenz number. The K_1 and K_0 tensors satisfy that

$$\boldsymbol{K}_{n} = \sum_{k} \tau(\boldsymbol{k}) \boldsymbol{v}(\boldsymbol{k}) \left[-\frac{df(\boldsymbol{\varepsilon})}{d\boldsymbol{\varepsilon}}(\boldsymbol{k}) \right] [\boldsymbol{\varepsilon}(\boldsymbol{k}) - E_{f}]^{n}.$$
(4)

Here, $\boldsymbol{\varepsilon}(\boldsymbol{k})$ is the band dispersion, $\boldsymbol{v}(\boldsymbol{k}) = \nabla_{\boldsymbol{k}}\boldsymbol{\varepsilon}(\boldsymbol{k})/\hbar$ is the carrier group velocity of the wave vector \boldsymbol{k} , $\tau(\boldsymbol{k})$ is the quasiparticle lifetime, $f(\boldsymbol{\varepsilon})$ is the Fermi distribution function, and E_f is the Fermi level (chemical potential). The electronic states within k_BT near the E_f always contribute largely to K_0 and K_1 according to $df(\boldsymbol{\varepsilon})/d\boldsymbol{\varepsilon}$. In the constant τ approximation [62], Eq. (4) is simplified as

$$K_0 = \tau \sum_{k} \left(v_{\text{above}}^2 + v_{\text{below}}^2 \right), \tag{5}$$

$$K_1 = \tau \sum_{k} \left(v_{\text{above}}^2 - v_{\text{below}}^2 \right), \tag{6}$$

where the v_{above} and v_{below} are the group velocities above and below the E_f (usually within k_BT). Because of the crossover of bands in metallic systems, the v_{above} and v_{below} usually share similar values; thus the K_1 tends to be zero and therefore the S is much smaller, while the σ is very large when either v_{above} or v_{below} is relative large. This approximation can explicitly explain the ultrahigh κ_e reported in carbon biphenylene [12]. According to $S \propto K_1/K_0$, a large difference between v_{above} and v_{below} leads to a large S. It is possible to achieve a large σ simultaneously if either $v_{\rm above}$ or $v_{\rm below}$ is large enough due to $\sigma \propto K_0$. This is realized in the "pudding-mold" type band structure in $Na_x CoO_2$ and $CuAlO_2$ [62,63], where the E_f drops slowly when the holes are introduced by the *p*-type doping because of the large electronic DOS. When the E_f is close to the bending point of the band, the flat band results in a small v_{above} and the dispersive portion leads to a large v_{below} ; thus the large K_1/K_0 is reached. In this band mold [62–64], the S and σ are simultaneously large in a wide p-doping range.

In the Boltzmann transport theory, the σ closely depends on the relaxation time τ ; thus a method to evaluate τ should be applied appropriately. To describe the charge transport in 2D materials, the deformation potential method has been widely employed in thermoelectric investigations [65,66]. According to this method, the electron relaxation time τ can be expressed



FIG. 1. (a) Structural schemes of CBN and C_4BN biphenylene with the electron localization functions. (b) Infrared response spectra as well as vibrational modes of the main peaks. (c) Lattice thermal conductivity versus temperature including three-phonon scattering as well as four-phonon scattering along the armchair (solid) and zigzag (dashed) directions. (d) Three- and four-phonon scattering rates of allowed scattering channels at 300 K.

as

$$\tau = \frac{\mu_{2D} m_d^*}{e} = \frac{\hbar^3 C_{2D}}{k_B T m^* E_1^2},\tag{7}$$

where T, k_B , and \hbar are temperature, the Boltzmann constant, and the reduced Planck constant, respectively. $\mu_{2D} =$ $e\hbar^3 C_{2D}/(k_B T m^* m_d E_1^2)$ is the carrier mobility of 2D materials. $C_{2D} = 2\partial^2 E / [\partial (\Delta l/l_0)^2 S_0]$ is the elastic modulus along the strain direction, where E is the total energy at a small deformation state, S_0 is the area in the x-y plane at equilibrium state, and Δl is the deformation of the lattice constant l_0 . The deformation potential constant E_1 is defined as $E_1 = \Delta E_{\text{CBM(VBM)}} / (\Delta l / l_0)$, which is the energy change of the conduction band minimum (CBM) and valence band maximum (VBM) with the small deformation $\Delta l/l_0$. $m^* =$ $\hbar^2 / [\partial^2 \boldsymbol{\varepsilon}(\vec{\mathbf{k}}) / \partial \vec{\mathbf{k}}^2]$ is the carrier effective mass; $m_d = \sqrt{m_x^* m_y^*}$ is average effective mass. In this work, the C_{2D} and E_1 are calculated along the armchair (x) and zigzag (y) directions. The analyses of PF are based on the electronic band structures within the HSE06 hybrid functional, whose accuracy has been extensively reported [67-69].

III. RESULTS AND DISCUSSION

Structural searches confirm the energetically favorable CBN and C₄BN biphenylene with the four-, six-, and eightmembered periodic rings in 2D $C_x(BN)_{1-x}$ alloys [see Fig. 1(a) and Table S1]. The dynamical and thermal stabilities are carefully checked in Sec. II in the Supplemental Material. Figure 1(b) displays the infrared (IR) response spectra, which are much stronger in C₄BN than in CBN. In CBN biphenylene, the alternate arrangement of C, B, and N atoms inspires the bending vibrational modes; therefore, the oscillator strengths are nearly negligible. In sharp contrast, in C₄BN biphenylene, the stretching vibrations of C atoms along the zigzag direction result in the very large variation of dipole moment and thus strengthen the anharmonic scattering. This is because there are two types of C-C bond along the zigzag direction in each eight-membered ring: (I) one C atom bonds with two B atoms and another with two N atoms; (II) the C atoms all bond with C atoms by the regular sp^2 hybridization. As a result, the net atomic forces along the zigzag direction are not zero in C₄BN biphenylene. Furthermore, the stronger anharmonicity is verified by the lower κ_L with the typical ~1/T character in C₄BN biphenylene [see Fig. 1(c)].

To ensure the κ_L accuracy, the four-phonon (4ph) scattering is included. Within the profile of three-phonon (3ph) scattering, the κ_{3ph} are 43.44 and 33.40 W/mK at room temperature in CBN and C₄BN biphenylene, respectively. After including the 3+4ph scattering, the corresponding κ_{3+4ph} are 33.19 and 18.72 W/mK, which are the 23.60 and 43.95% reductions. The reduction is further enlarged with increasing temperature, especially in C₄BN biphenylene, due to the four-phonon scattering $\tau_4^{-1} \sim T^2 \omega^4$, as displayed in Fig. 1(c). Figure 1(d) reveals the dominance of three-phonon processes in CBN biphenylene, which obeys the general notion of perturbation theory. In contrast, the four-phonon redistribution process $\mathbf{q} + \mathbf{q}_1 \rightarrow \mathbf{q}_2 + \mathbf{q}_3 + \mathbf{k}$ contributes the most to the scattering rate in the entire frequency range in C_4BN , where the k is zero for the normal process and nonzero for the umklapp process. On one hand, the small difference in atomic mass removes the *a-o* phonon gap and makes the optical branches available at low frequencies to strengthen the coupling between the acoustic and the optical branches. On the other hand, the strong covalency of C-C bonds makes the optical branches much more dispersive (see Fig. S3); therefore, the energy and momentum conservations are more easily satisfied during the four-phonon processes in C₄BN biphenylene.

CBN and C₄BN biphenylene networks have much higher κ_L than conventional high-*ZT* materials such as Pd₂Se₃ monolayer (1.5 and 2.85 W/mK along the *a* and *b* axes, respectively) [70], Penta-Silicene (1.66 and 1.29 W/mK along



FIG. 2. Figure of ZT along the armchair direction, the electrical conductivity σ , and the Seebeck coefficient S along the armchair (solid line) and zigzag (dashed line) directions versus the chemical potential E_f and temperature T in (a) CBN and (b) C₄BN biphenylene, together with the relative percentage κ_L/κ_{total} in the insets.

the *x* and *y* axes, respectively) [71], and PbTe (2.4–3.1 W/mK) [72,73]. This is ascribed to the very low atomic masses, although the other factors, i.e., the complex crystal structure, the weak interatomic bonding, and the strong anharmonicity [74], favor the low κ_L in biphenylene network. The high *ZT* is usually present in semiconductor materials with the ultralow κ_L . Here, it looks difficult to improve the *ZT* unless the electronic structure can significantly augment the *PF* in CBN and C₄BN biphenylene.

Figures 2 and S4 reveal that CBN has a much more excellent TE performance than C₄BN by systematically disclosing the relationships of ZT, σ and S versus E_f and T, although C₄BN shares a much lower κ_L . The optimum ZT is as high as 1.80 at 300 K at low hole concentration $n = 1.59 \times 10^{12}$ cm⁻² and rises quickly to the maximum value of 3.35 at 800 K along the armchair direction in CBN, which is a promising 2D *p*-type TE material. The high ZT in CBN is introduced by the electronic contributions that the σ and S, unexpectedly, remain large simultaneously. In general, one is high and another is low, since the σ and S have opposite dependence on the effective mass m^* . It is the case in C₄BN that the σ is low and the S is high. The anomalous behaviors of σ and S arise from the distinct band structures in CBN and C₄BN biphenylene.

As temperature increases, the four-phonon scattering is greatly strengthened and thus the carrier mobility μ is substantially reduced; meanwhile, a large carrier concentration *n* is inspired. Therefore, the σ and *S* usually decrease with increasing temperature, as displayed in Fig. 2. Because of the high σ , the $\kappa_e = L\sigma T$ contributes more to the thermal transport with increasing temperature in CBN. The $\kappa_L/(\kappa_L + \kappa_e)$ drops quickly from 55.53% at 300 K to 8.2% at 800 K along the armchair direction. When the electronic contribution is large enough, $ZT \approx S^2/L$, implying the dominance of *S* at high temperature. However, the $\kappa_L/(\kappa_L + \kappa_e)$ is insensitive to temperature along the zigzag direction in CBN, e.g., 97.69% at 300 K and 81.04% at 800 K (see the insets in Fig. 2). To explain the high *ZT* in CBN, the key is to explore why the σ is high along the armchair direction, while the *S* is high along both directions. Note that the σ and *S* are sensitive to the m^* , which is determined by the band shape near the E_f . In general, the high electronic DOS near the E_f corresponds to a large m^* .

Since the maximum ZT is achieved by the *p*-type doping, we focus on the valence band near the E_f to understand the anomalous S and σ in CBN and C₄BN biphenylene networks, as displayed in Fig. 3. In CBN, the three-dimensional (3D) band structure displays a weird funnel-shaped valence band, where the minimum is at the S and the second minimum at the Γ point, and the maximum at the X point and the second maximum at the Y point. This band structure is distinct from the ring-shaped bands with small- and largeradius rings alternately arranged on the contour plot [33], and is also different from the ideal "pudding-mold" band in $Na_x CoO_2$ [62–64]. The pudding-mold band originates from the $3d_{3r^2-r^2}$ -like orbital of a transition metal; however, such orbitals are unoccupied in CBN and C₄BN. Our investigations reveal that the constant τ approximation can demonstrate the excellent ZT based on the relationship of PF versus band structure in CBN.



FIG. 3. HSE06 three-dimensional band structures near the Fermi level, projected band structures along the high-symmetry path of the Brillouin zone (red, blue, and green symbols represent the inserted C-, N-, and $B-p_z$ orbitals, respectively), electronic density of states, and spatial distributions of valence band edge states at the high-symmetry points in (a) CBN and (b) C₄BN biphenylene networks.

There are two typical Brillouin zone pathways, depicted as paths I and II, from the X to the Y point in CBN and C_4BN biphenylene. In CBN, the valence band along path I is very dispersive and the valence band along path II is nearly flat, with the energy evolution illustrated in the projected band structure. The dispersive band between the X and S points corresponds to a small m^* of $0.69m_0$, a high μ of 9535.05 $cm^2V^{-1}s^{-1}$ and thus a large σ of 4.79×10^6 S/m at 300 K. The valence band along the Y-to-X direction is very flat and thus the large m^* greatly enhances the S. Therefore, the lowering of the E_f to the Y point by the p-type doping can result in high σ and S simultaneously, and thus a remarkable PF in CBN. In sharp contrast, in C₄BN, the valence bands along paths I and II are all very flat. Table I reveals that C₄BN has the larger deformation potential constant E_1 and elastic modulus C_{2D} than CBN. This is because C₄BN has a higher percentage of C-C covalent bonds, which makes the valence band edge states very localized. In C₄BN, the flat valence band leads

TABLE I. Hole effective mass m^* (m_0), deformation potential constant E_1 (eV), elastic modulus C_{2D} (N/m), and carrier mobility μ (cm²V⁻¹s⁻¹) at 300 K in CBN and C₄BN biphenylene.

Туре	Direction	m^*	$ E_1 $	C_{2D}	μ	
CBN	$X \to S$	0.69	0.88	246.61	9535.05	
	$X \to \Gamma$	1.38	3.72	204.95	205.47	
C ₄ BN	$\Gamma \to Y$	4.55	8.39	245.12	94.41	
	$\Gamma \to X$	1.85	4.23	270.00	1438.00	

to the large m^* and n simultaneously; e.g., the hole m^* is 4.55 m_0 along the Γ -to-Y direction. Because of the dominant contribution of m^* , the σ is low and the S is high, according to $\sigma = ne\mu$ and $S = 8\pi^2 k_B^2 m^* T [\pi/(3n)]^{2/3}/(3eh^2)$. Therefore, C₄BN has a smaller *PF* and thus a smaller *ZT* than CBN.

To explore why the peculiar funnel-shaped band structure is present in CBN not in C₄BN, we focus on the localization/delocalization of chemical bonds based on the electronic DOS and the spatial distributions of valence band edge states at different high-symmetry points, as plotted in Fig. 3. In CBN, the DOS near the E_f shares a unique steplike character, which usually prefers a large PF. This closely correlates with the strong hybridization between C-, B-, and $N-p_z$ orbitals, which form the delocalized π bonds at the X point. The different electronegativity introduces the strong ionicity into the π bonds, which pushes the energy level up and thus makes the VBM located at the X point. At the S point, the C-, C-, and B- p_7 orbitals form the delocalized π bonds and the strong covalency of C-C bonds significantly lowers the energy level with respect to the X point; thus the valence band near the E_f is much more dispersive between the S and X points. We further reveal that the $N-p_z$ orbital dominates the VBM state because of its high energy level (see Fig. 4) and the C- p_z orbital dominates the electronic state at the S point by projecting the C-, B-, and N- p_z orbitals into the valence band near the E_f . On the other hand, at the Y point, besides the delocalized π bonds formed by C-, C-, and B- p_z electrons, the N- and B- p_z orbitals form the localized π bonds; thus the Y point is in the energy range from the S to the X point. To check the effect of symmetry on the valence band edge states,



FIG. 4. Atomic orbital hybridization near the E_f in (a) CBN and (b) C₄BN biphenylene networks, where p_x , p_y , and p_z orbitals of C, B, and N atoms and symmetry are labeled.

we randomly select the W (0.078, 0.421, 0.000) between the X and Y points. The C- and C- p_z orbitals form the localized π bonds and so do the B- and N- p_z orbitals; thus the valence band near the E_f is relatively flat between the X and Y points, especially near the Y point, in CBN biphenylene.

The electronic DOS also confirms that, in C₄BN, the valence band near the E_f is dominated by the C- p_z orbital (see Fig. 3). At the typical S, X, and Y points, the C- and C- p_z orbitals form the localized π bonds and the N- p_z state is localized; thus the valence band near the E_f is very flat in the whole Brillouin zone. Figure 4 plots the band edge

- A. N. Enyashin and A. L. Ivanovskii, Phys. Status Solidi B 248, 1879 (2011).
- [2] X. L. Sheng, Q. B. Yan, F. Ye, Q. R. Zheng, and G. Su, Phys. Rev. Lett. **106**, 155703 (2011).
- [3] C. Sevik, A. Kinaci, J. B. Haskins, and T. Çağin, Phys. Rev. B 84, 085409 (2011).
- [4] M. Makaremi, S. Grixti, K. Butler, G. A. Ozin, and C. V. Singh, ACS Appl. Mater. Inter. 10, 11143 (2018).
- [5] Q. Fan, L. Yan, M. W. Tripp, O. Krejí, and J. M. Gottfried, Science 372, 852 (2021).
- [6] X. Yang, J. Wang, J. Zheng, M. Guo, and R. Zhang, J. Phys. Chem. C 124, 6379 (2020).
- [7] M. Liu, M. Liu, L. She, Z. Zha, J. Pan, S. Li, T. Li, Y. He, Z. Cai, J. Wang, Y. Zheng, X. Qiu, and D. Zhong, Nat. Commun. 8, 14924 (2017).

states and the relative positions of p_x , p_y , and p_z orbitals of C, B, and N atoms and Table S2 lists the irreducible representations of p_x , p_y , and p_z orbitals. The valence bands far away from the E_f are dominated by the σ bonds, which is consistent with the strong interatomic interaction, compared to the π bonds. Therefore, we can infer that, to make the funnel-shaped band structure available, the key is to tune the localization/delocalization of π bonds by properly controlling the carbon composition, which can result in the remarkable TE performance by improving σ and *S* simultaneously in $C_x(BN)_{1-x}$ biphenylene networks.

IV. CONCLUSIONS

In summary, inspired by the synthesis of carbon biphenylene and the properties induced by its metallic nature, we focus on two-dimensional $C_x(BN)_{1-x}$ biphenylene networks, which stabilize as CBN and C₄BN semiconductors via structural searches. Unexpectedly, the funnel-shaped band structure is present in CBN not in C₄BN. This band structure is distinct from the ideal pudding mold, but greatly improves the thermoelectric properties by enhancing the power factor, not by the usually ultralow lattice thermal conductivity, because of the small atomic masses. The four-phonon scattering plays a more dominant role in the thermal transport in C₄BN than in CBN because of the large carbon composition. Most importantly, we demonstrate how to tune the shape of the valence band near the Fermi level based on the delocalization/localization of π bonds by controlling the alloy composition. Therefore, it is promising to design the specified-shaped band structure in other biphenylene networks to achieve the desired thermal transport and thermoelectric performance.

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- [8] D.-B. Zhang, E. Akatyeva, and T. Dumitrică, Phys. Rev. Lett. 106, 255503 (2011).
- [9] I. Nikiforov, E. Dontsova, R. D. James, and T. Dumitrică, Phys. Rev. B 89, 155437 (2014).
- [10] T. Dumitrica, M. Hua, and B. I. Yakobson, Proc. Natl. Acad. Sci. USA 103, 6105 (2006).
- [11] T. Dumitrică and B. I. Yakobson, Appl. Phys. Lett. 84, 2775 (2004).
- [12] Z. Tong, A. Pecchia, C. Yam, T. Dumitrică, and T. Frauenheim, Adv. Energy Mater. 12, 2200657 (2022).
- [13] H. Wang, G. Qin, Z. Qin, G. Li, Q. Wang, and M. Hu, J. Phys. Chem. Lett. 9, 2474 (2018).
- [14] K. Zhao, Y. Guo, Y. Shen, Q. Wang, Y. Kawazoe, and P. Jena, J. Phys. Chem. Lett. 11, 3501 (2020).
- [15] Y. Liu, G. Wang, Q. Huang, L. Guo, and X. Chen, Phys. Rev. Lett. 108, 225505 (2012).

- [16] J. Deb, D. Paul, and U. Sarkar, J. Phys. Chem. A 124, 1312 (2020).
- [17] P.-F. Liu, J. Li, C. Zhang, X.-H. Tu, J. Zhang, P. Zhang, B.-T. Wang, and D. J. Singh, Phys. Rev. B 104, 235422 (2021).
- [18] X. Gu, Y. Wei, X. Yin, B. Li, and R. Yang, Rev. Mod. Phys. 90, 041002 (2018).
- [19] P. Rosenzweig, H. Karakachian, D. Marchenko, K. Küster, and U. Starke, Phys. Rev. Lett. 125, 176403 (2020).
- [20] Z. Tong, A. Pecchia, C. Yam, H. Bao, T. Dumitrică, and T. Frauenheim, Adv. Funct. Mater. 32, 2111556 (2022).
- [21] Y. Xiao, Z. Wang, L. Shi, X. Jiang, S. Li, and L. Wang, Sci. China Phys. Mech. 63, 277312 (2020).
- [22] M. A. Hudspeth, B. W. Whitman, V. Barone, and J. E. Peralta, ACS Nano 4, 4565 (2010).
- [23] S. Demirci, Ş. Çallıoğlu, T. Görkan, E. Aktürk, and S. Ciraci, Phys. Rev. B 105, 035408 (2022).
- [24] S. Nehate, A. Saikumar, A. Prakash, and K. Sundaram, Mater. Today Adv. 8, 100106 (2020).
- [25] Y. Wu, Y. Chen, C. Ma, Z. Lu, H. Zhang, B. Mortazavi, B. Hou, K. Xu, H. Mei, T. Rabczuk, H. Zhu, Z. Fang, R. Zhang, and C. M. Soukoulis, Phys. Rev. Mater. 4, 064001 (2020).
- [26] A. Bafekry, M. Naseri, M. M. Fadlallah, I. Abdolhosseini Sarsari, M. Faraji, A. Bagheri Khatibani, M. Ghergherehchi, and D. Gogova, J. Appl. Phys. 130, 114301 (2021).
- [27] B. Mortazavi, F. Shojaei, M. Yagmurcukardes, A. V. Shapeev, and X. Zhuang, Carbon 200, 500 (2022).
- [28] Z. Tang, G. J. Cruz, Y. Wu, W. Xia, F. Jia, W. Zhang, and P. Zhang, Phys. Rev. Appl. 17, 034068 (2022).
- [29] H. Chakraborty, S. Mogurampelly, V. K. Yadav, U. V. Waghmare, and M. L. Klein, Nanoscale 10, 22148 (2018).
- [30] I. Jo, M. T. Pettes, J. Kim, K. Watanabe, T. Taniguchi, Z. Yao, and L. Shi, Nano Lett. 13, 550 (2013).
- [31] B. Mortazavi, Carbon 182, 373 (2021).
- [32] H. Zhang, X. Zhang, G. Yang, and X. Zhou, J. Phys. Chem. C 122, 5291 (2018).
- [33] C. Rudderham and J. Maassen, Phys. Rev. B 103, 165406 (2021).
- [34] K. Biswas, J. He, I. D. Blum, C.-I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, and M. G. Kanatzidis, Nature (London) 489, 414 (2012).
- [35] J. P. Heremans, V. Jovovic, E. S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, and G. J. Snyder, Science 321, 554 (2008).
- [36] D. Wu, X.-H. Cao, P.-Z. Jia, Y.-J. Zeng, Y.-X. Feng, L.-M. Tang, W.-X. Zhou, and K.-Q. Chen, Sci. China Phys. Mech. 63, 276811 (2020).
- [37] G. Yang, Q. Yu, H. Geng, and Y. Wang, Sci. China Phys. Mech. 63, 217321 (2020).
- [38] T. Yue, Y. Sun, Y. Zhao, S. Meng, and Z. Dai, Phys. Rev. B 105, 054305 (2022).
- [39] T. Yue, P. Sui, Y. Zhao, J. Ni, S. Meng, and Z. Dai, Phys. Rev. B 105, 184304 (2022).
- [40] G. J. Snyder and E. S. Toberer, Nat. Mater. 7, 105 (2008).
- [41] H. Liang, H. Zhong, S. Huang, and Y. Duan, J. Phys. Chem. Lett. 12, 10975 (2021).
- [42] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, Nano Lett. 8, 902 (2008).

- [43] B. C. Sales, D. Mandrus, and R. K. Williams, Science 272, 1325 (1996).
- [44] H. Liang and Y. Duan, Chin. Phys. B 31, 076301 (2022).
- [45] R. Guo, X. Wang, Y. Kuang, and B. Huang, Phys. Rev. B 92, 115202 (2015).
- [46] L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and M. G. Kanatzidis, Nature (London) 508, 373 (2014).
- [47] H. Ma, C. Li, S. Tang, J. Yan, A. Alatas, L. Lindsay, B. C. Sales, and Z. Tian, Phys. Rev. B 94, 220303(R) (2016).
- [48] J. Kim, D. A. Evans, D. P. Sellan, O. M. Williams, E. Ou, A. H. Cowley, and L. Shi, Appl. Phys. Lett. 108, 201905 (2016).
- [49] T. Feng, L. Lindsay, and X. Ruan, Phys. Rev. B 96, 161201(R) (2017).
- [50] C. W. Glass, A. R. Oganov, and N. Hansen, Comput. Phys. Commun. 175, 713 (2006).
- [51] A. O. Lyakhov, A. R. Oganov, H. T. Stokes, and Z. Qiang, Comput. Phys. Commun. 184, 1172 (2013).
- [52] L. A. Burns, A. V. Mayagoitia, B. G. Sumpter, and C. D. Sherrill, J. Chem. Phys. 134, 084107 (2011).
- [53] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [54] J. Hafner, J. Comput. Chem. 29, 2044 (2008).
- [55] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
- [56] G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).
- [57] Y. Wang, S. L. Shang, H. Fang, Z. K. Liu, and L. Q. Chen, Npj Comput. Mater. 2, 16006 (2016).
- [58] W. Li, J. Carrete, N. A. Katcho, and N. Mingo, Comput. Phys. Commun. 185, 1747 (2014).
- [59] Z. Han, X. Yang, W. Li, T. Feng, and X. Ruan, Comput. Phys. Commun. 270, 108179 (2022).
- [60] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.107.045422 for more details on the computational details of four-phonon scattering, structural parameters, phonon spectrums, first-principles molecular dynamic simulations, figure of merit, and power factor.
- [61] G. Madsen and D. J. Singh, Comput. Phys. Commun. 175, 67 (2006).
- [62] K. Mori, H. Sakakibara, H. Usui, and K. Kuroki, Phys. Rev. B 88, 075141 (2013).
- [63] K. Kuroki and R. Arita, J. Phys. Soc. Jpn. 76, 083707 (2007).
- [64] H. Usui, K. Suzuki, K. Kuroki, S. Nakano, K. Kudo, and M. Nohara, Phys. Rev. B 88, 075140 (2013).
- [65] J. Bardeen and W. Shockley, Phys. Rev. 80, 72 (1950).
- [66] H. Lang, S. Zhang, and Z. Liu, Phys. Rev. B 94, 235306 (2016).
- [67] J. E. Peralta, J. Heyd, G. E. Scuseria, and R. L. Martin, Phys. Rev. B 74, 073101 (2006).
- [68] H. Liang and Y. Duan, Nanoscale 13, 11994 (2021).
- [69] Y. Duan, L. Qin, L. Shi, G. Tang, and H. Shi, Appl. Phys. Lett. 100, 022104 (2012).
- [70] S. S. Naghavi, J. He, Y. Xia, and C. Wolverton, Chem. Mater. 30, 5639 (2018).
- [71] Z. Gao and J.-S. Wang, ACS Appl. Mater. Inter. **12**, 14298 (2020).
- [72] S. Ju, T. Shiga, L. Feng, and J. Shiomi, Phys. Rev. B 97, 184305 (2018).
- [73] Y. Xiao and L.-D. Zhao, Npj Quantum Mater. 3, 55 (2018).
- [74] G. Slack, J. Phys. Chem. Solids 34, 321 (1973).