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Revealing the Roles of In-Plane and Out-of-Plane van der Waals Interactions in Modulating the Dimension-Dependent Ground- and Excited-State Properties of Quasi-1D Zigzag COFs

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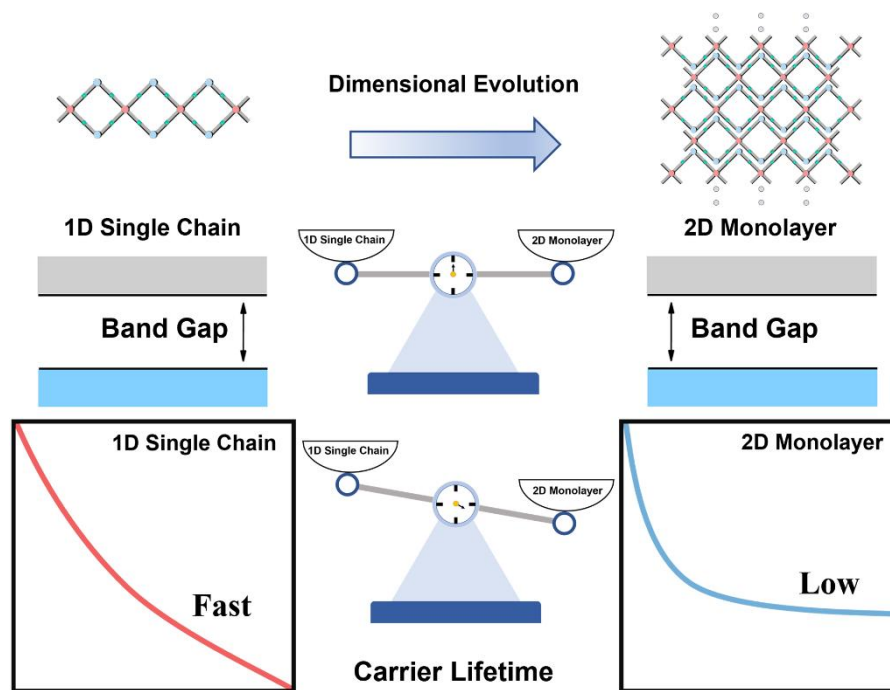
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Abstract

Van der Waals (vdW) interactions dictate the properties of low-dimensional materials, yet the role of in-plane interactions, and especially the synergy between in-plane and out-of-plane vdW forces, remains largely unexplored. Using first-principles and nonadiabatic molecular dynamics calculations on quasi-one-dimensional porphyrin COFs with zigzag boundary, we show how these dual vdW interactions modulate structural, electronic, and excited-state properties. In-plane vdW interactions minimally impact ground-state structures but suppress low-frequency vibrations and decrease nonadiabatic coupling due to the unique zigzag interface, extending the excited-state lifetime from 2.1 ns (1D) to 21.3 ns (2D). This behavior persists in other quasi-1D systems with identical interfaces but vanishes in configurations featuring non-zigzag interfaces. **In the 3D architecture, distinct stacking modes lead to marked variations in interlayer coupling strength, tuning the lifetime from 2.7 to 29.6 ns.** This work unravels the complex correlation between in-plane/out-of-plane vdW interactions, establishing critical design principles for tailored low-dimensional vdW materials.

Keywords: Van der Waals interactions, Quasi-one-dimensional, Covalent organic frameworks, Excited-state dynamics, Dimensional dependence.

TOC



■ INTRODUCTION

Low-dimensional quantum materials exhibit unique physical properties, such as tunable electronic band structures and excitonic effects that establish them as a key platform for exploring novel quantum effects and developing next-generation optoelectronic devices.¹⁻³ Van der Waals (vdW) materials, in particular, occupy a central role due to their distinctive structural characteristics of strong in-plane covalent/coordination bonds and weak out-of-plane vdW interactions.^{4, 5} This bonding anisotropy not only enables the mechanical exfoliation of monolayer or few-layer materials but also facilitates the design of tailored vdW heterojunctions.⁶ Representative examples include graphene,⁷ transition metal dichalcogenides,⁸ black phosphorus,⁹ two-dimensional (2D) metal-organic frameworks and covalent organic frameworks (COFs).¹⁰⁻¹² As research advances, a series of groundbreaking quantum phenomena and optoelectronic properties, such as various topological Hall effects, strongly correlated states in moiré superlattices, and long-lived interlayer excitons, have been discovered.¹³⁻¹⁹ These findings demonstrate that vdW interactions serve as a key tunable degree of freedom to actively govern the quantum and optoelectronic behavior of materials.

Weak vdW forces profoundly influence the interlayer coupling strength, charge distribution, and band structure of materials,²⁰⁻²⁴ while also modulating the anisotropic transport properties and isotropic optical responses.²⁵ **Consequently, the ability to engineer interlayer vdW coupling for precise control over the electronic and optical**

properties of 2D materials has emerged as a critical capability for designing next-generation quantum materials, driving the development of two main tuning strategies.²⁶⁻

³¹ However, a comprehensive understanding of the systematic control of vdW interactions and their underlying microscopic mechanisms remains limited. To date, prevailing research has predominantly focused on either interlayer stacking modulations or interfacial coupling effects in heterostructures.³²⁻³⁵ Consequently, the critical role of in-plane interactions remains largely overlooked. In particular, there is a conspicuous lack of systematic investigation into the synergistic and competitive interplay between in-plane and out-of-plane interactions, as well as how this intricate interplay governs the material's electronic structures and excited-state dynamics.

Quasi-one-dimensional (quasi-1D) COFs, as a new type of COF system with zigzag boundaries, have drawn extensive attention since they were first synthesized in 2019 due to their unique structural architectures.^{36, 37} Because they inherently integrate in-plane and out-of-plane vdW interactions to assemble the “1D ribbon-like” chains, this system offers an ideal platform to investigate the synergistic effects.³⁸ Crucially, the zigzag chain configuration yields a highly advantageous interfacial alignment for in-plane, interchain polymerization. Herein, we select the TAPP-PDA COF, experimentally synthesized from tetra-(4-aminophenyl)-porphyrin (TAPP) and 2,6-pyridinedialdehyde (PDA),³⁹⁻⁴¹ as the primary model (Figure 1). For validation, the TFPP-DAPB with a similar structure,⁴² is employed as a reference system. Integrating first-principles calculations with nonadiabatic molecular dynamics (NAMD) simulations, we systematically elucidate how in-plane and out-of-plane vdW

interactions synergistically modulate electronic structures and excited-state dynamics. Surprisingly, at the static electronic level, in-plane vdW interactions induce negligible bandgap variations in both 1D chains and 2D monolayer of TAPP-PDA. Similarly, 3D stacking leads to only a slight bandgap narrowing, a feature that sharply contrasts with conventional vdW materials possessing strong quantum confinement effects.⁴³

What is even more intriguing, however, is that these in-plane vdW interactions provoke a striking disparity in their excited-state dynamics: the carrier lifetime in the 2D monolayer is significantly prolonged to 21.3 ns, representing a tenfold enhancement compared to that of the 1D single chain (2.1 ns). Such a pronounced difference in excited-state dynamics primarily originates from the interchain vdW interactions governed by the zigzag interface within the 2D architecture, which effectively suppress atomic vibrations and thereby result in a weakened electron-phonon (*e-ph*) coupling. This trend is not only successfully reproduced in the reference TFPP-DAPB COF, but also consistently observed in another quasi-1D system with zigzag interface, poly(carbon nitride) (PCN, composed of s-triazine units).⁴⁴ In contrast, the significant difference in excited-state dynamics disappears in the black phosphorus nanoribbons (BPNRs) system without the zigzag interface,⁴⁵ further demonstrating how interfacial geometry governs *e-ph* coupling in quasi-1D systems. This study elucidates how dimensionality-dependent vdW interactions, particularly along the in-plane direction with zigzag interface, govern the physicochemical properties of the materials, providing atomic-scale theoretical guidance for the rational design of low-dimensional photocatalytic and optoelectronic systems.

■ RESULTS

Structure and Stability of Quasi-1D COFs

Figure 1a,b illustrate the strategy for constructing quasi-1D COFs. Specifically, the 1D chains are initially formed through the co-condensation of X-shaped nodes (X1=TAPP, X2=TFPP) and V-shaped linkers (V1=PDA, V2=DAPB), after which noncovalent interactions maintain the orderly stacking of the structure along the perpendicular 2D and 3D directions.⁴⁶ The distinct zigzag conformation of the 1D chains exposes abundant boundary sites, thereby expanding the possibilities for highly efficient in-plane self-assembly. As presented in Figure 1c, by systematically constructing structures ranging from 1D single-chain (1D-1C) to 1D double-chain (1D-2C), 1D triple-chain (1D-3C), 2D monolayer, and ultimately fully extended 3D bulk frameworks, we investigate the synergistic effects of in-plane and out-of-plane vdW interactions. The optimized lattice constants of 2D TAPP-PDA ($a = 21.45 \text{ \AA}$, $b = 41.67 \text{ \AA}$) are in excellent agreement with previously reported values.³⁹ The parameters of the other structures are summarized in Table S1 in the Supporting Information.

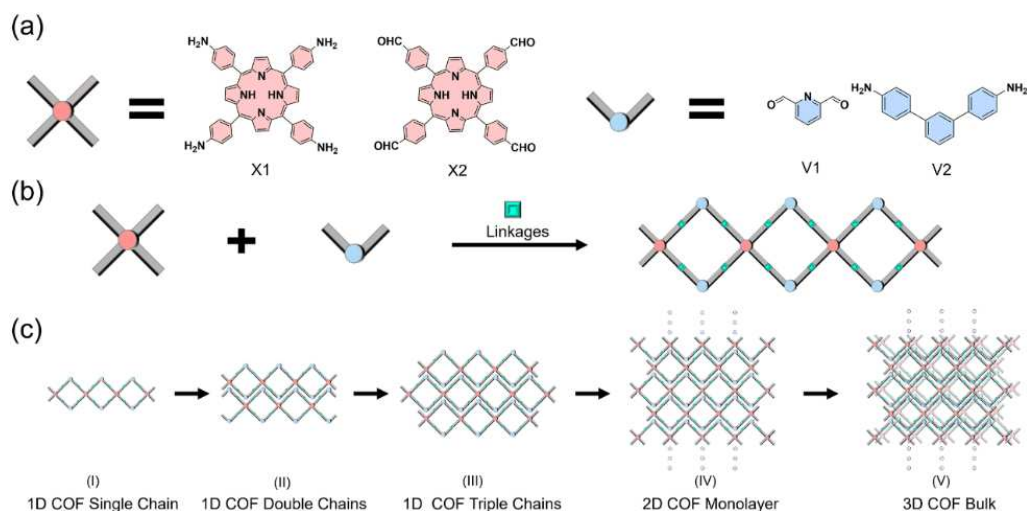


Figure 1. (a) Schematic structures of X-shaped nodes (X1=TAPP, X2=TFPP) and V-shaped linkers (V1=PDA, V2=DAPB). (b) 1D covalent chains composed of X-shaped and V-shaped building units. (c) Schematic illustration of the assembly for COF structures from a 1D-1C (I), 1D-2C (II), 1D-3C (III), 2D monolayer (IV), and to fully extended 3D bulk (V).

Following geometric optimization (Figure 2), the shortest interatomic distance between adjacent chains gradually decreases from 7.06 Å in the 1D-2C (Figure 2b) to 6.63 Å in the 1D-3C (Figure 2c), and ultimately reaches 6.61 Å in the 2D monolayer (Figure 2d) structure, indicating that increasing chain number strengthens interchain vdW interactions. Interestingly, the in-plane interchain distance reduces to 3.87 Å in the 3D bulk structure (Figure 2e), while the out-of-plane interlayer distance is maintained at 4.04 Å. Meanwhile, the in-plane molecular chains slide against each other to relieve steric hindrance, thereby allowing the 3D framework to achieve optimal thermodynamic stability. These structural changes reflect the counterbalance between interlayer vdW forces and in-plane steric constraints during COF assembly.⁴⁷ Evidently, such a large interchain distance signifies that vdW interactions, rather than hydrogen bonding, play the predominant role in stabilizing the 1D COF chains within the in-plane direction. As shown in Figure S1, the calculated binding energies are -13.41, -28.26, and -26.26 meV in the 1D-2C, 1D-3C, and 2D TAPP-PDA, respectively. Concurrently, the interlayer spacing in the 3D AA-stacked system indicates the predominance of out-of-plane π - π stacking interactions with a binding energy of -8.64 eV. Besides, the thermal stability of these quasi-1D COFs has also been validated by the AIMD

simulations (see Section S1 and Figure S2). Collectively, these findings demonstrate that our selected quasi-1D COF system serves as an efficacious vehicle for investigating the underlying mechanisms of vdW interactions.

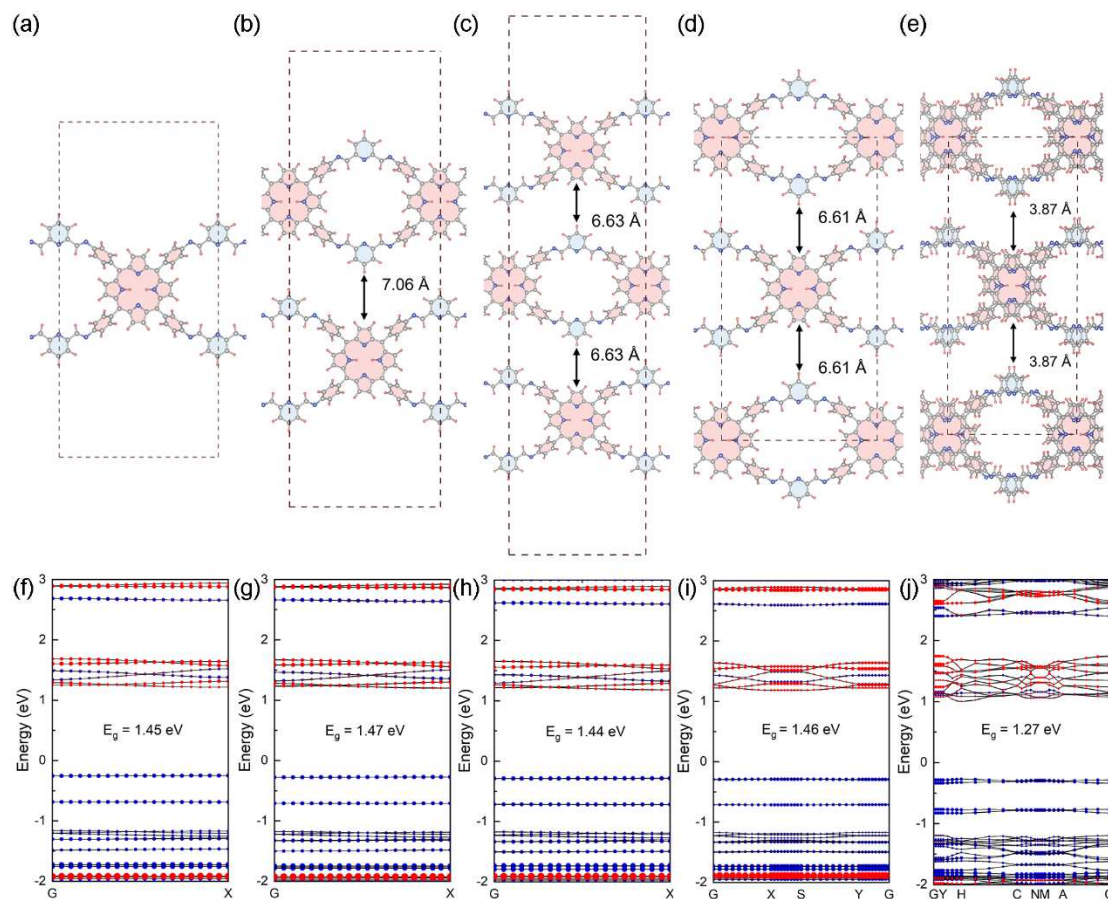


Figure 2. Upper panel: Optimized geometric structures of (a) 1D-1C, (b) 1D-2C, (c) 1D-3C, (d) 2D monolayer (2D), and (e) 3D TAPP-PDA, where the H, C, and N atoms are represented by pink, gray, and blue spheres, respectively. Lower panel: Band structures of (f) 1D-1C, (g) 1D-2C, (h) 1D-3C, (i) 2D, and (j) 3D TAPP-PDA, respectively. The blue and red dots represent the contributions of atoms in TAPP units and PDA units, respectively.

Evolution of Electronic Structures with Dimensionality in Quasi-1D COFs

The influence of vdW interactions on the electronic structure were further investigated. First, we calculated the band structure and projected charge density for the TAPP-PDA systems across different dimensions. As shown in Figure 2f-j, all the TAPP-PDA configurations exhibit direct bandgap semiconductor characteristics. For the 1D single, double, and triple chains, both the valence band maximum (VBM) and conduction band minimum (CBM) are localized at the Gamma point, yielding direct bandgaps of 1.45 eV, 1.47 eV, and 1.44 eV, respectively. Surprisingly, the bandgap increases by merely 0.02 eV in the 2D monolayer, demonstrating that large interchain distances confine electronic transitions intra-chain, thereby rendering the band structure unaffected by the stabilizing vdW interactions. The charge density distribution, Bader charge analysis, and projected density of states (PDOS) further confirm that the large vdW separation affects the electronic overlap between adjacent chains to be insufficient to change the fundamental electronic structure that is dominated by the intrachain covalent network, yielding the almost invariant bandgaps (Section S2 and Figures S3-S5).

A similar phenomenon is also observed during the transition from the 2D monolayer to the 3D bulk structure, where the bandgap of the TAPP-PDA decreases marginally from 1.46 eV to 1.27 eV. This reduction is attributed to the structural variations and interlayer electronic coupling due to the unique synergy between the in-plane and out-of-plane interactions within these quasi-1D COFs (Section S3 and Figure S6). This synergy alleviates the confinement required to hold these ribbon-like chains

in the vertical direction, resulting in an interlayer distance of 4.04 Å, which is significantly larger than that of traditional vdW materials.⁴⁸ Consequently, the electron motion is highly restricted along the out-of-plane direction, thereby weakening the interlayer quantum confinement effect in the quasi-1D TAPP-PDA.^{49, 50} The bandgaps obtained from the more accurate HSE06 hybrid functional successfully reproduce the same trend of negligible bandgap variation (Table S2). Moreover, the reference TFPP-DAPB COF exhibits the same feature of dimensional resilience (Figures S7 and S8). Crucially, the insensitivity of the electronic structure to dimensionality significantly lowers the stringency of material synthesis and facilitates broader practical applications.

Evolution of Excited-state Dynamics with Dimensionality in Quasi-1D COFs

The excited-state dynamics of charge carriers plays a pivotal role in dictating device performance. In non-radiative carrier recombination, the specific vibrational modes coupled with the lattice forces inherently determine the strength of *e-ph* coupling, which subsequently governs the carrier dynamical evolution rates. To elucidate the underlying mechanisms of in-plane and out-of-plane vdW interactions in modulating these excited-state carrier dynamics within quasi-1D COFs, we employ NAMD simulations to investigate the recombination processes of single chains, as well as 2D and 3D TAPP-PDA COFs. The lifetime (τ) of the excited-state carrier is determined by fitting the time-dependent population decay curves with the exponential function $f(t) = \exp(-t/\tau)$.⁵¹

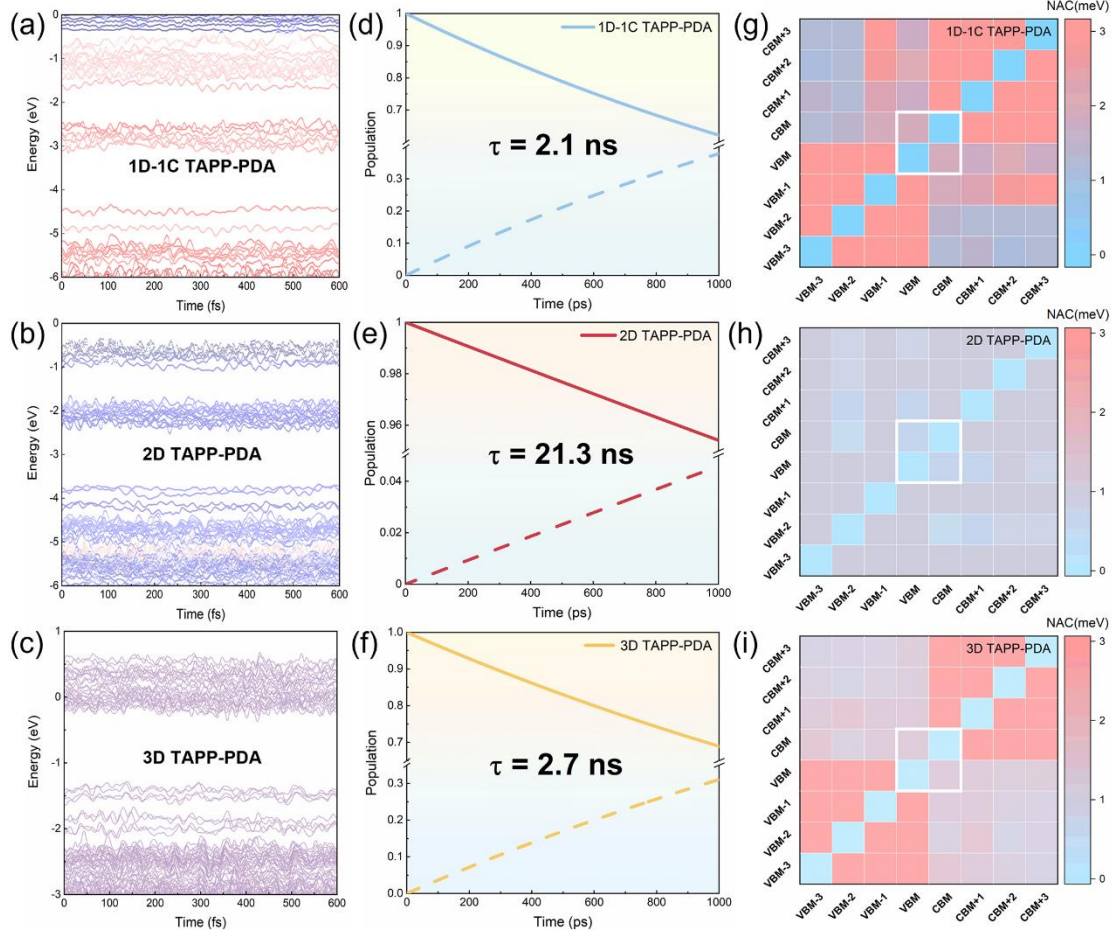


Figure 3. The time evolution of the energy levels at the Γ point close to the CBM and VBM in (a) 1D-1C, (b) 2D, and (c) 3D TAPP-PDA, respectively. Excited-state and ground-state populations of (d) 1D-1C, (e) 2D, and (f) 3D TAPP-PDA, respectively. Nonadiabatic coupling hotspot maps for the (g) 1D-1C, (h) 2D, and (i) 3D TAPP-PDA, respectively.

The energy levels of both the 1D-1C TAPP-PDA (Figure 3a) and the 2D TAPP-PDA (Figure 3b) exhibit excellent stability without significant fluctuation throughout the NAMD simulations. The average bandgaps are 1.44 eV and 1.40 eV for the 1D-1C and 2D systems, respectively (Table 1), which closely match their ground-state counterparts. The alignment indicates that the in-plane vdW interactions can effectively

maintain the electronic structures in the presence of the thermal disturbance. Intriguingly, the excited-state carrier dynamics of the two systems are completely opposite, in spite of both having a similar electronic stability. Figure 3d clearly illustrates that the excited-state carrier lifetime in the 1D-1C is 2.1 ns, whereas it is significantly prolonged to 21.3 ns in the 2D TAPP-PDA (Figures 3e and S9), representing a tenfold increase. These findings suggest that the interchain vdW interactions may affect the lattice vibrations, and hence potentially modulate the relaxation modes and lifetimes of the excited-state carriers.

To elucidate the origin of this significant lifetime prolongation in the 2D configuration, we analyzed the dimensional evolution of the nonadiabatic coupling (NAC) between the CBM and the VBM. According to the nonadiabatic transition theory, the NAC matrix element d_{jk} is defined as ⁵²:

$$d_{jk} = \langle \varphi_j | \frac{\partial}{\partial t} | \varphi_k \rangle = \sum_I \frac{\langle \varphi_j | \nabla_{R_I} H | \varphi_k \rangle}{\varepsilon_k - \varepsilon_j} \cdot \dot{R}_I \quad (1)$$

where the $\langle \varphi_j | \frac{\partial}{\partial t} | \varphi_k \rangle$ represents the time-dependent wavefunction overlap between different adiabatic states, $\varepsilon_k - \varepsilon_j$ denotes the energy gap between the adiabatic Kohn-Sham states j and k , and $\dot{R}_I$ represents the velocity of the atomic nuclei. As captured in the NAC heatmaps (Figure 3g,h and Table 1), a drastic reduction in the coupling magnitude is clearly observed upon dimensional expansion. Specifically, for the critical VBM-to-CBM transition, the average NAC value in the 1D-1C TAPP-PDA is as high as 1.95 meV. In contrast, the NAC value decreases sharply to 0.64 meV after assembling into the 2D structure. This approximately three-fold reduction of NAC magnitude

provides a compelling explanation for the suppressed non-radiative electron-hole (e-h) recombination in the 2D configuration.

Table 1. Average Band Gaps, NAC, Decoherence Times, and Carrier Lifetimes of 1D, 2D TAPP-PDA, TFPP-DAPB, PCN, BPNRs, and 3D TAPP-PDA, respectively.

System	Band gap (eV)	NAC (meV)	Lifetime (ns)	Decoherence time (fs)
1D-1C TAPP-PDA	1.44	1.95	2.1	9.5
2D TAPP-PDA	1.40	0.64	21.3	21.3
3D TAPP-PDA	1.17	1.37	2.7	18.5
1D-1C TFPP-DAPB	1.51	1.77	4.2	12.4
2D TFPP-DAPB	1.51	0.79	10.4	17.5
1D-1C PCN	2.39	2.30	8.9	15.1
2D PCN	2.46	0.92	35.8	16.9
1D-1C BPNR	0.94	0.97	1.6	4.1
2D BPNR	0.86	0.67	1.9	4.3

Mathematically, the magnitude of d_{jk} is proportional to both the electronic Hamiltonian gradient ($\nabla_{R_j} H$) and the nuclear velocity ($\dot{R}_I$), and inversely proportional to the energy gap $\varepsilon_k - \varepsilon_j$. In addition, dynamical evolution behaviors of the energy gap, which are mediated by specific lattice vibration modes, also play a key role in determining the NAC matrix elements. Obviously, all these parameters are intimately correlated with the dynamical structural fluctuations of the systems. As illustrated in Figure 4a, the 1D-1C exhibited significant fluctuations in root-mean-square deviation (RMSD) during the simulation, whereas the 2D structure exhibited weaker local fluctuations and higher structural stability, which stems from the in-plane vdW

constraints at the zigzag interfaces that suppress skeletal deformation (Figure S2a, d). Conversely, the more pronounced RMSD fluctuations observed in the 1D-1C TAPP-PDA imply higher average nuclear velocities ($\dot{R}_I$), which will accelerate the recombination of e-h pairs.

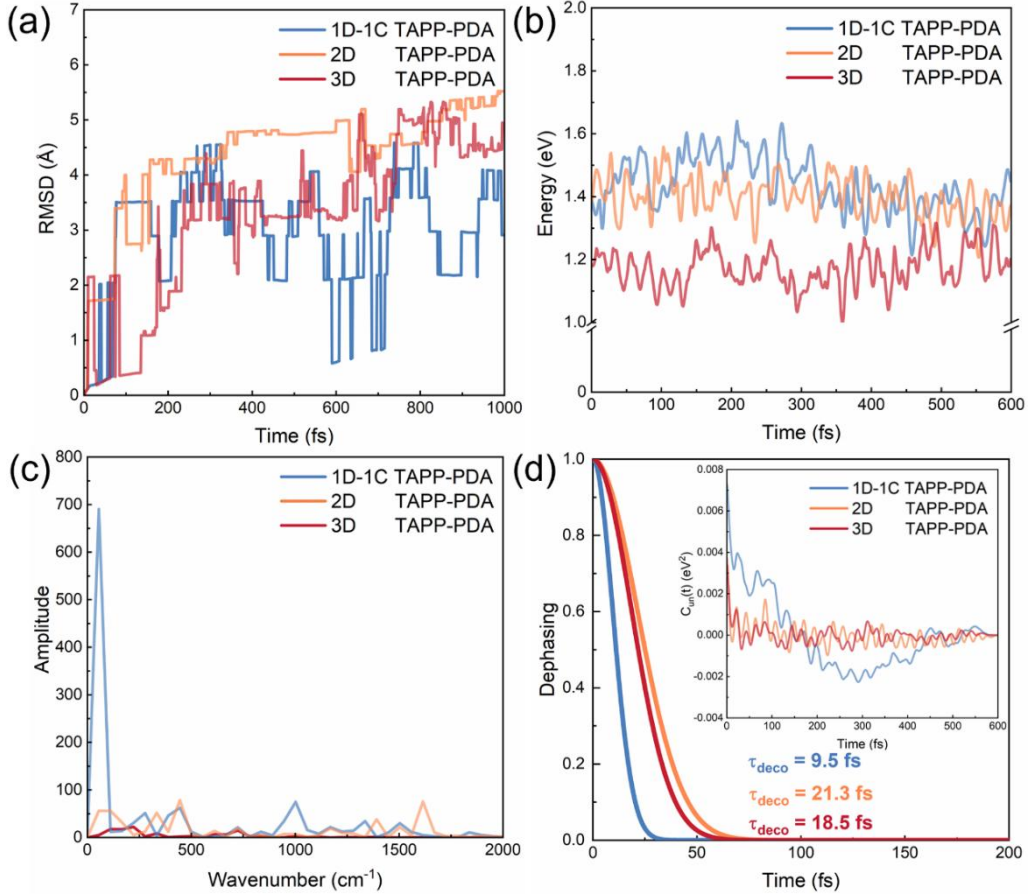


Figure 4. (a) Dynamic evolutions of the RMSD and (b) fluctuations of the energy gaps along the NAMD trajectories at 300 K. The blue, orange, and red curves represent the 1D-1C, 2D, and 3D TAPP-PDA, respectively. (c) Fourier-transformed vibrational spectra and (d) pure-dephasing functions of 1D-1C, 2D, and 3D TAPP-PDA, respectively. The insets show the ACFs of the VBM-CBM energy gap fluctuations.

Subsequently, the spatial overlap between the electron and hole wavefunctions, another decisive factor governing the electronic transition matrix element, was further

explored. As illustrated in Figure S10, for both the 1D-1C and 2D TAPP-PDA systems, the CBM charge is extensively distributed across both the TAPP and PDA units, while the VBM charge is predominantly localized on the TAPP units. Intriguingly, the spatial overlap between the CBM and VBM in the 2D TAPP-PDA remains visibly smaller than that in the 1D-1C TAPP-PDA throughout the dynamic evolution. The delocalization of charge caused by weak interchain interactions leads to significant differences in the overlap of the spatial wave functions, which directly suppresses the amplitude of the NAC in 2D systems.

The dynamical variance (instantaneous values and time evolution patterns) of the energy gap is also expected to modulate the *e-ph* coupling, thereby altering the relaxation behaviors of the excited-state carriers. In the single-chain system, stronger lattice vibrations result in a larger amplitude of bandgap fluctuations (1.21–1.64 eV), whereas the bandgap of the 2D structure fluctuates within the range of 1.20–1.55 eV (Figure 4b). In addition, these two systems also exhibit distinctly different trends in their temporal evolution. The Fourier-transformed vibrational spectra of the energy gaps directly illustrate this dynamic phenomenon (Figure 4c). For the 1D-1C TAPP-PDA, the lack of spatial confinement triggers pronounced out-of-plane vibrational modes, as evidenced by an intensely sharp peak at 100 and 1000 cm^{-1} . Conversely, the 2D TAPP-PDA shows a suppressed low-frequency response, yet features a prominent peak near 1600 cm^{-1} attributed to in-plane interchain vibrations. Such a spectral shift corroborates that, even with weak in-plane vdW interactions, the zigzag interface of the 2D structure efficiently locks low-frequency structural fluctuations. This conclusion is

further validated by subsequent investigations into counterpart systems devoid of the zigzag boundary. Consequently, the suppression of these large-amplitude, low-frequency skeletal movements effectively weakens the *e-ph* coupling, thereby minimizing the NAC matrix elements and extending the excited-state lifetime.

In addition to the NAC, quantum decoherence serves as the other competitive factor governing the excited-state dynamics. As illustrated in Figure 4d, the 1D-1C TAPP-PDA exhibits an ultra-fast decoherence time (τ_{deco}) of 9.5 fs. The autocorrelation function (ACF) reveals large-amplitude fluctuations, reflecting how the intense, unconstrained structural distortions in the 1D limit rapidly destroy the quantum phase coherence between the VBM and CBM. In contrast, the 2D TAPP-PDA displays a significantly prolonged τ_{deco} of 21.3 fs, with its ACF exhibiting sustained, smaller-amplitude oscillations that confirm the effective restriction of energy gap fluctuations by the in-plane vdW constraints. Obviously, the non-radiative decay process here is clearly dictated by the suppression of *e-ph* coupling, which offsets the counteractive influence of the prolonged quantum coherence. **Consequently, this suppressed NAC emerges as the dominant driver for the order-of-magnitude enhancement in the excited-state carrier lifetime, a trend further supported by NAMD simulations at 100 K (Section S4 and Figures S11, S12).⁵³**

For the AA-stacked 3D architecture, intensified vdW interactions restrict lattice vibrations, as shown in the Fourier-transform vibrational spectra (Figure 4c). **Although reduced vibrational damping typically weakens *e-ph* coupling and extends carrier lifetimes, this AA system yields a lifetime of only 2.7 ns, barely exceeding that of the**

single chain (1D-1C) and falling far short of the 2D value. NAMD simulations reveal the microscopic origin: strong out-of-plane electronic coupling in the 3D framework enhances CBM–VBM wavefunction overlap (Figure S13), raising the NAC coefficient (1.37 meV) and shortening decoherence time (18.5 fs) to match single-chain levels. Consequently, out-of-plane interlayer coupling dominates over in-plane interactions, opening extra non-radiative decay pathways that accelerate charge relaxation. Conversely, alternative stacking modes display distinctly different excited-state dynamics. Translating the top layer of the AA pattern by 0.5 and 0.25 unit cells along the x- and y-axes yields TAPP-PDA-X and TAPP-PDA-Y (Figure S14a,b), with carrier lifetimes of 6.1 ns and 29.6 ns (Figure S15c), respectively. Remarkably, e–h recombination in 3D TAPP-PDA-Y is even slower than in the 2D structure. This occurs because its 1D chains align with the interchain gaps of adjacent layers, significantly weakening interlayer coupling (NAC = 0.44 meV). Thus, suppressing out-of-plane factors via ultrathin 2D COF fabrication or stacking pattern engineering represents a highly effective strategy to prolong carrier lifetimes. A similar dimensionality-dependent evolution of excited-state dynamics was observed in the quasi-1D TFPP-DAPB COF (Table 1, Section S5 and Figure S16). Furthermore, the correlations among vdW interaction strengths, lattice vibrations, *e-ph* coupling, and excited-state lifetimes have been systematically discussed (Section S6).

Dimensionality and Interface Dependence of Quasi-1D PCN and BPNRs

To further verify the universality of this dimension-resilient electronic behavior, we extended our computational framework to another representative quasi-1D system

with zigzag interface, polymeric carbon nitride (PCN).⁵⁴ As illustrated in Figures 5a and S17, hydrogen bonding and vdW interactions collectively drive chain assembly, yielding much shorter interchain separations (1.93-2.14 Å) and stronger interchain coupling (binding energies from -1.85 to -3.92 eV) than quasi-1D COFs. This implies that not only weak vdW forces, but even stronger in-plane noncovalent interactions such as hydrogen bonding, fail to fundamentally alter the intrinsic electronic properties dictated by the covalent chain backbone (Figure S18).

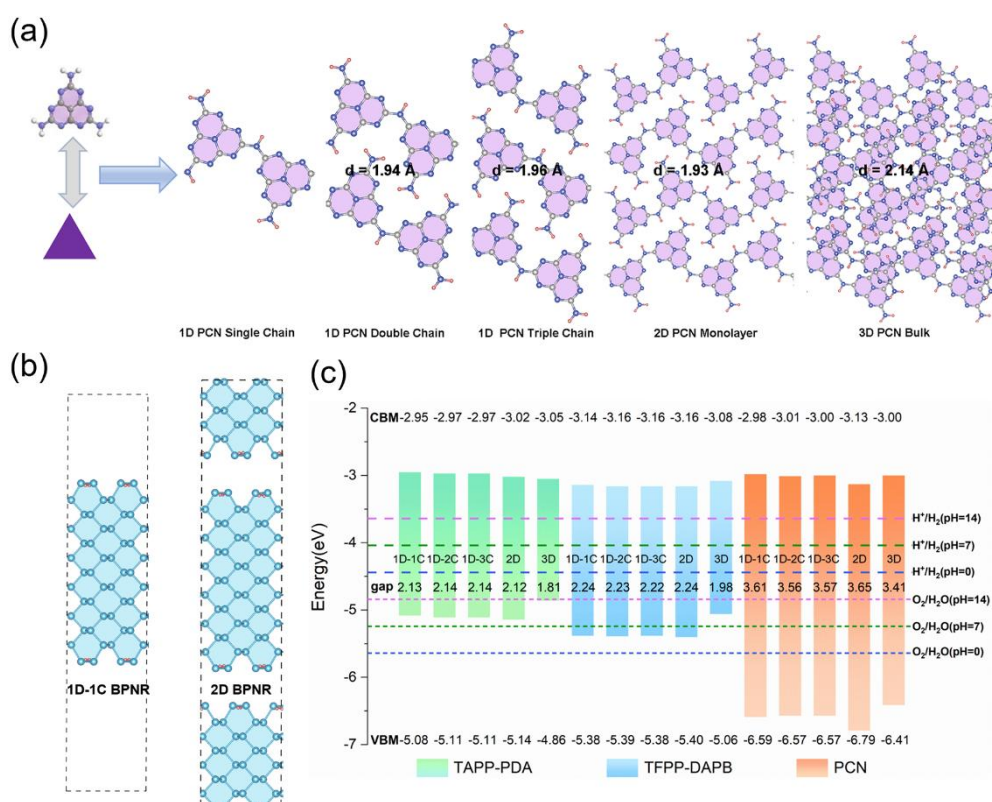


Figure 5. (a) Schematic illustration of the structural assembly of PCN. (b) Schematic atomic structures of 1D-1C and 2D BPNRs. (c) Band alignment of the TAPP-PDA, TFPP-DAPB, and PCN across different dimensions relative to the vacuum level, calculated using the HSE06 functional. The standard redox potentials for water splitting at different pH values are indicated by dashed lines.

Likewise, the excited-state carrier dynamics of the PCN system has been found to be dimensionality dependent. The carrier lifetime of the single-chain structure is 8.9 ns, significantly shorter than 35.8 ns in the 2D system as shown in Figure S19. For 1D-1C and 2D systems, the values of calculated NAC are 2.30 meV and 0.92 meV, respectively, and the values of calculated decoherence time are 15.1 fs and 16.9 fs, respectively. Obviously, this highlights the role of NAC as the main factor controlling the dynamical migration of excited-state carriers (Section S7 and Figure S20). Finally, the results provide a further valid indicator of the dimensional robustness of the ground-state electronic structures, and the dimensional sensitivity of excited-state properties of quasi-1D systems assembled by zigzag interfaces.

Subsequently, BPNRs with linear boundary were employed as a reference to clarify how zigzag interfaces alter the ground- and excited-state properties of these quasi-1D systems (Figure 5b).^{45, 55} The optimized interchain distance of 2D BPNR is 3.67 Å, notably shorter than that of the quasi-1D COFs. Accordingly, the 2D BPNR exhibits a much stronger interchain interaction (with a binding energy of -847.12 meV) than the COFs. However, this robust interaction similarly exerts negligible impact on the ground-state electronic structure, with the 1D-1C and 2D BPNRs yielding bandgaps of 0.98 eV and 0.93 eV, respectively (Figure S21). However, excited-state dynamics show similar relaxation behaviors for 1D-1C and 2D BPNRs, with carrier lifetimes of 1.6 ns and 1.9 ns, respectively (Table 1 and Figure S22). This negligible discrepancy contrasts sharply with quasi-1D COFs, where lifetimes differ by over an order of magnitude. Unlike the quasi-1D systems featuring zigzag boundaries, the 1D-1C and

2D BPNRs display nearly identical vibrational modes, with the 1D-1C structure showing only a slightly higher vibrational intensity. This clearly demonstrates that the vdW interactions at the linear interface fail to effectively suppress the out-of-plane vibrations of 2D BPNRs, thereby failing to modulate the *e-ph* coupling strength. Consequently, the unique zigzag boundary in quasi-1D COFs, which mediates in-plane vdW interactions, plays a crucial role in steering excited-state dynamics, offering valuable design guidelines for low-dimensional vdW materials. More interestingly, dimensionality exerts a negligible influence on the band edge positions of quasi-1D systems, and all configurations meet the requirements for overall water splitting under alkaline conditions (Section S8 and Figure 5c). Therefore, by integrating these robust static electronic properties with the dimension-sensitive excited-state dynamics, we propose that the fabrication of ultrathin 2D layered structures represents an optimal strategy for highly efficient solar energy conversion.

CONCLUSIONS

In summary, by integrating first-principles calculations based on density functional theory with NAMD simulations, we successfully deciphered the role of in-plane and out-of-plane vdW interactions in regulating the electronic structures and carrier recombination dynamics of quasi-1D TAPP-PDA, TFPP-DAPB, and PCN. Intriguingly, the static bandgap and dynamic carrier lifetime exhibit contrasting sensitivities to vdW interactions. During the 1D-to-2D structural evolution, the bandgaps remain virtually unaltered (variation less than 0.04 eV). Conversely, the structural constraints imposed by 2D spatial confinement significantly suppress low-

frequency atomic vibrations due to the zigzag in-plane interface, thereby weakening the NAC. This leads to a remarkable prolongation of carrier lifetimes from 2.1 ns, 4.2 ns, and 8.9 ns in the 1D chains to 21.3 ns, 10.4 ns, and 35.8 ns in the 2D monolayers. However, upon transitioning to 3D bulk phases, distinct stacking modes alter the out-of-plane interlayer coupling strength, thereby significantly modulating excited-state carrier relaxation processes and tuning carrier lifetimes across a broad range—from near-1D single-chain levels to exceeding 2D values. Our findings reveal that the in-plane structural confinement derived from zigzag interface-induced vdW interactions, rather than static electronic modulation, plays a primary role in governing carrier dynamics. This work provides critical insights for the rational design of low-dimensional optoelectronic and photocatalytic platforms.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/XXX>.

Computational methods and details; additional details (Sections S1–S9); binding energies; AIMD simulations; charge density; differential charge density; PDOS; optimized geometric structures; band structures; dynamic evolution of charge density; NAMD simulations; Table S1–S2 (data including binding energies, lattice parameters, interchain distance and band gaps)

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The authors declare no competing financial interests.

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