

Supplementary Information

Manipulating Quantum Criticality in Light-induced 2D superconductivity

Bin Chen^{1,2}, Kenichiro Hashimoto³, Motoi Kimata⁴, Takahiko Sasaki⁴, Shu Seki², Hiroshi M. Yamamoto⁵, Masayuki Suda^{1,6*}

¹Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan

²Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

³Department of Advanced Materials Science, University of Tokyo, Kashiwa, Chiba 277-8561, Japan.

⁴Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

⁵Institute for Molecular Science, Myodaiji, Okazaki, 444-8585, Japan

⁶JST-FOREST, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan

SUPPLEMENTARY TEXT

Angular dependence of the upper critical field

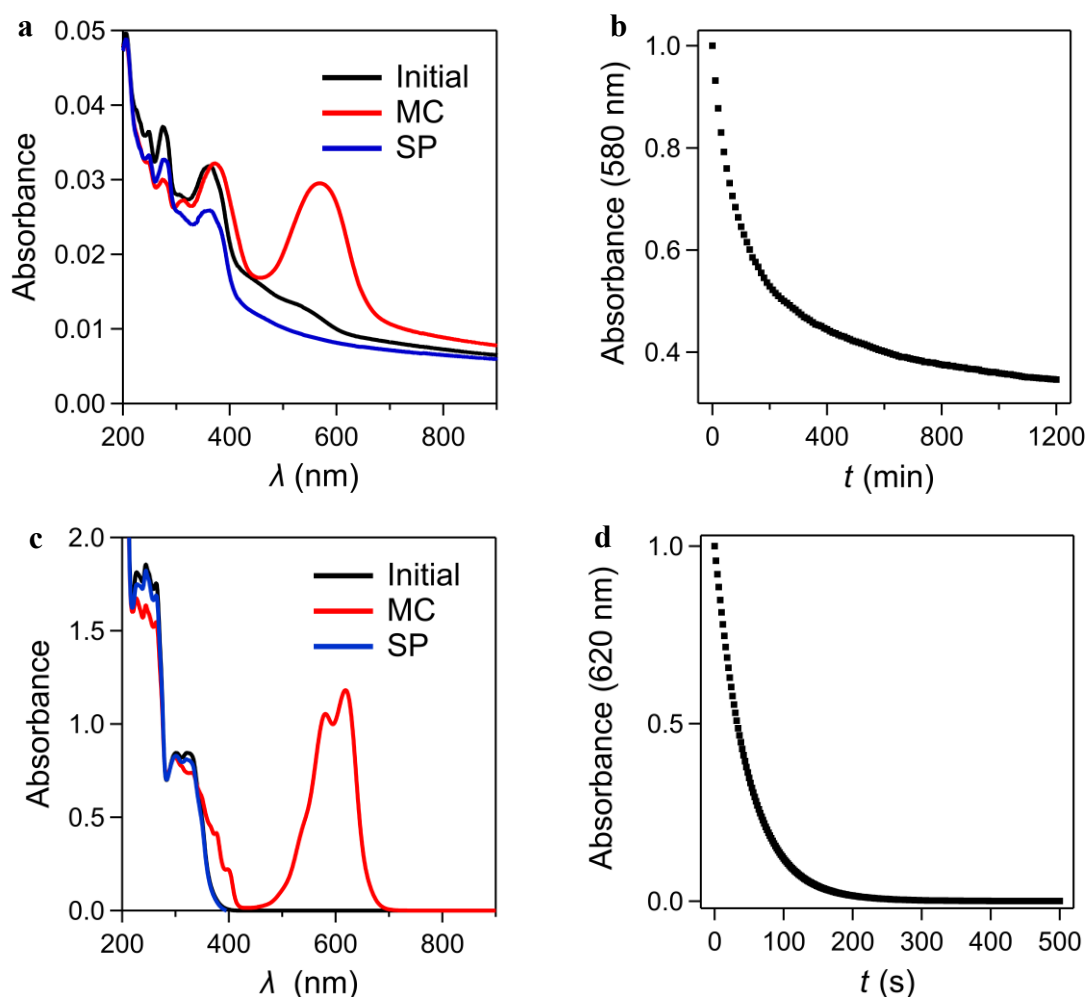
For bulk layered superconductors, typically, the angular dependence of the upper critical field $\mu_0 H_{c2}$ is represented by the 3D anisotropic mass model expressed as²:

$$\left(\frac{H_{c2}(\theta)\sin\theta}{H_{c2}^{\parallel}}\right)^2 + \left(\frac{H_{c2}(\theta)\cos\theta}{H_{c2}^{\perp}}\right)^2 = 1$$

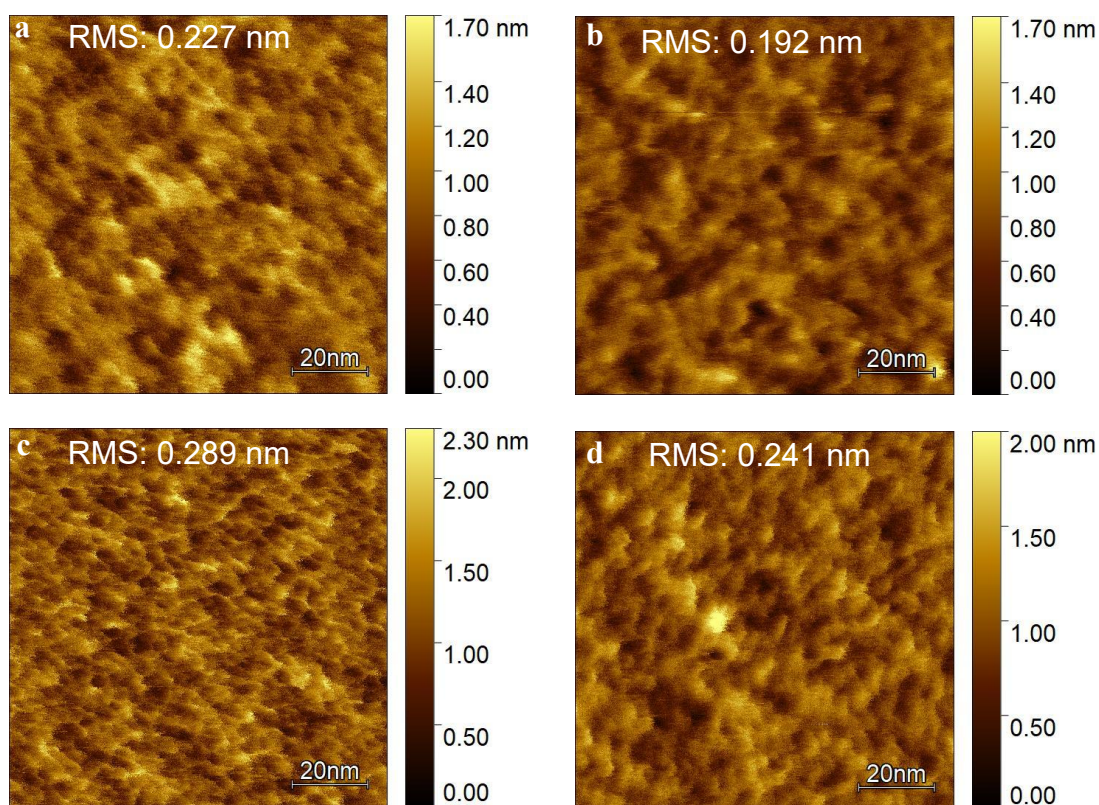
where $H_{c2}^{\parallel}$ and $H_{c2}^{\perp}$ are the parallel ($\theta=90^\circ$) and perpendicular ($\theta=0^\circ$) upper critical fields with respect to the conducting planes, respectively. In 2D thin films, $\mu_0 H_{c2}$ can be described by 2D Tinkham model as follows²:

$$\left(\frac{H_{c2}(\theta)\sin\theta}{H_{c2}^{\parallel}}\right)^2 + \left|\frac{H_{c2}(\theta)\cos\theta}{H_{c2}^{\perp}}\right| = 1$$

As the field direction approaches the conducting plane at an angle of 90° , the two models diverge. Figure 3c in the main text displays the fits to 3D anisotropic model and 2D Tinkham model simultaneously. As shown in the inset of Figure 3c, 2D Tinkham model gives a best fit to the experimental results between 89° and 91° .

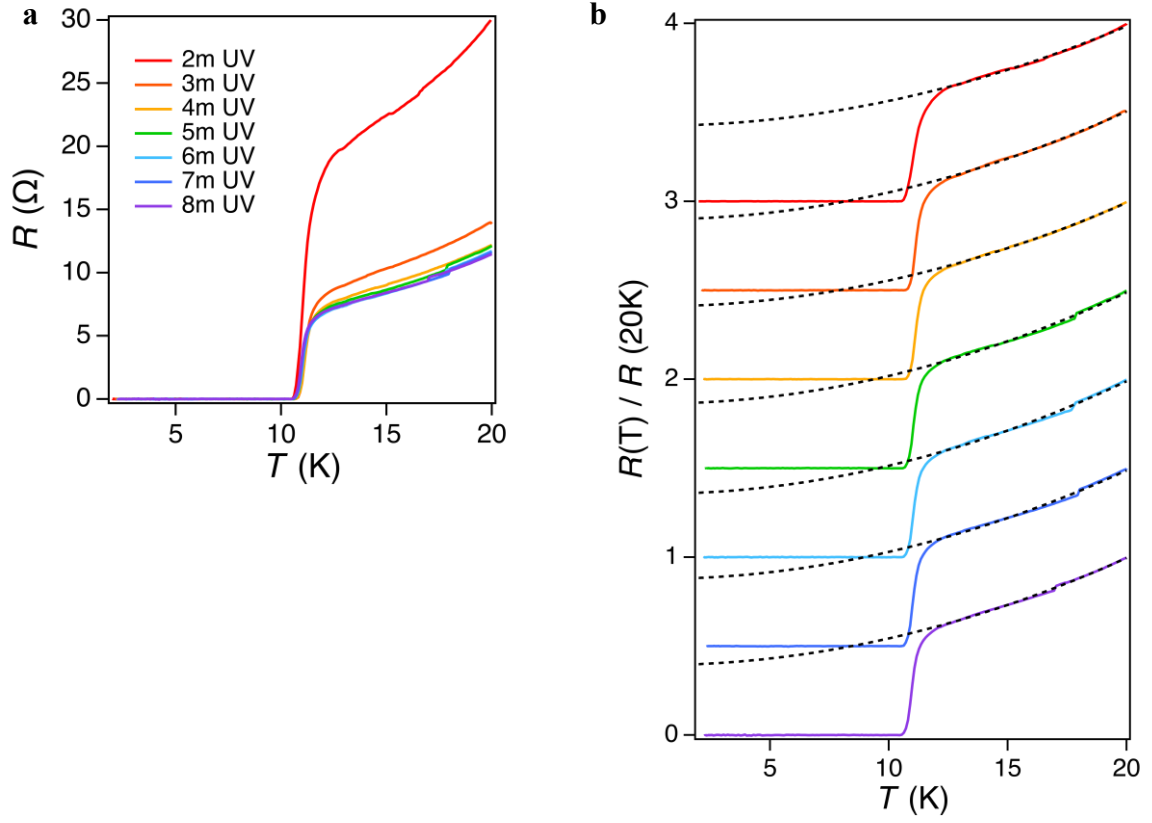


Supplementary Figure 1: Optical absorbance spectra of SP-C18. (a) Absorbance spectra of the SP-C18 solution in cyclohexane (0.05 mg mL⁻¹) at the initial state (black), the SP solution after irradiation with UV light (red, with a wavelength of 365 nm), and the SP solution after 10 minutes of thermal recovery (blue). (b) Time trace of the normalized solution absorbance (at 580 nm) following irradiation with UV light (c) SP-C18-SAM absorbance spectra on film, obtained by spin-coating the SP solution in cyclohexane (1 mg mL⁻¹) onto a quartz slide. Absorbance spectra of initial spin-coated film (black), spin-coated film following UV irradiation (red, with a wavelength of 365 nm), and film after 72 hours of thermal recovery (blue) (d) Time trace of the normalized film absorbance (at 620 nm) following irradiation of UV light. Notably, the SP spin-coated on film recovered considerably more slowly than that in solution.

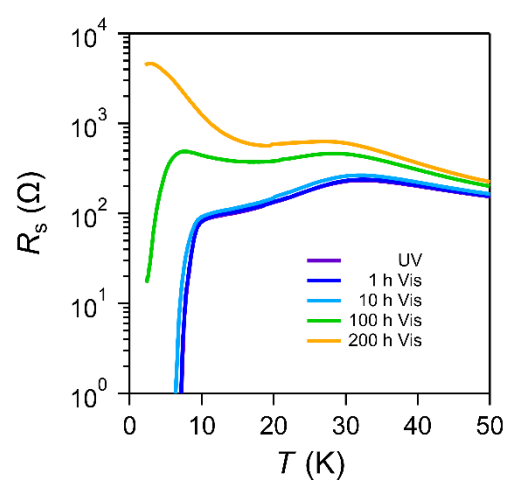


Supplementary Figure 2: Light-induced topographical reorganization of SP monolayer on κ -Cl at 100 nm scale. (a) Surface topography of κ -Cl. (b) Topography of initial state of SP- κ -Cl following SP-SAM spin-coating. (c) Topography of SP- κ -Cl following 1 hour of irradiation of UV light with a wavelength of 365 nm. After UV irradiation, a dramatic rearrangement of the SP-SAM was detected. (d) Topography of SP- κ -Cl after 72 hours of irradiation of visible light with a wavelength of 580 nm.

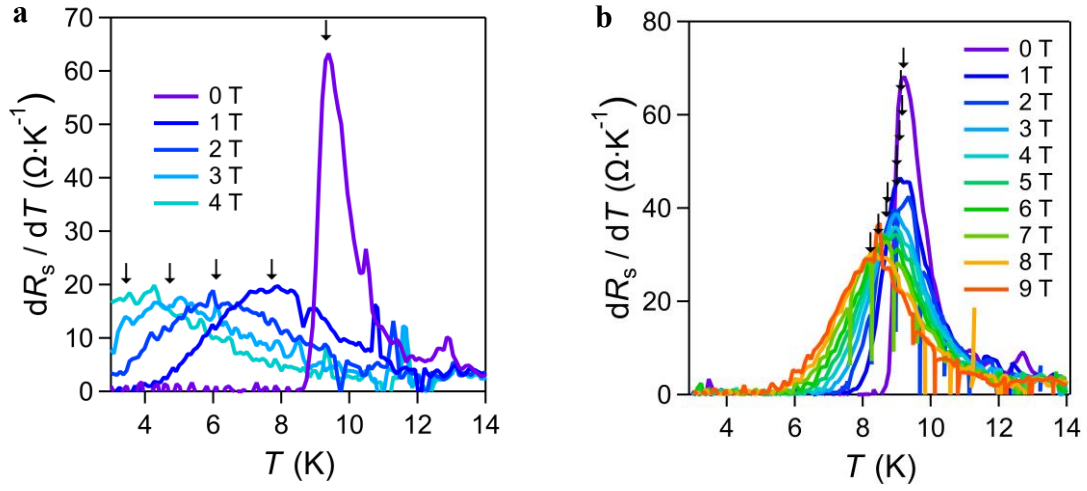
Above the image is the corresponding root mean square (RMS) roughness. The initial RMS in κ -Cl bulk crystal is comparable to the value reported in a κ -Cl film with a thickness of tens of nanometers³. RMS roughness decreased after spin-coating with SP-SAM because SP-SAM modified and smoothed the surface of κ -Cl. Due to the extensively stretched and rigidly ordered structure of the MC state, the RMS roughness rebounded significantly following UV irradiation, in accordance with the previous findings derived from density functional theory (DFT) calculation¹. With the irradiation of visible light, the RMS roughness dropped to a value greater than the initial state, indicating a partial recovery. This partial recovery is also reflected in the low resistance after prolonged exposure to visible light displayed the main text.



Supplementary Figure 3: Fermi liquid behavior in SP- κ -Cl. (a) The UV irradiation time dependence of resistance R . (b) Resistance normalized at 20 K. Each curve is shifted by 0.5. The black dashed lines indicate that $R(T)$ has a strictly quadratic form at the vicinity of superconducting transition. Thus, Fermi liquid behavior is observed in SP- κ -Cl with various UV irradiation time.

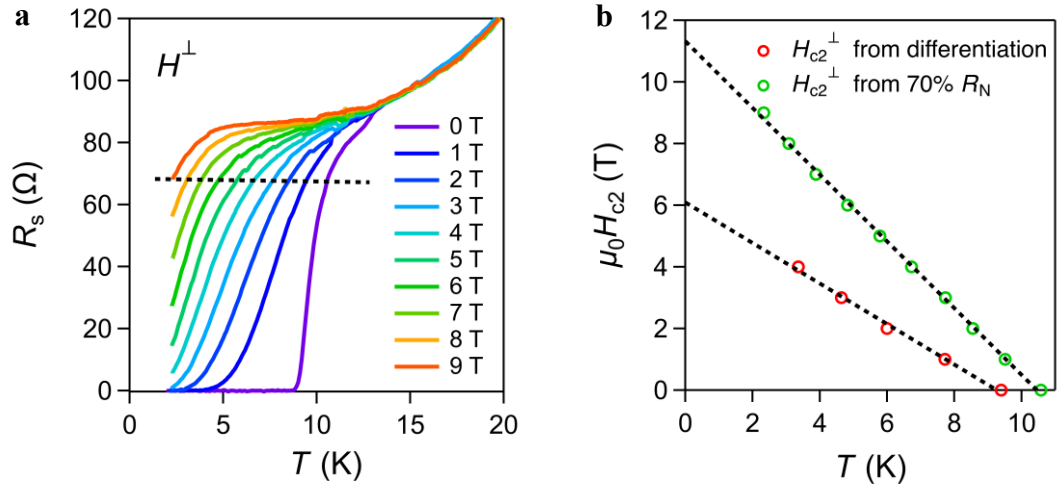


Supplementary Figure 4: Sheet resistance versus temperature for the SP- κ -Cl device after various times of irradiation with visible light.

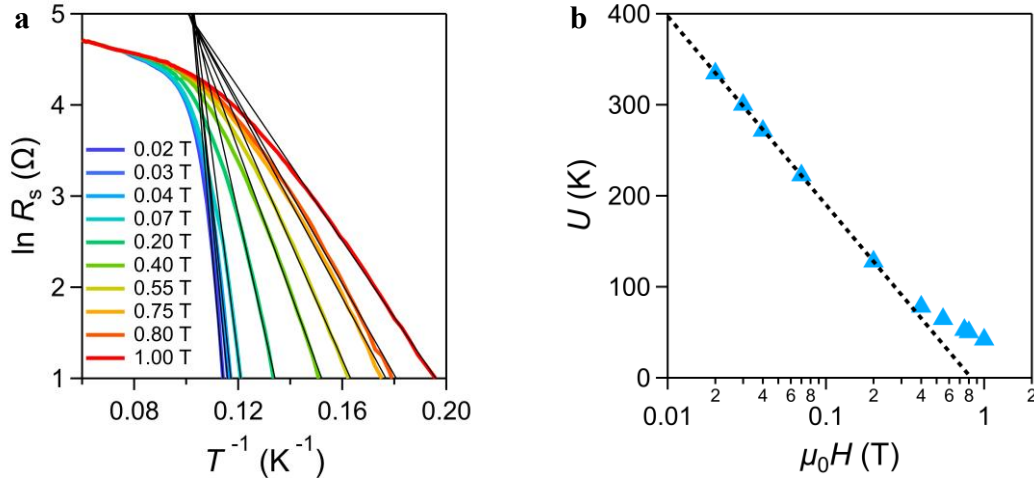


Supplementary Figure 5: Determination of upper critical field H_{c2} for SP- κ -Cl. (a) Differentiation of out-of-plane magnetoresistance of SP- κ -Cl **(b)** Differentiation of in-plane magnetoresistance of SP- κ -Cl.

Analogue to cuprate superconductors⁴, the broadening of superconducting transition under magnetic field results in varied onset as well as midpoint in resistive drop, which brings large ambiguities to the determination of upper critical field H_{c2} from the electrical transport measurement⁵. Thus, here the upper critical field H_{c2} is defined to be the peak values of the differentiation of resistance.



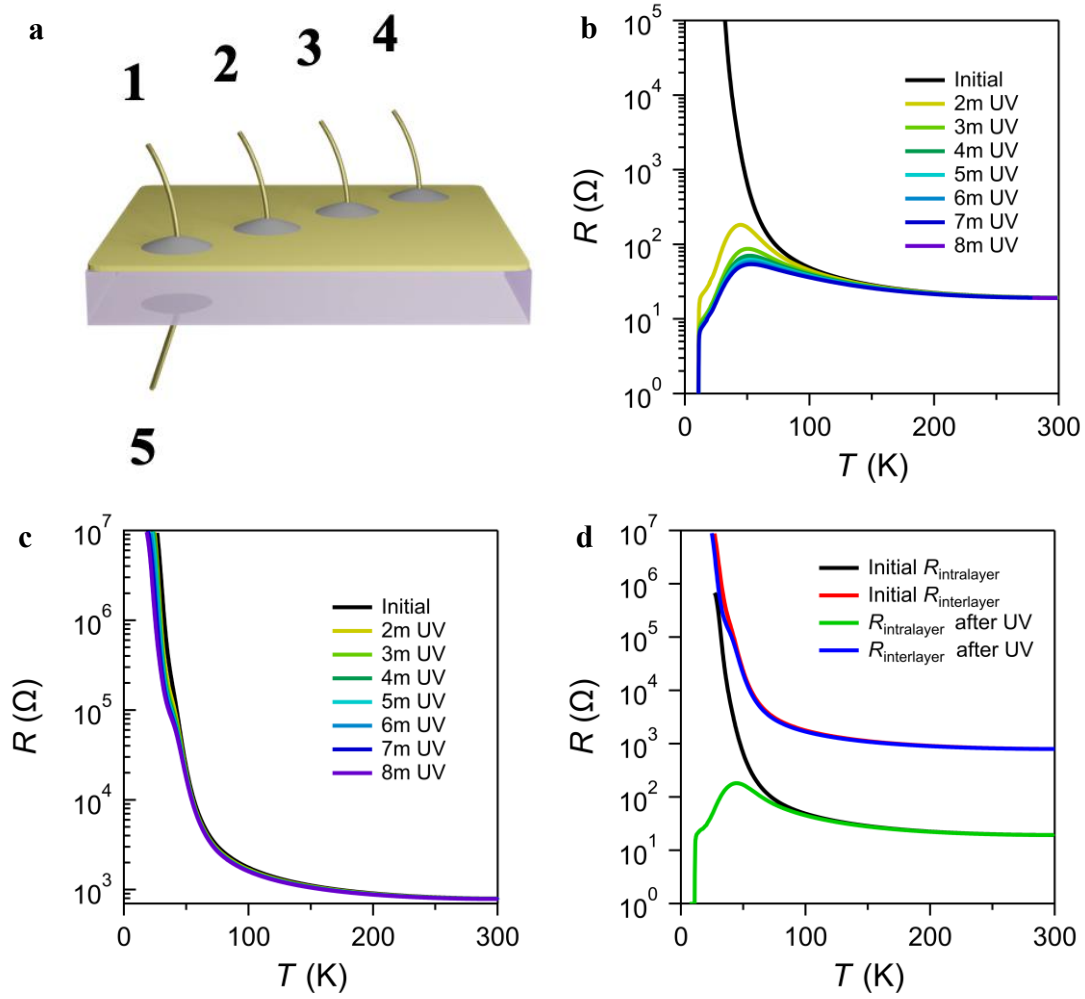
Supplementary Figure 6: Out-of-plane upper critical field H_{c2} of SP- κ -Cl. (a) Determination of out-of-plane H_{c2} in SP- κ -Cl. The dashed line indicates the resistance that is equal to 70% of R_N . (b) Comparison of the temperature-dependent upper critical field defined in two different ways. Despite the different methods to determine the H_{c2} , both results show a linear behavior which is consistent with 2D Ginzburg-Landau model.



Supplementary Figure 7: Vortex dynamics in SP- κ -Cl. (a) Arrhenius plot of sheet resistance of κ -Cl in perpendicular magnetic fields. (b) Field-dependent activation energies extracted from the Arrhenius plot of sheet resistance on a semi-logarithmic scale. Dashed line gives fitting result using the formula $U(H) = U_0 \ln(H_0/H)$, which suggests a 2D vortex lattice in low fields regime.

Compared to the zero-field superconducting transition, remarkable broadening of the resistive transition in magnetic field was observed (Fig. 3a, b). The Arrhenius plots of R_{sheet} for out-of-plane magnetic fields are well described by thermally assisted flux flow (TAFF) theory with the formula $\ln R(H, T) = \ln R_0(H) - U(H)/T$, as indicated by the black lines, where $U(H)$ is the field-dependent activation energy of a vortex and it is given by the slope of the linear fit⁶⁻⁸. The formula $U(H) = U_0 \ln(H_0/H)$ (Fig.S 7b) describes finely the relationship between $U(H)$ and H in low field regime, suggesting a 2D vortex lattice in SP- κ -Cl⁹. As the applied magnetic field increases, the vortex density increases and thereby the repulsion between them appears. Notably, a deviation emerges above 0.2 T, which can be explained by a crossover from individual flux pinning to collective pinning in 2D vortex lattice¹⁰. For fields below ~ 0.2 T, the activation energy decreases logarithmically as $U(H) = U_0 \ln(H_0/H)$, consistent with 2D TAFF theory. At higher fields, U begins to saturate, which we attribute to a crossover into a regime of collective pinning, where vortices move in correlated bundles rather than individually. At still higher fields, vortex lattice melting could in principle occur, as reported in other κ -(BEDT-TTF)₂ salts¹², leading to a decrease of the activation energy with increasing field. However, such a reversal was not observed within our accessible experimental range. On the other hand,

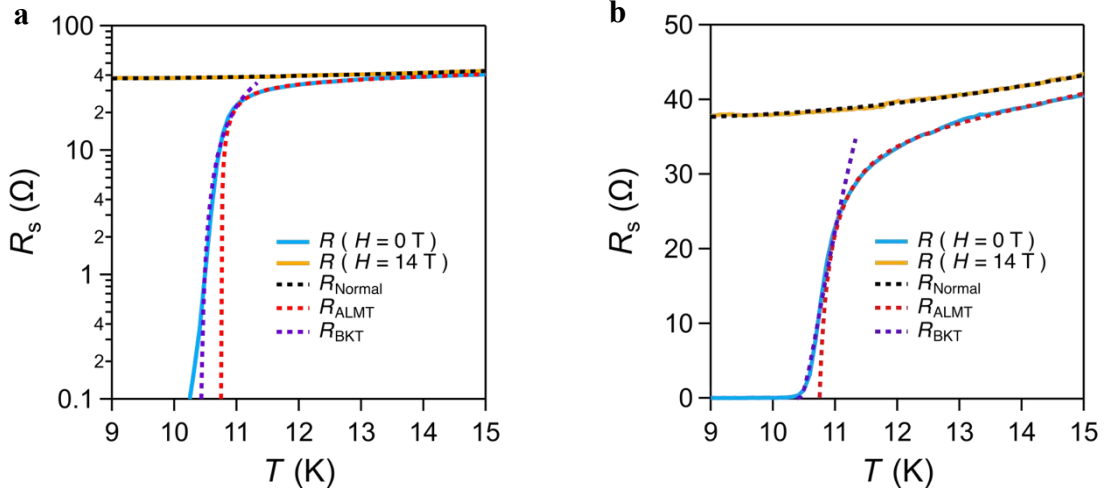
for its superconducting counterparts, κ -(BEDT-TTF)₂[CuN(CN)₂]Br (κ -Br) and κ -(BEDT-TTF)₂Cu(NCS)₂ (κ -NCS), a relationship of $U \propto H^{-0.5}$ corresponding to a 3D vortex lattice in low fields has been reported^{11,12}. In addition, a dimensional crossover from 3D in low fields to 2D in high fields has been demonstrated in terms of vortex dynamics in κ -type of BEDT-TTF based salts¹². On the other hand, our distinctive results suggest a 2D nature of superconductivity in SP- κ -Cl even in low fields regime.



Supplementary Figure 8: Anisotropic electrical transport in the SP- κ -Cl. (a) Electrode geometry for resistance anisotropy measurement in SP- κ -Cl. (b) Resistance versus temperature for the SP- κ -Cl device after various irradiation times of UV light, with the electrodes 1, 2, 3, and 4. (c) Resistance versus temperature for the SP-SAM κ -Cl after various irradiation times of UV light, with the electrode 1 and 5. (d) Comparison of the changes of resistance after UV light irradiation for in-plane and out-of-plane configurations.

κ -Br and κ -NCS have been intensively studied for decades due to their extremely high anisotropy among layered superconductors. Their resistivity anisotropy ρ_{zz}/ρ_{xx} is about 10^3 at ambient temperature and increases to several thousand at low temperatures slightly above T_c ^{13,14}. In contrast, as shown in Supplementary Figure 8d, the resistance anisotropy R_{zz}/R_{xx} in SP- κ -Cl at its initial state is $\sim 10^2$ at room temperature, which is the same value as reported for κ -Cl¹⁵. As the temperature is lowered, the resistance anisotropy can be

readily extrapolated to exceed 10^6 or even 10^7 above T_c , which is more than three orders of magnitude higher than that in κ -Br and κ -NCS. This tremendously high resistance anisotropy in SP- κ -Cl evidences the 2D nature in it.



Supplementary Figure 9: Superconducting fluctuation in SP- κ -Cl. (a) Sheet resistance versus temperature for SP- κ -Cl in log-linear scale. The solid and dashed lines indicate the experimental and fitting results, respectively. **(b)** Sheet resistance versus temperature for SP- κ -Cl in linear-linear scale.

Both the phase and amplitude of the order parameter are significantly affected by thermal fluctuations in 2D superconductor¹⁶. Phase fluctuations produce paraconductivity below the mean-field transition temperature T_{c0} , whereas amplitude fluctuations produce excess conductivity $\Delta\sigma$ above T_{c0} . The resistive transition is broadened and rounded as a result of the overall effect of them.

In addition to the enhanced phase fluctuation in the immediate vicinity of superconducting transition described by BKT scenario, the amplitude fluctuation above T_{c0} is remarkable as well in SP- κ -Cl.

This excess conductivity approximately composed of two principal contributions: Aslamaxov-Larkin (AL) contribution stemmed from the fluctuating Cooper pairs¹⁷⁻¹⁹, and Maki-Thompson (MT) contribution taking into account coherent scattering of electrons by impurity¹⁸⁻²¹.

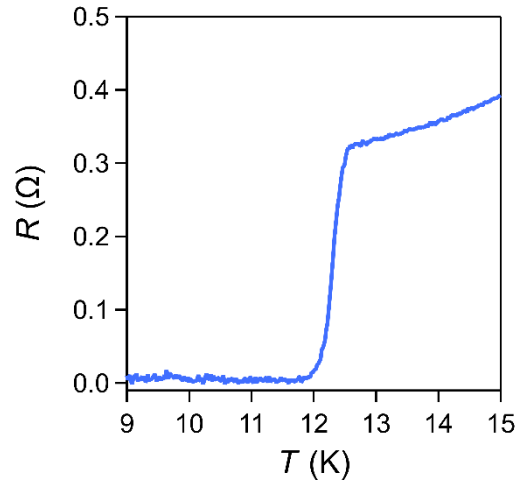
In 2D system, AL contribution is expressed as: $\sigma_{\text{AL}} = \frac{e^2}{16h} \frac{1}{\epsilon^2}$, where $\epsilon = \frac{T-T_{c0}}{T_{c0}}$, and T_{c0} is mean field transition temperature.

MT contribution is expressed as: $\sigma_{\text{MT}} = \frac{e^2}{8h} \frac{1}{\epsilon - \delta} \ln \frac{\epsilon}{\delta}$, where δ is a pair-breaking parameter.

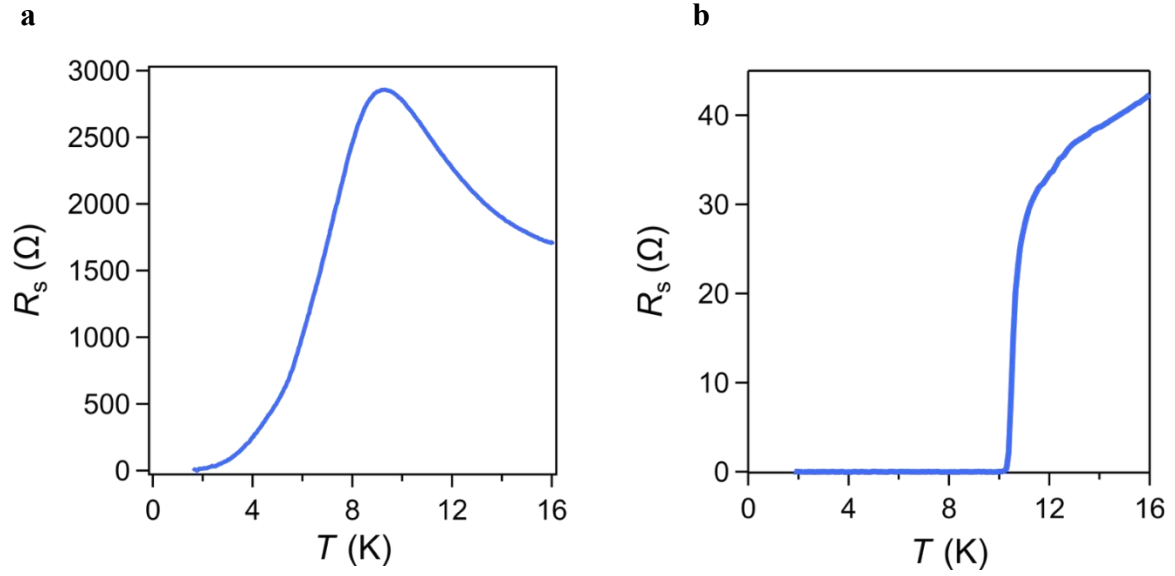
Thus, consider the Aslamaxov-Larkin theory in 2D case with the Maki-Thompson correction (ALMT), we have:

$$\Delta \sigma = \frac{1}{R_{\text{Normal}}} + \frac{1}{R_{\text{sheet}}} = \sigma_{\text{AL}} + \sigma_{\text{MT}} = \frac{e^2}{16\hbar} \left(\frac{1}{\epsilon} + \frac{2}{\epsilon - \delta} \ln \frac{\epsilon}{\delta} \right)$$

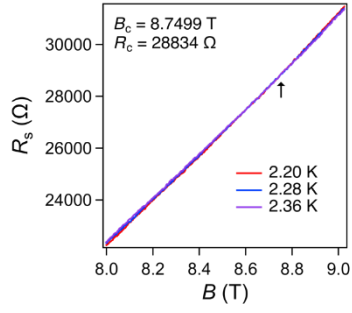
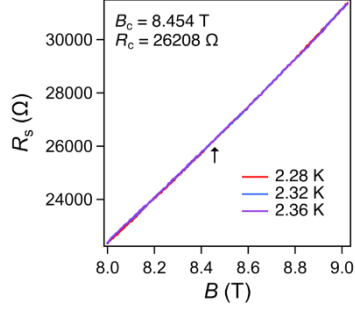
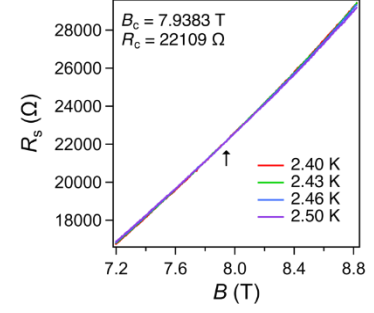
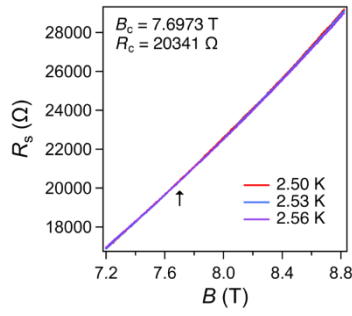
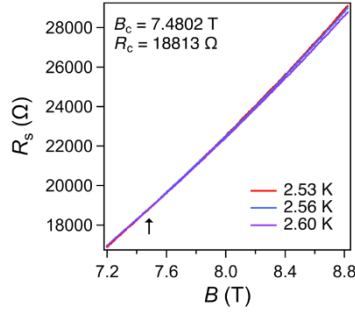
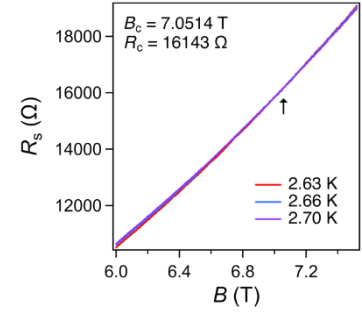
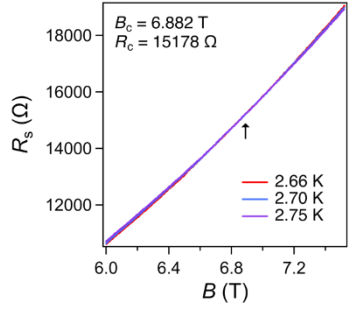
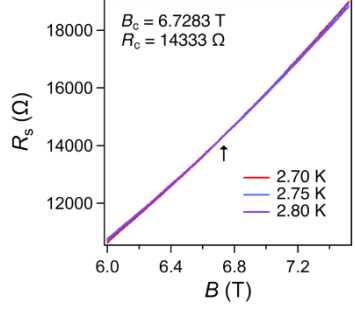
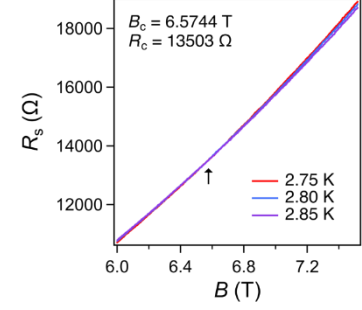
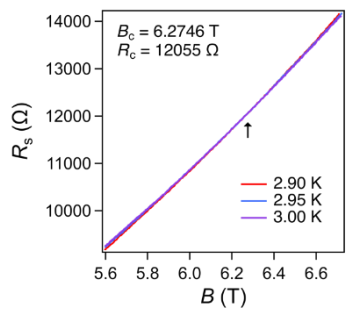
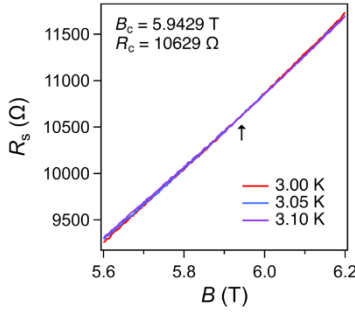
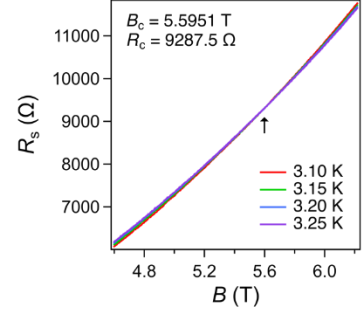
where R_{Normal} is the normal state resistance and R_{sheet} here is the zero-field sheet resistance. We use the resistance under a magnetic field up to 14 Tesla as the R_{Normal} to fit this equation. The fitting is shown in Supplementary Figure 9, which gives $T_{c0} = 10.75$ K and $\delta = 1 \times 10^{-8}$. We note that this pair-breaking parameter δ is extremely large in comparison to other crystalline 2D systems^{22,23}, which could be attributed to the clean-limit superconductivity in κ -BEDT-TTF salts. As shown in Supplementary Figure 9, the mean field temperature T_{c0} is very near to T_{BKT} , which evidences the clean-limit superconductivity also¹⁰.

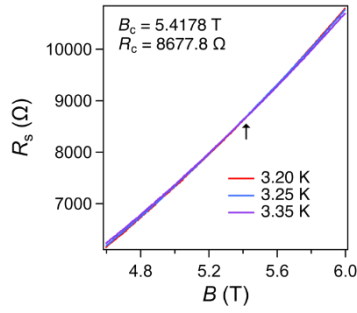
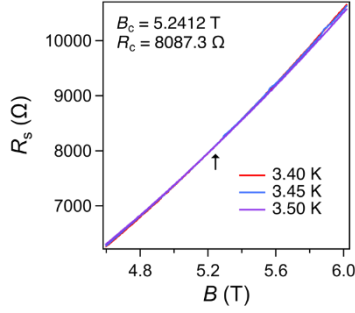
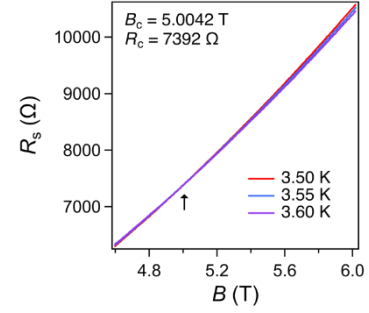
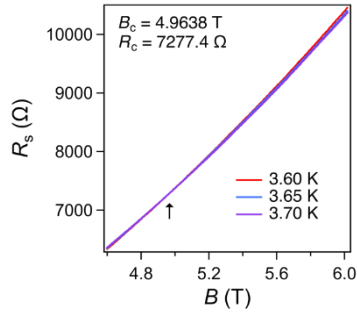
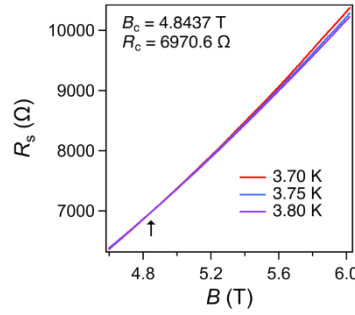
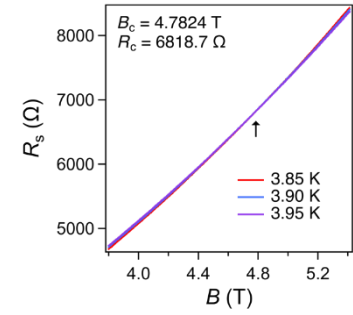
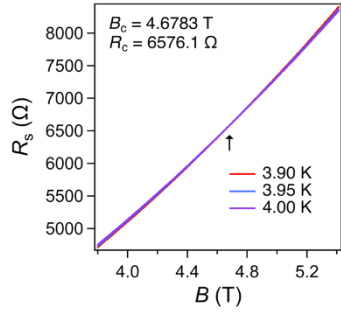
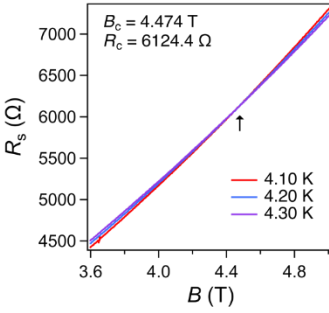
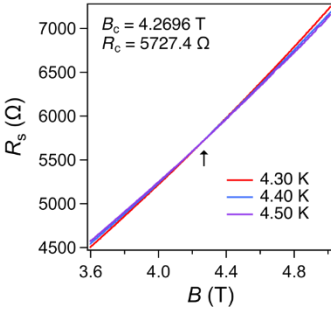
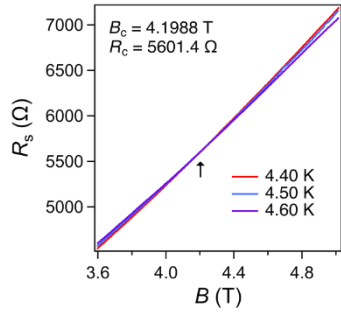
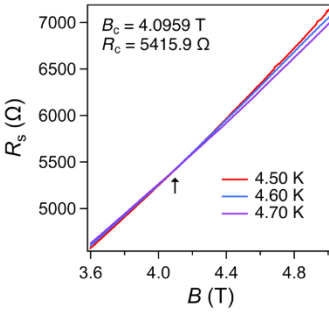
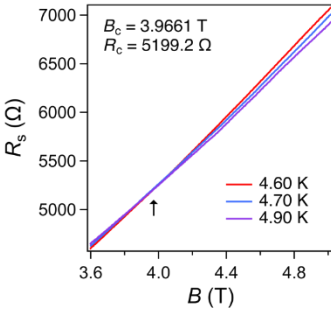


Supplementary Figure 10: Superconducting transition in κ -Br. In-plane resistance versus temperature in κ -Br. In comparison to the rounded superconducting transition originated from enhanced superconducting fluctuation in SP- κ -Cl, in-plane resistive transition in κ -Br behaves like a quasi-2D superconductor, as in previous report²⁴.

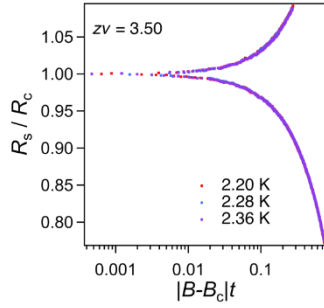
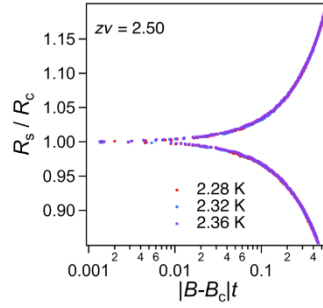
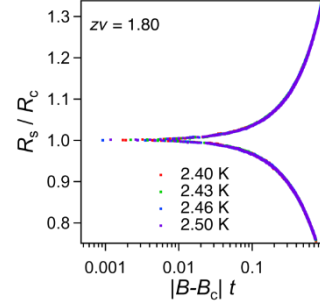
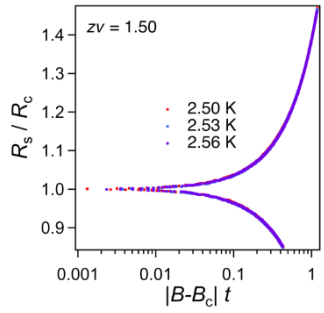
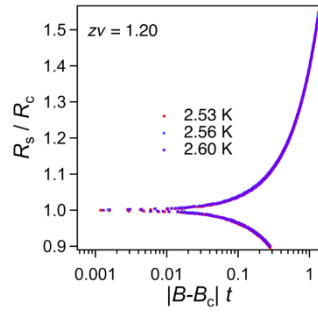
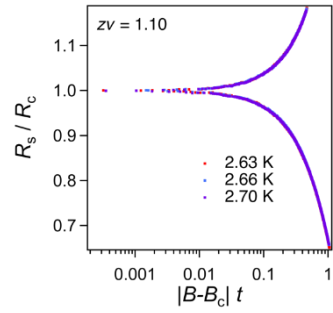
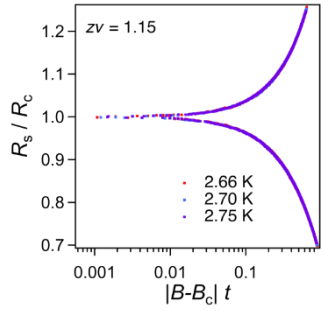
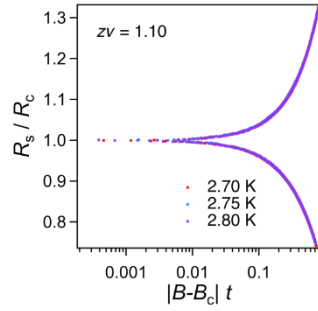
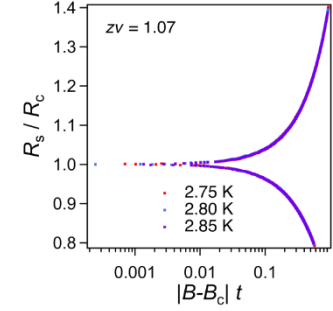
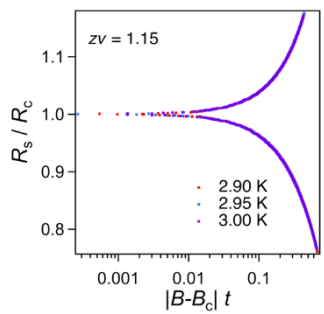
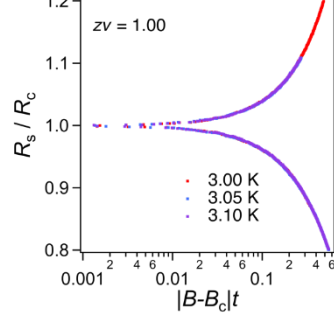
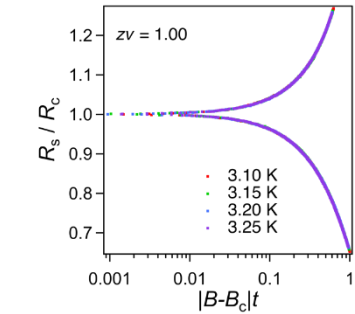


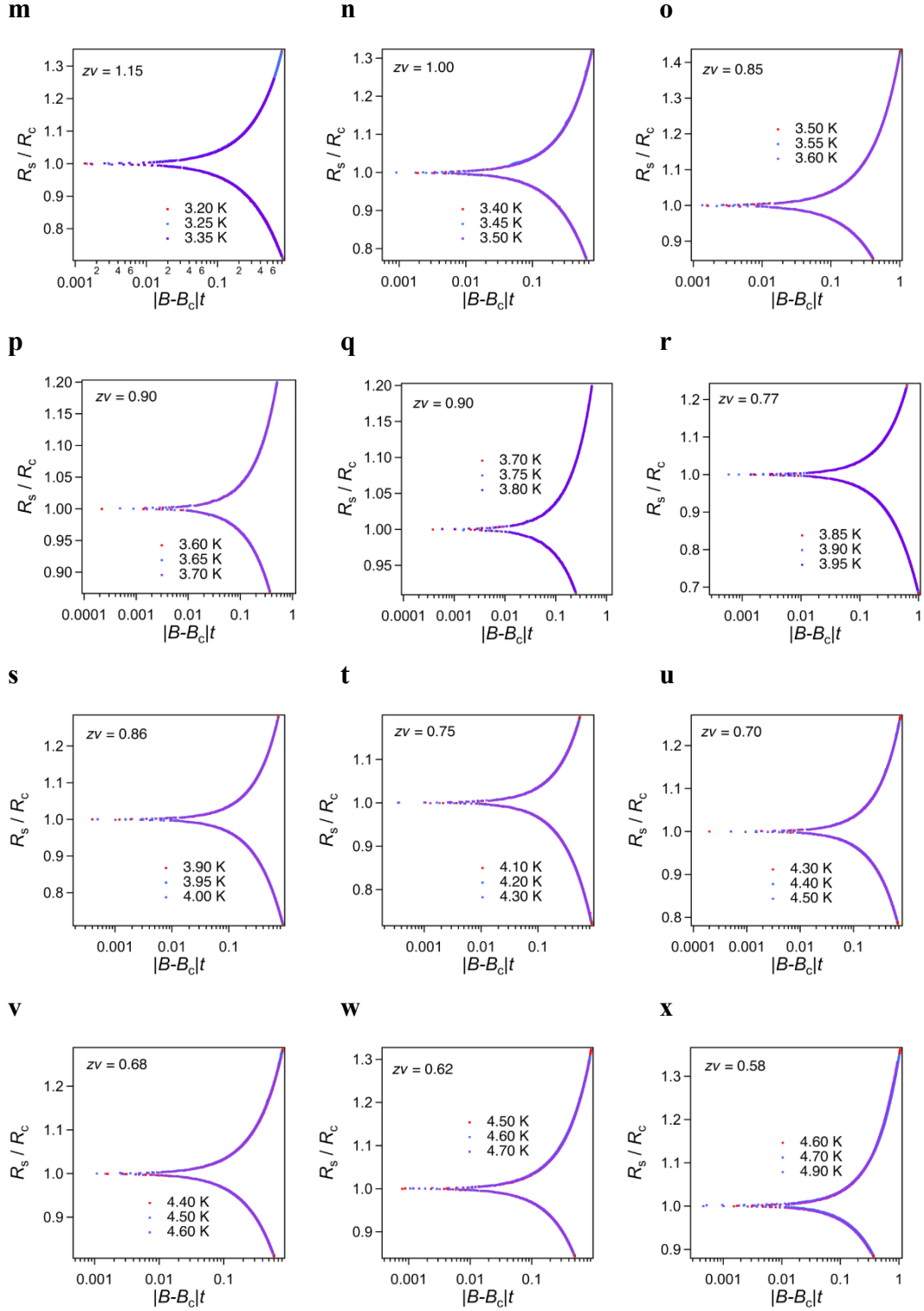
Supplementary Figure 11: Photo-switching Inhomogeneous and homogeneous superconducting states in SP- κ -Cl. (a) Sheet resistance versus temperature for SP- κ -Cl in inhomogeneous state realized with a short irradiation time, which shows the features of granular superconductivity indicated by broadened transition. (b) Sheet resistance versus temperature for SP- κ -Cl in the homogeneous state realized with a longer irradiation time, which displays a relatively sharp transition.

a**b****c****d****e****f****g****h****i****j****k****l**

m**n****o****p****q****r****s****t****u****v****w****x**

Supplementary Figure 12: The sheet resistance as a function of magnetic field at different temperatures (a~x).

a**b****c****d****e****f****g****h****i****j****k****l**



Supplementary Figure 13: Finite-size scaling analysis. Normalized R_s extracted from Supplementary Figure 12 as a function of the scaling variable $|B-B_c|t$, where $t = (T/T_0)^{-1/zv}$ and T_0 denotes the lowest temperature in each set of $R(B)$ curves²⁵.

References

- 1 Gobbi, M. *et al.* Collective molecular switching in hybrid superlattices for light-modulated two-dimensional electronics. *Nat. Commun.* **9**, 2661 (2018).
- 2 Tinkham, M. *Introduction to superconductivity.* (Courier Corporation, 2004).
- 3 Sato, Y., Kawasugi, Y., Suda, M., Yamamoto, H. M. & Kato, R. Critical behavior in doping-driven metal–insulator transition on single-crystalline organic Mott-FET. *Nano Lett.* **17**, 708-714 (2017).
- 4 Welp, U., Kwok, W., Crabtree, G., Vandervoort, K. & Liu, J. Magnetic measurements of the upper critical field of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals. *Phys. Rev. Lett.* **62**, 1908 (1989).
- 5 Kwok, W. *et al.* Unusual behavior in the upper critical magnetic fields of the ambient-pressure organic superconductor $\kappa\text{-(BEDT-TTF)}_2\text{Cu[N(CN)}_2\text{]Br}$ [where BEDT-TTF represents bis (ethylenedithio) tetrathiofulvalene]. *Phys. Rev. B* **42**, 8686 (1990).
- 6 Palstra, T., Batlogg, B., Schneemeyer, L. & Waszczak, J. V. Thermally activated dissipation in $\text{Bi}_{2.2}\text{Sr}_2\text{Ca}_{0.8}\text{Cu}_2\text{O}_{8+\delta}$. *Phys. Rev. Lett.* **61**, 1662 (1988).
- 7 Palstra, T., Batlogg, B., Van Dover, R. B., Schneemeyer, L. & Waszczak, J. Dissipative flux motion in high-temperature superconductors. *Phys. Rev. B* **41**, 6621 (1990).
- 8 Blatter, G., Feigel'man, M. V., Geshkenbein, V. B., Larkin, A. I. & Vinokur, V. M. Vortices in high-temperature superconductors. *Rev. Mod. Phys.* **66**, 1125 (1994).
- 9 Feigel'Man, M., Geshkenbein, V. & Larkin, A. Pinning and creep in layered superconductors. *Phys. C: Supercond.* **167**, 177-187 (1990).
- 10 Hsu, J. & Kapitulnik, A. Superconducting transition, fluctuation, and vortex motion in a two-dimensional single-crystal Nb film. *Phys. Rev. B* **45**, 4819 (1992).
- 11 Ito, H., Ishiguro, T., Nakamura, T., Komatsu, T. & Saito, G. Resistive transition of $\kappa\text{-(BEDT-TTF)}_2\text{Cu[N(CN)}_2\text{]Br}$ superconductor under magnetic field. *Synth. Met.* **56**, 2251-2256 (1993).
- 12 Friemel, S. & Pasquier, C. Activation energies in the vortex liquid state of $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$. *Phys. C: Supercond.* **265**, 121-125 (1996).
- 13 Buravov, L. *et al.* Anisotropic resistivity and thermopower of the organic superconductor $(\text{ET})_2\text{Cu[N(CN)}_2\text{]Br}$. *J. Phys. I* **2**, 1257-1262 (1992).
- 14 Ito, H., Ishihara, A., Hanada, M., Saito, G. & Yamada, J. Resistivity Anisotropy and Phase Diagram of the κ -Type BEDT-TTF Salts. *Synth. Met.* **137**, 1221-1222 (2003).
- 15 Ito, H., Ishiguro, T., Kubota, M. & Saito, G. Metal-nonmetal transition and superconductivity localization in the two-dimensional conductor $\kappa\text{-(BEDT-TTF)}_2\text{Cu[N(CN)}_2\text{]Cl}$ under pressure. *J. Phys. Soc. Jpn.* **65**, 2987-2993 (1996).
- 16 Fisher, D. S., Fisher, M. P. & Huse, D. A. Thermal fluctuations, quenched disorder, phase transitions, and transport in type-II superconductors. *Phys. Rev. B* **43**, 130 (1991).
- 17 Aslamasov, L. & Larkin, A. The influence of fluctuation pairing of electrons on the conductivity of normal metal. *Phys. Lett. A* **26**, 238-239 (1968).

- 18 Larkin, A. & Varlamov, A. *Theory of fluctuations in superconductors*. Vol. 127 (OUP Oxford, 2005).
- 19 Skocpol, W. & Tinkham, M. Fluctuations near superconducting phase transitions. *Rep. Prog. Phys.* **38**, 1049 (1975).
- 20 Maki, K. The critical fluctuation of the order parameter in type-II superconductors. *Prog. Theor. Phys.* **39**, 897-906 (1968).
- 21 Thompson, R. S. Microwave, flux flow, and fluctuation resistance of dirty type-II superconductors. *Phys. Rev. B* **1**, 327 (1970).
- 22 Saito, Y., Kasahara, Y., Ye, J., Iwasa, Y. & Nojima, T. Metallic ground state in an ion-gated two-dimensional superconductor. *Science* **350**, 409-413 (2015).
- 23 Devarakonda, A. *et al.* Clean 2D superconductivity in a bulk van der Waals superlattice. *Science* **370**, 231-236 (2020).
- 24 Mu, H. *et al.* Temperature dependent anisotropy and two-band superconductivity revealed by lower critical field in organic superconductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Br. *arXiv preprint arXiv:2302.02604* (2023).
- 25 Sondhi, S. L., Girvin, S., Carini, J. & Shahar, D. Continuous quantum phase transitions. *Rev. Mod. Phys.* **69**, 315 (1997).