Supporting Information

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Unusual Molecular Material formed through Irreversible Transformation and Revealed by 4D Electron Microscopy

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Supporting Figure S1: Tilt dependence of bright-field images before the irreversible phase transformation. The angle of rotation is denoted in the upper left corner for each image. The electron beam is approximately perpendicular to the substrate surface for 0° tilt angle. The scale bar amounts to 200 nm. The contrast changes quite sensitively as a function of tilt angle (as compared to the contrast change after the phase transformation, see Fig. S4).
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Supporting Figure S2: Tilt dependence of single-nanoparticle diffraction patterns before the irreversible phase transformation. The electron beam is nearly perpendicular to the $a,b$-plane, coinciding with the large flat surface of the nanoparticle. Kinematical electron diffraction simulations are shown to the right of each diffraction pattern. It is noted that a satisfactory agreement between experiment and simulation could only be achieved for a particle thickness of $\sim 4-6$ nm; for a thicker nanoparticle the higher-order reflections at large scattering angles cannot be simulated simultaneously at symmetrically at both sides of the direct beam. In reciprocal-space terms: the thicker the particle (along the $c$-axis), the sharper the reciprocal lattice points, and the more sensitive the diffraction pattern becomes for tilt changes. For very thin particles, the reciprocal lattice points are broadened into rods, and the Ewald sphere intercepts for a range of tilt angles without large changes in peak position and intensity.
Supporting Figure S3: Tilt dependence of single-nanoparticle diffraction patterns after the irreversible phase transformation. The pattern hardly changes as a function of tilt angle. Compared to the original particles (Fig. S3), this indicates a material with reduced crystallinity and/or smaller thickness along the crystallographic c-axis.
**Supporting Figure S4**: Tilt dependence of bright-field images after the irreversible phase transformation. The diffraction contrast hardly changes as a function of tilt angle (compared to the original particles, see Fig. S2).
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Temperature jump simulation

The aim of the heat diffusion calculations is to estimate the laser-induced temperature jump in the graphite substrate and the nanoparticle (dashed curve in Figure 6A of the main text) under the specific experimental conditions. We consider the situation of three objects in thermal contact: the nanoparticle (600x600 nm², 5 nm thickness), the graphite film (7.5x7.5 um², 3 nm thickness) and the Cu frame, which is assumed to act as a heat sink at constant temperature (90 K). The following heat diffusion equation was solved numerically for an \( x,y \) grid with mesh size 500 nm.

\[
\frac{dQ}{dt} = C_p \cdot \frac{dT}{dt} = k \nabla^2 T - k' \Delta T
\]

The asymmetry of the nanoparticle position with respect to the Cu frame was taken into account. It was verified that the calculation for mesh size of 500 nm gave the same result as one with smaller mesh sizes (e.g., 200 nm). We assume thermalization in both graphite and the particle is very fast (faster than the excitation pulse) and the thermal contact at the interface between the graphite and the nanoparticle (represented by the interface conductance \( k' \)) is very efficient.

The heat capacity of the nanoparticle is estimated to be 250 J K\(^{-1}\) mol\(^{-1}\), independent of temperature. The temperature dependence of the heat capacity and thermal conductivity of graphite are taken from the literature\(^4,5\) and adapted in order to match the diffraction dynamics of bare graphite (see Supporting Figure S6). The solid lines in Figure S6 are the corresponding simulated curves using an optical absorption cross section of \( \alpha = 0.037 \) nm\(^{-1}\) calculated from the imaginary component of refractive index for polarization perpendicular to the \( c \)-axis at 532 nm. The temperature dependence of the heat diffusivity of graphite from the literature\(^5\) was scaled in order to match the data at low fluence. A simultaneous match for all fluences could not be achieved, which we believe is due to a slightly different zero-crossing temperature for the thermal expansion coefficient (the temperature at which
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the coefficient becomes positive). However, the simulations are sufficient in order to estimate the temperature jumps induced in the graphite substrate, which are used in the heat diffusion simulations.

Note that graphite itself also exhibits a negative thermal expansion coefficient in the \(a,b\)-plane of \(-2 \times 10^{-6}\) K\(^{-1}\) \(^{6}\), but this small graphite contraction (<<1\% for a temperature jump of \(~700\) K) does not affect the much larger particle expansion dynamics (at least 10 times larger). The laser energy was deposited as a Gaussian profile in space and time (8 mJ/cm\(^2\), FWHM 30x30 um\(^2\), 7 ns).
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Supporting Figure S5: Time-resolved diffraction data (relative diffraction peak shifts) of bare graphite substrate for three different laser fluences (open circles). The simulated profiles are drawn as solid lines. Note that the momentum transfer values increase upon excitation, implying a contraction of the graphite lattice in the $a,b$-plane. This is in agreement with the well-known negative thermal expansion of graphite, in the temperature range of 10 – 500 K.
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**Comparison of \{110\} peak positions**

In order to test whether the pyrazine-deprived compound generated *in situ* using pulsed laser excitation in the electron microscope can also be formed through static (steady-state, slow) thermal treatment of the nanoparticles, we compare the peak positions in the single-nanoparticle electron diffraction pattern with those from the powder X-ray diffraction measurement after thermal treatment at 623 K.

Fig. S7 shows a zoom into the \{110\} and \{220\} peaks of the powder X-ray diffraction patterns taken at RT before and after the thermal treatment. The \{110\} and \{220\} reflections at 16.86° and 34.08°, respectively, are two of the most intense peaks in the whole pattern. In both cases, after thermal treatment two peaks at 17.14° and 34.65° remain, while all the other reflections disappear. Based on the fact that crystallinity along the c-axis is reduced in the new phase, we assign the two remaining peaks to the \{110\} and \{220\} reflections in the new phase, which are shifted to higher momentum transfer values compared to Fe(pyrazine)Pt(CN)$_4$. This is in qualitative agreement with the single-nanoparticle electron diffraction results.

Quantitatively, the increase in momentum transfer after static heating is 

\[
\frac{\sin(17.14^\circ)}{\sin(16.86^\circ)} = 1.016 \ (1.6\%) \ \text{for the} \ \{110\} \ \text{reflection and}
\]

\[
\frac{\sin(34.65^\circ)}{\sin(34.08^\circ)} = 1.014 \ (1.4\%) \ \text{for the} \ \{220\} \ \text{reflection. In the single-nanoparticle diffraction experiment the increase is} \ 2.10 \ \text{nm}^{-1}/1.96 \ \text{nm}^{-1} = 1.071 \ (7.1\%) \ \text{for} \ \{110\} \ \text{and} \ 4.18 \ \text{nm}^{-1}/3.92 \ \text{nm}^{-1} = 1.066 \ (6.6\%) \ \text{for} \ \{220\}. \ \text{The peak shifts, and thus the contraction, achieved by static heating are thus about four times smaller than those observed in the pulsed single-nanoparticle experiment.}
Supporting Figure S6: Zooms into the \{110\} (A) and \{220\} (B) reflections of the powder X-ray diffraction pattern before and after static heating at 623 K. Only the \{110\}/\{220\} reflections are assumed to survive the phase transformation; first, because they are the strongest reflections and much more intense than the neighbouring \{101\} and \{202\} reflections. Second, the crystallinity along the \(c\)-direction is expected to be considerably reduced after the phase transformation, which would reduce the intensity of all \{hkl\} reflections (with \(l>0\), but not that of the \{hk0\} reflections.
**Supporting Figure S7:** Infrared spectra of Fe(pyrazine)Pt(CN)₄ before and after thermal treatment at 310 °C (40% pyrazine weight loss), after thermal treatment at 350 °C (95% pyrazine weight loss), and after thermal treatment at 800 °C (complete loss of pyrazine and cyanide). The bottom graph shows a zoom into the absorption peaks of the cyanide ligands. The peaks at lower wavenumbers belong to pyrazine.
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Supporting Figure S8: Relative momentum transfer change of the \{110\} diffraction peaks as a function of temperature (without laser excitation). The steady increase corresponds to a linear expansion coefficient of \(-30\pm5\cdot10^{-6}\) K\(^{-1}\). Because the \(a\)- and \(b\)-unit cell directions are equivalent in the tetragonal crystal symmetry, the \{110\} peak family directly probes the thermal expansion properties of the entire \(a,b\)-plane.
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Supporting Movie 1:
Bright-field image dynamics showing the laser-induced negative expansion dynamics of a single molecular framework nanoparticle (on the right). The dark particle on the left side exhibits positive expansion dynamics due to laser-induced spin crossover, as described in reference 14 of the main article.

Supporting Movie 2:
Difference image movie referenced to the images before $t = 0$.


(5) Uher, C. *Temperature dependence of thermal conductivity of graphite*, Landolt-Börnstein.

(6) Morgan, W. C. *Carbon* 1972, 10, 73–79.