

Supporting Information for

Topology-Guided Design of the 3D Penta-COFs

with Superior Ultraviolet Optical Response

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Note S1. Geometric feasibility analysis of four topologies (ung, unn, unh, unj).

As shown in **Table S1**, all of the topologies in this table are four-coordinate. Due to the bonding preference of 3D COFs, four-coordinate nodes typically form a 3D network in a tetrahedral arrangement with an ideal bond angle of $\theta_0 = 109.471^\circ$. Although COFs generally exhibit some tolerance for structural distortion, it is undesirable to deviate too much from ideal geometric features as they may lead to structural deformation or collapse.^{1,2} To quantify this geometric suitability, we introduce the bond angle average deviation $\nabla\bar{\theta}$ ($\nabla\bar{\theta} = \frac{\sum_i |\theta_i - \theta_0|}{N} \times 100\%$, where N is the number of four-coordinate bond angles). In addition, the edge length ratio ($|m|/|n|$) compares the difference of two types edges in the topology. A larger edge length difference implies greater difficulty in forming an ordered 3D framework. The results presented in this table indicate that among the four topologies, **unj** exhibits the smallest $\nabla\bar{\theta}$ and edge length ratio. In contrast, the other three topologies (**ung**, **unn**, and **unh**) show larger $\nabla\bar{\theta}$ (more than 25%) and edge ratios, making them less feasible for constructing stable 3D penta-COFs. Consequently, **unj** is selected as the target topology for further exploration.

Table S1. Structural parameters of the four topologies: including space group, bond angle average deviation $\nabla\bar{\theta}$ and edge length ratio $|m|/|n|$ for **unj**, **unh**, **ung** and **unn**.

Topology	Space group	$\nabla\bar{\theta}$ (%)	($ m / n $)
ung	<i>R</i> -3c (No. 167)	25.77	1.22
unn	<i>R</i> -3c (No. 167)	27.61	1.26
unh	<i>P</i> 6 ₁ 22 (No. 178)	29.29	1.32
unj	<i>P</i> 6 ₁ 22 (No. 178)	19.25	1.12

Note S2. Intrinsic chirality in the unj topology.

As shown in **Figure S1**, the **unj** topology intrinsically exhibits chirality, which can be classified into left-handed (*L*-) and right-handed (*R*-) structures due to the symmetry differences in the helical channels. The *L*-structure exhibits a counterclockwise helical arrangement, while the *R*-structure exhibits a clockwise helical arrangement. Despite this distinction, most properties of the *L*- and *R*-structures are identical, as the difference lies solely in the helical direction of the channels. Therefore, this study focuses on the *L*-structure as the representative for exploration in this study.

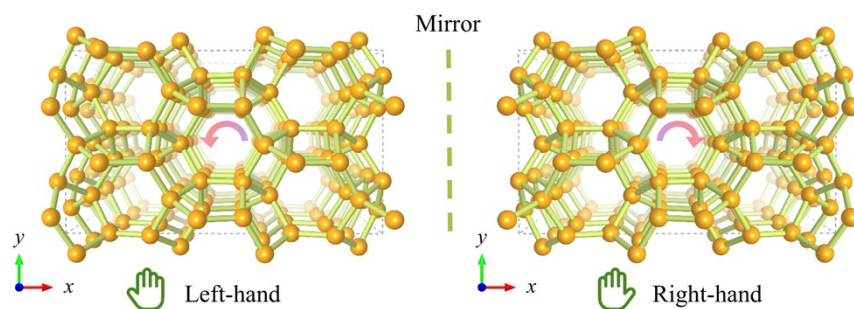


Fig. S1 Schematic illustration of the intrinsic chirality in the unj topology.

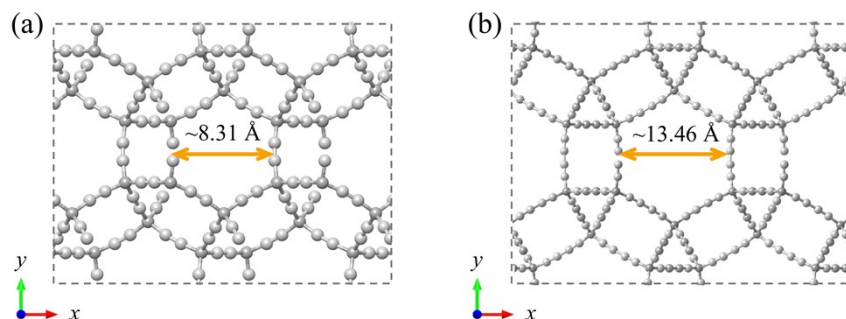


Fig. S2 Top views of unj-1 and unj-2, respectively.

Table S2. Structural parameters of the optimized unj-1 and unj-2: including lattice constants, primitive cell volume V_{cell} , bond angle average deviation $\nabla\bar{\theta}$, edge length ratio ($|m|/|n|$) and Wyckoff atomic positions.

Structure	Lattice constants (Å)	V_{cell} (Å ³)	$\nabla\bar{\theta}$ (%)	$ m / n $	Wyckoff Atomic Positions
unj -1	$a = 9.54$ $c = 9.17$	722.07	1.05	1.01	$12c$ (0.631, 0.699, 0.858)
					$12c$ (0.341, 0.572, 1.131)
					$6b$ (0.766, 0.234, 1.083)
unj -2	$a = 15.44$ $c = 14.84$	3062.88	0.62	1.02	$12c$ (0.594, 0.726, 0.881)
					$12c$ (0.639, 0.686, 0.850)
					$12c$ (0.768, 0.468, 0.823)
					$12c$ (0.768, 0.414, 0.883)
					$6b$ (0.766, 0.234, 1.083)

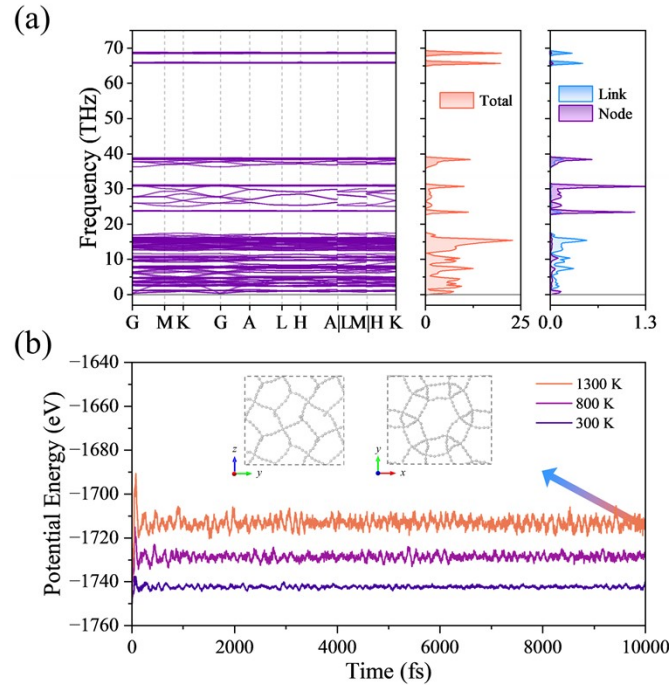


Fig. S3 Dynamical and thermal stability of unj-2: (a) phonon spectrum and phonon DOS. (b) AIMD simulations at 300, 800, and 1300 K, with insets showing the crystal structure snapshots in the end of the simulation at 1300 K.

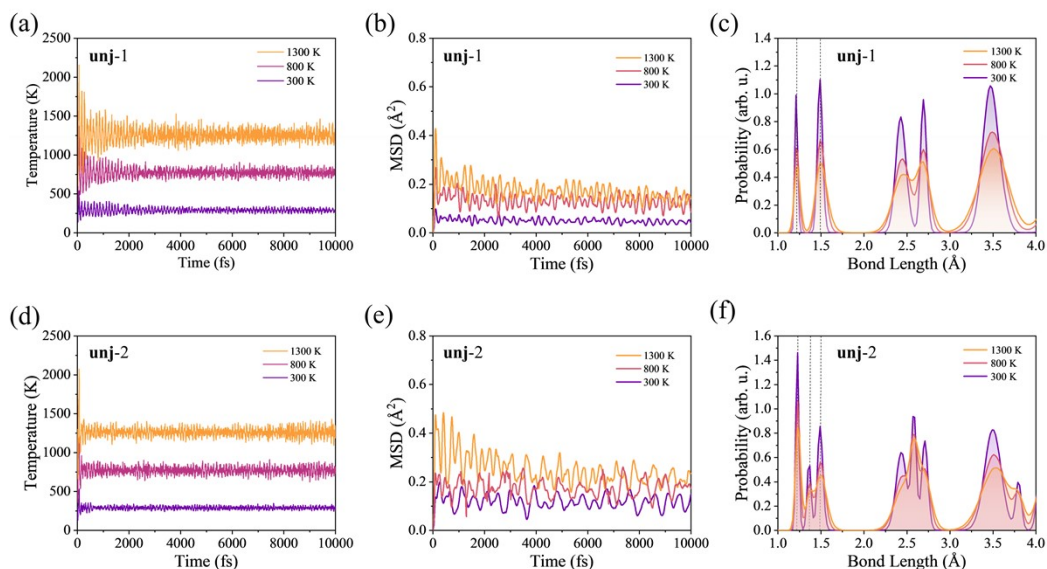


Fig. S4 AIMD simulations of unj-1 (a–c) and unj-2 (d–f) at 300, 800, and 1300 K: (a, d) temperature evolution, (b, e) mean square displacements (MSD), and (c, f) bond length distributions. The black dashed lines indicate the characteristic bond lengths in each structure.

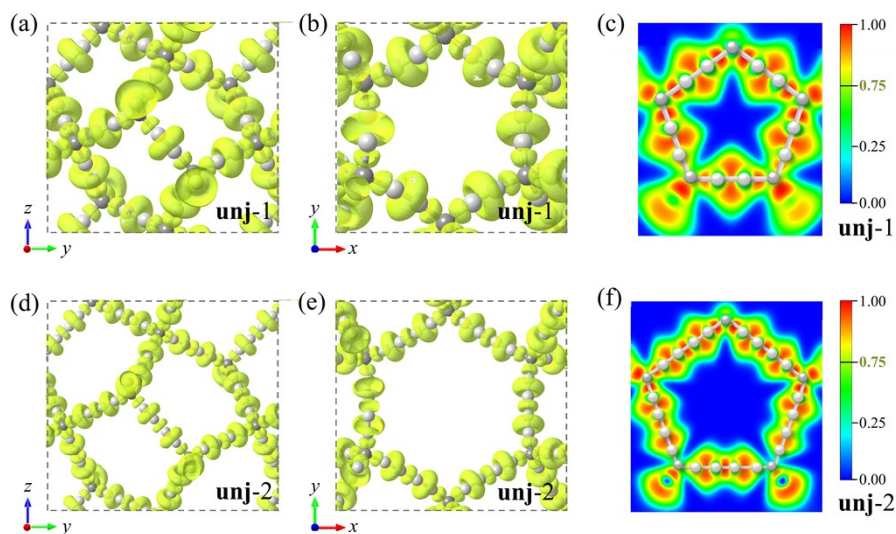


Fig. S5 ELF distribution of unj-1 and unj-2: (a, d) perspective views (isovalue = $0.75 \text{ \AA}^{-3}$), (b, e) top views (isovalue = $0.75 \text{ \AA}^{-3}$), (c, f) sectional views along the pentagonal ring.

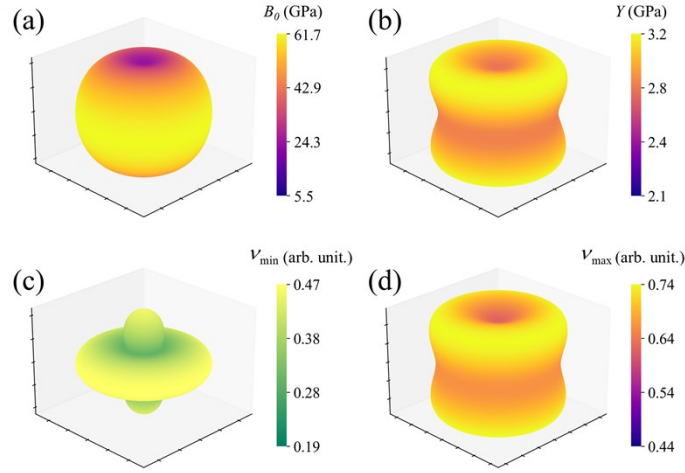
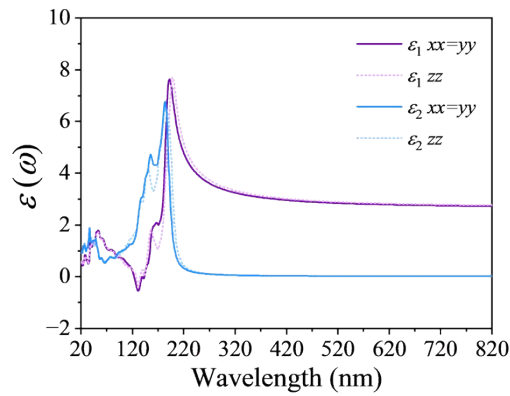


Fig. S6 3D Anisotropy mechanical properties of unj-2: (a) bulk modulus B_0 , (b) Young's modulus Y , and the (c) minimum and (d) maximum Poisson's ratios $v_{\min}$, $v_{\max}$.

Table S3. Statistical summary of mechanical properties: including the topology, coordination number (CN) and ratio, density, bulk modulus B_0 and the Poisson's ratio v . For comparability, reference materials containing at most a single alkyne bond between two carbon nodes were selected.

No.	Material	Topology	CN (ratio)	Density (g/cm ³)	B_0 (GPa)	v (arb.unit.)
1	unj-1	unj	2,4 (4:1)	0.82	73.69	0.44
2	Cubic a-Graphyne ³	pbz	2,3 (1:1)	1.04	99.80	0.42
3	Cubic b-Graphyne ³	pbz	2,3 (1:1)	1.44	150.45	0.45
4	Rh12 ⁴	pcu-h	2,3 (1:1)	1.77	108.60	0.34
5	Cubic Graphiteyne ³	pbz	2,3 (2:1)	1.04	110.82	0.31
6	TY carbon ⁵	dia-a	2,4 (1:1)	0.83	84.51	0.44
7	supercubane C32 ⁶	pcb	2,4 (1:1)	1.33	135.71	0.35
8	Y-II carbon ⁷	dia	2,4 (1:1)	1.78	167.51	0.43
9	1-Yne ⁸	crb	2,4 (2:1)	1.911	160.00	0.35

10	2-Yne ⁸	crb	2,4 (2:1)	1.650	114.80	0.33
11	Y-carbon ⁵	dia	2,4 (4:1)	0.90	84.40	0.47
12	6.82 P ⁹	pbp	3	2.01	226.09	0.38
13	Cubic Graphite ⁹	pbz	3	2.14	248.25	0.29
14	Squaroglitter ¹⁰	mjb	3,4 (1:1)	2.35	275.01	0.30
15	bcc-C20 ¹¹	tfh	3,4 (1:1)	2.42	203.84	0.20
16	T6 ¹²	tfi	3,4 (1:1)	2.95	326.71	0.29
17	3D-(4,0) ¹³	xca	3,4 (1:2)	3.24	368.88	0.13
18	Diamond	dia	4	3.50	432.90	0.07
19	T-carbon ⁷	dia	4	1.50	169.00	0.33
20	T12 ¹⁴	cdp	4	3.47	424.80	0.09
21	L-carbon ¹²	lon-a	4	1.52	162.40	0.37
22	HP3 ¹⁵	qtz	4	3.69	447.06	0.06
23	CA2 ¹⁶	acs-a	4	2.23	234.59	0.26
24	C8 ¹⁷	pcb	4	2.79	311.00	0.22



Fig, S7 Frequency-dependent dielectric function of unj-1.

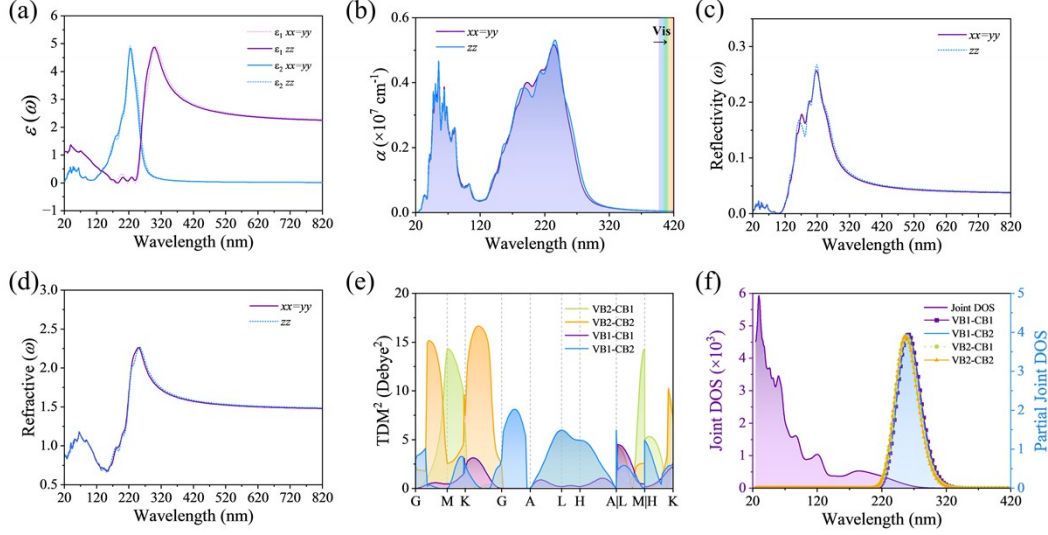


Fig. S8 Linear optical properties of unj-2: (a) frequency-dependent dielectric function, (b) absorption spectrum, (c) reflection spectrum, (d) refractive index spectrum. (e) Squared transition dipole moments, (f) joint DOS and partial joint DOS, where the VB1, VB2, CB1 and CB2 refer to the energy bands near the band edge.

Note S3. SHG susceptibilities $\chi_{ij}^{(2)}$ for *L*-unj-1 and *R*-unj-1.

As shown in **Figure S9**, the crystal symmetry restricts the nonzero components of the $\chi_{ij}^{(2)}$, requiring $\chi_{14} = -\chi_{25}$ (where the subscripts denote the tensor components, with 1=x, 2=y, 4=yz=zy, 5=xz=zx). Consequently, the analysis focuses on the χ_{14} component. The maximum values of the real part of $\chi_{14}(\omega)$ are -1.03 pm/V for ***L*-unj-1** and 1.07 pm/V for ***R*-unj-1**, both located at 3.34 eV. For imaginary part, the corresponding maxima are 0.80 pm/V for ***L*-unj-1** and -1.28 pm/V for ***R*-unj-1**, both occur at 3.28 eV. These values exhibit comparable magnitudes but opposite signs, consistent with their opposite chirality.

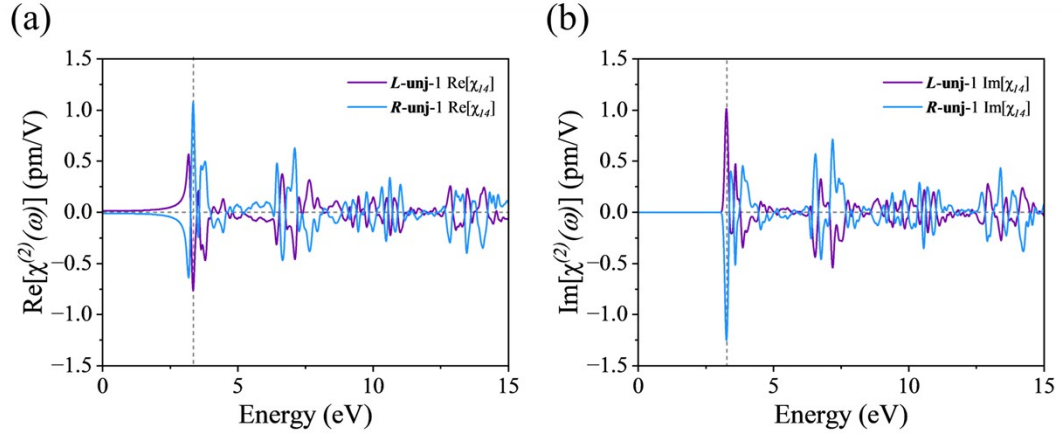


Fig. S9 Real part and imaginary part of the SHG susceptibilities $\chi_{ij}^{(2)}$ for *L*-unj-1 and *R*-unj-1.

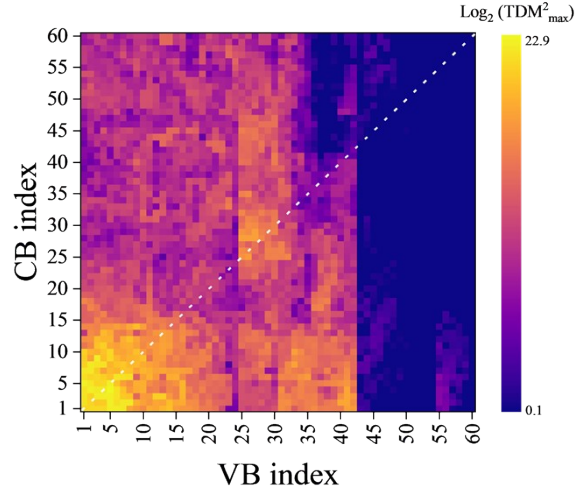


Fig. S10 Squared transition dipole moments (TDM²) between 60 valence bands and 60 conduction bands of *unj*-1. The white dashed line is included for visual guidance along the band-index diagonal.

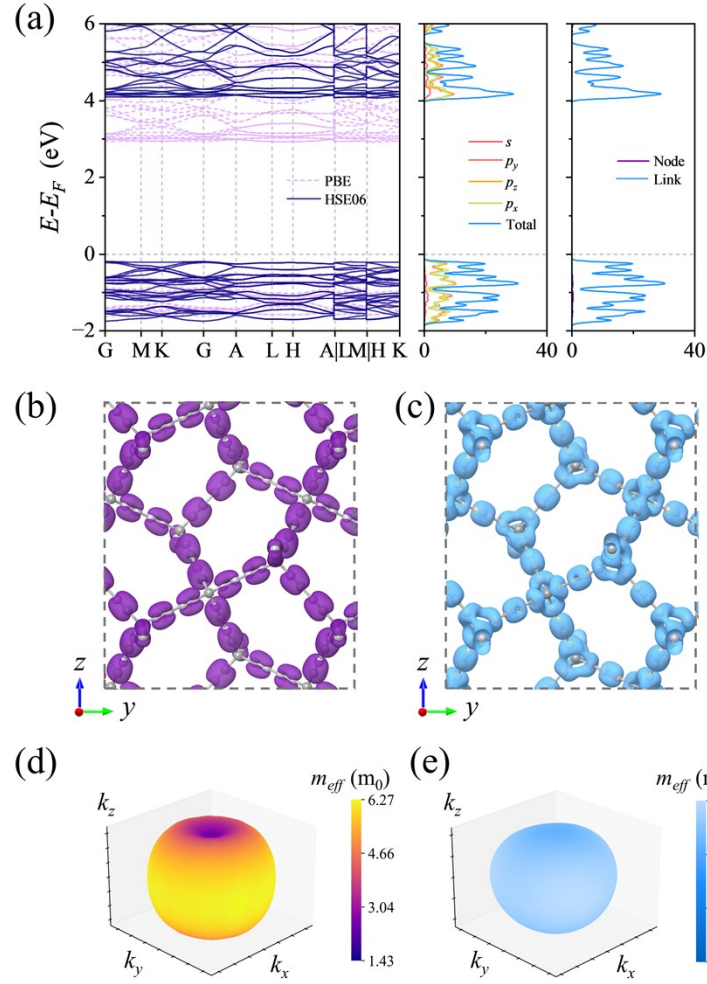


Fig. S11 Electronic properties of unj-2: (a) band structure with the bandgap of 4.28 eV and partial DOS at the HSE06 level, (b, c) band-partial charge distributions at the VBM and CBM (isovalue = 0.0008 Å⁻³). (d, e) 3D anisotropic effective mass (m_{eff}) at the VBM (absolute values for better visualization) and the CBM.

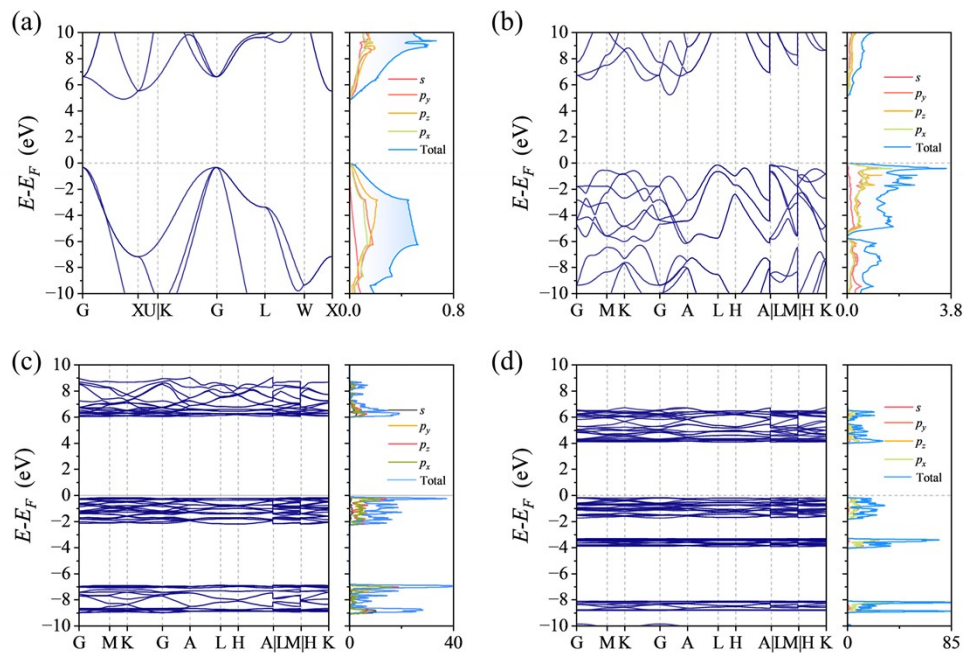


Fig. S12 Band structures and DOS at the HSE06 level: (a) dia, (b) unj, (c) unj-1, and (d) unj-2.

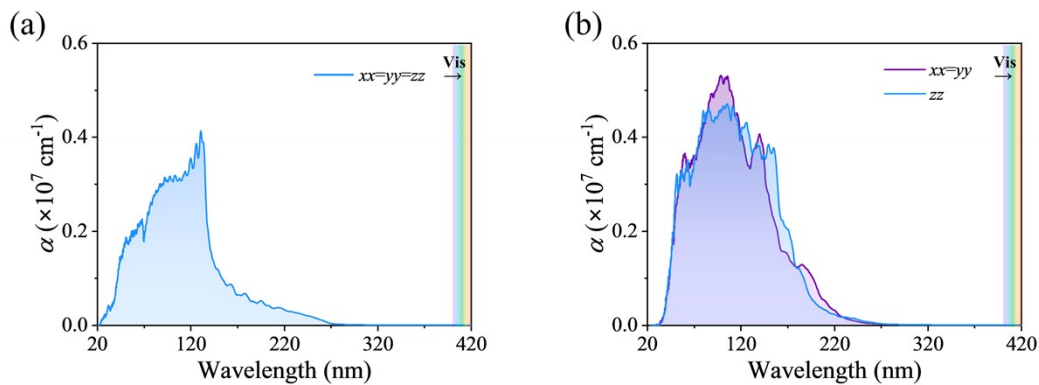


Fig. S13 Absorption spectra of (a) dia and (b) unj.

Appendix: POSCAR files of the main structures.

dia

```
1.000000000
  2.5253059067    0.0000000000    0.0000000000
  1.2626529533    2.1869790675   -0.0000000000
  1.2626529533    0.7289930225    2.0619036386
```

C

2

Direct

```
0.2500000000  0.2500000000  0.2500000000
-0.0000000000 -0.0000000000  0.0000000000
```

unj

1.0

```
  3.5734000206    0.0000000000    0.0000000000
 -1.7867000103    3.0946551957    0.0000000000
  0.0000000000    0.0000000000    3.3787999153
```

C

6

Direct

```
0.767430000    0.232570000    0.916666687
0.767430000    0.534860000    0.250000020
0.465140000    0.232570000    0.583333353
0.232570000    0.767430000    0.416666687
0.232570000    0.465140000    0.750000020
0.534860000    0.767430000    0.083333353
```

unj-1

1.0

```
  9.5366001129    0.0000000000    0.0000000000
 -4.7683000565    8.2589379635    0.0000000000
  0.0000000000    0.0000000000    9.1676998138
```

C

30

Direct

```
0.631140000    0.698850000    0.858370000
0.301150000    0.932290000    0.525036667
```

0.067710000	0.368860000	0.191703333
0.368860000	0.301150000	0.358370000
0.698850000	0.067710000	0.025036667
0.932290000	0.631140000	0.691703333
0.698850000	0.631140000	0.808296667
0.932290000	0.301150000	0.141630000
0.368860000	0.067710000	0.474963333
0.301150000	0.368860000	0.308296667
0.067710000	0.698850000	0.641630000
0.631140000	0.932290000	0.974963333
0.340870000	0.572400000	0.131430000
0.427600000	0.768470000	0.798096667
0.231530000	0.659130000	0.464763333
0.659130000	0.427600000	0.631430000
0.572400000	0.231530000	0.298096667
0.768470000	0.340870000	0.964763333
0.572400000	0.340870000	0.535236667
0.768470000	0.427600000	0.868570000
0.659130000	0.231530000	0.201903333
0.427600000	0.659130000	0.035236667
0.231530000	0.572400000	0.368570000
0.340870000	0.768470000	0.701903333
0.766000000	0.234000000	0.083333336
0.766000000	0.532000000	0.750000002
0.468000000	0.234000000	0.416666669
0.234000000	0.766000000	0.583333336
0.234000000	0.468000000	0.250000002
0.532000000	0.766000000	0.916666669

unj-2

1.0

15.4399995804	0.0000000000	0.0000000000
-7.7199997902	13.3714318710	0.0000000000
0.0000000000	0.0000000000	14.8355998993

C

54

Direct

0.594100000	0.725660000	0.880990000
-------------	-------------	-------------

0.274340000	0.868440000	0.547656667
0.131560000	0.405900000	0.214323333
0.405900000	0.274340000	0.380990000
0.725660000	0.131560000	0.047656667
0.868440000	0.594100000	0.714323333
0.725660000	0.594100000	0.785676667
0.868440000	0.274340000	0.119010000
0.405900000	0.131560000	0.452343333
0.274340000	0.405900000	0.285676667
0.131560000	0.725660000	0.619010000
0.594100000	0.868440000	0.952343333
0.639270000	0.686290000	0.850320000
0.313710000	0.952980000	0.516986667
0.047020000	0.360730000	0.183653333
0.360730000	0.313710000	0.350320000
0.686290000	0.047020000	0.016986667
0.952980000	0.639270000	0.683653333
0.686290000	0.639270000	0.816346667
0.952980000	0.313710000	0.149680000
0.360730000	0.047020000	0.483013333
0.313710000	0.360730000	0.316346667
0.047020000	0.686290000	0.649680000
0.639270000	0.952980000	0.983013333
0.767570000	0.467640000	0.823240000
0.532360000	0.299930000	0.489906667
0.700070000	0.232430000	0.156573333
0.232430000	0.532360000	0.323240000
0.467640000	0.700070000	0.989906667
0.299930000	0.767570000	0.656573333
0.467640000	0.767570000	0.843426667
0.299930000	0.532360000	0.176760000
0.232430000	0.700070000	0.510093333
0.532360000	0.232430000	0.343426667
0.700070000	0.467640000	0.676760000
0.767570000	0.299930000	0.010093333
0.768030000	0.413950000	0.883310000
0.586050000	0.354080000	0.549976667
0.645920000	0.231970000	0.216643333
0.231970000	0.586050000	0.383310000

0.413950000	0.645920000	0.049976667
0.354080000	0.768030000	0.716643333
0.413950000	0.768030000	0.783356667
0.354080000	0.586050000	0.116690000
0.231970000	0.645920000	0.450023333
0.586050000	0.231970000	0.283356667
0.645920000	0.413950000	0.616690000
0.768030000	0.354080000	0.950023333
0.765920000	0.234080000	0.083333336
0.765920000	0.531840000	0.750000002
0.468160000	0.234080000	0.416666669
0.234080000	0.765920000	0.583333336
0.234080000	0.468160000	0.250000002
0.531840000	0.765920000	0.916666669

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