

Charge-cluster glass in an organic conductor

F. Kagawa^{1,2*}, T. Sato¹, K. Miyagawa¹, K. Kanoda¹, Y. Tokura^{1,3}, K. Kobayashi⁴, R. Kumai^{2,4}
and Y. Murakami⁴

Geometrically frustrated spin systems often do not exhibit long-range magnetic ordering, resulting in either quantum-mechanically disordered states, such as quantum spin liquids¹, or classically disordered states, such as spin ices^{2,3} or spin glasses⁴. Geometric frustration may play a similar role in charge ordering^{5,6}, potentially leading to unconventional electronic states without long-range order; however, there are no previous experimental demonstrations of this phenomenon. Here, we show that a charge-cluster glass evolves on cooling in the absence of long-range charge ordering for an organic conductor with a triangular lattice. A combination of time-resolved transport measurements and X-ray diffraction reveals that the charge-liquid phase has two-dimensional charge clusters that fluctuate extremely slowly (<10–100 Hz) and heterogeneously. On further cooling, the cluster dynamics freezes, and a charge-cluster glass is formed. Surprisingly, these observations correspond to recent ideas regarding the structural glass formation of supercooled liquids^{7–10}. Glassy behaviour has often been found in transition-metal oxides, but only under the influence of randomly located dopants^{11,12}. As organic conductors are very clean systems, the present glassy behaviour is probably conceptually different.

Wigner-type charge ordering is a phenomenon in which an equal number of charge-rich and charge-poor sites occupy a lattice such that rich–rich (or poor–poor) neighbouring pairs are avoided as much as possible. However, in a geometrically frustrated lattice, this constraint is insufficient to determine a specific charge ordering among the various charge configurations, analogously to spin-frustrated systems (Fig. 1a); thus, the geometric frustration potentially undermines the tendency towards long-range charge ordering, as was first suggested in ref. 5. As a result, exotic electronic states may be exhibited at low temperatures when long-range charge ordering is avoided.

The material investigated in this study is the organic conductor θ -(BEDT-TTF)₂RbZn(SCN)₄ (denoted θ -RbZn), where BEDT-TTF (ET) denotes bis(ethylenedithio)tetrathiafulvalene¹³. The crystal structure consists of alternating layers of conducting ET molecules and insulating anions, and the ET molecules form a geometrically frustrated triangular lattice (Fig. 1b), where the ratio of two different inter-site Coulomb interactions is calculated to be ~ 0.86 (ref. 14). The ET conduction band is hole-1/4-filled; thus, the charge-delocalized state (the charge-liquid phase) is subject to charge ordering instability¹⁵. However, the charge frustration created by the triangular lattice may prevent long-range ordering. Experimentally, a structural transition with the modulation $\mathbf{q}_0 = (0\ 0\ 1/2)$ occurs at ~ 200 K and relaxes the degree of charge frustration; consequently, a horizontal charge order that matches \mathbf{q}_0 is stabilized^{16–18}. This charge order is a strong first-order

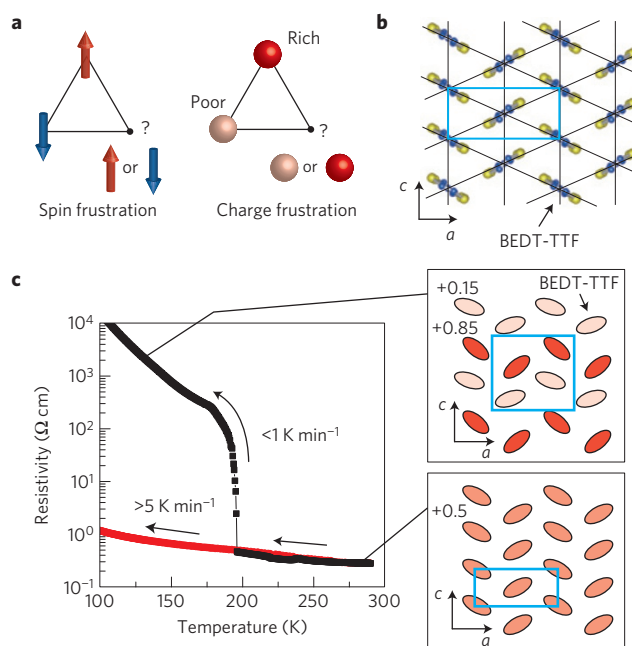


Figure 1 | Charge frustration and crystal structure of θ -(BEDT-TTF)₂RbZn(SCN)₄. **a**, An illustration of the analogy between spin frustration and charge frustration. **b**, The structure of the BEDT-TTF layer. The lattice parameters are $a \approx 10.2$ Å and $c \approx 4.6$ Å at 220 K (ref. 16). **c**, The temperature dependence of the resistivity during cooling for different temperature-sweeping rates. The insets indicate the crystal structures of the high-temperature phase (lower inset) and the low-temperature phase (upper inset). Colours as for **a**. In the upper inset, the charge-ordering pattern is also shown. To emphasize the two-fold structural modulation of the c axis, the upper inset is depicted in an exaggerated manner. In each panel, the unit cell is indicated by a blue rectangle.

transition accompanied by a sudden increase in resistivity (Fig. 1c). When rapidly cooled ($> 5\text{ K min}^{-1}$), the charge/structure order at 200 K vanishes, giving way to a charge-liquid phase with a frustrated triangular lattice, which is maintained at lower temperatures^{19,20} (Fig. 1c). As there is no resistivity anomaly at 200 K during rapid cooling (Fig. 1c), the phase exhibited above 200 K is considered a continuation of the rapidly cooled phase. The electronic states above 200 K may be exotic, as suggested in the literature: the optical conductivity measurements revealed that the charge liquid cannot be ascribed to a conventional metal that has a Drude response²¹. More interestingly, previous NMR measurements, which are a probe of local spin dynamics, implied the existence of slow charge

¹Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan, ²CREST, Japan Science and Technology Agency (JST), Tokyo 102-0076, Japan, ³RIKEN Center for Emergent Matter Science (CEMS), Wako 351-0198, Japan, ⁴Condensed Matter Research Center (CMRC) and Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba 305-0801, Japan. *e-mail: kagawa@ap.t.u-tokyo.ac.jp

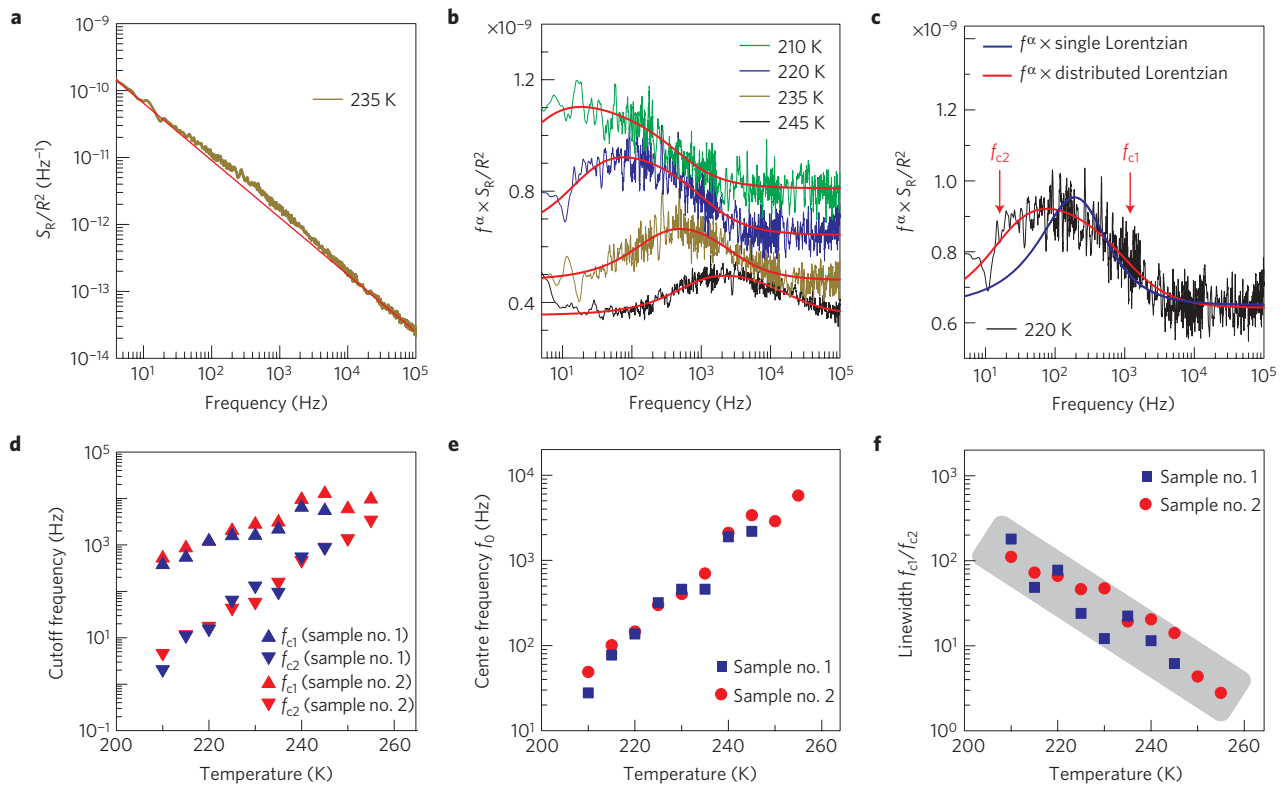


Figure 2 | Resistance fluctuations in the charge-liquid phase. **a**, A typical resistance power spectrum density S_R normalized by the resistance squared R^2 . S_R/R^2 is found to be independent of an applied current as long as the current is low enough, indicating that the detected fluctuations reflect the nature of the equilibrium state (see also Supplementary Fig. S3). **b**, Power spectra densities for various temperatures with $f^\alpha \times S_R/R^2$ representations. The red lines are fits to the distributed Lorentzian model (Supplementary Information). **c**, A comparison of the S_R/R^2 characterizations using different schemes. The notations f_{c1} and f_{c2} represent the high- and low-frequency cutoffs, respectively, in the distributed Lorentzian model. **d**, Temperature profiles of the fitting parameters f_{c1} and f_{c2} . **e**, **f**, Slowing of the centre frequency (**e**) and concomitant growth of the dynamic heterogeneity (**f**). The shaded area in **f** is intended as a guide for the eyes.

dynamics of the order of kilohertz above 200 K (ref. 22). These slow dynamics may indicate that the charge liquid above 200 K, where the triangular lattice is held, is transforming into a classically disordered state, that is, an electronic glass, but the relevance of this result to known glass formers is far from clear at present. To demonstrate possible electronic-glass-forming behaviour, several key concepts need to be tested, for example, the temperature evolution of the slow charge dynamics, the spatial and dynamic heterogeneity, and the electronic-glass transition.

First, to directly detect the evolution of possible slow charge dynamics by determining their frequency, we implemented noise measurements, that is, resistance fluctuation spectroscopy²³. The typical resistance power spectrum density S_R is shown in Fig. 2a. The global S_R can be well fitted by $f^{-\alpha}$ with $\alpha \sim 0.8\text{--}0.9$ (weakly temperature dependent, f denotes frequency). This fitting reflects the prevalent $1/f$ noise, where the frequency exponent is not necessarily 1 (ref. 24). The origin of the ubiquitous $1/f$ noise was not identified for the present case and is beyond the scope of this study. Instead, we note that there is a finite deviation from the background $1/f$ noise over a certain frequency range (Fig. 2a). This deviation indicates that resistance fluctuations with a characteristic frequency are superimposed on the featureless $1/f$ noise (see Supplementary Information). For clarity, $f^\alpha \times S_R$ versus f is plotted for select temperatures in Fig. 2b, where the additional contribution appears as a broad peak rising out of a constant background (for this material, our methods are applicable only above 200 K; see Methods).

On quantifying the non- $1/f$ contributions, we found that the linewidth of the power spectrum density in the $f^\alpha \times S_R$ representation was broader than the expected linewidth for

a single Lorentzian multiplied by f^α (Fig. 2c). To evaluate the linewidth, we introduced a hypothetical superposition of continuously distributed Lorentzians with high-frequency f_{c1} and low-frequency f_{c2} cutoffs (see Supplementary Information). We found that the spectrum shape is well reproduced using this scheme (Fig. 2b,c). The extracted values for f_{c1} and f_{c2} (Fig. 2d) reflect the fastest and slowest fluctuators, respectively, that are relevant to the non- $1/f$ contributions, from which we can estimate the centre frequency f_0 (defined as the geometric mean $(f_{c1}f_{c2})^{1/2}$) and the linewidth (defined as the ratio f_{c1}/f_{c2}). The temperature profiles of f_0 and f_{c1}/f_{c2} are shown in Fig. 2e,f, respectively, and two features can be emphasized. First, f_0 slows down by several orders of magnitude as the temperature decreases; remarkably, just above the frustration-relaxing structural transition (approximately 200 K), the lifetime of the long-lived fluctuator is less than 10 Hz (Fig. 2d). Second, the ratio f_{c1}/f_{c2} noticeably increases, that is, the dynamics become more heterogeneous, as the temperature decreases. These results are reproducible and are therefore considered to arise from the intrinsic nature of θ -RbZn. We note that slow dynamics accompanied by dynamic heterogeneities are known to be key experimental properties for the vitrification process in supercooled normal liquids²⁵.

Some simulation results for supercooled normal liquids argued that medium-range crystalline clusters are critical for understanding the heterogeneous slow dynamics at a microscopic level^{7–10}, although the importance of these crystalline clusters is controversial^{26–29}, and there are still no clear experimental observations of crystalline clusters. To obtain further insight into the observed heterogeneous slow dynamics for the charge liquid, it is

necessary to determine whether a type of charge cluster evolves with the slow dynamics. We conducted X-ray diffuse scattering measurements. A typical photographic oscillation image is shown in Fig. 3a. As previously reported¹⁶, diffuse scattering characterized by $\mathbf{q}_d \sim (\pm 1/3 k \pm 1/4)$ is observed near the Bragg spots, where k denotes negligible coherence between the ET layers; that is, the diffuse modulation evolves in two dimensions. This is a clear indication of two-dimensional charge clusters comprised of a 3×4 -period charge order and cannot represent the nucleation of the horizontal charge order with $\mathbf{q}_0 = [(0 0 1/2)]$, which is almost absent above 200 K; in fact, the \mathbf{q}_d and \mathbf{q}_0 modulations compete with each other, as demonstrated in the literature²⁰. The new feature shown in this study is the temperature profile of the charge clusters. In Fig. 3b,c, the evolution of both the intensity and the correlation length ξ as a function of temperature can be observed, although the \mathbf{q}_d modulation is replaced with \mathbf{q}_0 below 200 K because of the emergence of the twofold horizontal charge order through the first-order transition. The value of ξ is not short-ranged, but it is $\sim 140 \text{ \AA}$ at 210 K, which corresponds to ~ 25 triangular spacings. This behaviour is essentially distinct from conventional critical phenomena, where ξ diverges for a continuous transition. On the basis of a comparison of Figs 3c and 2e, the growth of the slow dynamics and of ξ seem well correlated, indicating that the charge clusters cause the heterogeneous slow dynamics. We also note that of the many different ideas regarding the liquid–glass transition in supercooled normal liquids, our experimental observations for the charge liquid agree phenomenologically with the proposals that consider the crystalline clusters to be the main source of heterogeneous slow dynamics^{7–10}.

All of the physical properties discussed so far indicate that the charge-liquid phase above 200 K is transforming into a charge-cluster glass. Thus, the last issue to be studied is the glass transition of the charge clusters, which is expected to occur only if the frustration-relaxing transition at 200 K is avoided by rapid cooling (Fig. 1c; see also Supplementary Information). A charge-cluster glass transition is observed in the ξ temperature profile measured during heating after rapid cooling ($\sim 90 \text{ K min}^{-1}$; Fig. 3d). From 120 to 150 K, ξ is temperature insensitive with a significantly shorter length than expected (see also Fig. 3c), and no superlattice reflections attributable to a deformation of the triangular lattice are observed. This frozen metastable state with no long-range order is characteristic of a glassy state, indicating that a charge-cluster glass is formed in the charge-frustrated triangular lattice. On further heating, ξ increases sharply to the expected value at $T_g \sim 160\text{--}170 \text{ K}$ and becomes temperature dependent for temperatures above T_g . This behaviour demonstrates that the charge-liquid nature is recovered above T_g , and T_g can therefore be regarded as the charge-cluster glass-transition temperature. The temperature evolution of ξ is not critical-like above T_g , suggesting that what occurs at T_g is not a thermodynamic transition but of dynamic origin (see also Supplementary Information). Interestingly, previous a.c. conductance measurements reported a broad anomaly at approximately 167 K during rapid cooling¹⁹, which we think is another indication of the charge-cluster glass transition. The observations of frozen charge clusters, glass-transition behaviour, and glass-forming characteristics of the charge-liquid phase (that is, the heterogeneous slow dynamics) demonstrate that a charge liquid confined to a charge-frustrated triangular lattice is subject to charge-cluster vitrification in an organic system. As the frustration-relaxing structural transition interrupts the charge vitrification process, we suggest that the charge frustration plays a primary role in the charge-glass-forming nature.

Inhomogeneous electronic states are often found in strongly correlated electron systems that contain dopants^{11,12,30,31}, such as manganites and high-transition-temperature cuprates, in which randomly distributed dopants are considered to play a key role in the emergent inhomogeneity^{32,33}. This issue has been investigated systematically in manganites^{12,32,34}, where ferromagnetic metal and

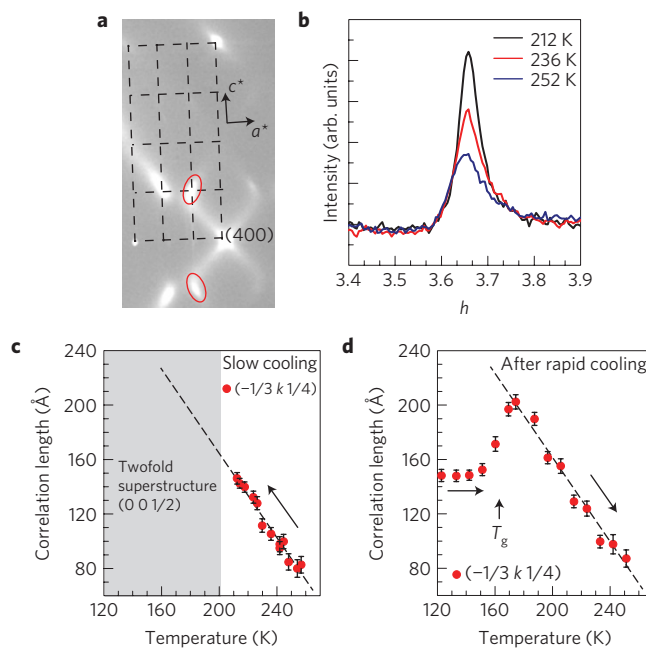


Figure 3 | Spatial correlation of the charge clusters investigated using X-rays. **a**, Photographic oscillation image of the a^*c^* plane at 225 K. Diffuse rods characterized by $\mathbf{q} \sim (\pm 1/3 k \pm 1/4)$ are observed near the Bragg reflections (some are indicated by red ellipsoids in the image). **b**, Line profile of $\mathbf{q} \sim (11/3 k 1/4)$ along the $-2a^* + c^*$ direction. The slight asymmetry in the line shape is due to the background asymmetry, which is temperature independent and irrelevant to the temperature-dependent diffuse scattering. **c,d**, Temperature dependence of the charge-cluster correlation length ξ during slow cooling (**c**) and during heating after rapid cooling to 120 K (**d**). The value of ξ is estimated along the $-2a^* + c^*$ direction on the $(11/3 k 1/4)$ diffuse rod. The broken lines in **c,d** are drawn as guides for the eyes. The error bars represent the numerical ambiguity of the fitting.

charge ordered insulator phases are competing and separated by a first-order transition when nominally disorder-free. The two phases, when perturbed by quenched disorders, result in a mixture in a mesoscopic scale, which is the inhomogeneity widely observed in manganites. Conversely, the organic conductor used in this study is nominally dopant-free, and the charge clusters that show up above the first-order transition temperature ($\sim 200 \text{ K}$) are not attributable to a phase mixture, because their symmetry is different from that of the low-temperature charge ordered phase. These situations imply that the microscopic mechanism of the charge-cluster glass formation is conceptually distinct from the mechanism discussed in manganites.

Methods

Crystal growth. Single crystals of θ -(BEDT-TTF)₂RbZn(SCN)₄ were synthesized by the galvanostatic anodic oxidation of BEDT-TTF (50 mg) in a N₂ atmosphere, in accordance with ref. 13.

Noise measurements. The noise measurements were conducted using the conventional four-terminal d.c. method. A steady current along the c axis was supplied from a low-noise voltage source, and the voltage between the voltage-probing electrodes was fed into a spectrum analyser (Agilent 35670A) after amplifying it with a low-noise preamplifier. A large-load resistor was used to eliminate the resistance fluctuation effect at the contacts. For the material used in this study, this method cannot be applied below 200 K because the centre frequency f_0 is too slow; the relaxation from the supercooled charge liquid to the more stable horizontal charge order occurs before the measurements are completed.

Diffraction scattering experiments. The diffraction of a θ -RbZn single crystal ($0.4 \times 0.3 \times 2.5 \text{ mm}^3$) was measured using a Rigaku DSC imaging plate diffractometer and Si(111) monochromatized synchrotron radiation X-rays

($\lambda = 0.689 \text{ \AA}$) at the BL-8B beamline of the Photon Factory (PF) at the High Energy Accelerator Research Organization (KEK). The correlation length of the charge clusters is defined as $\xi = \text{FWHM}^{-1}$, where FWHM (\AA^{-1}) denotes the height of the full-width at half-maximum of the Lorentzian fit to the data.

Received 11 January 2013; accepted 29 April 2013; published online 9 June 2013

References

- Balents, L. Spin liquids in frustrated magnets. *Nature* **464**, 199–208 (2010).
- Ramirez, A. P., Hayashi, A., Cava, R. J., Siddharthan, R. & Shastry, B. S. Zero-point entropy in 'spin ice'. *Nature* **399**, 333–335 (1999).
- Bramwell, S. T. & Gingras, M. J. P. Spin ice state in frustrated magnetic phyllosilicates. *Science* **294**, 1495–1501 (2001).
- Bouchaud, J. P., Cugliandolo, L., Kurchan, J. & Mezard, M. in *Spin-Glasses and Random Fields* (ed. Young, A. P.) (World Science, 1998).
- Anderson, P. W. Ordering and antiferromagnetism in ferrites. *Phys. Rev.* **102**, 1008–1013 (1956).
- Merino, J., Seo, H. & Ogata, M. Quantum melting of charge order due to frustration in two-dimensional quarter-filled system. *Phys. Rev. B* **71**, 125111 (2005).
- Doye, J. P., Wales, D. J., Zetterling, F. H. M. & Dzugutov, M. The favored cluster structures of model glass formers. *J. Chem. Phys.* **118**, 2792–2799 (2003).
- Widmer-Cooper, A., Harrowell, P. & Fynwever, H. How reproducible are dynamic heterogeneities in a supercooled liquid? *Phys. Rev. Lett.* **93**, 135701 (2004).
- Shintani, H. & Tanaka, H. Frustration on the way to crystallization in glass. *Nature Phys.* **2**, 200–206 (2006).
- Tanaka, H., Kawasaki, T., Shintani, H. & Watanabe, K. Critical-like behaviour of glass-forming liquids. *Nature Mater.* **9**, 324–331 (2010).
- Dagotto, E. Complexity in strongly correlated electronic systems. *Science* **309**, 257–262 (2005).
- Tokura, Y. Critical features of colossal magnetoresistive manganites. *Rep. Prog. Phys.* **69**, 797–851 (2006).
- Mori, H., Tanaka, S. & Mori, T. Systematic study of the electronic state in θ -type BEDT-TTF organic conductors by changing the electronic correlation. *Phys. Rev. B* **57**, 12023–12029 (1998).
- Mori, T. Non-stripe charge order in the θ -phase organic conductors. *J. Phys. Soc. Jpn* **72**, 1469–1475 (2003).
- Seo, H. Charge ordering in organic ET compounds. *J. Phys. Soc. Jpn* **69**, 805–820 (2000).
- Watanabe, M., Noda, Y., Nogami, Y. & Mori, H. Transfer integrals and the spatial pattern of charge ordering in θ -(BEDT-TTF)₂RbZn(SCN)₄ at 90 K. *J. Phys. Soc. Jpn* **73**, 116–122 (2004).
- Miyagawa, K., Kawamoto, A. & Kanoda, K. Charge ordering in a quasi-two-dimensional organic conductor. *Phys. Rev. B* **62**, R7679–R7682 (2000).
- Yamamoto, K., Yakushi, K., Miyagawa, K., Kanoda, K. & Kawamoto, A. Charge ordering in θ -(BEDT-TTF)₂RbZn(SCN)₄ studied by vibrational spectroscopy. *Phys. Rev. B* **65**, 085110 (2002).
- Nad, F., Monceau, P. & Yamamoto, H. M. Effect of cooling rate on charge ordering in θ -(BEDT-TTF)₂RbZn(SCN)₄. *Phys. Rev. B* **76**, 205101 (2007).
- Nogami, Y. *et al.* Charge order competition leading to nonlinearity in organic thyristor family. *J. Phys. Soc. Jpn* **79**, 044606 (2010).
- Tajima, H., Kyoden, S., Mori, H. & Tanaka, S. Estimation of charge-ordering patterns in θ -ET₂MM'(SCN)₄ (MM' = RbCo, RbZn, CsZn) by reflection spectroscopy. *Phys. Rev. B* **62**, 9378–9385 (2000).
- Chiba, R., Hiraki, K., Takahashi, T., Yamamoto, H. M. & Nakamura, T. Extremely slow charge fluctuations in the metallic state of the two-dimensional molecular conductor θ -(BEDT-TTF)₂RbZn(SCN)₄. *Phys. Rev. Lett.* **93**, 216405 (2004).
- Müller, J. Fluctuation spectroscopy: A new approach for studying low-dimensional molecular metals. *ChemPhysChem* **12**, 1222–1245 (2011).
- Dutta, P. & Horn, P. M. Low-frequency fluctuations in solids: $1/f$ noise. *Rev. Mod. Phys.* **53**, 497–516 (1981).
- Ediger, M. D. Spatially heterogeneous dynamics in supercooled liquids. *Annu. Rev. Phys. Chem.* **51**, 99–128 (2000).
- Debenedetti, P. G. & Stillinger, F. H. Supercooled liquids and the glass transition. *Nature* **410**, 259–267 (2001).
- Toninelli, C., Wyart, M., Berthier, L., Biroli, G. & Bouchaud, J.-P. Dynamical susceptibility of glass formers: Contrasting the predictions of theoretical scenarios. *Phys. Rev. E* **71**, 041505 (2005).
- Adam, G. & Gibbs, J. H. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *J. Chem. Phys.* **43**, 139–146 (1965).
- Kurita, R. & Weeks, E. R. The glass transition of two-dimensional binary soft disk mixtures with large size ratios. *Phys. Rev. E* **82**, 041402 (2010).
- Emery, V. J. & Kivelson, S. A. Frustrated electronic phase separation and high-temperature superconductors. *Physica C* **209**, 597–621 (1993).
- Schmalian, J. & Wolynes, P. G. Stripe glasses: Self-generated randomness in a uniformly frustrated system. *Phys. Rev. Lett.* **85**, 836–839 (2000).
- Akahoshi, Y. *et al.* Random potential effect near the bicritical region in perovskite manganites as revealed by comparison with the ordered perovskite analogs. *Phys. Rev. Lett.* **90**, 177203 (2003).
- Zeljko, I. *et al.* Imaging the impact of single oxygen atoms on superconducting Bi_{2+y}Sr_{2-y}CaCu₂O_{8+x}. *Science* **337**, 320–323 (2012).
- Dagotto, E., Hotta, T. & Moreo, A. Colossal magnetoresistant materials: The key role of phase separation. *Phys. Rep.* **344**, 1–153 (2001).

Acknowledgements

We thank H. Tanaka, K. Kuroki, H. Seo, M. Watanabe, H. Sakai, R. Kurita, Y. Kohsaka, M. Udagawa, T. Ito and M. Imada for fruitful discussions. T.S. was supported by the JSPS Program for Leading Graduate Schools (ALPS). This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 2012G115). This work was partially supported by the Funding Program of World-Leading Innovative R&D on Science and Technology (FIRST program) on Quantum Science on Strong Correlation initiated by the Council for Science and Technology Policy, Japan, and by JSPS KAKENHI (Grant Nos 24684020, 24224009, 20110002, and 24654101).

Author contributions

F.K. and T.S. conducted the noise measurements. T.S., K. Kobayashi, R.K., Y.M., K.M. and F.K. conducted the X-ray measurements. K.M. grew the single crystals used for the study. F.K. and K. Kanoda planned and headed the project. F.K. wrote the letter with assistance from Y.T. and K. Kanoda.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to F.K.

Competing financial interests

The authors declare no competing financial interests.