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Introduction 1.

Pentagons, as distinctive geometric structural units, have catalyzed a paradigm shift in advanced material design.¹ Following our first discovery of penta-graphene,² pentagonal materials have been expanded dramatically with immense potential applications in various fields, including thermoelectrics, ferroelectrics, piezoelectricity, water splitting, biosensors and beyond,^{1,3-6} highlighting the profound significance of the structure-property relationship in pentagonal materials. Building on this foundation, as a class of emerging framework materials, COFs inherently accommodate molecular building blocks and pre-designed topologies, providing an effective approach for exploring diverse pentagonal materials beyond atomic-level designs.^{1,3,7} This unique adaptability has established COFs as a versatile platform with tunable pore sizes and architectures, large surface areas, lightweight frameworks, and robust stability.8-10 Recent progress in the design and synthesis of 2D pentagonal COFs has been particularly encouraging. For instance, Lan et al.11 theoretically predicted 2D penta-COFs using molecular units with twofold (C_2) and fourfold (C_4)

Topology-guided design of the first 3D penta-COFs with superior ultraviolet optical response⁺

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Covalent organic frameworks (COFs) have gained significant attention in the past two decades due to their porous geometries, high stability and diverse functional applications. Very recently, 2D Cairo pentagon tessellated COFs (penta-COFs) have been successfully synthesized, going beyond conventional 2D COFs with a unique topology and exceptional properties. However, 3D penta-COFs remain unexplored, despite the inherent advantages of 3D frameworks over their 2D counterparts. Here, based on the combination of the topology-guided screening approach with rationally selected building blocks and first-principles calculations, we theoretically design the first 3D penta-COFs. The resulting two distinct 3D COFs, unj-1 and unj-2, exhibit high thermal stability up to 1300 K, intriguing mechanical hyperelasticity, and exceptional ultraviolet optical properties with absorption coefficients in the order of 10⁷ cm⁻¹, far surpassing conventional UV-absorbing materials. Further analysis of their electronic structures uncovers the underlying mechanism, which is attributed to the augmented electron-hole wavefunction overlap and valence bandwidth compression synergistically driven by the pentagonal topology and building blocks of the studied 3D penta-COFs. This study expands penta-COFs from two dimensions to three dimensions, demonstrating the unique role of the pentagonal topology in designing new functional materials

> symmetry based on the mcm topology. Subsequently, Liu et al.12 employed TBPP as the C_4 unit and BPY or QPTA as C_2 units to construct the corresponding 2D penta-COFs with remarkable near-infrared light absorption and efficient photothermal conversion properties. Similarly, Tian et al.13 synthesized 2D penta-COFs using TAPP as the C_4 unit and BATA as the C_2 unit, which exhibited outstanding photocatalytic hydrogen evolution performance. Wen et al.14 further advanced the field by utilizing TAPP as the C_4 unit and PBTD as the C_2 unit to create pentagonal frameworks that act as efficient electrocatalysts for the oxygen reduction reaction, achieving one of the highest halfwave potentials reported for COF-based electrocatalysts. These breakthroughs provide new insights and strategies for expanding the family of 2D COFs with tailored properties and varied functionalities by harnessing molecular building units and pentagon tessellations.

> Compared to 2D penta-COFs, 3D pentagonal frameworks inherently offer more freedom and flexibility in arranging molecular units, significantly enlarging the chemical design space and stable spatial network for designing more complex penta-COFs with diverse topologies and novel properties.10,15 In particular, the added dimensionality accommodates both planar and nonplanar building blocks and facilitates covalent bonding throughout the entire skeleton, thus enhancing structural robustness, enriching transport channels, and increasing active site density.16 These advantages are

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particularly relevant to low-symmetry pentagonal motifs, where expanding geometric tiling into three dimensions is not merely a spatial extension but may also substantially reshape electronic structures, giving rise to emergent mechanical and optical behaviors. For instance, it was demonstrated that light-induced crosslinking of a 2D layered COF into a 3D framework results in a marked bandgap widening and a pronounced blue-shift in absorption,¹⁷ underscoring the intrinsic link between spatial topology and electronic properties. Such structure-property relationships further reinforce the necessity for pursuing 3D penta-COFs. However, to date, neither theoretical prediction nor experimental synthesis of 3D penta-COFs has been reported. This absence is primarily due to the limited types of topologies reported and the obstacles associated with synthesizing specific frameworks.¹⁶ Consequently, constructing COFs with pentagonal tiling in 3D space is challenging.

For bridging this gap, we carry out the first theoretical study on the design of 3D penta-COFs. Using a topology-guided screening approach, we identify the **unj** topology, which enables pentagonal tiling in 3D space. Based on the rational selection of alkyl and alkynyl molecules as the building blocks and combined with first-principles calculations, two prototypical 3D penta-COFs are designed with high stability and superior ultraviolet optical response.

2. Computational methods

All first-principles calculations are performed using the Vienna Ab Initio Simulation Package (VASP)18 based on density functional theory (DFT). The projector augmented wave (PAW) method¹⁹ is employed to describe ion-core and valence electron interactions. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)²⁰ is used to treat the exchange-correlation interaction of electrons for most calculations, while the hybrid functional (HSE06)²¹ is applied to refine the band structure for improved accuracy. Plane-waves with a kinetic energy cutoff of 520 eV are used to expand the valence electron $(2s^22p^2)$ wavefunctions, and the first Brillouin zone is sampled using a gamma-centered k-point grid with a density of $2\pi \times 0.02$ Å⁻¹. Structure optimization is conducted with convergence criteria of 1 \times 10^{-6} eV for total energy and 1 \times 10⁻⁴ eV Å⁻¹ for atomic forces. Dynamical stability is evaluated with a 2 \times 2 \times 2 supercell by using the finite displacement method as implemented in the Phonopy code.²² For *ab initio* molecular dynamics (AIMD) simulations, the simulation time is set to 10 ps with a time step of 2 fs, and temperature control is achieved via the Nosé-Hoover thermostat. The linear optical properties are calculated based on the independent-particle approximation, which involves the frequency-dependent complex dielectric function, $\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$ $i\varepsilon_2(\omega)$. The imaginary part $\varepsilon_2(\omega)$ is derived from momentum matrix elements between the occupied and unoccupied wavefunctions, while $\varepsilon_1(\omega)$ is obtained from $\varepsilon_2(\omega)$ using the Kramers– Kronig transformations^{23,24}

$$arepsilon_2(\omega) = rac{2e^2\pi}{arOmegaarepsilon_0} \sum_{
m k,v,c} \left| \left\langle \psi^{
m c}_{
m k} | \hat{u} imes \hat{r} | \psi^{
m v}_{
m k}
ight
angle \Big|^2 \delta igl(E^{
m c}_{
m k} - E^{
m v}_{
m k} - E igr)$$
(1)

$$\varepsilon_{1}(\omega) = 1 + \left(\frac{2}{\pi}\right) \int_{0}^{\infty} d\omega' \frac{\omega'^{2} \varepsilon_{2}\left(\omega'\right)}{\omega'^{2} - \omega^{2}}$$
(2)

where \hat{u} , ψ_k^v and ψ_k^c represent the incident electric field polarization vector and the wavefunctions of valence and conduction bands, respectively. To improve the accuracy of the optical response range, a scissors correction is applied to account for the difference between the band gaps obtained at the PBE and HSE06 levels. The correction values are set to 1.41 eV for **unj**-1 and 1.15 eV for **unj**-2, respectively. This correction only shifts the absorption range and does not affect the intensity or shape of the optical spectra.²⁵ Then, main optical constants including absorption coefficient ($a(\omega)$), reflectivity ($R(\omega)$) and refractive index ($n(\omega)$) are subsequently calculated *via* standard formulae

$$a(\omega) = \sqrt{2}\omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}$$
(3)

$$R(\omega) = \left| \frac{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} - 1}{\sqrt{\varepsilon_1(\omega) + i\varepsilon_2(\omega)} + 1} \right|^2$$
(4)

$$n(\omega) = \left(\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}\right)^{\frac{1}{2}}$$
(5)

The second-harmonic generation (SHG) susceptibility tensor, $\chi_{ii}^{(2)}(-2\omega, \omega, \omega)$, is computed using the package developed at the independent-particle level by Zhang's group.²⁶ A consistent scissors correction is applied here with a denser *k*point grid of $2\pi \times 0.008$ Å⁻¹. Detailed computational parameters can be found in our previous work.²⁷

3. Results and discussion

3.1 Rational design of 3D penta-COFs

3D COFs are highly ordered structures that can be abstracted as 3D periodic networks composed of vertices, edges, and tiles, with specific topologies classified by reticular chemistry. To design 3D penta-COFs, we first identify the potential topology types by undertaking the screening process, as illustrated in Fig. 1a. From the Reticular Chemistry Structure Resource (RCSR) database,28 3587 3D periodic topologies are initially extracted for screening with the following steps: (1) geometric filtering: topologies containing pentagonal tiles are selected, reducing the number of candidates to sixteen; (2) simplicity filtering: topologies with single-vertex connectivity and embed type 1 are chosen for their simplicity and robust topological connectivity to reduce the options to five, where embed type 1, most commonly observed in simple nets, is characterized by maximum-symmetry embeddings in the form of sphere packings;^{8,29} (3) viability filtering: the remaining five candidates are carefully analyzed. Among them, the wgt topology is excluded due to its five-coordinated nodes, which are incompatible for 3D COFs owing to geometric symmetry restrictions and covalent bonding limitations,16,30 while the unh, unn, and ung topologies

Paper



Fig. 1 Design of 3D penta-COFs: (a) schematic of the topology-guided screening process for 3D pentagonal topologies and (b and c) perspective view and top view of the target **unj** topology, respectively. (d) Selection of building blocks and (e and f) side views of **unj**-1 and **unj**-2, using a single layer supercell for clarity.

have large bond angle average deviation, the details are given in Note S1 and Table S1 in the ESI,† so their geometries are unfavorable for COF formation. Ultimately, the **unj** topology emerges as the viable candidate for designing 3D penta-COFs.

Fig. 1b presents a perspective view of the **unj** topology, where the 2D projection of the pentagonal network corresponds to the well-known Cairo tiling.² It has two unequal edges, labeled as *m* and *n*. Moreover, the **unj** topology is a self-dual net, meaning that the nodes and voids are topologically interchangeable,²⁸ thus enhancing framework flexibility and stability. In the top view (Fig. 1c), pentagonal rings form a series of low-density 1D helical channels along the *z*-axis, breaking inversion symmetry and displaying intrinsic chirality (Fig. S1†). These unique topology features are promising to produce intriguing properties in framework materials with the **unj** topology. Notably, the **unj** topology was identified in the early synthesis of the Zintlphase NaGeSn₂ material,³¹ implying the possibility of 3D penta-COFs based on **unj** topology.

Furthermore, unlike the recently reported 3D COFs based on specific topologies that rely on complex building blocks,^{32–34} the **unj** topology can be realized using simple components. As shown in Fig. 1d, four-connected tetrahedral (T_d) nodes and two-connected (C_2) linear linkers can serve as viable building blocks, significantly enhancing synthetic feasibility. Tetrahedral nodes,¹⁶ commonly used in experiments, naturally correspond to sp³-hybridized organic units, while linear linkers, such as acetylene,³⁵ are simple, tunable, and widely used in organic synthesis. Additionally, the near-equal edge lengths of the **unj** topology allow the use of a single type of linker. As the first case, we designed two 3D penta-COFs, **unj**-1 and **unj**-2, using sp³-hybridized alkyl carbon as the nodes and acetylene-based (L₁) and diacetylene-based (L₂) links as the edges of the **unj** topology, respectively. The optimized primitive cells belong to the hexagonal crystal system with space group *P*6₁22 (no. 178), where the two types of edges are nearly equal ($|m|/|n| \sim 1$), indicating that the pentagonal motifs are nearly regular pentagons in 3D space. Also, the corresponding volumes of the two primitive cells are 722.07 Å³ and 3062.88 Å³, respectively. The perspective and top views are shown in Fig. 1e, f and S2,† illustrating the tunable pore sizes with varying linker lengths and the 3D anisotropy of their structures.

To check the stability of **unj**-1 and **unj**-2, we first studied the lattice dynamics by calculating their phonon dispersions. The calculated results are plotted in Fig. 2a and S3a,† respectively, showing that there are no any imaginary frequencies in their entire Brillouin zones, confirming that the two structures are dynamically stable. Then, AIMD was performed in the canonical ensemble for 10 ps to evaluate their thermal stability, as commonly used for COF systems.^{36,37} As shown in Fig. 2b and S3b,† the total potential energies remain almost constant during the simulations, and no significant structural distortions occur even at a high temperature of 1300 K, which is nearly twice the typical temperature range (500–800 K) for most



Fig. 2 Stability and structural characterization of 3D penta-COFs: (a) phonon spectrum and DOS of **unj**-1. (b) AIMD simulations at 300 K, 800 K, and 1300 K of **unj**-1, with insets showing crystal structure snapshots after 10 ps simulation at 1300 K. (c) Simulated XRD patterns for **unj**-1 and **unj**-2, respectively.

reported 3D COFs,32,33 resulting from the carefully screened topology structure and rationally selected building blocks. Additional calculation results are shown in Fig. S4,† including the temperature evolution, mean square displacement (MSD) and bond length distributions, to further corroborate the thermal robustness of the structures. Finally, mechanical stability is evaluated through elastic constant calculations using the finite distortion method (Table 1). Both structures satisfy the Born-Huang criteria for hexagonal lattices³⁸ ($C_{11} > |C_{12}|$; $2C_{13}^{2} < C_{33} (C_{11} + C_{12}); C_{44} > 0$, ensuring their mechanical robustness. Microscopically, the exhibited excellent stability is attributed to the strong chemical bonding. The calculated electron localization functions of unj-1 and unj-2 (Fig. S5[†]) show the values exceeding 0.75 at all bonding regions, confirming the covalent bonding features39 in the frameworks with localized electrons concentrated on the linkers. For future

Table 1	The elastic	constants (C	_{ij} , in GPa) of	unj-1 and unj	-2
	C	C	C	C	

	011	0_{12}	013	033	0_{44}
unj-1	88.75	74.11	67.34	76.26	11.60
unj-2	34.31	32.90	29.79	28.46	1.33

experimental characterization, the simulated X-ray diffraction (XRD) patterns are provided in Fig. 2c.

3.2 Mechanical hyperelasticity

Next, given that materials with small elastic constants usually exhibit flexibility, we explored the mechanical properties of 3D penta-COFs. Based on the calculated elastic constants, the 3D anisotropic distributions of the bulk modulus (B_0) , Young's modulus (Y), and the minimum and maximum Poisson's ratios (v_{\min}, v_{\max}) are presented in Fig. 3a for **unj-1** and Fig. S6[†] for unj-2, displaying cylindrical symmetry in the xy-plane but significant anisotropy along the z-axis because of the topologyinduced anisotropy. Based on the Voigt-Reuss-Hill approximation,⁴⁰ the bulk modulus ($B_0 = 73.69$ GPa) and Poisson's ratio (v = 0.44) of **unj**-1 are obtained, which are further benchmarked against some reported carbon structures with similar compositions and bonding characteristics (Fig. 3b and Table S3[†]). An approximately inverse relationship between B_0 and v is observed across the carbon-based materials. Remarkably, unj-1 shows the lowest B_0 and exceptionally large ν among the studied materials. Its B_0 is only 17.02% of that of diamond and 22.56% of T6 carbon, but its ν exceeds these by 528.57% and 51.72%, respectively, highlighting its extraordinary hyperelasticity. When the linker length is increased, as in unj-2, the corresponding values become lower ($B_0 = 29.54$ GPa) and larger ($\nu =$ 0.48, approaching the theoretical upper limit of 0.50), displaying the tunability with linker length.

To understand the origin of such intriguing mechanical properties of the 3D penta-COFs, we analyzed the relationships between B_0 , v, average coordination number and density (Fig. 3c and d), because the average coordination number reflects building block characteristics, while density captures the influence of the topology structure. A clear trend is found: the lower the coordination numbers and density, the smaller the B_0 and the larger the v. In fact, the average coordination number of **unj**-1 is 2.40 and the density is 0.82 g cm⁻³, while these values change to 2.22 and 0.35 g cm⁻³ in **unj**-2, respectively. The hyperelasticity observed in 3D penta-COFs suggests their potential for applications in flexible devices and advanced mechanical processing.

3.3 Ultraviolet optical properties

The exceptional optical performance of the recently reported 2D penta-COFs^{12,13} motivates us to explore the optical properties of 3D penta-COFs, which are analyzed with the Kubo–Greenwood method.^{23,24} Although this method may underestimate the optical responses, it can effectively capture the optical characteristics of materials for analyzing the structure–property relationship within a solid physical framework.⁴¹ From the frequency-dependent dielectric constants (Fig. S7†), we derive the absorption, reflection, and refractive index spectra of **unj**-1 (Fig. 4a and b). Structural anisotropy introduces slight optical differences between the lateral (xx = yy) and axial (zz) directions. Notably, **unj**-1 exhibits pronounced absorption in the ultraviolet region (<224 nm), which contrasts with the predominantly visible light responses of the reported 2D penta-



Fig. 3 Mechanical properties of unj-1: (a) 3D anisotropy of the bulk modulus B_0 , Young's modulus Y, and the minimum and maximum Poisson's ratios v_{min} , v_{max} , (b) comparison of Poisson's ratio and bulk modulus with the reported materials in Table S3,† with the gray line for visual guidance, correlations of (c) bulk modulus B_0 and (d) Poisson's ratio v with density and the average coordination number.

COFs¹²⁻¹⁴ and typical 3D COFs.⁴² Impressively, unj-1 achieves an absorption coefficient in the order of 10⁷ cm⁻¹, far surpassing typical organic ultraviolet absorbers such as benzophenone and triazines $(\sim 10^4 \text{ cm}^{-1})$,^{43,44} as well as inorganic counterparts like TiO_2 and $ZnO (\sim 10^5 \text{ cm}^{-1})$.^{45,46} Meanwhile, **unj**-1 shows a low reflectivity (~ 0.28) and a high refractive index (~ 2.85), indicating its efficient light absorption. Further inspection reveals that the optical absorption of **unj**-1 is divided into two regions: in the extreme ultraviolet range (<66 nm, denoted as Region 1), discrete absorption peaks are observed alongside strong absorption, and in the mid-ultraviolet range (66-224 nm, denoted as Region 2), the absorption is continuous, accompanied by a sharp absorption edge and some absorption peaks, indicating a direct bandgap semiconductor-like absorption behavior.^{47,48} Besides, the optical response of unj-2 (Fig. S8[†]) is also primarily in the ultraviolet region (<352 nm), exhibiting exceptional absorption characteristics. This outstanding ultraviolet absorption performance underscores the potential of 3D penta-COFs for ultraviolet protection, photodetectors, and photocatalysis.

In addition, we also investigated the effect of the intrinsic chirality from the **unj** topology on the optical response. Chirality primarily affects nonlinear optical properties, particularly in second harmonic generation (SHG).⁴⁹ Taking **unj**-1 as a representative (Note S3 and Fig. S9†), our calculations reveal that both left-handed *L*-**unj**-1 (space group $P6_522$, no. 179) and right-handed *R*-**unj**-1 (space group $P6_122$, no. 178) structures exhibit

pronounced SHG responses, with comparable magnitudes but opposite signs. This phenomenon can be attributed to the chirality-induced reversal of polarization,^{49,50} and such a phenomenon has also been observed in chiral carbon nanotubes,⁵¹ thus providing a possible approach for experimentally identifying these chiral configurations.

Since the optical response of materials usually originates from interband transitions of charge carriers, we analyzed the interband transition probabilities governed by Fermi's golden rule, which depend on both the squared transition dipole moment (TDM^2) and the joint density of states $(JDOS)^{24,47}$

$$\mathrm{TDM}^{2} = \left| \frac{i\hbar}{(E_{\mathrm{c}} - E_{\mathrm{v}})m_{0}} \langle \psi_{\mathrm{c}} | \mathbf{p} | \psi_{\mathrm{v}} \rangle \right|^{2} \tag{6}$$

$$JDOS(\omega) = \sum_{v,c} \frac{Q}{4\pi^3} \int \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega) d^3k$$
(7)

where ψ_v , ψ_c , and E_v , E_c correspond to the wavefunctions and energies of the valence and conduction bands, respectively. The TDM² is the transition probability between two states, ψ_v and ψ_c . As shown in Fig. 4c, the TDM² is calculated for the four states near the band edge, where it reaches a maximum value of 17.33 Debye² near the *G* point. Moreover, relatively high transition probabilities are observed along the entire high-symmetry path with local maxima occurring near high-symmetry points. As the transition energy increases, TDM² exhibits a clear decreasing trend, reflecting weaker wavefunction overlap and less favorable



Fig. 4 Optical properties of **unj**-1: (a) absorption spectrum (α), (b) reflection spectrum (R) and refractive index (n). (c) Squared transition dipole moments (TDM²), (d) joint and partial joint DOS, where VB1, VB2, CB1 and CB2 refer to the energy bands near the band edge, respectively.

transition at higher excitation energies (see Fig. S10[†]). The JDOS reflects the total possible interband transition state densities from the valence band to the conduction band, while the partial JDOS captures the transition densities between the specific states. As illustrated in Fig. 4d, the JDOS of **unj**-1 exhibits a trend consistent with its absorption spectrum with values in the order of 10³. This strong correlation suggests that the higher absorption intensity observed in Region 1 is primarily due to the abundance of available transition channels with high JDOS. Additionally, the partial JDOS for the four energy bands near the band edge features sharp Gaussian-type peaks with highly similar profiles, correlated with the sharp absorption edge observed in Fig. 4a. The intricate interband optical transitions are intrinsically rooted in the materials' electronic structures, as discussed below.

3.4 Electronic properties

As shown in Fig. 5a, the energy bandgap of **unj**-1 is calculated to be 4.83 eV at the PBE level and 6.24 eV using the HSE06 hybrid functional, indicating that it is an ultrawide-bandgap semiconductor. Its partial DOS reveals a significant increase in the electronic states near the band edges, mainly arising from the porbitals of the linking units, which is consistent with the charge spatial distributions of the valence band maximum (VBM) and conduction band minimum (CBM) shown in Fig. 5b and c. Moreover, **unj**-1 exhibits an indirect bandgap, with the VBM located along the *G*-*M* path and the CBM at the *G* point. However, due to the sub-VBM at the *G* point being close to the VBM in energy, it can be classified as a quasi-direct bandgap material. In comparison, **unj**-2 (Fig. S11†) displays a lower bandgap of 3.13 eV (PBE level) and 4.28 eV (HSE06 hybrid functional), while retaining a similar quasi-direct bandgap to **unj**-1. The reduced bandgap in **unj**-2 is due to its L_2 linkers, which generate more delocalized states at the VBM compared to **unj**-1. These results highlight the wide-bandgap feature of 3D penta-COFs, which enables their optical response in the ultraviolet region. Additionally, the quasi-direct bandgap nature favors the sharp optical absorption edge observed above.

Detailed analysis of the electronic structures of **unj**-1 and **unj**-2 reveals a quasi-flat band phenomenon near the band edges, indicating a larger carrier effective mass (m_{eff}). As shown in Fig. 5d, e, S11d and e,† the spatial distribution of m_{eff} shows pronounced anisotropy with the maximum values of $|m_{eff}|$ reaching 11.92 m_0 (VBM) and 18.57 m_0 (CBM) for **unj**-1, and 6.27 m_0 (VBM) and 3.07 m_0 (CBM) for **unj**-2. This large effective mass, coupled with the relatively low dielectric constant of organic materials, implies the potential for a notable excitonic effect in the 3D penta-COFs, which is common in organic widebandgap semiconductors.⁵² This effect aligns with the appearance of peaks near the absorption edge and the specific partial



Fig. 5 Electronic properties of unj-1: (a) band structure and partial DOS, (b and c) band-partial charge distributions at the VBM and CBM (isovalue $= 0.0043 \text{ Å}^{-3}$). (d and e) 3D anisotropy of the effective mass (m_{eff}) at the VBM (absolute values for better visualization) and CBM. (f) Comparison of bandgap and valence bandwidth between dia and unj topologies at the HSE06 level. (g) Schematic of the enhancement mechanism for optical properties.

JDOS near the band edges. Generally, the quasi-flat band phenomenon is commonly attributed to diminished orbital interactions resulting from electronic localization within the building blocks, as discussed in previous studies.⁵² However, we identify an additional factor: the valence bandwidth compression induced by the pentagonal topology defined as the energy difference between the valence band maximum and minimum across all occupied valence states.

To understand the effect of valence bandwidth compression on optical absorption, we introduce two pristine topological models: one is dia, the most common topology of 3D COFs,16 and the other is **uni**, which is composed purely of sp³-hybridized carbon atoms without additional linker units. As shown in Fig. 5f, S12, and S13,[†] although dia and uni exhibit nearly identical bandgaps, the valence bandwidth of unj is compressed by 11.46% from 23.72 eV to 21.02 eV, owing to the geometric constraints and reduced symmetry of the pentagonal framework. This compression enhances electronic localization, reduces band dispersion, and increases the state density, enabling a greater number of optically allowed transitions in a similar excitation energy range. Consequently, unj exhibits a markedly steeper absorption edge and stronger initial absorption compared to dia. After incorporating the L₁ linker, the electronic localization is enhanced, and the valence bandwidth is further reduced (17.67 eV, -15.94%) in **unj**-1 due to the synergy of the pentagonal topology and linker unit, leading to an even sharper absorption edge and higher overall absorption intensity. Conversely, the conjugated L₂ linker in unj-2 induces partial charge delocalization, resulting in a slightly broader valence bandwidth (18.31 eV) and a moderate reduction in absorption sharpness and intensity, while still outperforming **dia**. These findings illustrate how the interplay between the topological geometry and linker design modulates the electronic structures and enhances the UV optical performance of 3D penta-COFs. Moreover, they provide insight into the dual-region absorption behavior observed in **unj**-1 and **unj**-2, where the discrete peaks in Region 1 arise from deep subband transitions,⁵³ while the continuous and intense absorption in Region 2 stems from near-edge transitions facilitated by enhanced state density near band edges.

Based on the above analysis, we further elucidate how these electronic properties of 3D penta-COFs govern their exceptional ultraviolet optical response. As shown in Fig. 5g, the strong optical adsorption is mainly related to two factors: (1) the synergy of the pentagonal topology and the alkynyl-based linkers enhances electronic localization, leading to the emergence of quasi-flat bands with reduced band dispersion and increased effective masses. This narrows the energy difference between the electronic states at different k-points, increasing the number of allowed transitions within similar excitation energy ranges. Meanwhile, the localization of wavefunctions can reduce the Coulomb screening and improve their spatial overlap, thereby changing the transition dipole matrix elements. Similar effects have been observed in materials such as hBN and V₂O₅.^{54,55} (2) The intriguing valence bandwidth compression effect induced by the pentagonal topology significantly enhances the state density near the band edges, further increasing the number of available interband optical transitions, as described by JDOS. These findings provide a deep understanding of the structure-property relationships in 3D penta-COFs, correlating the structural topology with the electronic properties and optical characteristics.

4. Conclusions

In summary, motivated by the recent experimental synthesis of 2D penta-COFs that integrate the pentagonal topology with COF chemistry, we have carried out the first study on designing 3D penta-COFs based on the unj topology. The resulting two structures, unj-1 and unj-2, exhibit dynamic, mechanical and exceptional thermal stability up to 1300 K. In particular, the studied 3D penta-COFs display intriguing mechanical hyperelasticity and remarkable ultraviolet optical response with absorption coefficients in the order of 10^7 cm⁻¹, far exceeding typical organic and inorganic ultraviolet-absorbing materials, originating not only from the quasi-direct bandgap related to the quasi-flat band feature, but also from the valence bandwidth compression that enhances the interband transition probability and joint density of states. These unique effects can be attributed to the synergy between the pentagonal topology and the building blocks, thus showing the profound structuremechanical-electronic-optical relationships in 3D penta-COFs. These intriguing features highlight the role of the pentagonal topology in regulating functionalities and would stimulate experimental effort in synthesizing 3D penta-COFs for ultraviolet protection and novel optical devices.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

The authors declare no competing financial interest.

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