

Supplementary Information for

Multifunctional van der Waals PdSe₂ for light detection, guiding and modulation

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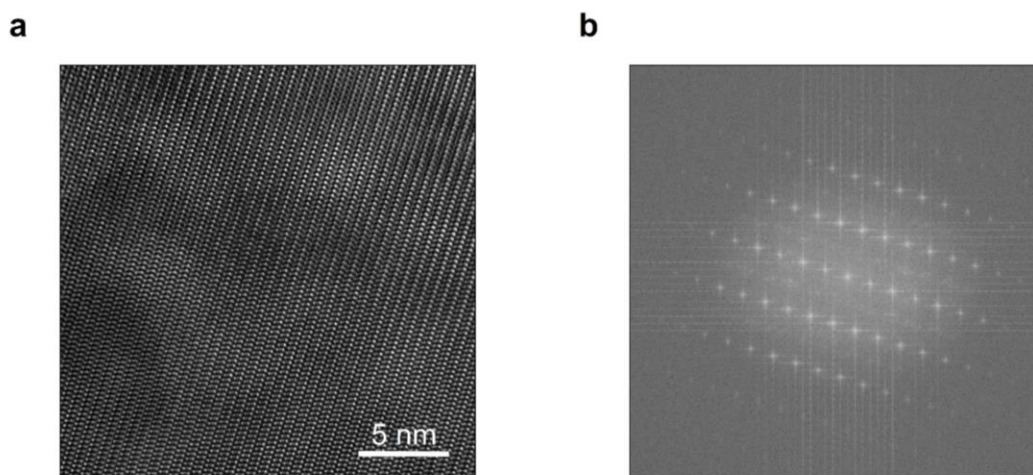
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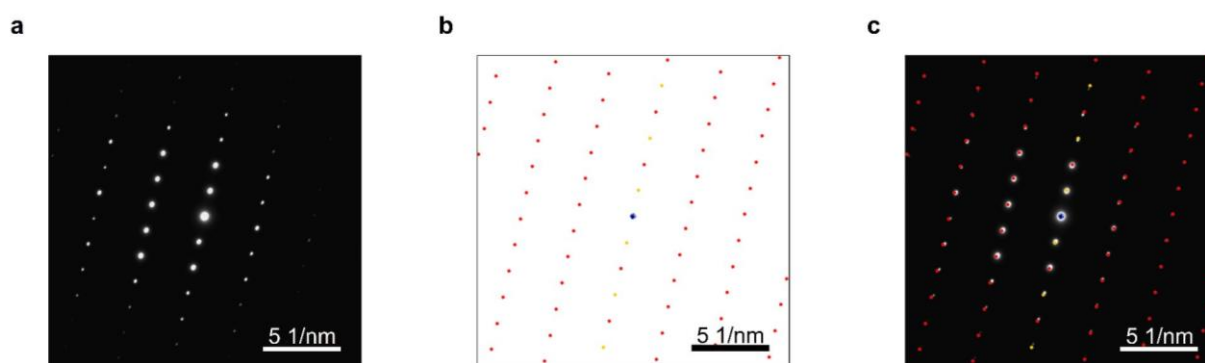
Supplementary Note 1: PdSe₂ crystal characterization

We observed the atomic structure of PdSe₂ thin flakes using transmission electron microscopy (TEM) technique in high-resolution imaging mode (Supplementary Figure 1a). Despite the crystalline plane image being noisy, we clearly see an atomic line pattern. The lines parallelism and straightness prove the absence of structural defects. Moreover, to ensure that the resulting image of the atomic layers corresponds to the pentagonal crystal lattice of PdSe₂ we processed high-resolution data using fast Fourier transform (FFT), see Supplementary Figure 1b. Obtained pattern fits previous data from better quality high-resolution TEM images¹.



Supplementary Figure 1. TEM imaging. **a** High-resolution TEM image of a few-layer PdSe₂ flake. **b** Corresponding FFT image.

Selected area electron diffraction (SAED) pattern analysis, along with TEM imaging, provides additional confirmation of phase structure and crystal quality. In this regard, we performed transmission electron microscopy measurement. The experimental SAED pattern (Supplementary Figure 2a) sufficiently matches with literature experimental data^{1,2}. Also, we simulated a diffraction pattern (Supplementary Figure 2b) using cif-file that we then used in our ab initio computations. Finally, we overlaid the simulated points onto the experimental image, see Supplementary Figure 2c. The accuracy of the reflections' coincidence proves the high reliability of the data in the file we use.

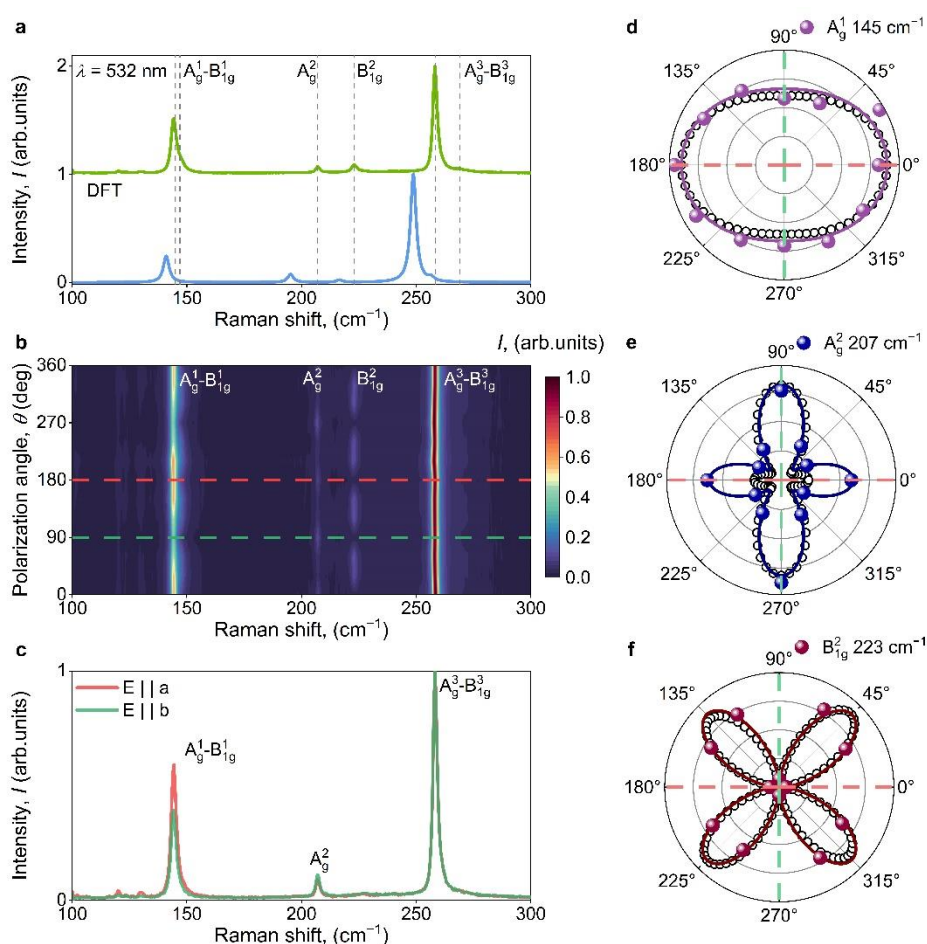


Supplementary Figure 2. Electron diffraction analysis. **a** Selected area electron diffraction (SAED) image. **b** Simulated SAED pattern. **c** Overlaying of simulated and experimental data.

Supplementary Note 2: PdSe₂ angle-resolved Raman spectroscopy

Crystallographic directions in PdSe₂ flakes

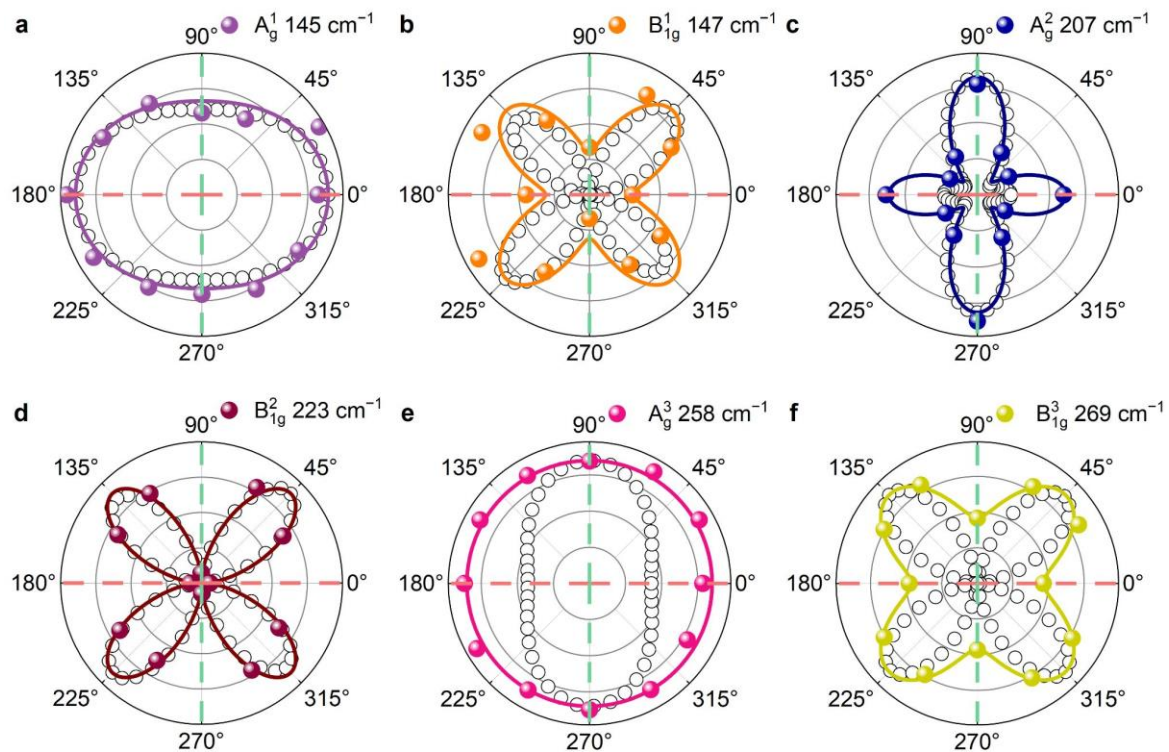
Angle-resolved Polarized Raman spectroscopy (ARPRS) is a powerful tool for studying crystallographic orientations and defects in vdW materials. In order to identify in-plane crystallographic axes of PdSe₂ flakes we utilized polarized Raman spectroscopy in combination with density functional theory (DFT) Raman calculations. All the Raman spectra of PdSe₂ were measured using a Horiba LabRAM HR Evolution (HORIBA Ltd., Kyoto, Japan) confocal Raman microscope, equipped with a 100× objective (N.A. = 0.9) and an 1800 lines/mm diffraction grating. A 532 nm laser was used as a source of linearly polarized light, along with an additional analyzer placed in the way of the scattered beam, which allowed us to measure Raman spectra in parallel configuration. Raman spectra were acquired with laser power of 0.35 mW and a spot size of ~1 μm. The samples were rotated in a full circle with 30° step, and the spectra at all sample rotation angles were accumulated over 10 different points on the flake over 10 s integration time. After the measurements, all spectra were processed by subtracting baseline and fitting Raman peaks with Lorentz function.



Supplementary Figure 3. Raman spectroscopy for crystallographic axes determination. **a** Experimental angle-averaged Raman spectra of PdSe₂ flake (green line, $\lambda = 532$ nm) and DFT calculations (blue line). **b** angle-resolved Raman spectrum map. Dashed red and green lines denote orientations of *a*- and *b*-axes, correspondingly. **c** Raman spectra of the bulk PdSe₂ flake with laser polarized along *a* and *b* crystallographic axes. **d-f** polar diagrams of Raman resonance peaks. Colored points denote experimental data, solid lines represent fitted curves and blank circles depict DFT calculated diagrams. The data in polar diagrams are normalized to their maximum values, respectively.

Supplementary Figure 3a represents in-plane angle-averaged experimental and calculated Raman spectra. We identified six Raman-active vibrational modes between 100 and 300 cm^{-1} : three symmetric A_g modes and three antisymmetric B_{1g} modes. Experimental Raman active modes are marked with dashed gray lines. These findings are in complete agreement with our calculations and previous reports³⁻⁵. Further details on vibration response analysis are presented in the next subsection.

The intensities of Raman modes are sensitive to the polarization angle of the incident light. Using the orientation-invariant relationship between in-plane crystallographic axes and polarized Raman mode profiles, we determined the lattice orientation of PdSe₂ flakes. Supplementary Figure 3b shows a polarization-dependent Raman intensity map. By applying Raman tensor calculations, we matched polarization dependencies of each experimental mode to theoretical predictions with known directions of the in-plane crystal axes (see Supplementary Figure 4). Thus, we determined the a - and b -axes of crystallographic directions. Supplementary Figure 3c represents Raman spectra for incident laser-beam polarization along the crystalline axes. Most of the experimental peaks showed remarkable congruence with the vibrational modes calculated using DFT, as depicted in the polar diagrams for A_g^1 (145 cm^{-1}), A_g^2 (207 cm^{-1}), B_{1g}^2 (223 cm^{-1}) mode (see Supplementary Figure 3d-f). The red and green dashed lines represent the laser-beam polarization directions parallel to the crystallographic a - and b -axes, respectively. We observe additional peaks coming from second-order Raman scattering since the laser energy exceeds PdSe₂ optical bandgap, which we prove by calculating the two-phonon density of states, see below.



Supplementary Figure 4. Anisotropy of vibrational modes. a-f Polar diagrams of ARPRS peaks with their experimental positions. Color dots represent experimental data, solid lines are fitted curves and blank circles denote theoretical (DFT) dependencies.

PdSe₂ vibrational response analysis

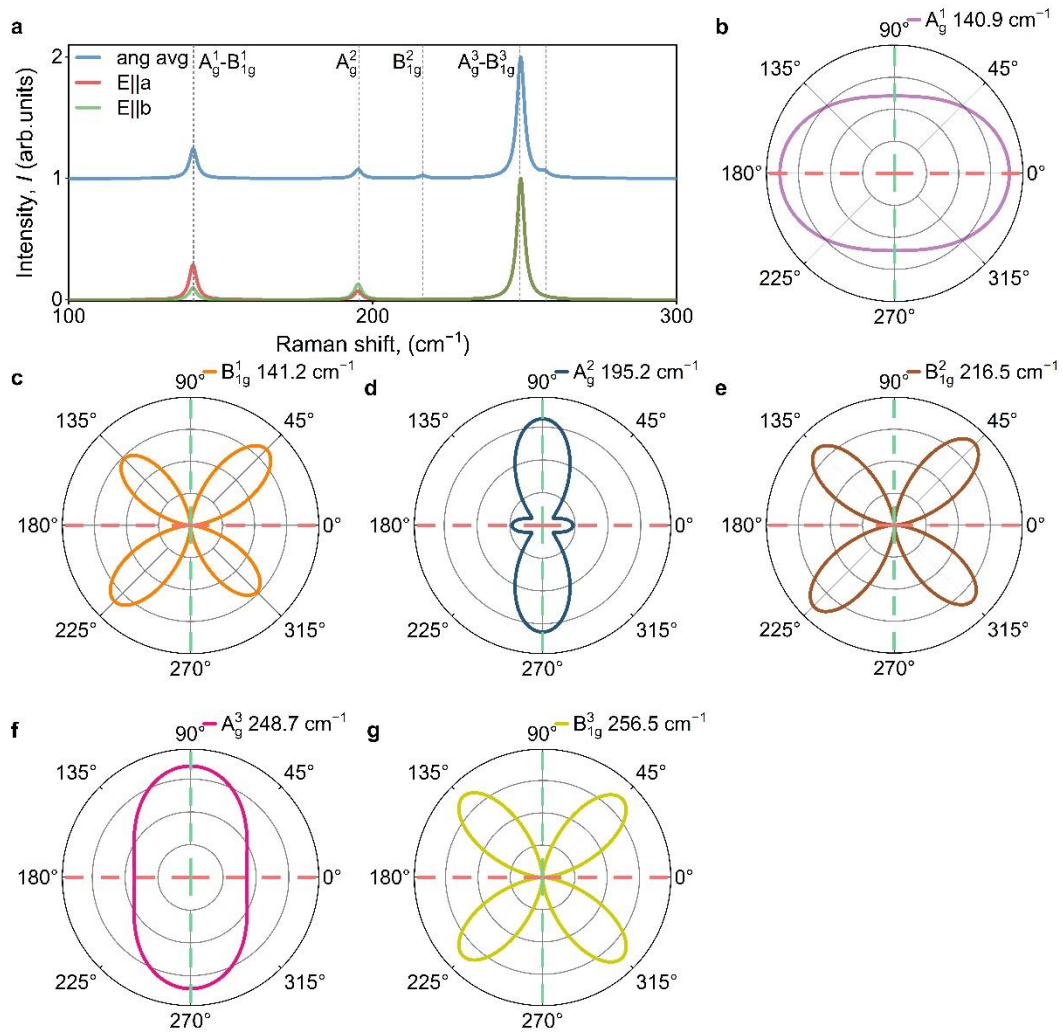
Ab-initio calculations were performed using Vienna ab initio simulation package (VASP) code⁶. The core electrons are described with projector augmented wave (PAW) pseudopotentials treating the Pd 4d, 5s

and the Se 4s and 4p electrons as valence. A kinetic energy cutoff for the plane-wave basis was set to 400 eV. The lattice parameters of PdSe₂ crystal were taken from literature⁷. Raman spectra and polar diagrams were computed based on the Phonopy-Spectroscopy package with our modifications.

PdSe₂ belongs to the orthorhombic system and has the space group Pbca. Representation for the lattice modes is as follows:

$$\begin{aligned}\Gamma &= \Gamma_{\text{acoustic}} + \Gamma_{\text{optical}}, \\ \Gamma_{\text{acoustic}} &= B_{1u} + B_{2u} + B_{3u}, \\ \Gamma_{\text{optical}} &= 3A_g + 3B_{1g} + 3B_{2g} + 6A_u + 5B_{1u} + 5B_{2u} + 5B_{3u}.\end{aligned}\quad (1)$$

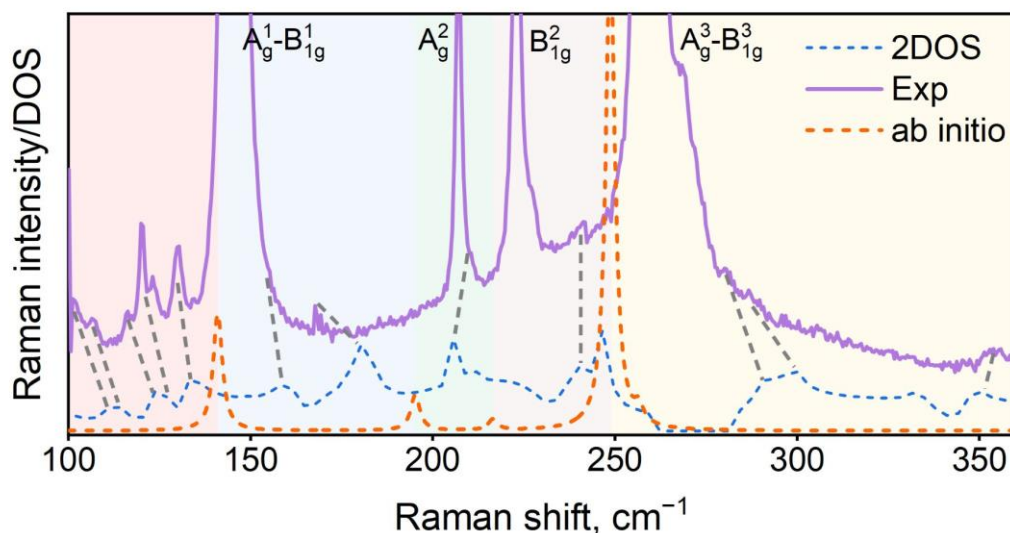
In total we have 36 phonon modes which is 3×12 (12 atoms per unit cell). Vibrations having A_g , B_{1g} , B_{2g} and B_{3g} irreducible representations are Raman-active. In the experimental geometry used in our measurements (laser beam is directed parallel to the c -axis, and the polarization of the incident light is parallel to the in-plane axes) we observe only $3A_g$ and $3B_{1g}$ modes (6 in total).



Supplementary Figure 5. Theoretical Raman response of PdSe₂. **a** Theoretical Raman spectra with light polarized along crystallographic axes. **b-g** Polar diagrams of theoretical Raman active peaks with their computed positions.

Applying Phonopy code^{8,9}, we calculated eigenvibrations and eigenfrequencies. Raman tensors were computed based on frequency-dependent dielectric tensors (within the independent particle approach) for all phonon modes above 100 cm^{-1} . Experimental and theoretical angle-averaged Raman spectra in Supplementary Figure 3a and along crystallographic axes (see Supplementary Figure 3c and Supplementary Figure 5a) are in good agreement. The experimental positions of 6 Raman-active modes in the range from 100 to 300 cm^{-1} are: 145, 147, 207, 223, 258 and 269 cm^{-1} . Corresponding theoretical positions are: $140.9\text{ (A}_g\text{)}$, $141.2\text{ (B}_{1g}\text{)}$, $195.2\text{ (A}_g\text{)}$, $216.5\text{ (B}_{1g}\text{)}$, $248.7\text{ (A}_g\text{)}$ and $256.5\text{ (B}_{1g}\text{)}\text{ cm}^{-1}$. In Supplementary Figure 5b-g angle-resolved Raman intensities for calculated Raman-active vibrations are shown. Their geometrical origin is demonstrated in Figure 4c of the previous research¹⁰.

Notably, we observed additional experimental peaks associated with the second-order processes, which is favored by the high laser energy of 2.33 eV. We confirm this fact by constructing an overtone density of states (DOS), that is phonon DOS on its 2-fold range (see Supplementary Figure 6). It is seen that additional lines on the Raman spectrum are in good agreement with the overtone DOS which justifies their second-order nature. We also observe a new peak beyond the range from 100 to 300 cm^{-1} (the maximum phonon frequency in computations is 258 cm^{-1} corresponding to B_{2g} mode which is of zero intensity in the experiment geometry) which is not first-order line.



Supplementary Figure 6. Experimental (purple solid line) and DFT (orange dashed line) Raman spectra for angle-averaged in-plane parallel polarizations. Density of overtone phonon states (blue dashed line). Gray dashed lines connect the experimental peaks to the DFT overtones. We chose these spectra scales for clarity.

Supplementary Note 3: PdSe₂ principal optical axes determination

The comparison of dielectric tensor principal axes and crystallographic axes is an important step in the investigation of optical properties. For the attribution of n_a and n_b to the main crystallographic axes, we determined the in-plane crystallographic directions of PdSe₂ flakes via polarization-resolved Raman spectroscopy method as described in the previous section. To find the principal optical axes, we performed polarized micro-reflectance measurements (see Methods). Supplementary Figure 7a shows the experimental polarization-dependent reflectance map measured with 10° steps in a visible range (500–800 nm) from 0° to 360°. The extracted spectra were approximated linearly with a $\Delta\lambda$ of 1 nm. Subsequently, each $R_\lambda(\alpha)$ at fixed λ was fitted (see Supplementary Figure 7b) with the following formula:

$$R_\lambda(\alpha) = \left| \frac{E^1}{E^0} \right|^2 = \quad (2)$$

$$= |A_\lambda \sin^2 \alpha + B_\lambda e^{i\Delta\phi} \cos^2 \alpha|^2 = A_\lambda^2 \sin^4 \alpha + B_\lambda^2 \cos^4 \alpha + 2A_\lambda B_\lambda \sin^2 \alpha \cos^2 \alpha \cos \Delta\phi,$$

that can be derived from the complex Fresnel coefficients r_a and r_b :

$$\begin{cases} E_b^0 = E^0 \cos \alpha \\ E_a^0 = E^0 \sin \alpha \\ E_b^1 = r_b E_b^0 \\ E_a^1 = r_a E_a^0 \end{cases} \Rightarrow$$

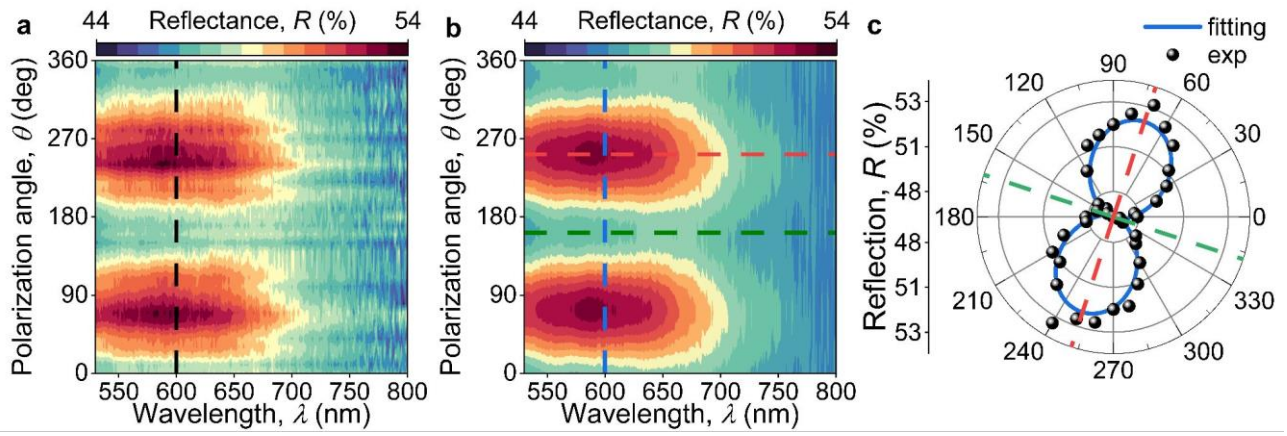
$$E^1 = E_a^1 \sin \alpha + E_b^1 \cos \alpha = r_a E_a^0 \sin \alpha + r_b E_b^0 \cos \alpha = r_a E^0 \sin^2 \alpha + r_b E^0 \cos^2 \alpha$$

$$\begin{aligned} R &= \left| \frac{E^1}{E^0} \right|^2 = |r_a \sin^2 \alpha + r_b \cos^2 \alpha|^2 = |r_a' \sin^2 \alpha + r_b' \cos^2 \alpha + i(r_a'' \sin^2 \alpha + r_b'' \cos^2 \alpha)|^2 = \\ &= |r_a' \sin^2 \alpha + r_b' \cos^2 \alpha|^2 + |r_a'' \sin^2 \alpha + r_b'' \cos^2 \alpha|^2 + 2r_a' r_b' \sin^2 \alpha \cos^2 \alpha + \\ &\quad + 2r_a'' r_b'' \sin^2 \alpha \cos^2 \alpha + 2r_a' r_b'' \sin^2 \alpha \cos^2 \alpha = \begin{cases} R_a = |r_a|^2 \\ R_b = |r_b|^2 \end{cases} = R_a \sin^4 \alpha + R_b \cos^4 \alpha + \\ &\quad + 2 \sin^2 \alpha \cos^2 \alpha (r_a' r_b' + r_a'' r_b'') = \begin{cases} \vec{a}\vec{b} = |a||b|\cos\Delta\phi \\ \vec{a}\vec{b} = a_x b_x + a_y b_y \end{cases} = R_a \sin^4 \alpha + R_b \cos^4 \alpha + \\ &\quad + 2 \sin^2 \alpha \cos^2 \alpha \sqrt{R_a R_b} \cos \Delta\phi = \begin{cases} R_a = A_\lambda^2 \\ R_b = B_\lambda^2 \end{cases} = A_\lambda^2 \sin^4 \alpha + B_\lambda^2 \cos^4 \alpha + 2 \sin^2 \alpha \cos^2 \alpha A_\lambda B_\lambda \cos \Delta\phi \end{aligned}$$

where α can be expressed as:

$$\alpha = \theta - \varphi_0, \quad (3)$$

where θ is the polarization angle, φ_0 is the angle identifying the principal optical axis position. The angle for the second principal axis is $\varphi_0 + 90^\circ$. A_λ^2 and B_λ^2 are the reflectance spectra with light polarized along in-plane optical axes and $\Delta\phi$ is the phase difference between reflected beams polarized along a - and b -axes, correspondingly. Next, to determine optical axes, we used the fitted curves (Supplementary Figure 7c). Then, we matched principal optical and crystallographic axes directions to designate n_a and n_b refractive-index-tensor components.

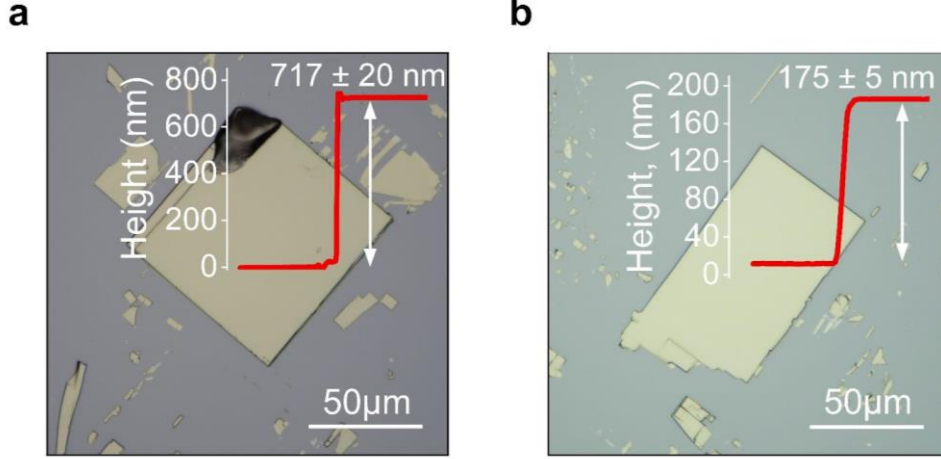


Supplementary Figure 7. In-plane principal optical axes determination. **a,b** Polarized micro-reflectance experimental and fitting maps of PdSe₂ flake respectively. **c** Angle-dependent reflectance diagram is taken along vertical dashed lines in the panels (**a,b**). The green and red dashed lines denote the optical axes (**b,c**).

Supplementary Note 4: PdSe₂ optical constants

PdSe₂ optical constants determination from reflectance and ellipsometry measurements

To obtain the refractive index complex tensor we performed spectroscopic ellipsometry (250–1700 nm) measurements of PdSe₂ flakes on Si substrates. Optical images of PdSe₂ flakes used in the measurement of optical constants are provided in Supplementary Figure 8.



Supplementary Figure 8. Sample thickness characterization. **a, b** Optical images of 717-nm-thick and 175-nm-thick PdSe₂ flakes respectively. The insets demonstrate height profiles of samples measured via AFM.

We also obtained the reflectance spectra in the wavelength region from VIS to FIR by combining A_λ^2 and B_λ^2 from angle-resolved measurements (see Supplementary Note 3) and reflectance spectra with polarization of incident light along in-plane principal optical axes from Fourier-transform infrared spectroscopy measurements, as demonstrated in Supplementary Figure 9. Then we acquired the full dielectric tensor of PdSe₂ by fitting of ψ , Δ spectra at different angles (see an exemplified graphs in Supplementary Figure 10) and the resulted reflectance spectra (see Supplementary Figure 9c) simultaneously. To further improve the accuracy of the measurements, we apply Mueller matrix analysis. As a result, we measured the Mueller Matrix in the spectral range (400–900 nm) and added the Mueller Matrix in the analysis of optical properties. The experimental Mueller Matrix spectra and their fitting curves are presented in Supplementary Note 10. The fitting model incorporates Tauc-Lorentz oscillators model to describe excitonic response¹¹ and Drude oscillator model to take into account metallic response in infrared wavelength range for in-plane light polarization:

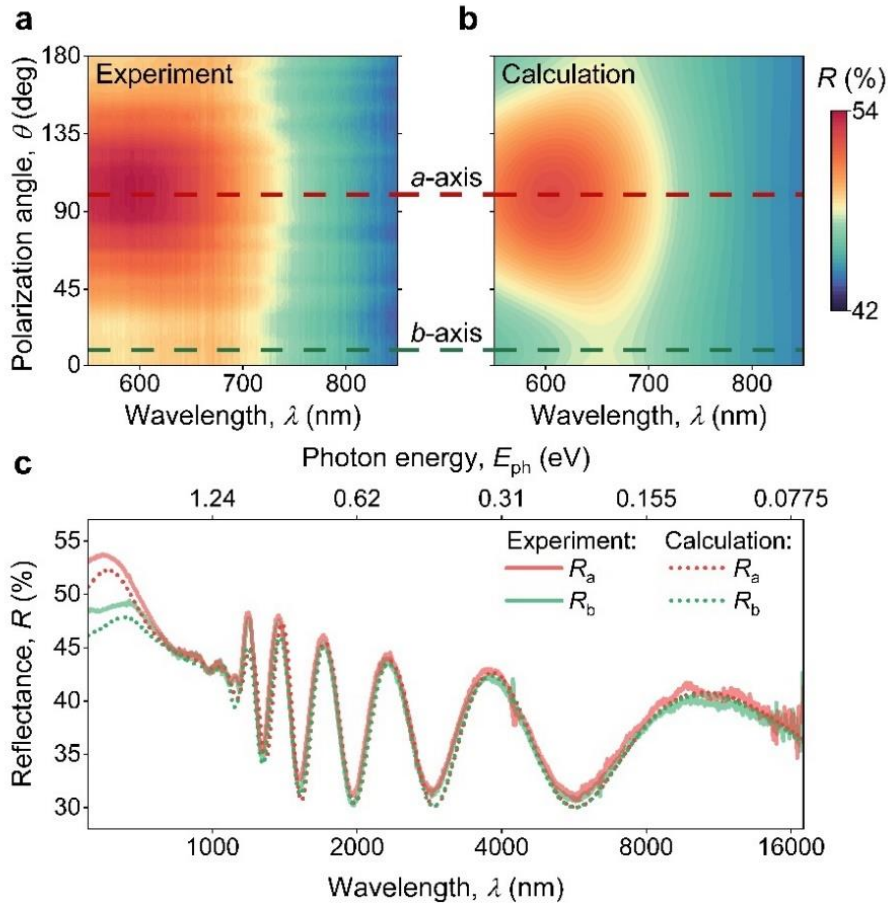
$$\begin{aligned} \varepsilon_x &= \varepsilon_{\infty,x} + \varepsilon_{\text{Drude},x} + \sum_{j=1}^n (\varepsilon'_{\text{TL},jx} + i\varepsilon''_{\text{TL},jx}) = \\ &= \varepsilon_{\infty,x} - \frac{A_{\text{Drude},x} B_x}{E^2 + iB_x E} + \sum_{j=1}^n \left(\frac{2}{\pi} \text{v. p.} \int_{E_{g,jx}}^{\infty} \frac{\xi \varepsilon''_{\text{TL},jx}(\xi)}{\xi^2 - E^2} d\xi + iH_{E_{g,jx}}(E) \frac{1}{E} \frac{A_{jx} E_{0,jx} C_{jx} (E - E_{g,jx})^2}{(E^2 - E_{0,jx}^2)^2 + C_{jx}^2 E^2} \right). \end{aligned} \quad (4)$$

where x represent a, b with respect to crystal in-plane anisotropy, ε_{∞} is a contribution in the dielectric function of high energy interband transition, E is photon energy, ε_0 is vacuum permittivity, A_{Drude} and B amplitude and damping coefficient of Drude oscillator, n is a number of Tauc-Lorentz oscillators, E_g is optical band gap, H_{E_g} is

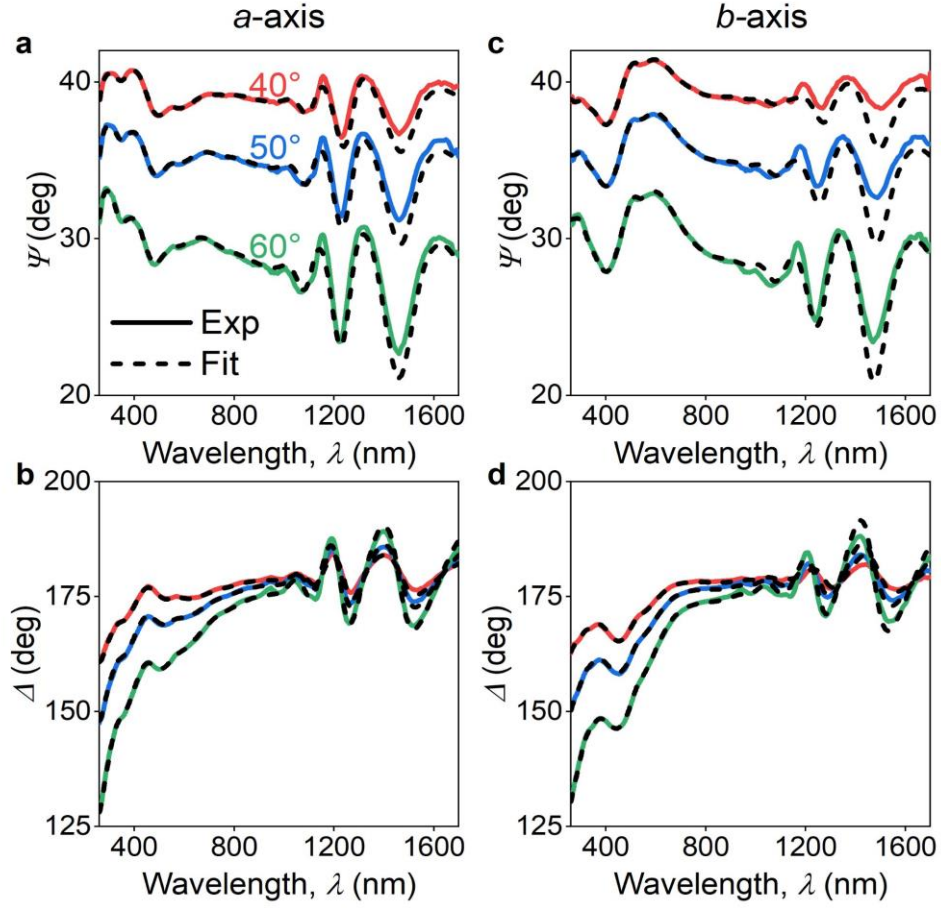
Heaviside step function equal one if $E > E_{g,x}$ and zero otherwise, A_j , C_j , and $E_{0,j}$ are strength, broadening term, and peak central energy of j^{th} Tauc-Lorentz oscillator, respectively. The out-of-plane component of permittivity tensor does not have Drude tail because electron jumps between layers along c -axis are neglectable. Therefore, the fitting formula has a different form:

$$\begin{aligned} \varepsilon_c &= \varepsilon_{\text{pole},c} + \varepsilon'_{\text{TL},1c} + i\varepsilon''_{\text{TL},1c} = \\ &= \frac{A_{\text{pole}}}{E_{\text{pole}}^2 + E^2} + \frac{2}{\pi} \text{v. p.} \int_{E_{g,1c}}^{\infty} \frac{\xi \varepsilon''_{\text{TL},1c}(\xi)}{\xi^2 - E^2} d\xi + iH_{E_{g,1c}}(E) \frac{1}{E} \frac{A_{1c}E_{0,1c}C_{1c}(E - E_{g,1c})^2}{(E^2 - E_{0,1c}^2)^2 + C_{1c}^2 E^2}. \end{aligned} \quad (\text{S5})$$

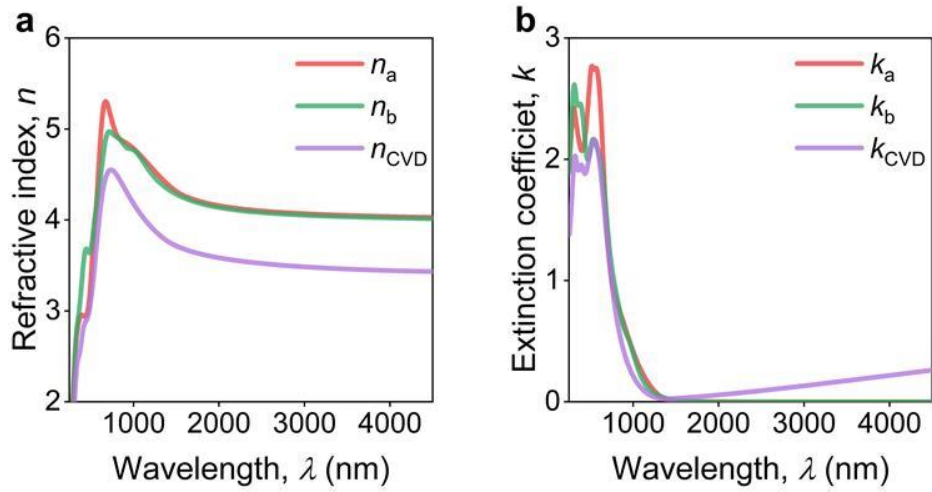
where A_{pole} and E_{pole} are magnitude and pole position respectively. For the initial approximation we used PdSe₂ CVD film optical constants¹², see Supplementary Figure 11. The calculated reflectance spectra based on the obtained optical constants are in good agreement with experimental data, as shown in Supplementary Figure 9. Final parameters of the optical model are collected in Supplementary Table 1, Supplementary Table 2 and Supplementary Table 3 for a , b and c principal optical axes respectively. Tabulated optical constants are represented in Supplementary Note 11.



Supplementary Figure 9. Angle-resolved reflectance spectra. **a,b** Experimental and calculated polarization-resolved micro-reflectance maps of the 717-nm-thick PdSe₂ flake respectively. Red and green dashed lines illustrate a - and b -axes. **c** Experimental reflectance spectra with light polarized along a - and b -axes are presented by solid lines. Calculated spectra are drawn with dotted lines.



Supplementary Figure 10. Spectroscopic ellipsometry data. **a,b** ψ and Δ of 717 nm thick PdSe₂ flake with light polarized along *a*-axis. **c,d** ψ and Δ of 717-nm-thick PdSe₂ flake with light polarized along *b*-axis. Dashed lines denote fitting curves, solid lines represent experimental data.



Supplementary Figure 11. Comparison of in-plane PdSe₂ refractive index and extinction coefficient of bulk crystal (**a**) and CVD film (**b**).

Supplementary Table 1. Tauc-Lorentz oscillators model parameters of *a*-axis ($\epsilon_\infty = 2.6376 \pm 0.2633$; $A_{\text{Drude}} = 1.0021 \pm 0.6310$ eV; $B = 0.008491 \pm 0.006325$ eV).

Tauc-Lorentz oscillators	<i>A</i> , eV	<i>E</i> ₀ , eV	<i>C</i> , eV	<i>E</i> _g , eV
1b	5.756 ± 1.369	1.2949 ± 0.0236	0.3566 ± 0.0244	0.6221 ± 0.0402
2b	91.78 ± 23.05	1.4998 ± 0.0517	0.5617 ± 0.1244	1.2193 ± 0.0573
3b	158.32 ± 45.05	1.8149 ± 0.0396	0.6268 ± 0.1541	1.5045 ± 0.0787
4b	25.33 ± 11.55	2.3192 ± 0.0916	0.6480 ± 0.1353	1.4747 ± 0.9475
5b	206.49 ± 46.15	2.8207 ± 0.0770	1.0517 ± 0.1361	2.3050 ± 0.1714

Supplementary Table 2. Tauc-Lorentz oscillators model parameters of *b*-axis ($\epsilon_\infty = 1.5543 \pm 0.3923$; $A_{\text{Drude}} = 0.9981 \pm 0.6201$ eV; $B = 0.008478 \pm 0.006384$ eV).

Tauc-Lorentz oscillators	<i>A</i> , eV	<i>E</i> ₀ , eV	<i>C</i> , eV	<i>E</i> _g , eV
1a	165.09 ± 19.02	1.9469 ± 0.0104	0.62919 ± 0.03438	1.4983 ± 0.0174
2a	30.563 ± 7.156	2.3595 ± 0.0273	0.2963 ± 0.0605	2.0314 ± 0.1922
3a	55.74 ± 6.12	1.6324 ± 0.0443	1.5781 ± 0.1642	0.82115 ± 0.00781
4a	115.76 ± 27.49	3.3556 ± 0.1417	1.9309 ± 0.1150	2.3195 ± 0.1658
5a	0.9378 ± 0.2926	3.9696 ± 0.0261	0.6709 ± 0.1962	0.0001 ± 0.0122
6a	131.060 ± 50.13	6.322 ± 2.557	8.7633 ± 2.9938	4.4271 ± 0.6681

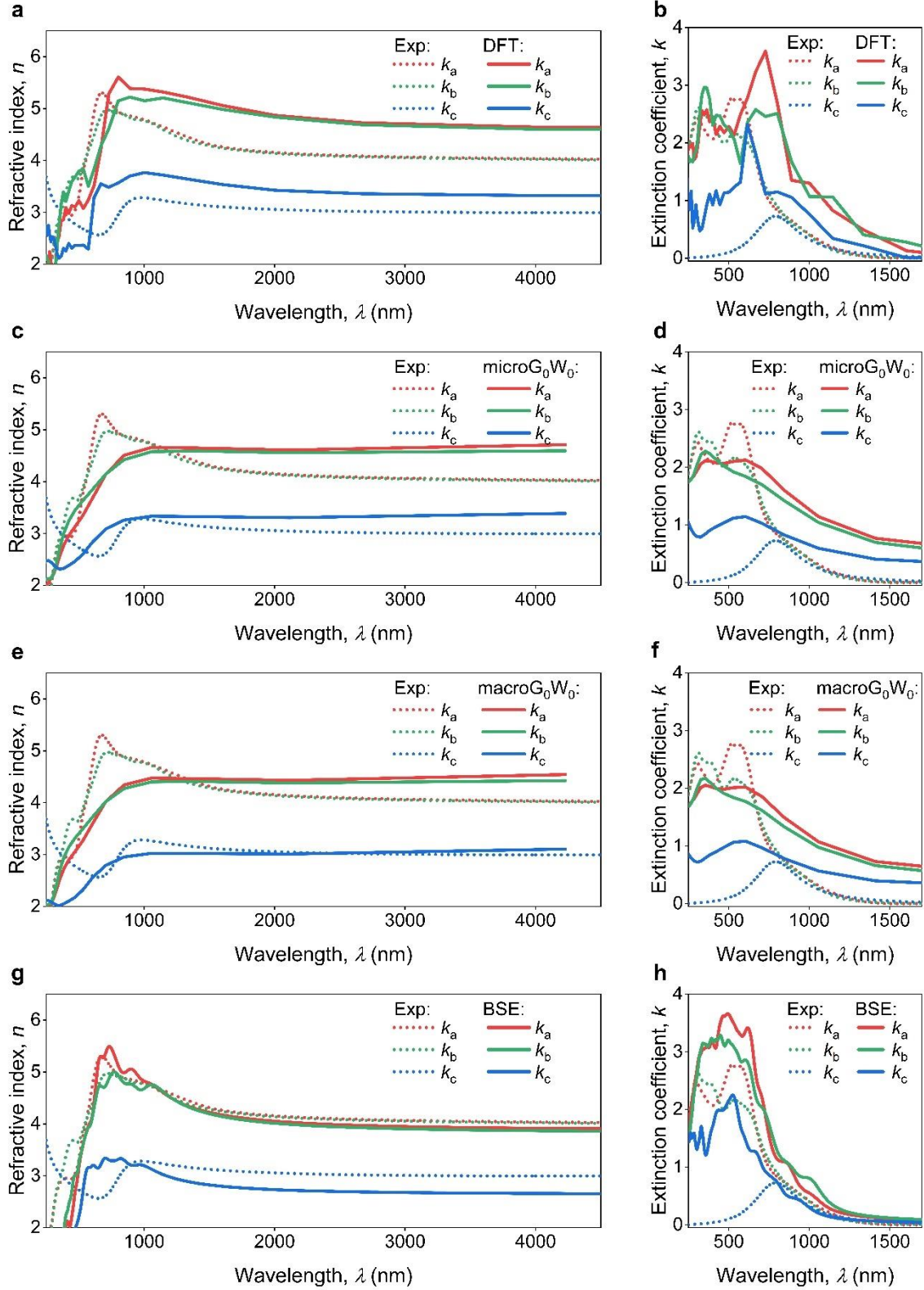
Supplementary Table 3. Tauc-Lorentz oscillators model parameters of *c*-axis ($A_{\text{pole}} = 395.38 \pm 30.87$ eV²; $E_{\text{pole}} = 7.297 \pm 0.251$ eV).

Tauc-Lorentz oscillators	<i>A</i> , eV	<i>E</i> ₀ , eV	<i>C</i> , eV	<i>E</i> _{gn} , eV
1c	5.783 ± 0.927	1.5290 ± 0.0198	0.6490 ± 0.0413	0.4661 ± 0.0678

PdSe₂ ab initio optical constants computation

The optical constants of the PdSe₂ crystal were calculated within the DFT, GW approximation, and Bethe-Salpeter equation (BSE), as implemented in VASP package^{13–16}. We first obtained the one-electron ground-state wavefunctions from a single-shot DFT calculation and used them to initialize the GW run. Next, we calculated the imaginary and real parts of the frequency dependent dielectric function within the GW approximation and derived the refractive indices and extinction coefficients of the material. Finally, we used the GW wavefunctions and screened Coulomb interaction components to solve the BSE and account for the excitonic effects. The cutoff energy for the plane wave basis was set to 400 eV, while the first Brillouin zone was sampled with a Γ -centered 7×7×5 grid. The exchange correlation effects were described with a generalized gradient approximation (Perdew-Burke-Ernzerhof functional)¹⁷, and the behavior of the wavefunctions in the core region was reconstructed with the projector augmented wave pseudopotentials of a GW type. We used 256 bands in the DFT run to initialize the dielectric function, and performed the GW calculation on a total of 64 lowest-energy bands. In the BSE run, we used 12 occupied and 12 valence bands to describe the excitonic effects. All results are collected in Supplementary Figure 12 and compared to experimental constants.

We first note that although the pure DFT results can quantitatively reproduce the experimental peak in the refractive index around 700 nm, the long wavelength behavior is mostly inconsistent (see Supplementary Figure 12a). This effect is often due to the underestimation of the electron correlation effects in the PBE exchange-correlation functional, and therefore one would expect the GW results to be in much better agreement with the experimental data. Nevertheless, both the microscopic and macroscopic dielectric functions obtained from the GW calculation also diverge significantly from the experimental data. Finally, taking into account the excitonic effects by solving the Bethe–Salpeter equation, we were able to reproduce the two excitonic peaks in the refractive index around 700 nm and the long wavelength asymptotics of the dielectric function. Tabulated BSE optical constants are listed in Supplementary Note 12.



Supplementary Figure 12. Optical properties of PdSe₂ calculated within (a,b) DFT, (c,d) GW (from micro dielectric tensor), (e,f) GW (from macro dielectric tensor), (g,h) BSE. Theoretically calculated data for refractive index and extinction coefficient are shown with solid line, experimental data - with dotted lines.

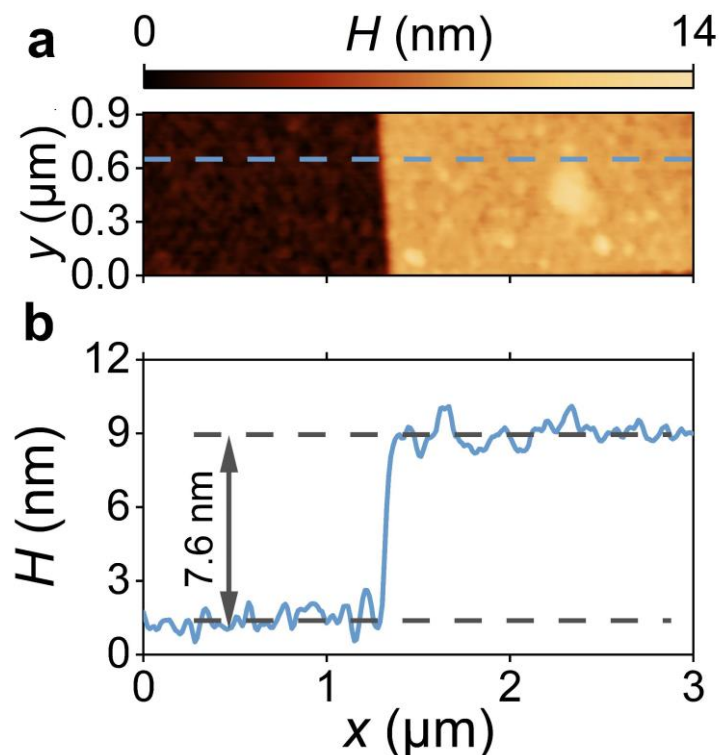
Supplementary Note 5: PdSe₂ plasma frequency and effective transport mass

In Figure 2c of the main text the first Brillouin zone of orthorhombic PdSe₂ is shown. In Figure 2d its bandstructure along high-symmetry paths is demonstrated. For these calculations we used PBE exchange-correlation functional with SOC taken into account. For calculation of free carrier density at room temperature we found the effective masses and separation from Fermi level of the valence band maximum (at Γ point) and conduction band minima (at $S - X$ and $S - Y$ paths). A band with Fermi-level F with respect to the extremum point (positive F meaning that Fermi level is above the conduction band minimum or below the valence band maximum) contains free carriers of a density of $n = \int_0^\infty g f_{\text{FD}}(E, F, T) \text{DOS}(E) dE$, where g is degeneracy factor (not including spin degeneracy which is accounted in DOS), f_{FD} is the Fermi-Dirac distribution function and $\text{DOS}(E)$ is electronic density of states within the considered band according to the parabolic band approximation.

Next, the contributions of each band to the plasma frequency were calculated as $\omega_{\text{band}}^2 = \frac{ne^2}{\epsilon_0 m_t}$, where the effective transport mass was found as $m_t = 3/(1/m_a + 1/m_b + 1/m_c)$. Plasma frequency defined from ellipsometry fit (Supplementary Note 4) is 0.37 eV. Independent predictions based on the DFT-calculated band structure yield free charge carrier concentration of $5.75 \times 10^{19} \text{ cm}^{-3}$ and $\omega_p = 0.43 \text{ eV}$ which is quite close to the measured value. To put these values into perspective, we note that free carrier density in extremely heavily doped semiconductors may reach up to $2 \times 10^{19} \text{ cm}^{-3}$, whereas the free electron density in gold is $5.9 \times 10^{22} \text{ cm}^{-3}$, corresponding to the plasma frequency of 9 eV. Therefore, the calculated free carrier density in our not intentionally doped PdSe₂ is of the same order of magnitude as in extremely heavily doped semiconductors and much lower than in noble bulk metals.

Supplementary Note 6: PdSe₂-based mid-IR photodetector

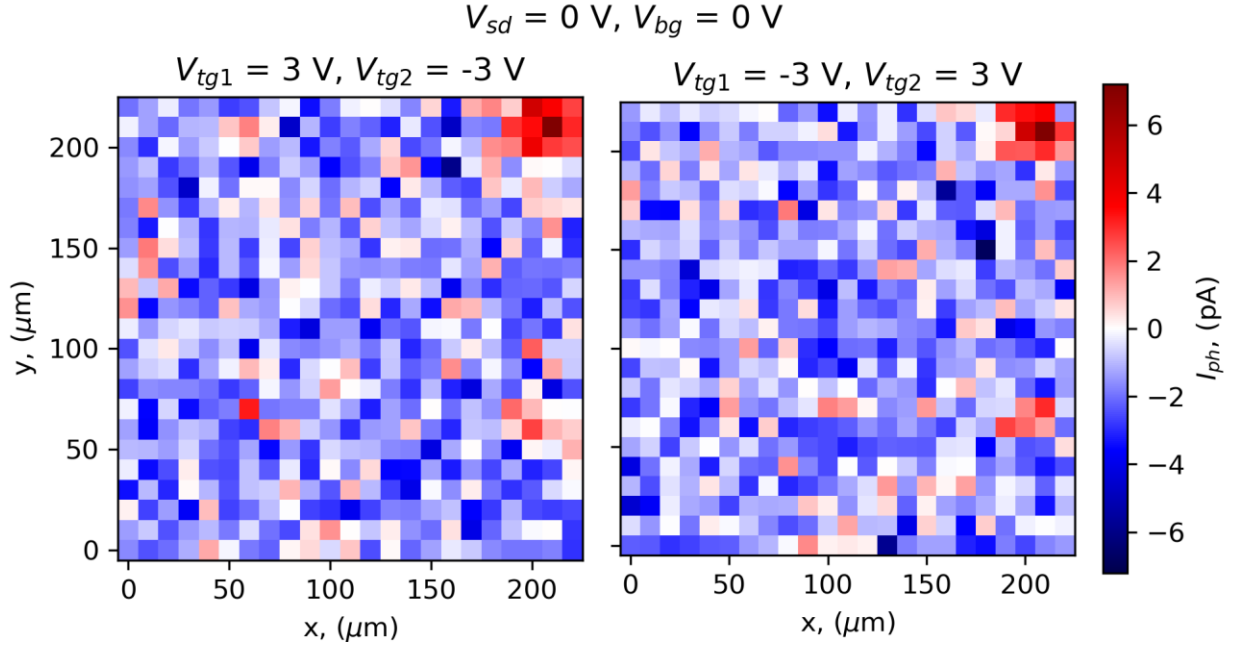
Here we demonstrate extended measurements of a PdSe₂-based mid-IR photodetector. Supplementary Figure 13a represents an AFM image of the edge of a PdSe₂ flake used for mid-infrared photoresponse measurements. The height profile (see Supplementary Figure 13b) across the dashed line in Supplementary Figure 13a shows a step with a thickness of 7.6 nm. The 7.6 nm thickness corresponds to ~12 PdSe₂ layers.



Supplementary Figure 13. AFM characterization of the PdSe₂ flake in mid-IR photodetector. a Topography map. **b** Cross-section analysis along the dashed line in (a).

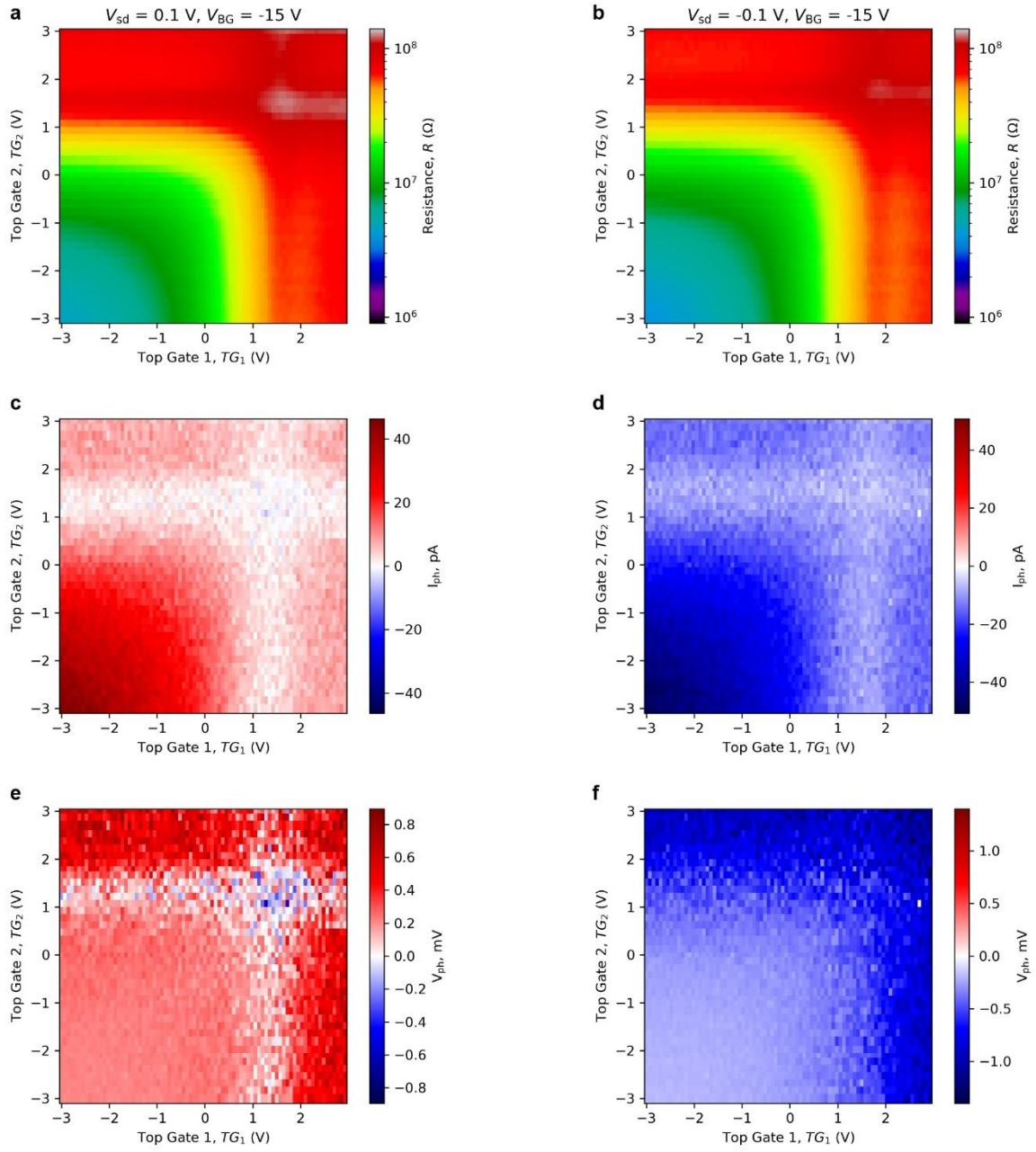
Measurements were carried out in parallel for photocurrent and resistance using lock-in amplifier (LIA) and DC sourcemeter (SM). SM applied DC bias voltage V_{sd} and recorded appearing current I_{sd} , which then were recalculated into device resistance $R = V_{sd}/I_{sd}$. LIA measured photocurrent, that was generated under modulated at $f_{mod} = 911$ Hz mid-IR illumination. Directly measured resistance and photocurrent then were recalculated into photovoltage as $V_{ph} = I_{ph}R$.

To check photogeneration at the central p-n junction, we measured spatial maps of the photocurrent at asymmetric voltages on the two top gates, with no bias voltage applied to the channel (Supplementary Figure 14). In both cases, we did not observe any photocurrent generation.

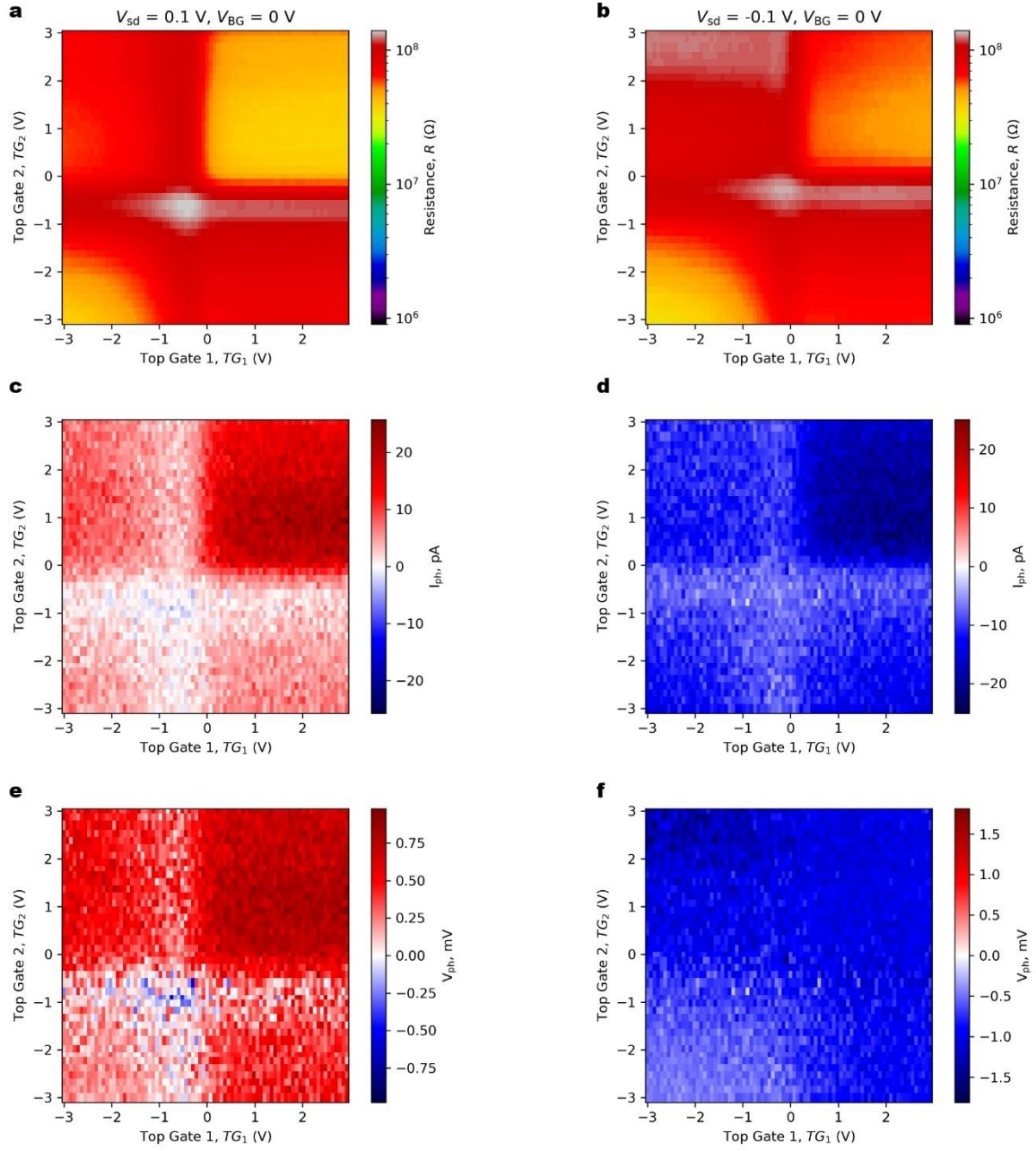


Supplementary Figure 14. Spatial maps of photocurrent I_{ph} when p-n and n-p junctions are formed, demonstrating the absence of photoresponse. Channel bias voltage V_{sd} and global back gate voltage V_{BG} are 0 V.

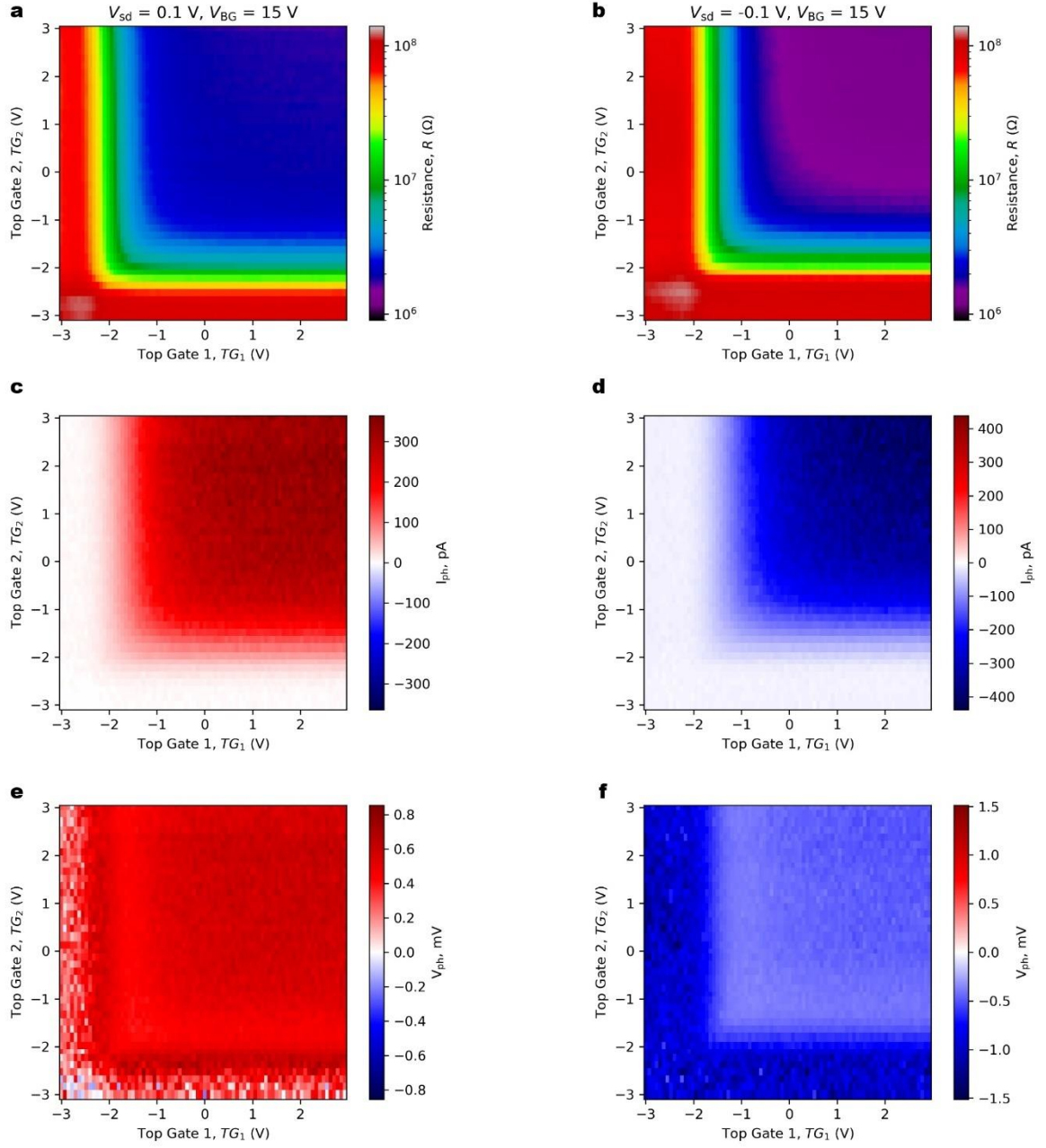
Supplementary Figure 15-17 show the maps for dependencies on top gate voltages TG_1 and TG_2 for resistance R , photocurrent I_{ph} and photovoltage V_{ph} . Maps divided into three Figures, obtained at different initial doping levels provided by the back gate voltages V_{BG} : hole doping at $V_{BG} = -15 \text{ V}$ (Supplementary Figure 15), light electron doping at $V_{BG} = 0 \text{ V}$ (Supplementary Figure 16) and electron doping at $V_{BG} = +15 \text{ V}$ (Supplementary Figure 17). Left columns obtained at source-drain bias voltage $V_{sd} = 0.1 \text{ V}$, right columns at $V_{sd} = -0.1 \text{ V}$.



Supplementary Figure 15. Hole-doped PdSe₂-based mid-IR photodetector ($V_{BG} = -15 \text{ V}$). Resistance R (a,b), photocurrent I_{ph} (c,d) and photovoltage V_{ph} (e,f) dependencies on top gate voltages TG_1 and TG_2 at forward (a,c,e) and backward (b,d,f) bias voltage V_{sd} .

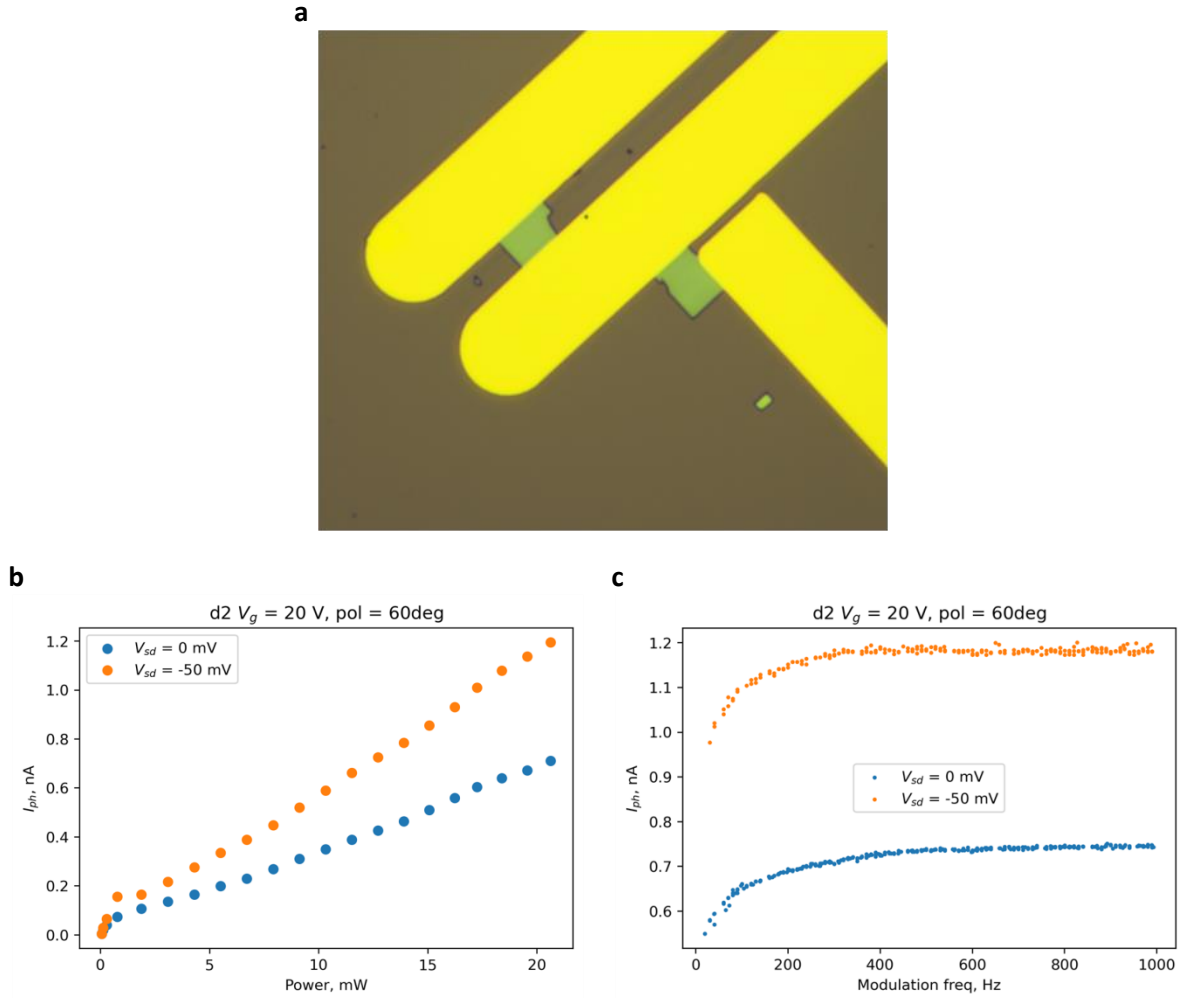


Supplementary Figure 16. Slightly electron-doped PdSe₂-based mid-IR photodetector ($V_{BG} = 0 \text{ V}$). Resistance R (a,b), photocurrent I_{ph} (c,d) and photovoltage V_{ph} (e,f) dependencies on top gate voltages TG_1 and TG_2 at forward (a,c,e) and backward (b,d,f) bias voltage V_{sd} .



Supplementary Figure 17. Electron-doped PdSe₂-based mid-IR photodetector ($V_{BG} = +15$ V). Resistance R (a,b), photocurrent I_{ph} (c,d) and photovoltage V_{ph} (e,f) dependencies on top gate voltages TG_1 and TG_2 at forward (a,c,e) and backward (b,d,f) bias voltage V_{sd} .

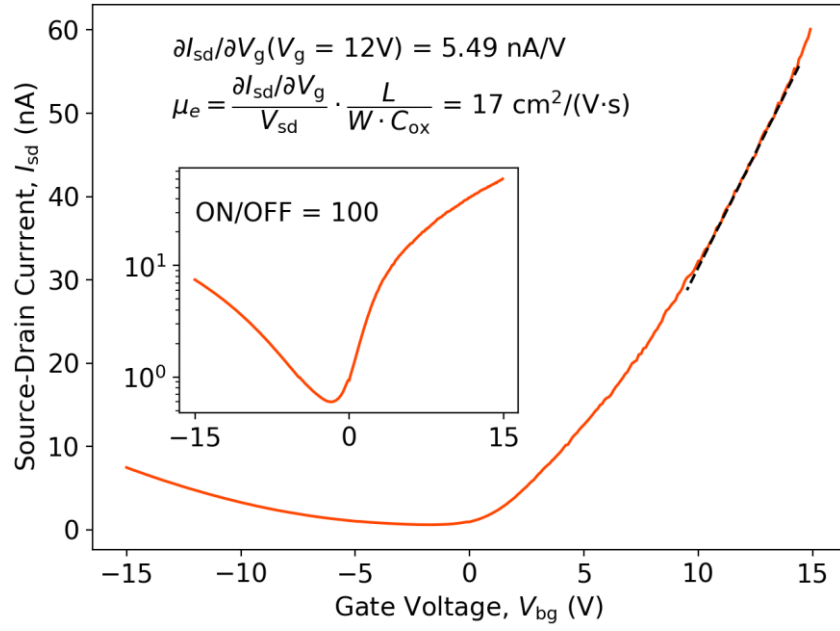
Finally, we present the dependences of photocurrent on the modulation frequency and laser power. The measurements were performed on a PdSe₂ flake with mutually orthogonal metal contacts, described in our prior work¹⁸. Micro-photograph of the device is shown in Supplementary Figure 18a; the device with parallel metal contacts serves as a reference. Both the detector described in the main text and that of Ref. [18] were fabricated within the same transfer batch, therefore their power- and frequency-dependent responsivities are expected to closely match each other.



Supplementary Figure 18. Power- and frequency-dependent responsivity of PdSe₂ infrared detectors. **a** Micro-photograph of the samples. **b** Power dependence of the photoresponse in the bias-free (blue) and in the biased (orange) modes. **c** Dependence of the photocurrent on infrared laser modulation frequency (internal modulation). Deviations from power linearity at low power levels are due to the unstable laser operation, so are the deviations from flat response at low modulation frequency.

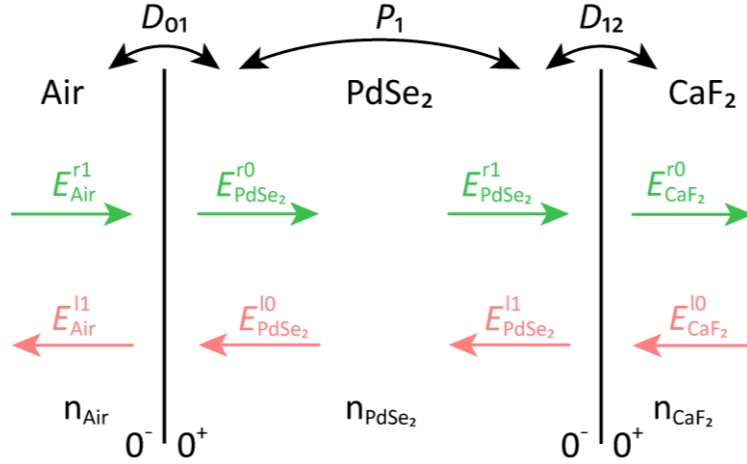
The relevant dependences of the photoresponse are shown in Supplementary Figure 18b,c. The photocurrent appears linear in laser power in a broad range from units of mW to ~20 mW. Nonlinearity at small power is attributed to the unstable laser operation at small drive currents. The photocurrent also does not display any significant frequency dependence for modulation up to $f_{mod} = 911$ Hz. Again, a small reduction in photocurrent at low modulation frequencies is associated with reduction in average laser power in the continuous mode.

Transfer curve of the fabricated detector is shown in Supplementary Figure 19. The obtained values of ON/OFF ratio and carrier mobility based on two-point measurements are also given (see inset in Supplementary Figure 19).



Supplementary Figure 19. Transfer curve of PdSe₂ mid-IR photodetector and carrier mobility estimation. Curve is measured at $V_{sd} = 0.1 \text{ V}$, device sizes are $L = 9.3 \text{ }\mu\text{m}$ and $W = 2.6 \text{ }\mu\text{m}$, specific capacitance of 300 nm SiO₂ is 11.5 nF/cm². The inset shows the same curve on a logarithmic scale with ON/OFF ratio.

Supplementary Note 7: Transfer matrix maps calculations



Supplementary Figure 20. Transfer matrix representation of the transmission through the studied structure.

To analyze the interaction of electromagnetic waves with a layered medium, we used the matrix transfer method. This method allows us to generalize the accounting of all reflections within a layered system. To do this, the problem is divided into taking into account propagation matrices P between the interfaces and transmission matrices D on the interfaces of the system. These matrices express the relationships between various electromagnetic fields Supplementary Figure 20:

$$\begin{pmatrix} E_{Air}^{r1} \\ E_{Air}^{l1} \end{pmatrix} = D_{01} \begin{pmatrix} E_{PdSe_2}^{r0} \\ E_{PdSe_2}^{l0} \end{pmatrix}, \quad (6)$$

$$\begin{pmatrix} E_{PdSe_2}^{r0} \\ E_{PdSe_2}^{l0} \end{pmatrix} = P_1 \begin{pmatrix} E_{PdSe_2}^{r1} \\ E_{PdSe_2}^{l1} \end{pmatrix}. \quad (7)$$

The propagation P matrix can be expressed simply by taking into account the phase shift in the medium:

$$P = \begin{pmatrix} e^{ikl} & 0 \\ 0 & e^{-ikl} \end{pmatrix}. \quad (8)$$

The transmission D matrix can be expressed in terms of complex Fresnel coefficients using:

$$E_{Air}^{l1} = r_{01} E_{Air}^{r1} + t_{10} E_{PdSe_2}^{l0}, \quad (9)$$

$$E_{PdSe_2}^{r0} = r_{10} E_{PdSe_2}^{l0} + t_{01} E_{Air}^{r1}. \quad (10)$$

Knowing matrices P and D for every part of the system, we can simply multiply them to obtain the transfer matrix M for the connection between the fields at the ends of the layered structure:

$$\begin{pmatrix} E_{Air}^{r1} \\ E_{Air}^{l1} \end{pmatrix} = M \begin{pmatrix} E_{CaF_2}^{r0} \\ E_{CaF_2}^{l0} \end{pmatrix}, \quad (11)$$

$$M = D_{01} P_1 D_{12}. \quad (12)$$

If we take into account that there is no field, because we do not illuminate the structure from the reverse side, then we can obtain complex Fresnel coefficients for the entire structure. This allows us to construct the dispersion of waveguide modes (see Figure 4d,g of the main text) and a reflectance map (see Supplementary Figure 9b) for the system. It is worth noting that for our calculations we used a bit more complex approach described in previous research¹⁹, but similar principles are applied.

Supplementary Note 8: Scanning near-field microscopy

To unequivocally validate out-of-plane components of the PdSe₂ dielectric tensor, we investigated properties of TM₀ modes supported by PdSe₂ planar waveguides. For this purpose, we exfoliated two flakes of different thicknesses (≈ 225 nm and ≈ 1.12 μ m) on a CaF₂ substrate, which formed planar waveguides in the near- and mid-infrared wavelength ranges, respectively. To study mode properties, we used scattering-type Scanning Near-field Optical Microscopy (s-SNOM) in reflection mode. A parabolic mirror focused the TM-polarized light on the apex of an atomic force microscope tip covered with metal. We chose TM polarization due to probe's much higher sensitivity to TM polarized light compared to TE²⁰⁻²². The atomic force microscope operated in tapping mode, allowing us to filter the near-field signal through tip oscillations. The light scattered from the probe and the flake edges was collected using the same parabolic mirror.

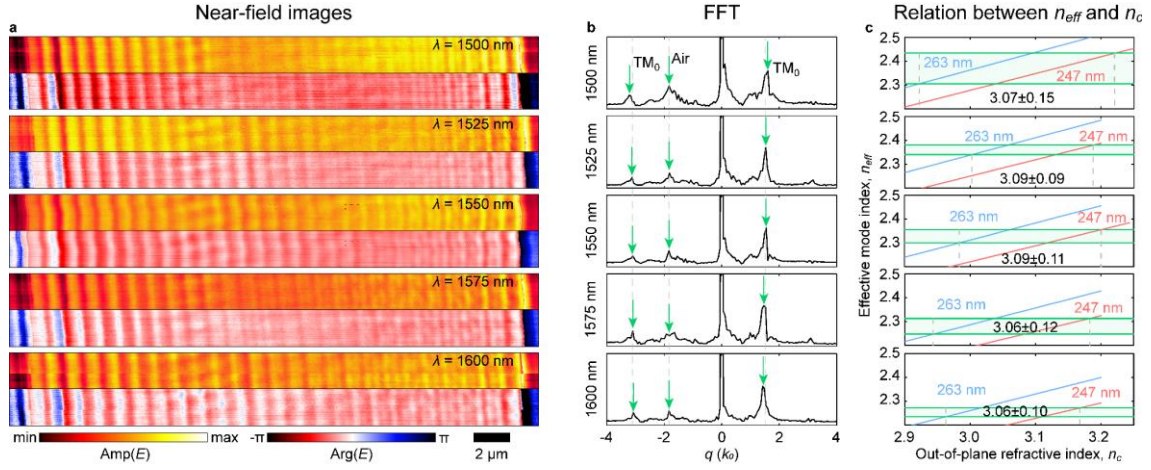
The oscillations observed in the measurements originated from the interference between light scattered directly from the tip to the detector and light that propagated in the form of a waveguide mode before scattering at the flake edge. These shifts are linked to the relative orientation between the scattering edge of the flake and the spatial geometry of the s-SNOM setup, and can be described by the equation:

$$n_{\text{eff}} = n_{\text{obs}} + \sin(\beta)\cos(\alpha) \quad (13)$$

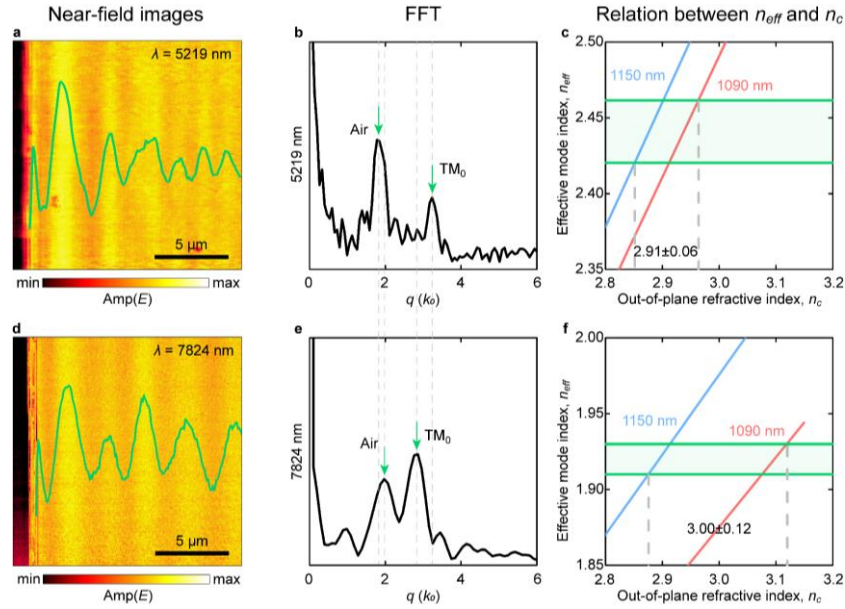
Where α is the angle between the illumination wavevector (k) and its projection on the sample's surface plane ($k_{||}$), β is the angle between the projection of the wavevector ($k_{||}$) and the scattering edge, n_{eff} is the effective index of the mode, and n_{obs} is the observable effective mode index.

To extract the exact value of the frequency shift, we used the air mode as our marker. Due to it having no dispersion and always having an effective mode index close to one. The frequency shift for peak positions in Supplementary Figure 21b of the TM₀ mode for positive and negative $q(k_0)$ values is attributed to its counter-propagating directions, which vary based on the edge of the flake from which it scatters. The air mode for positive $q(k_0)$ is not observable due to the frequency shift, which results in its effective mode index being near zero. The asymmetry in the zero-frequency peak is possibly due to its merging with the shifted air mode. At the same time due to the unresolved near-field phase for measurements in mid-infrared region Supplementary Figure 22, the FFT shows only positive $q(k_0)$. There are three peaks: the left peak corresponds to the zero-frequency background, and the other two are the result of traveling air and TM₀ waves. Two measurements were made with different orientations of the sample, thus the frequency shift effect for the air mode can be observed.

Lastly, to study the correlation between effective mode index in the planar waveguides and the out-of-plane refractive index of the material, we performed dispersion calculations for all the measurements (Supplementary Figure 21c and Supplementary Figure 22c,f). The extracted out-of-plane refractive index components are in good agreement with plotted constants from Figure 2a of the main text.



Supplementary Figure 21. **a** Near-field amplitude $\text{Amp}(E)$ and phase $\text{Arg}(E)$ in the near-infrared wavelength range of 1500 nm to 1600 nm. **b** Fast Fourier transformation of the complex near-field signal taken from (**a**). Green arrows denote observable effective mode indexes: air and TM_0 . **c** Dependency of the effective TM_0 mode index (n_{eff}) on the out-of-plane refractive index (n_c), calculated for a 263 nm flake (blue line) and a 247 nm flake (red line). The thicknesses were derived from the errors in the AFM measurements. Green horizontal lines represent the effective mode index extracted from the near-field measurements, with the line thickness indicating the expected experimental error. Dashed gray vertical lines represent the extracted out-of-plane refractive index of the material. The in-plane refractive index for the calculations was taken from the extrapolated optical functions (Figure 2a of the main text).



Supplementary Figure 22. **a,d** Near-field amplitude $\text{Amp}(E)$ in the mid-infrared wavelength range for 5219 nm and 7824 nm. **b,e** Fast Fourier transformation of the complex near-field signal taken from (**a,d**). Green arrows denote observable effective mode indexes: air and TM_0 . **c,f** Dependency of the effective TM_0 mode index (n_{eff}) on the out-of-plane refractive index (n_c), calculated for a 1150 nm flake (blue line) and a 1090 nm flake (red line). The thicknesses were derived from the errors in the AFM measurements. Green horizontal lines represent the effective mode index extracted from the near-field measurements, with the line thickness indicating the expected experimental error. Dashed gray vertical lines represent the extracted out-of-plane refractive index of the material. The in-plane refractive index for the calculations was taken from the extrapolated optical functions (Figure 2a of the main text).

Supplementary Note 9: Nanoparticles

Nanoparticles fabrication

To synthesize the palladium diselenide (PdSe₂) nanoparticles (NPs), we utilized a diode-pumped Teta 20 laser system (Avesta) operating at a wavelength of 1,030 nm. The laser emitted pulses with an energy of 30 μ J and duration of 250 fs at a repetition rate of 1 kHz. A 100 mm focal length lens was employed to focus the laser beam onto the surface of a synthetically grown PdSe₂ crystal immersed in deionized water (18.2 MOhm-cm, Milli-Q, Merck Millipore, Germany). The focusing resulted in a laser spot size of approximately 50 μ m on the crystal surface, providing sufficient energy density for effective ablation. The laser ablation process was conducted for a duration of 30 minutes at room temperature. Throughout this period, the laser pulses interacted with the crystal surface, causing plasma plume generation with a subsequent cavitation bubble formation. The vapor within the bubble is a zone where solid crystallization and the formation of atomic clusters take place. The collapse of the cavitation bubble led to the ejection of PdSe₂ particles into the surrounding water forming a colloidal suspension of nanoparticles. The resulting colloidal solution exhibited a uniform appearance, indicating a well-dispersed nanoparticle suspension. The concentration of PdSe₂ nanoparticles in the solution was approximately 0.1 mg/mL, as determined by measuring the weight change of PdSe₂ crystal before and after laser ablation. The nanoparticle suspension was stable at room temperature, showing no visible signs of sedimentation or aggregation over time. The laser ablation in liquid technique provides a straightforward and chemical-free method for synthesizing high-quality PdSe₂ nanoparticles.

Nanoparticles photoresponse calculations

For calculating the extinction, scattering and absorption cross-section (σ_{abs}) of the nanospheres, we used the extended Mie theory with radial anisotropy²³. For PdSe₂, the radial and tangential dielectric functions, ϵ_r and ϵ_t respectively were assumed as follows:

$$\epsilon_r = \epsilon_c, \quad (14)$$

$$\epsilon_t = (\epsilon_a + \epsilon_b)/2. \quad (15)$$

where the complex dielectric function is related to the refractive index and extinction coefficient as $\epsilon_j = (n_j + ik_j)^2$ where $j=a, b, c$.

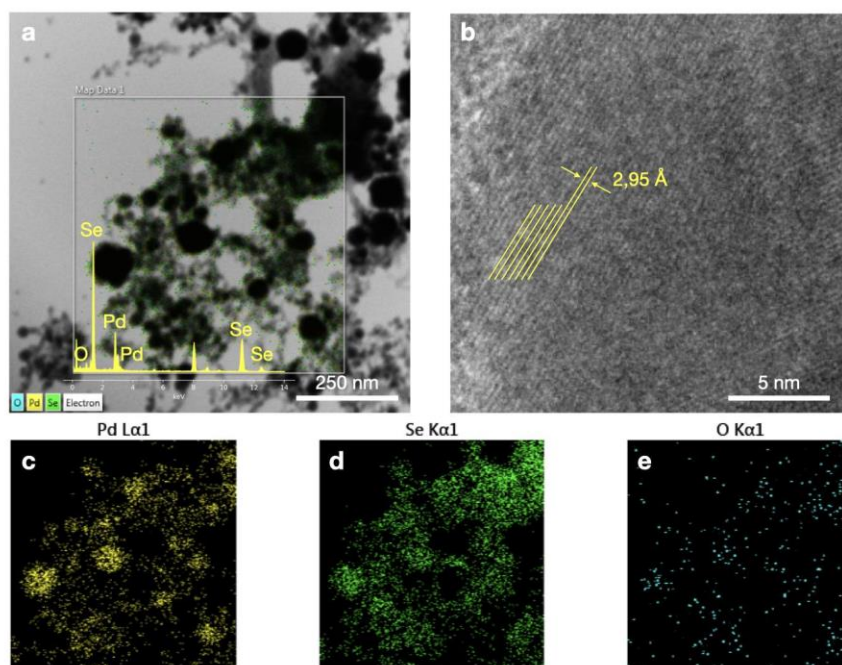
Next, to estimate the temperature rise caused by the incident radiation, we used the expression²⁴:

$$\Delta T = \frac{Q_0 f_N V_r}{Nu A k}. \quad (16)$$

Here, $Q_0 = I_0 \sigma_{abs}$ represents the heating power per single particle. We assumed $I_0 = 3.2 \times 10^5$ W m⁻². V , A , and $r = 1$ cm are the volume, surface area, and characteristic length of the particle solution, respectively. k and $Nu \sim 5$ are the thermal conductivity of water and the Nusselt number, correspondingly. To ensure realistic conditions for photothermal therapy, the concentration of nanoparticles in the target organ was set to 0.67 mg L⁻¹ (number density of $f_N = 4.2 \times 10^{14}$ m⁻³ at $d=80$ nm) aligning with the conditions described by Rastinehad et al.²⁵

Nanoparticles characterization

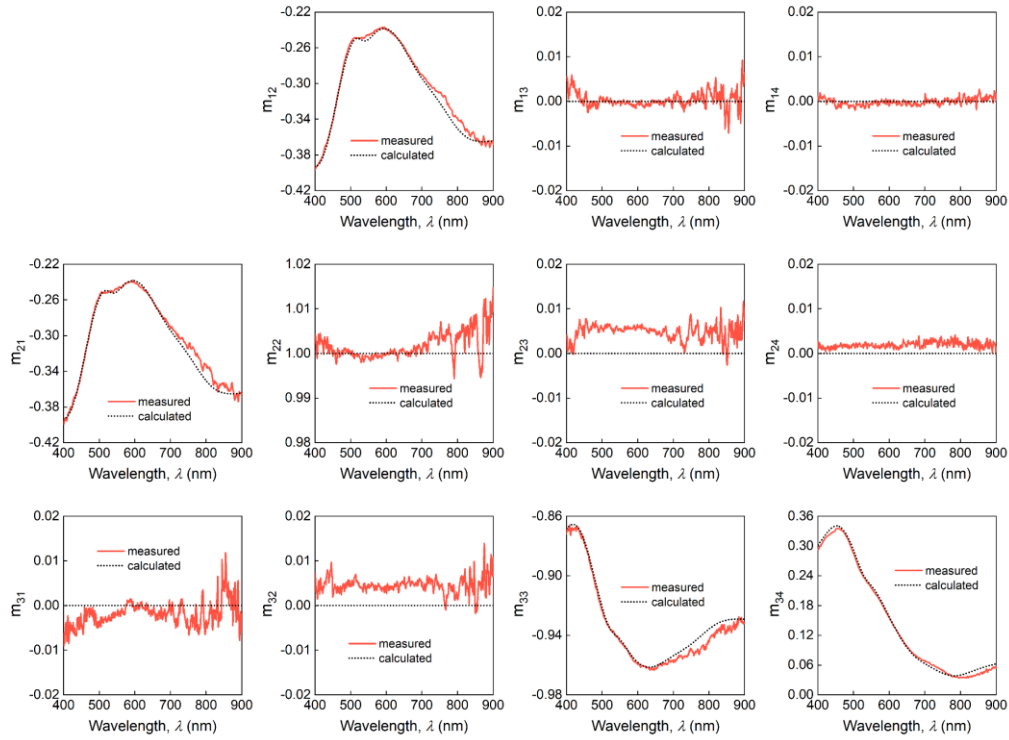
The results of transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) measurements revealed the nanoparticles with atomic concentrations of O, Se and Pd are 2.95%, 61.58% and 35.47% as shown in Supplementary Figure 23. Interplanar distance of NP (see Supplementary Figure 23b) corresponds to the value of 2.93 Å for the (0 2 0) plane.



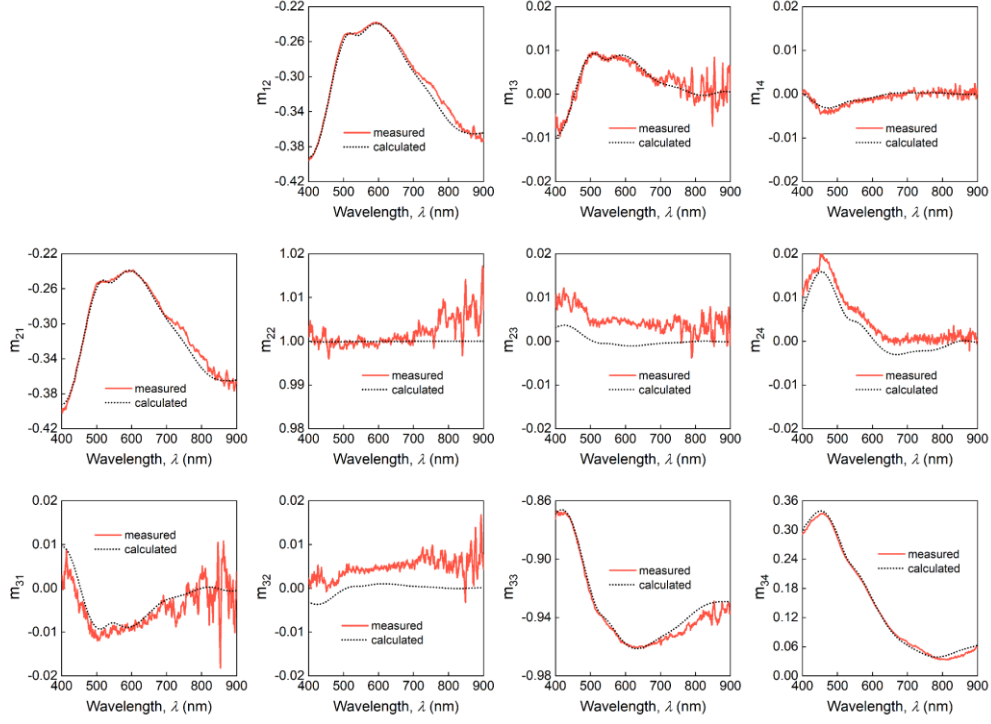
Supplementary Figure 23. TEM (a,b) and EDX (c,d,e) characterization of PdSe₂ nanoparticles obtained by femtosecond PLAL of PdSe₂ crystal in aqueous solution.

Supplementary Note 10: Mueller Matrix of PdSe₂

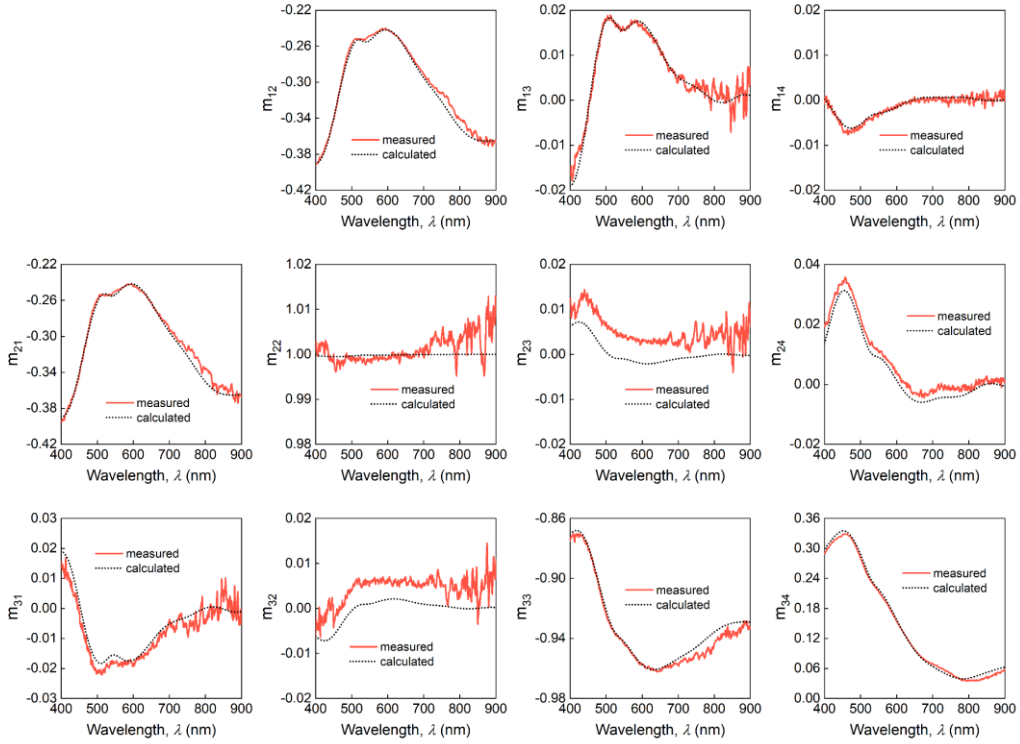
To support our ellipsometry and reflectance analysis of optical properties, we also added a Mueller Matrix spectra for 175-nm-thick PdSe₂ flake, which are shown in Supplementary Figures 24–42.



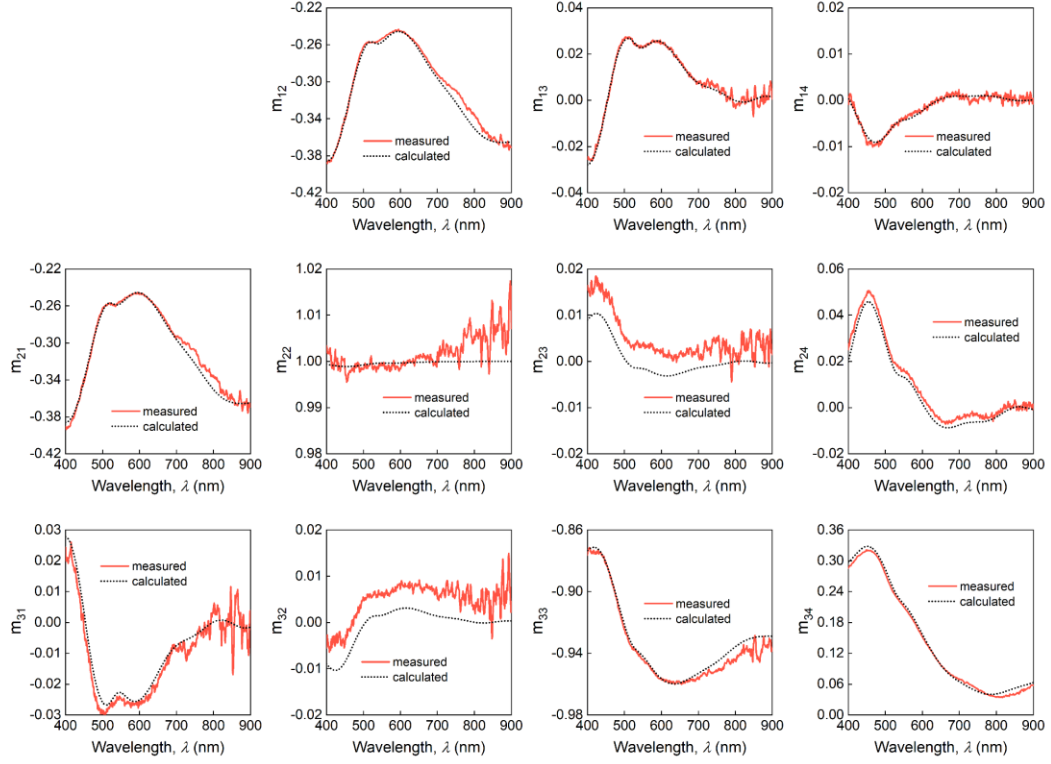
Supplementary Figure 24. Mueller Matrix spectra with the plane of incidence aligned with *b*-axis.



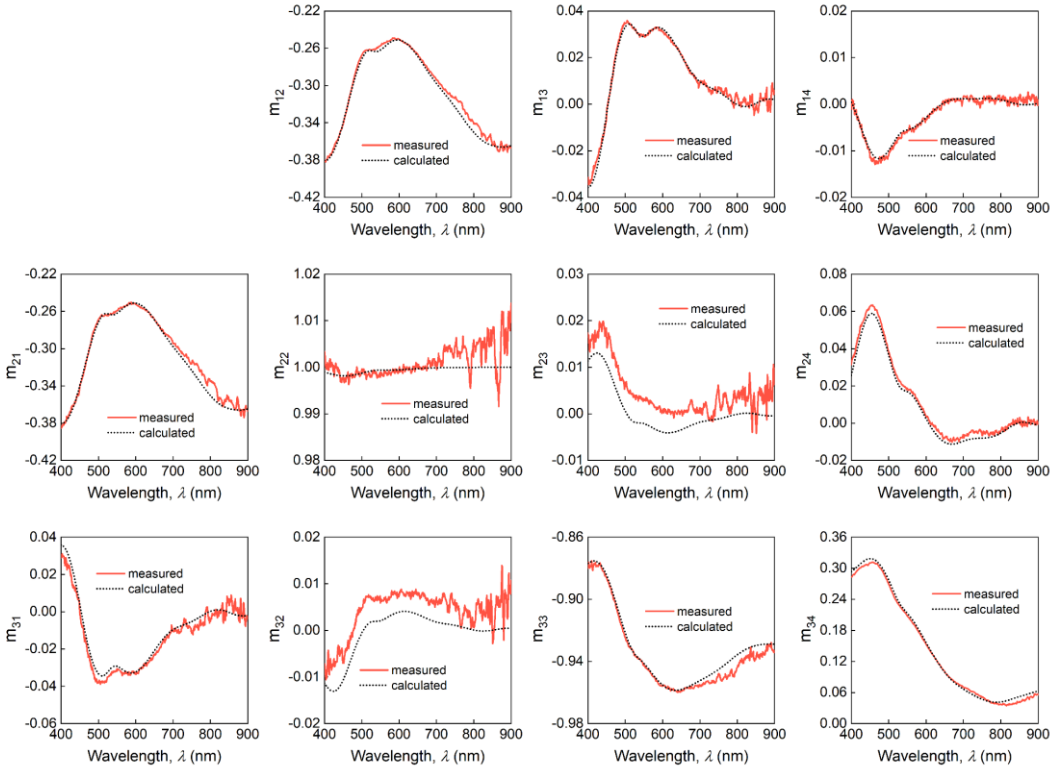
Supplementary Figure 25. Mueller Matrix spectra with the plane of incidence having the angle of 5° with respect to b -axis and 85° with respect to a -axis.



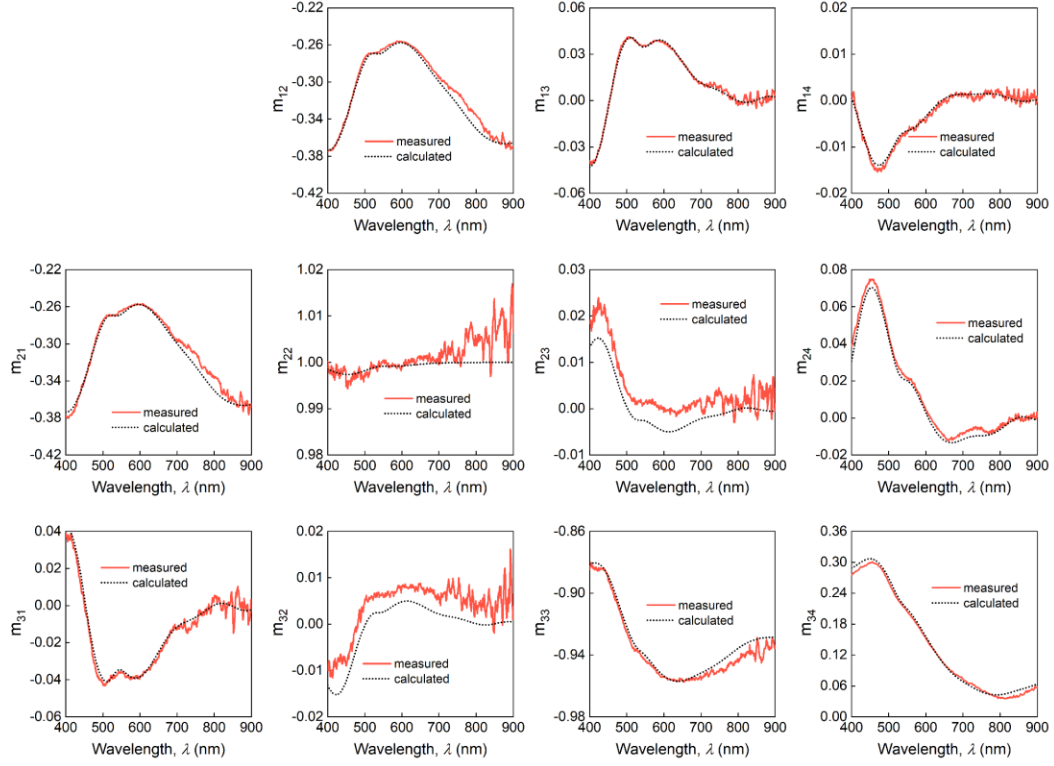
Supplementary Figure 26. Mueller Matrix spectra with the plane of incidence having the angle of 10° with respect to b -axis and 80° with respect to a -axis.



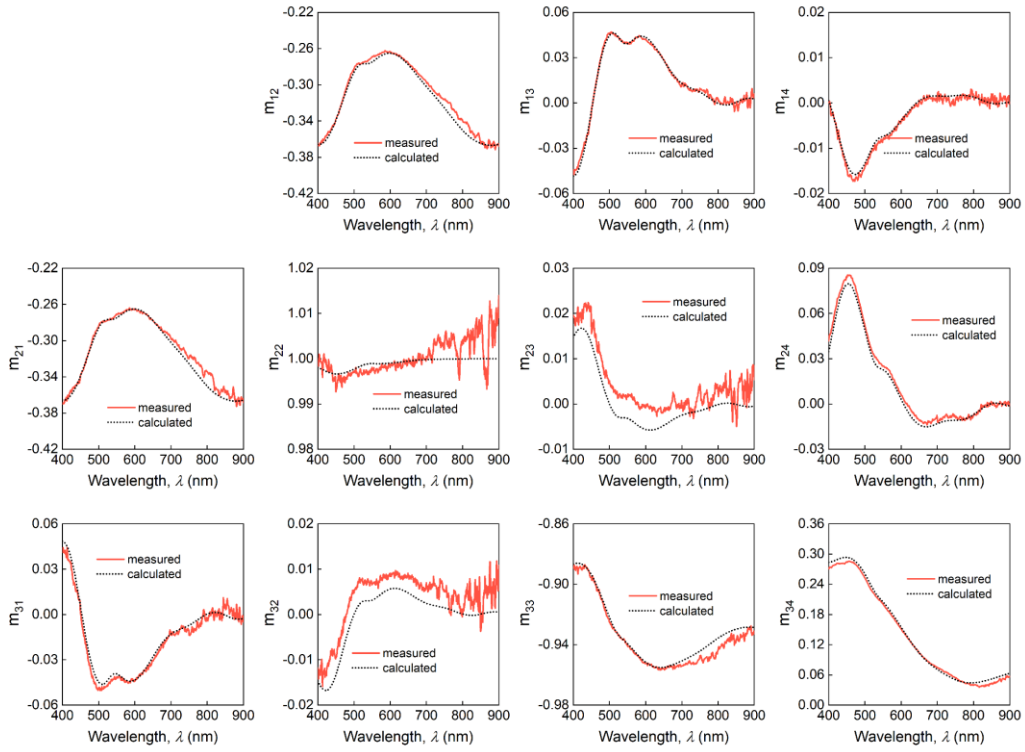
Supplementary Figure 27. Mueller Matrix spectra with the plane of incidence having the angle of 15° with respect to b -axis and 75° with respect to a -axis.



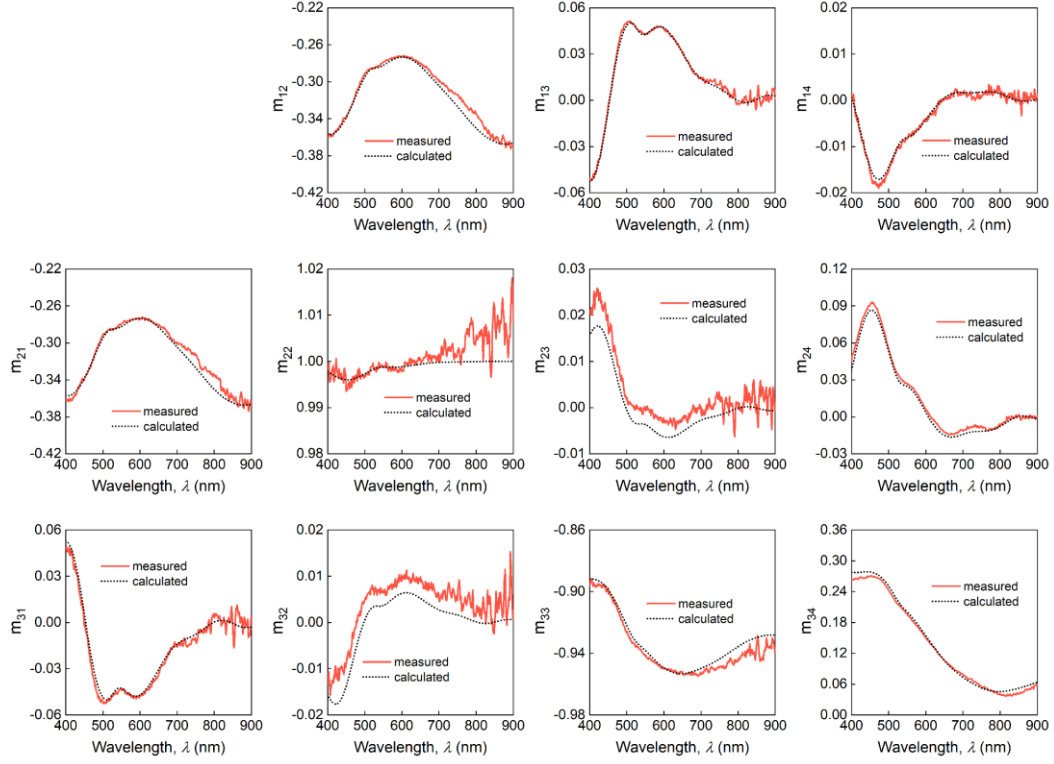
Supplementary Figure 28. Mueller Matrix spectra with the plane of incidence having the angle of 20° with respect to b -axis and 70° with respect to a -axis.



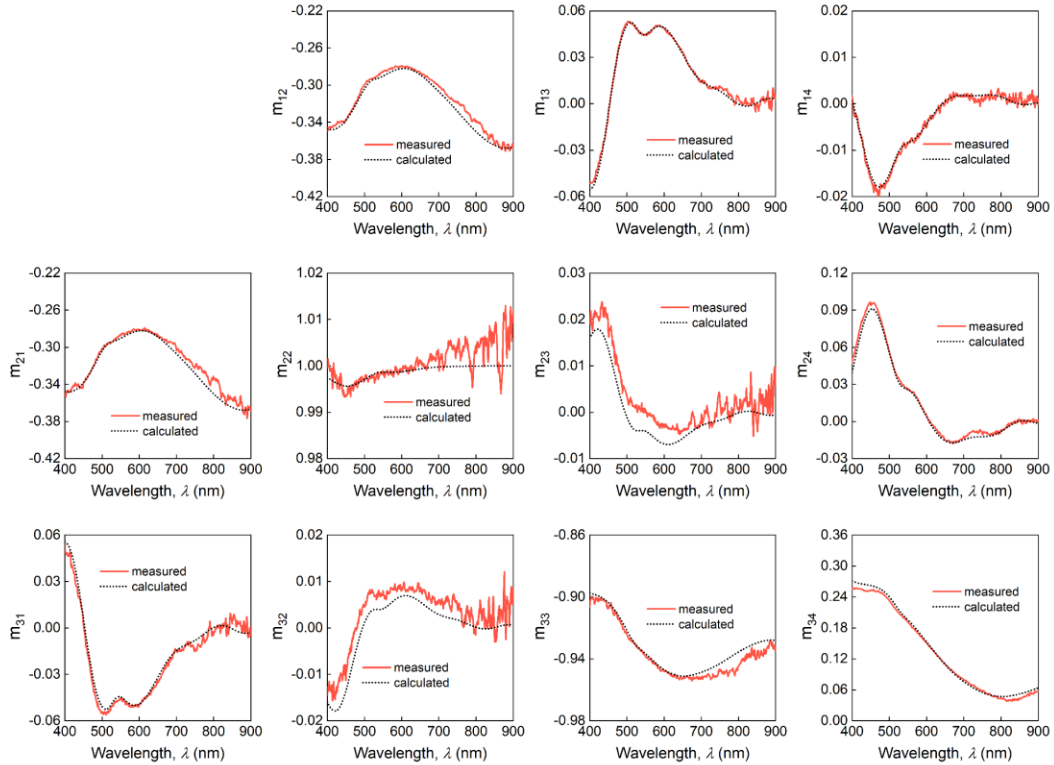
Supplementary Figure 29. Mueller Matrix spectra with the plane of incidence having the angle of 25° with respect to b -axis and 65° with respect to a -axis.



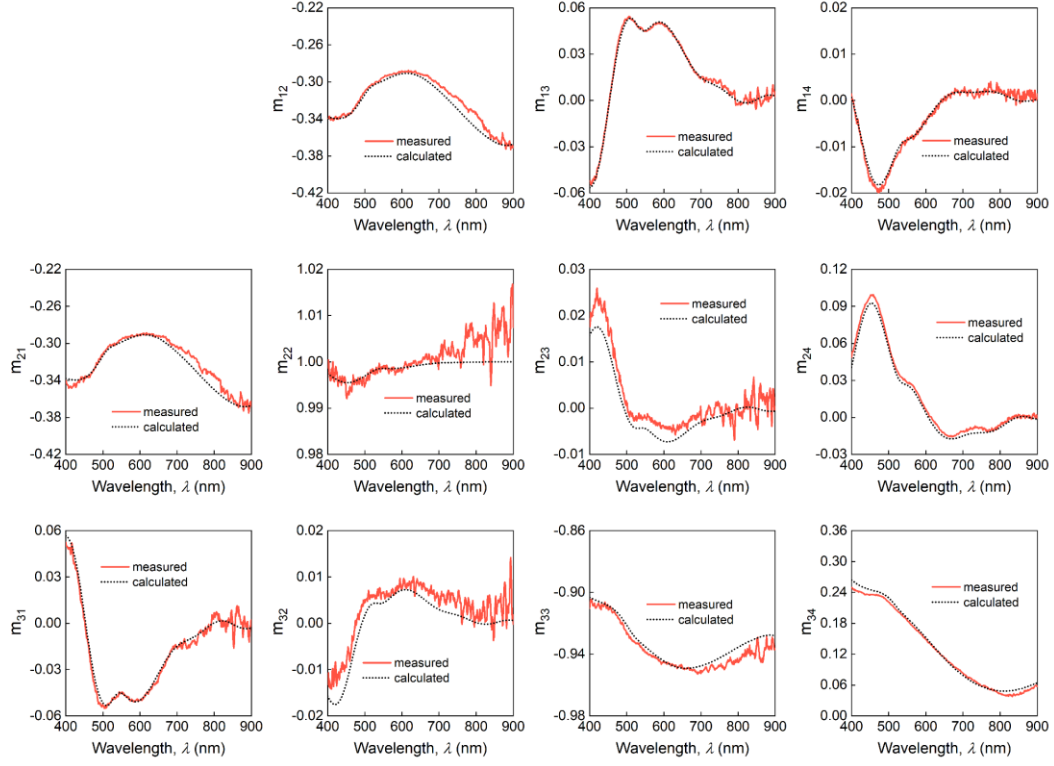
Supplementary Figure 30. Mueller Matrix spectra with the plane of incidence having the angle of 30° with respect to b -axis and 60° with respect to a -axis.



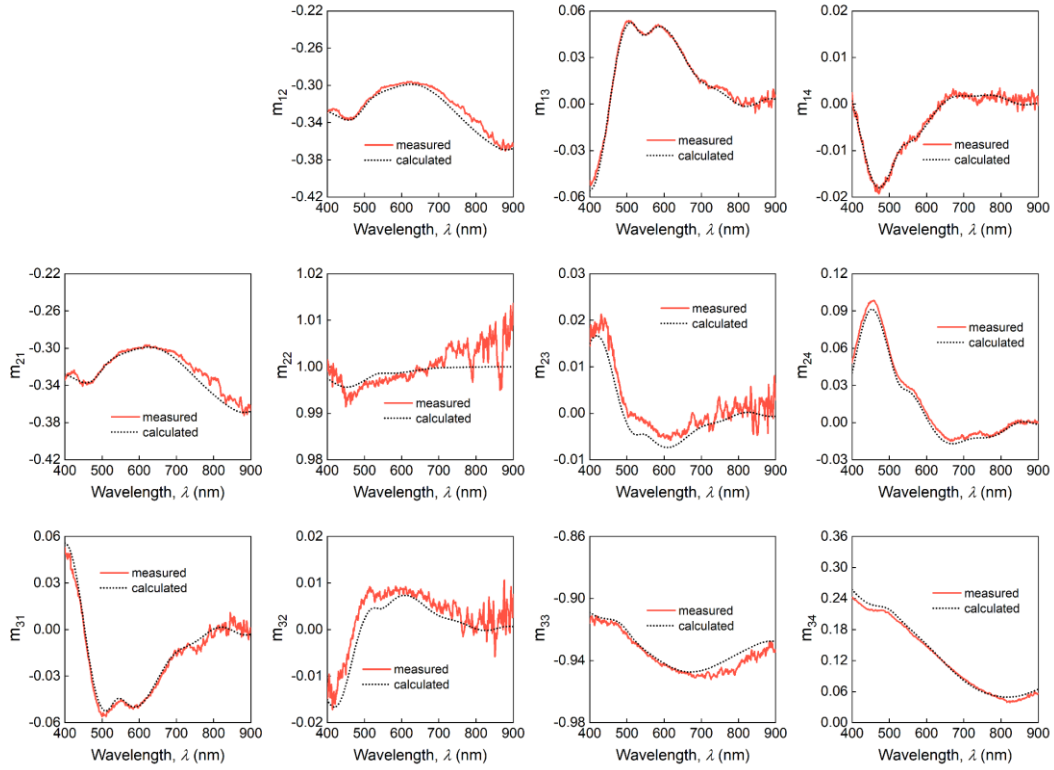
Supplementary Figure 31. Mueller Matrix spectra with the plane of incidence having the angle of 35° with respect to b -axis and 55° with respect to a -axis.



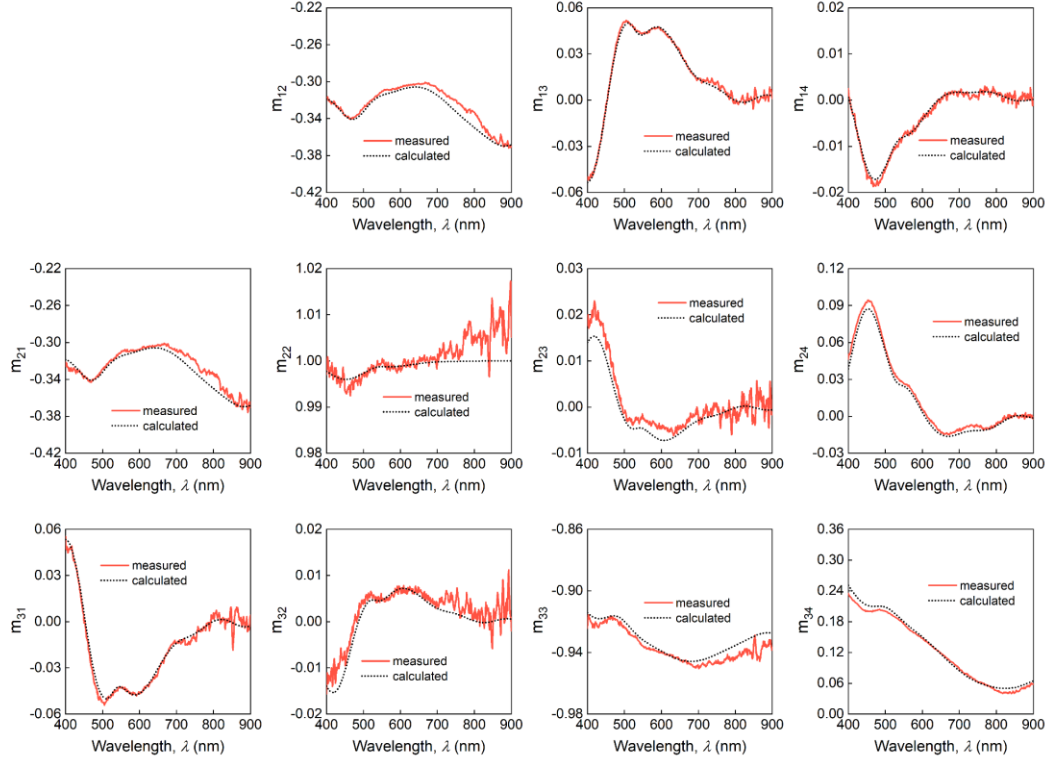
Supplementary Figure 32. Mueller Matrix spectra with the plane of incidence having the angle of 40° with respect to b -axis and 50° with respect to a -axis.



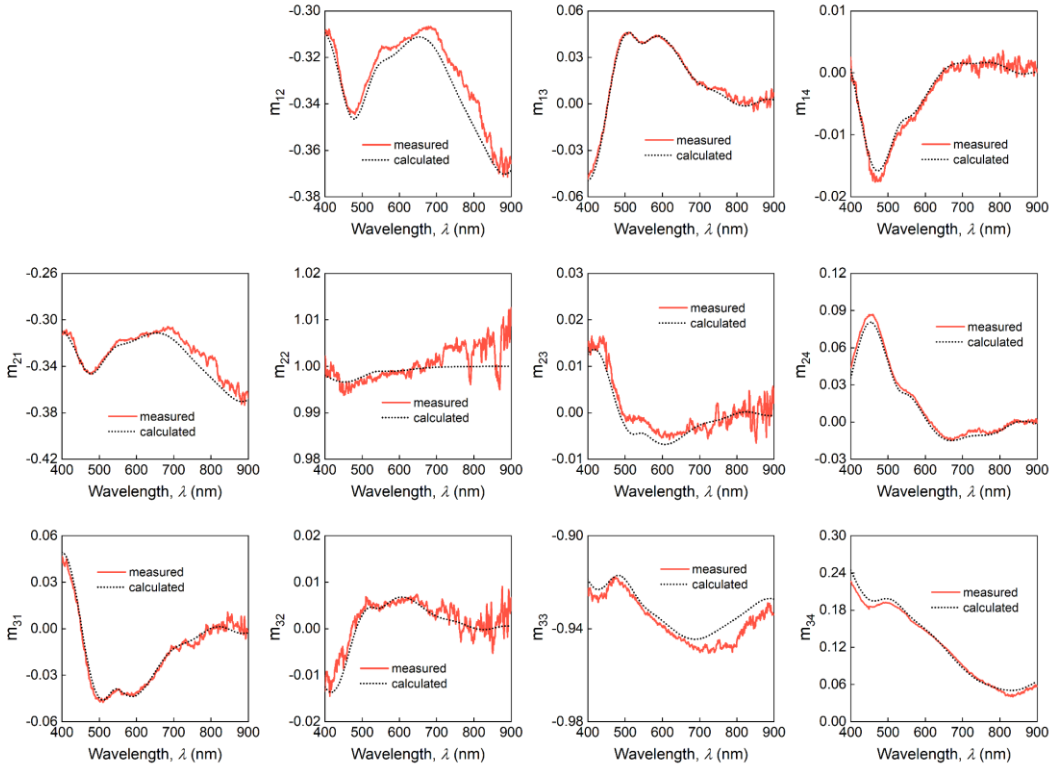
Supplementary Figure 33. Mueller Matrix spectra with the plane of incidence having the angle of 45° with respect to b -axis and 45° with respect to a -axis.



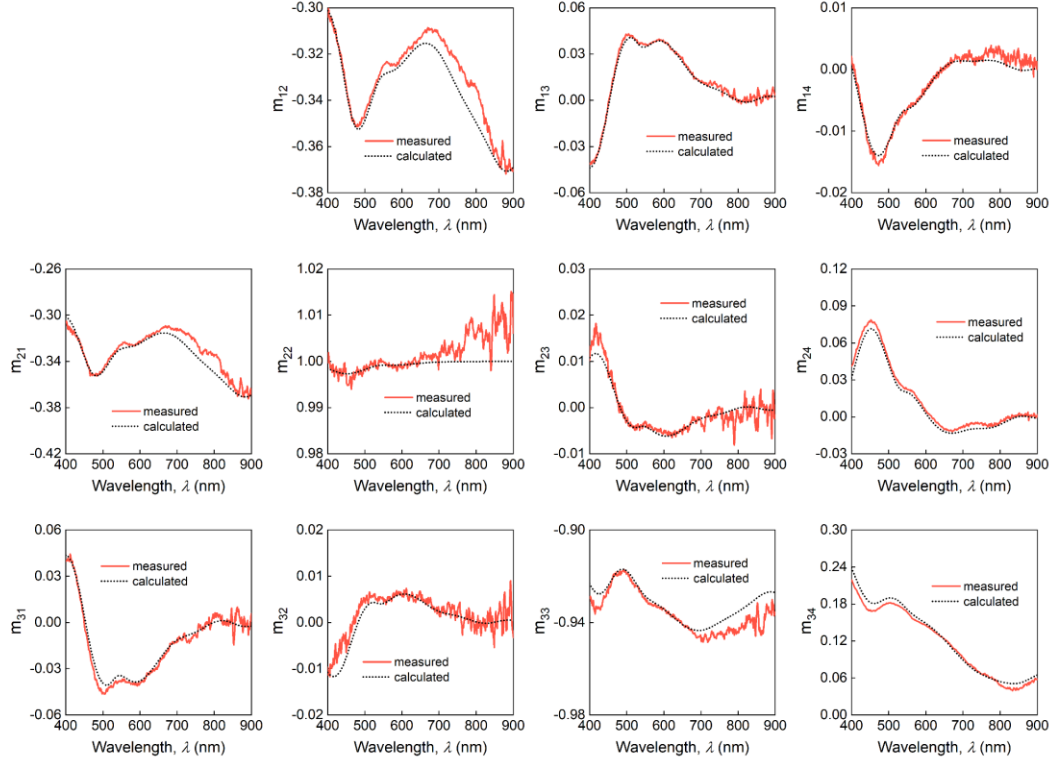
Supplementary Figure 34. Mueller Matrix spectra with the plane of incidence having the angle of 50° with respect to b -axis and 40° with respect to a -axis.



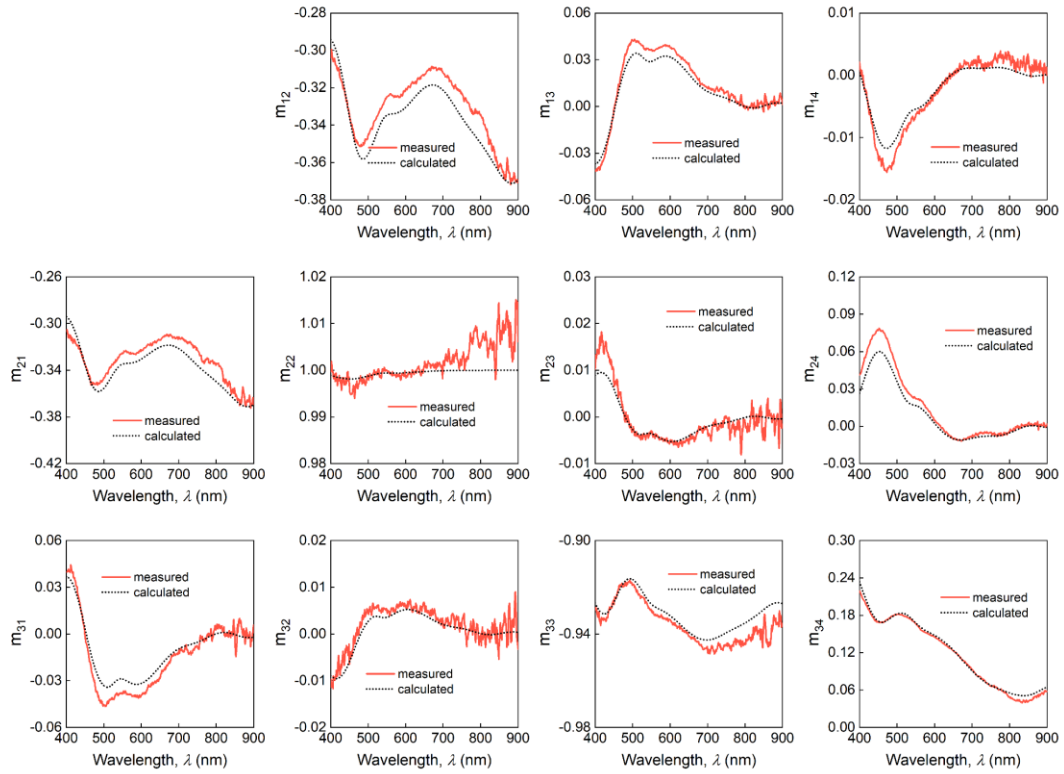
Supplementary Figure 35. Mueller Matrix spectra with the plane of incidence having the angle of 55° with respect to b -axis and 35° with respect to a -axis.



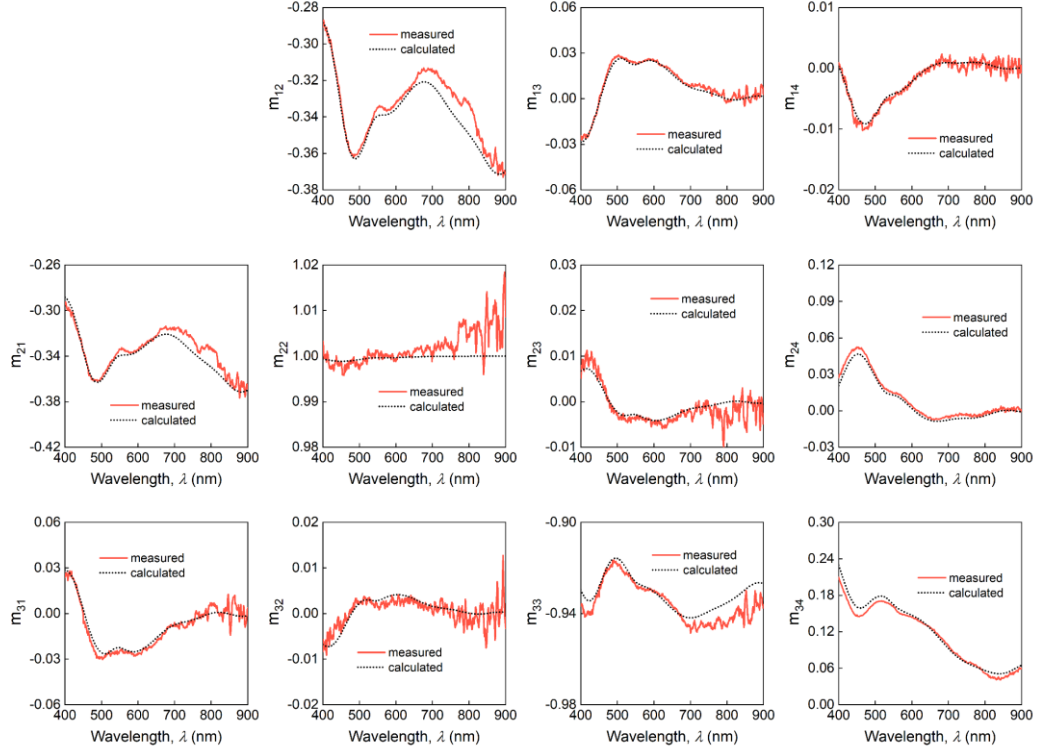
Supplementary Figure 36. Mueller Matrix spectra with the plane of incidence having the angle of 60° with respect to b -axis and 30° with respect to a -axis.



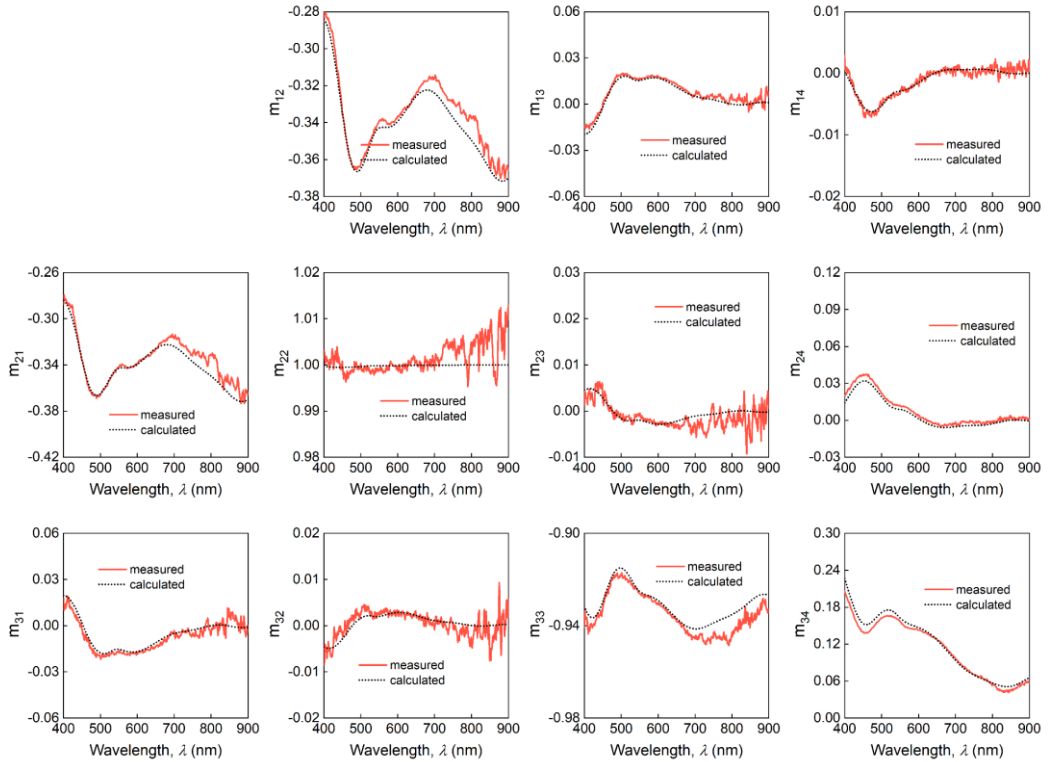
Supplementary Figure 37. Mueller Matrix spectra with the plane of incidence having the angle of 65° with respect to b -axis and 25° with respect to a -axis.



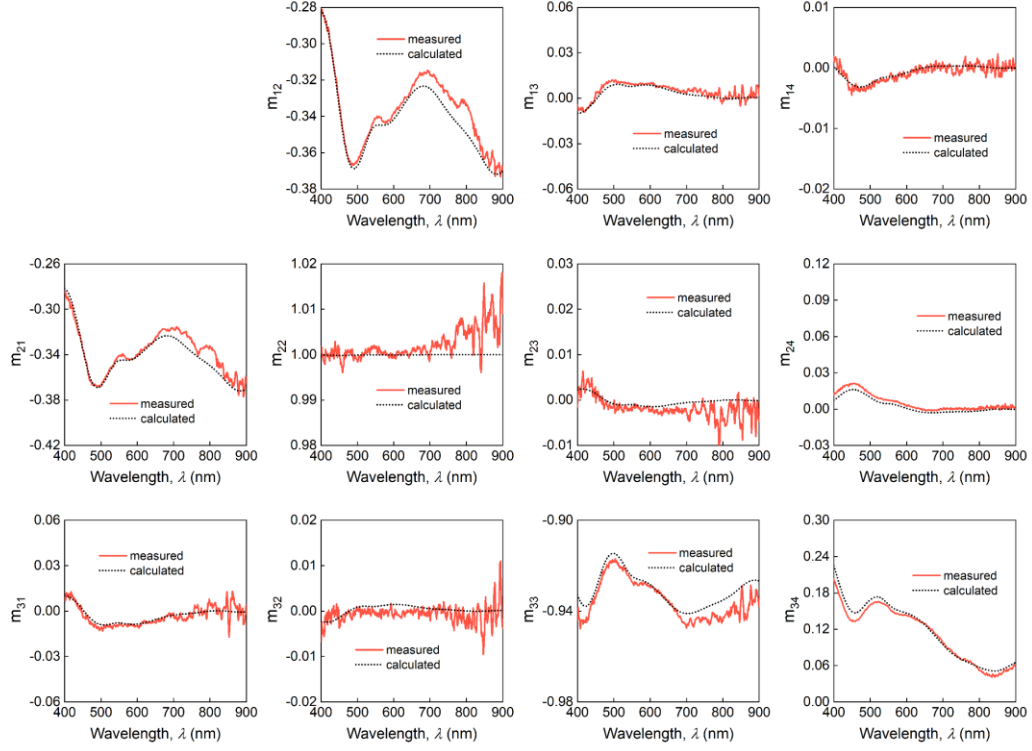
Supplementary Figure 38. Mueller Matrix spectra with the plane of incidence having the angle of 70° with respect to b -axis and 20° with respect to a -axis.



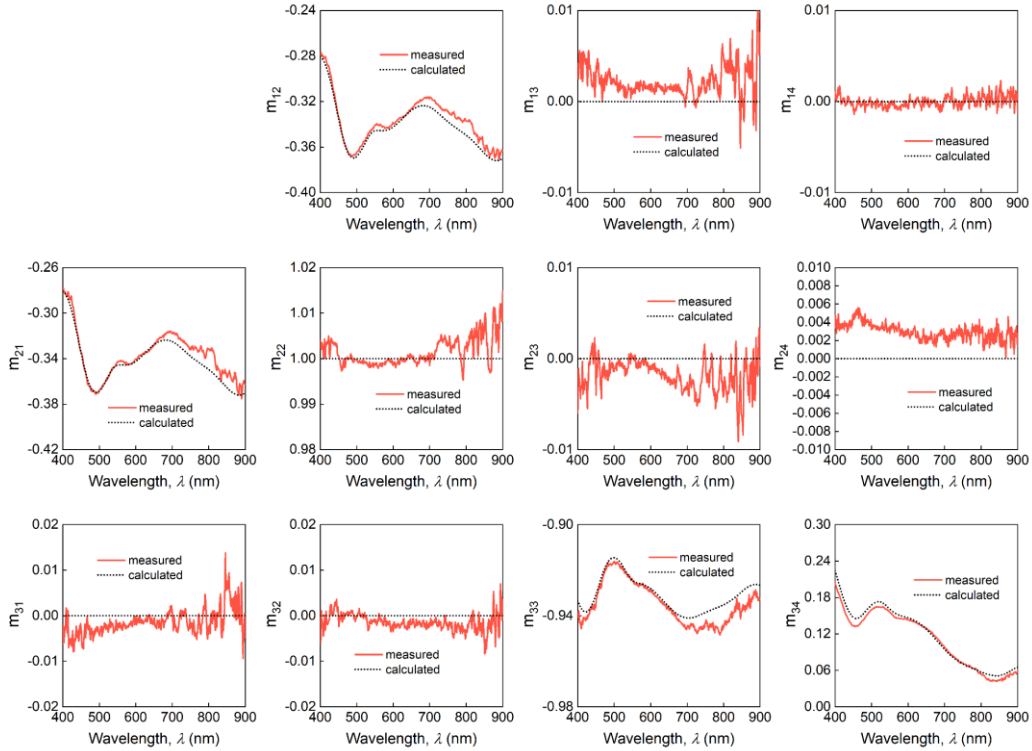
Supplementary Figure 39. Mueller Matrix spectra with the plane of incidence having the angle of 75° with respect to b -axis and 15° with respect to a -axis.



Supplementary Figure 40. Mueller Matrix spectra with the plane of incidence having the angle of 80° with respect to b -axis and 10° with respect to a -axis.



Supplementary Figure 41. Mueller Matrix spectra with the plane of incidence having the angle of 85° with respect to b -axis and 5° with respect to a -axis.



Supplementary Figure 42. Mueller Matrix spectra with the plane of incidence aligned with a -axis.

Supplementary references

1. Lin, Z. *et al.* Planar-coordination PdSe₂ nanosheets as highly active electrocatalyst for hydrogen evolution reaction. *Adv. Funct. Mater.* **31**, 2102321 (2021).
2. Yu, J. *et al.* Giant nonlinear optical activity in two-dimensional palladium diselenide. *Nat. Commun.* **12**, 1083 (2021).
3. Nishiyama, W. *et al.* Quantitative determination of contradictory bandgap values of bulk PdSe₂ from electrical transport properties. *Adv. Funct. Mater.* **32**, 2108061 (2022).
4. Lu, L.-S. *et al.* Layer-dependent and in-plane anisotropic properties of low-temperature synthesized few-layer PdSe₂ single crystals. *ACS Nano* **14**, 4963–4972 (2020).
5. Jiang, S. *et al.* Anisotropic growth and scanning tunneling microscopy identification of ultrathin even-layered PdSe₂ ribbons. *Small* **15**, e1902789 (2019).
6. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B* **47**, 558–561 (1993).
7. Irvine, C. T. *et al.* Diselenide dianion's dual powers: PdSe₂ polymorph control and Pd₃Se₁₀ superatomic crystal creation. *Chem. Mater.* **35**, 4404–4411 (2023).
8. Togo, A., Oba, F. & Tanaka, I. First-principles calculations of the ferroelastic transition between rutile-type and CaCl₂-type SiO₂ at high pressures. *Phys. Rev. B Condens. Matter Mater. Phys.* **78**, (2008).
9. Togo, A. & Tanaka, I. First principles phonon calculations in materials science. *Scr. Mater.* **108**, 1–5 (2015).
10. Oyedele, A. D. *et al.* PdSe₂: Pentagonal two-dimensional layers with high air stability for electronics. *J. Am. Chem. Soc.* **139**, 14090–14097 (2017).
11. Ermolaev, G. A., Yakubovsky, D. I., Stebunov, Y. V., Arsenin, A. V. & Volkov, V. S. Spectral ellipsometry of monolayer transition metal dichalcogenides: Analysis of excitonic peaks in dispersion. *J. Vac. Sci. Technol. B Nanotechnol. Microelectron.* **38**, 014002 (2020).
12. Ermolaev, G. *et al.* Topological phase singularities in atomically thin high-refractive-index materials. *Nat. Commun.* **13**, 2049 (2022).
13. Shishkin, M. & Kresse, G. Self-consistent GW calculations for semiconductors and insulators. *Phys. Rev. B* **75**, 235102 (2007).
14. Kresse, G. & Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
15. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **6**, 15–50 (1996).
16. Sander, T., Maggio, E. & Kresse, G. Beyond the Tamm-Dancoff approximation for extended systems using exact diagonalization. *Phys. Rev. B* **92**, 045209 (2015).
17. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
18. Semkin, V. A. *et al.* Zero-bias photodetection in 2D materials via geometric design of contacts. *Nano Lett.* **23**, 5250–5256 (2023).
19. Passler, N. C. & Paarmann, A. Generalized 4 × 4 matrix formalism for light propagation in anisotropic stratified media: study of surface phonon polaritons in polar dielectric heterostructures: erratum. *J. Opt. Soc. Am. B* **36**, 3246 (2019).
20. Govyadinov, A. A. *et al.* Recovery of permittivity and depth from near-field data as a step toward infrared nanotomography. *ACS Nano* **8**, 6911–6921 (2014).

21. Novotny, L. & Stranick, S. J. Near-field optical microscopy and spectroscopy with pointed probes. *Annu. Rev. Phys. Chem.* **57**, 303–331 (2006).
22. Cvitkovic, A., Ocelic, N. & Hillenbrand, R. Analytical model for quantitative prediction of material contrasts in scattering-type near-field optical microscopy. *Opt. Express* **15**, 8550–8565 (2007).
23. Qiu, C.-W., Li, L.-W., Yeo, T.-S. & Zouhdi, S. Scattering by rotationally symmetric anisotropic spheres: potential formulation and parametric studies. *Phys. Rev. E* **75**, 026609 (2007).
24. Panova, D. A. *et al.* Broadband optical properties of TiC MXene revisited. *Opt. Lett.* **49**, 25–28 (2024).
25. Rastinehad, A. R. *et al.* Gold nanoshell-localized photothermal ablation of prostate tumors in a clinical pilot device study. *Proc. Natl. Acad. Sci. U. S. A.* **116**, 18590–18596 (2019).