Supplementary Information

Exploring fingerprints of ultrafast structural dynamics in molecular solutions with an x-ray laser

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S1 Data collection and processing

The data were collected in the form of scans over the time-delay t, where a typical scan (run) contains ~37k detector measurements of different kinds (scattering images, diagnostics, etc). In the analysis of experimental x-ray scattering from $[Ir_2(dimen)_4]^{2+}$ presented below we used data measured in 10 such runs, containing about 370k scattering images in total. Most of the images contain measured intensity $I_{on}(q, t)$ from the excited sample measured at a time delay t after the optical pump pulse, while every 7th recorded image contains signal from the unpumped sample $I_{off}(q)$ (i.e., when the optical pump pulse was not applied). Each individual image is labelled according to its type and recorded along with additional metadata on x-ray and optical laser pulse properties. This allows one to identify pump-probe events and their time delays t, perform data filtering, and eventually determine the difference images for different time delays.

The raw 2D images measured with the ePix10K detector were preprocessed using established calibration pipeline at XCS, which includes pedestal subtraction, common mode correction, masking [1]. The calibrated 2D images were filtered using reliable ranges of the recorded parameters of the timing tool (0.05 < /tt/AMPL < 0.25, 100 < /tt/FLTPOS < 700, 10 < /tt/FLTPOSFWHM < 200). Another pair of parameters used for event filtering were measured total scattering intensity I_{scatt} of an image, and incident intensity I_{in} recorded by the beam intensity monitor ipm4. Images with too low and too high values of these parameters, as well as images corresponding to large deviations from the linear dependence of $I_{scatt}(I_{in})$, were filtered out (see Fig. S1).

Additional image processing has been applied to all remaining images. A *q*-resolved pixel intensity filter has been applied considering each image centered in polar coordinate system $I(q) = I(q, \phi)$. For each radius *q*, pixels (q, ϕ) with intensity values that do not satisfy the inequality $\langle I(q, \phi) \rangle_{\varphi} - 3\sigma < I(q, \phi) < \langle I(q, \phi) \rangle_{\varphi} + 3\sigma$, where σ is the standard deviation of $I(q, \phi)$ for a given *q*, were masked. Additional pixels at the edges of four central detector modules were masked due to their visibly higher response. Remaining nonlinearities in the response of individual detector pixels due to x-ray pulse energy and pulse intensity fluctuations were corrected using the approach described in [2]. Finally, images were corrected for differences in solid angle covered by each pixel, as well as for x-ray polarization. Before computing the difference images (see next section on CCF determination), each image was normalized by its total intensity determined within a region of interest in the form of annulus defined in the range $1.2 \text{ Å}^{-1} < q < 3.5 \text{ Å}^{-1}$.



Figure S1. Example of the correlation plot of the total scattered image intensity I_{scatt} and incident pulse intensity I_{in} for one of the measured datasets. A solid line defines the linear regression model $I_{\text{scatt}}(I_{\text{in}})$ determined from the measured dataset, and dashed lines define the acceptance thresholds for the images. All images with large deviations from the identified linear dependence (black dots) were filtered out, while majority of the images (red dots) were considered for further analysis.

S2 Determination of the time-dependent angular cross-correlation function

The content of $C_{\text{diff}}(q_1, q_2, \Delta, t)$ can be examined by substituting Eq. (1) in the main text into Eq. (2),

$$\begin{split} C_{\text{diff}}(q_1, q_2, \Delta, t) &= \langle [I_{\text{on}}(q_1, \varphi, t) - I_{\text{off}}(q_1, \varphi)] [I_{\text{on}}(q_2, \varphi + \Delta, t) - I_{\text{off}}(q_2, \varphi + \Delta)] \rangle_{\varphi} = \\ &= \langle I_{\text{on}}(q_1, \varphi, t) I_{\text{on}}(q_2, \varphi + \Delta, t) \rangle_{\varphi} - \langle I_{\text{on}}(q_1, \varphi, t) I_{\text{off}}(q_2, \varphi + \Delta) \rangle_{\varphi} - \\ &\quad \langle I_{\text{off}}(q_1, \varphi) I_{\text{on}}(q_2, \varphi + \Delta, t) \rangle_{\varphi} + \langle I_{\text{off}}(q_1, \varphi) I_{\text{off}}(q_2, \varphi + \Delta) \rangle_{\varphi} \\ &= C_{\text{on}}(q_1, q_2, \Delta, t) + C_{\text{off}}(q_1, q_2, \Delta) - C_{\text{on-off}}(q_1, q_2, \Delta, t), \end{split}$$
(S1)

where

$$C_{\rm on}(q_1, q_2, \Delta, t) = \langle I_{\rm on}(q_1, \varphi, t) I_{\rm on}(q_2, \varphi + \Delta, t) \rangle_{\varphi}$$
(S2)

$$C_{\rm off}(q_1, q_2, \Delta) = \langle I_{\rm off}(q_1, \varphi) I_{\rm off}(q_2, \varphi + \Delta) \rangle_{\varphi}$$
(S3)

and

$$C_{\text{on-off}}(q_1, q_2, \Delta, t) = \langle I_{\text{on}}(q_1, \varphi, t) I_{\text{off}}(q_2, \varphi + \Delta) \rangle_{\varphi} + \langle I_{\text{off}}(q_1, \varphi) I_{\text{on}}(q_2, \varphi + \Delta, t) \rangle_{\varphi}.$$
(S4)

As one can see, the CCF $C_{\text{diff}}(q_1, q_2, \Delta, t)$ has a composite structure and can be represented as a sum of the angular CCF $C_{\text{on}}(q_1, q_2, \Delta, t)$ determined for a sample in the pumped state at a time *t*, the CCF $C_{\text{off}}(q_1, q_2, \Delta)$ determined for a sample in the ground (unpumped) state, and the cross-term $C_{\text{on-off}}(q_1, q_2, \Delta, t)$, where the latter depends both on the pumped and unpumped sample states.

Alternatively, one can describe the difference image correlations in terms of the Fourier components (FCs) of the CCFs,

$$C^{n}_{\text{diff}}(q_1, q_2, t) = C^{n}_{\text{on}}(q_1, q_2, t) + C^{n}_{\text{off}}(q_1, q_2) - C^{n}_{\text{on-off}}(q_1, q_2, t),$$
(S5)

where the angular FCs are determined as [see also Eq. (3) in the main text]

$$C_{\rm on}^{n}(q_1, q_2, t) = \frac{1}{2\pi} \int_0^{2\pi} C_{\rm on}(q_1, q_2, \Delta, t) \exp(-in\Delta) d\Delta,$$
(S6)

$$C_{\rm off}^{n}(q_1, q_2) = \frac{1}{2\pi} \int_0^{2\pi} C_{\rm off}(q_1, q_2, \Delta) \exp(-in\Delta) \, d\Delta, \tag{S7}$$

$$C_{\rm on-off}^{n}(q_1, q_2, t) = \frac{1}{2\pi} \int_0^{2\pi} C_{\rm on-off}(q_1, q_2, \Delta, t) \exp(-in\Delta) \, d\Delta.$$
(S8)

One can readily show that Eqs. (S6-S7) can be expressed in terms of the angular FCs of the measured intensities as [3],

$$C_{\rm on}^n(q_1, q_2, t) = I_{\rm on}^n(q_1, t)I_{\rm on}^{n*}(q_2, t),$$
(S9)

$$C_{\rm off}^n(q_1, q_2) = I_{\rm off}^n(q_1) I_{\rm off}^{n*}(q_2), \tag{S10}$$

$$C_{\rm on-off}^{n}(q_1, q_2, t) = I_{\rm on}^{n}(q_1, t)I_{\rm off}^{n*}(q_2) + I_{\rm off}^{n}(q_1)I_{\rm on}^{n*}(q_2, t),$$
(S11)

where the angular FCs of intensities measured from the pumped $I_{on}^{n}(q, t)$ and unpumped $I_{off}^{n}(q)$ samples are determined as,

$$I_{\rm on}^n(q,t) = \frac{1}{2\pi} \int_0^{2\pi} I_{\rm on}(q,\varphi,t) \exp(-in\varphi) d\varphi, \tag{S12}$$

$$I_{\text{off}}^{n}(q) = \frac{1}{2\pi} \int_{0}^{2\pi} I_{\text{off}}(q,\varphi) \exp(-in\varphi) \, d\varphi.$$
(S13)

In practice $C_{\text{diff}}^n(q_1, q_2, t)$ need to be averaged at each t over a large number M_t of difference patterns determined in the chosen range of pump-probe delay times $[t_1, t_2)$ to reduce statistical fluctuations and improve the signal-to-noise (SNR) ratio, i.e. $\tilde{C}_{\text{diff}}^n(q_1, q_2, t) = \frac{1}{M_t} \sum_{t_1 \le t_i < t_2} C_{\text{diff}}^n(q_1, q_2, t_i)$, while formally assuming $t = (t_1 + t_2)/2$, and the tilde "~" denotes the statistically averaged quantities. The averages of the time-

independent quantities, i.e. $\tilde{C}_{off}^{n}(q_1, q_2)$ and $\tilde{I}_{off}^{n}(q)$, can be determined similar way using the available set of *M* scattering patterns from the unpumped sample measurements.

At this point one may notice, that the measured intensities $I_{on}(q, \varphi, t)$ and $I_{off}(q, \varphi)$, and thus the corresponding FCs $I_{on}^{n}(q, t)$ and $I_{off}^{n}(q)$, are mutually independent since they are always measured from the independent sample realizations. This means that statistically averaged cross-term $C_{on-off}^{n}(q_1, q_2, t)$ reduces to the form,

$$\tilde{\mathcal{L}}_{\text{on-off}}^{n}(q_{1},q_{2},t) = \tilde{I}_{\text{on}}^{n}(q_{1},t)\tilde{I}_{\text{off}}^{n*}(q_{2}) + \tilde{I}_{\text{off}}^{n}(q_{1})\tilde{I}_{\text{on}}^{n*}(q_{2},t) = \delta_{n,0}[\tilde{I}_{\text{on}}^{0}(q_{1},t)\tilde{I}_{\text{off}}^{0}(q_{2}) + \tilde{I}_{\text{off}}^{0}(q_{1})\tilde{I}_{\text{on}}^{0}(q_{2},t)],$$
(S14)

where only the zero-order FC survives after averaging, since higher-order (n>0) crossterms $\tilde{I}_{off}^{n}(q_1)$ vanish (assuming a uniform distribution of molecular orientations in the unpumped sample). Considering Eq. (S14), one can write the statistically averaged version of Eq. (S5) as

$$\tilde{C}_{\text{diff}}^{n}(q_{1},q_{2},t) = \tilde{C}_{\text{on}}^{n}(q_{1},q_{2},t) + \tilde{C}_{\text{off}}^{n}(q_{1},q_{2}) - \delta_{n,0}[\tilde{I}_{\text{on}}^{0}(q_{1},t)\tilde{I}_{\text{off}}^{0}(q_{2}) + \tilde{I}_{\text{off}}^{0}(q_{1})\tilde{I}_{\text{on}}^{0}(q_{2},t)].$$
(S15)

As one can see from Eq. (S15), generally $\tilde{C}_{\text{diff}}^n(q_1,q_2,t)$ can be represented as a sum of time-dependent and time-independent terms. In a conventional pump-probe experiment one expects that $I_{\text{on}}(q,\varphi,t<0) \equiv I_{\text{off}}(q,\varphi)$ at any negative time delay t<0, since both $I_{\text{off}}(q,\varphi)$ and $I_{\text{on}}(q,\varphi,t<0)$ are measured from an unpumped sample. This allows one to determine the time-dependent contribution to the correlation function $C_{\text{td}}^n(q_1,q_2,t)$ as,

$$C_{\rm td}^n(q_1, q_2, t) = \tilde{C}_{\rm diff}^n(q_1, q_2, t) - \tilde{C}_{\rm diff}^n(q_1, q_2, t < 0), \tag{S16}$$

where $\tilde{C}_{diff}^{n}(q_1, q_2, t < 0)$ can be determined by substituting $\tilde{I}_{on}(q, \varphi, t < 0)$ with $\tilde{I}_{off}(q, \varphi)$, and $\tilde{C}_{on}^{n}(q_1, q_2, t < 0)$ with $\tilde{C}_{off}^{n}(q_1, q_2)$ in Eq. (S15), that is

$$\tilde{C}_{\text{diff}}^{n}(q_{1}, q_{2}, t < 0) = 2[\tilde{C}_{\text{off}}^{n}(q_{1}, q_{2}) - \delta_{n,0}\tilde{I}_{\text{off}}^{0}(q_{1})\tilde{I}_{\text{off}}^{0}(q_{2})].$$
(S17)

Eq. (S16) ensures that $C_{td}^n(q_1, q_2, t)$ vanishes at negative time delays (t < 0), when the sample is in the ground state, and can be applied to analyze structural dynamics triggered with the optical pump at t = 0.

In our diffraction simulations we employed a model of a dilute many-particle ensemble of molecules in gas phase (without solvent). At such conditions the term $\tilde{C}^n_{diff}(q_1, q_2, t < 0)$ is significantly smaller compared to $\tilde{C}^n_{diff}(q_1, q_2, t > 0)$ due to orientational alignment of the molecules in the pumped state at t > 0 (see also Section S5 and Fig. S6). Therefore, we neglected $\tilde{C}^n_{diff}(q_1, q_2, t < 0)$ in our simulations, and assumed $C^n_{td}(q_1, q_2, t) \approx$ $\tilde{C}^n_{diff}(q_1, q_2, t)$. At the same time, the magnitude of the experimental $\tilde{C}^n_{diff}(q_1, q_2, t < 0)$ is large and need to be subtracted to obtain the time-dependent term $C^n_{td}(q_1, q_2, t)$. We attribute a relatively high magnitude of $|\tilde{C}_{diff}^n(q_1, q_2, t < 0)|$ observed in our experiment to the equilibrium solvent structure and solvent-solute interactions, that were not implemented in our simulations, as well as to the remaining uncompensated background contribution. A good agreement of the simulated $|\tilde{C}_{diff}^n(q_1, q_2, t)|$ and experimental FCs $|C_{td}^n(q_1, q_2, t)|$ [compare Figs. 10(a) and 5(c) in the main text] confirms the validity of such assumptions.

S3 Visualization of the Fourier components of the CCFs

The definition of the CCF in Eq. (2) in the main text implies a mirror symmetry of the correlation plots with respect to the diagonal $q_1 = q_2$ [see a dashed line in Fig. S2(a)]. In spite of the obvious data redundancy, in our plots of FCs we show the full range of data, that facilitates identification of distinct features in the correlation maps. Notice, that generally FCs defined in Eq. (3) in the main text are complex numbers, therefore, the amplitude and phase information can be accessed separately, or combined in a single plot (see Fig. S2). This offers additional dimensionality and flexibility for data analysis, while the phase contrast might be more sensitive in certain cases. For simplicity, in this work we focus on the amplitude information, like it is presented in Fig. S2(a).



Figure S2. Experimentally determined (a) amplitude $|C_{td}^0(q_1, q_2, t)|$ (log scale) and (b) phase $\arg[C_{td}^0(q_1, q_2, t)]$, as well as the combined plot (c) of $\operatorname{sgn}[C_{td}^0(q_1, q_2, t)] \cdot |C_{td}^0(q_1, q_2, t)|^{1/2}$, determined for *n*=0, at *t*=2 ps. In the case of FC order *n*=0, the FCs $C_{td}^0(q_1, q_2, t)$ are real-valued, and the phase is simply defined by the sign of the FC (noted here as $\operatorname{sgn}[C_{td}^0(q_1, q_2, t)]$), that is $\arg[C_{td}^0(q_1, q_2, t)]=0$ or π .

S4 Atomic models of the [lr₂(dimen)₄]²⁺ molecules

Examples of the ground state (GS) and excited state (ES) structures from both DFT and BOMD calculations, visualized as ball-and-stick models in VMD software [4] are shown in Fig. S3. One may notice that the BOMD structures are generally more disordered and asymmetric compared to the DFT structures. Histograms of interatomic distances between selected pairs of atoms in the ES molecules from BOMD simulations plotted in Fig.S4 show notable spread of distances reaching ~1 Å for some distant pairs of atoms.



Figure S3. Representative GS and ES structures of $[Ir_2(dimen)_4]^{2+}$ molecule from DFT (a-c) and BOMD (d-f) calculations. The ball-and-stick models are presented with the Ir-Ir bond oriented perpendicular to the paper plane. The structure type (GS or ES) and Ir-Ir distance d_{Ir-Ir} are specified above each structure, and distinct atomic species are specified in the legend.



Figure S4. Histograms of interatomic distances between selected pairs of distinct atoms in the ES molecules, extracted from 44 BOMD trajectories in the 30 fs wide interval of pump-probe time delays, 3.30 ps < t < 3.33 ps.

S5 Simulations of samples with mixed orientations of TDMs and distinct excitation probabilities

We consider here several models with mixed distributions of orientations of the TDMs. Particularly, assuming the possibility of coexistence of orthogonal orientations of TDMs like in the ES₁ and ES₂ models, the "laser-on" intensity can be modelled as:

$$I_{\rm on} = I(\text{ES}_1, p_1 N, \cos^2) + I(\text{ES}_2, p_2 N, \cos^2) + I\left(\text{GS}_{\text{SH}}, [1 - p_1 - p_2]\frac{N}{2}, \text{Uniform}\right) + I\left(\text{GS}_{\text{LG}}, [1 - p_1 - p_2]\frac{N}{2}, \text{Uniform}\right),$$
(S18)

where p_1 and p_2 are the probabilities of the ES₁ and ES₂ -type excitations, respectively, and the total excitation fraction is $p = p_1 + p_2$.

The correlation plots computed using Eq. (S18) for a fixed $p_1 = 10\%$, and several distinct values of p_2 are shown in Fig. S5. One can observe deformation and widening of one of the features on the plot of FC of the order n = 0, indicated with a white arrow in Fig.

S5(d). Notable changes in $|\tilde{C}_{diff}^n(q_1, q_2, t)|$ can already be observed at $p_2 = 5\%$, while such a feature is not present in our experimental correlation plots (compare Fig.S5 and Fig.6 in the main text), indicating that excitations with the TDM orientations parallel to the Ir-Ir axis have low probability or are entirely absent. Therefore, we employed the ES₁ model of the TDM orientations in our further simulations.



Figure S5. (Log scale, arb. units) The simulated amplitudes of FCs $|\tilde{C}_{diff}^n(q_1, q_2, t)|$ of the orders *n*=0,2 determined at *t*=2 ps for the models with mixed (ES₁ and ES₂) distributions of TDM orientations. The corresponding excitation fractions p_1 and p_2 [%] of the ES₁ and ES₂ -type excitations are specified for each model. White arrow in (d) indicates widening of one of the features with increasing excitation probability p_2 .

We also performed simulations with the ES₁ model where we considered different excitation fractions *p* in Eq. (6) in the main text, the corresponding correlation plots are shown in Fig. S6. As one can see, the magnitudes of FCs grow with the increasing excitation fraction *p*. This happens because for higher *p* the fraction of molecules that become oriented according to the cos² orientational distribution becomes larger, leading to a more pronounced signal in the difference scattering patterns, and subsequently larger $|\tilde{C}_{diff}^{n}(q_{1},q_{2},t)|$.

Theoretical consideration of the cross-correlation functions for dilute two-dimensional (2D) disordered and partially ordered ensembles of molecules shows that the magnitudes of FCs of the CCFs are much higher in the case of partial orientational order, as compared to a uniform distribution of particle orientations [3, 5, 6]. For instance, provided a fixed number of molecules *N* in the system, the magnitudes of FCs (for n > 0) of the two-point CCF are proportional to *N* in the case of a uniform distribution of particle orientations, and

proportional to $N[1 + (N - 1) \exp(-\sigma^2 n^2)]$ in the case of a Gaussian distribution of orientations about a fixed direction in 2D with standard deviation σ . Our simulations of disordered ensembles of molecules in the absence of solvent show that similar arguments are also valid in the three-dimensional (3D) case.



Figure S6. (Log scale, arb. units) The simulated amplitudes of FCs $|\tilde{C}_{diff}^n(q_1, q_2, t)|$ of the orders *n*=0,2 determined at *t*=2 ps for the ES₁ model at different excitation fractions (a) *p*=5%, (b) *p*=10%, (c) *p*=15% and (d) *p*=20%.

S6 Simulations with solvated [Ir₂(dimen)₄]²⁺ molecules

We performed simulations with sets {GS_{LG}} and {ES} of BOMD structures surrounded by *k* nearest acetonitrile molecules using Eq. (9) in the main text, and assuming the excitation fraction p = 11%. The results of the correlation analysis for k=0,2,10 and 20 are presented in Fig.S7, where k=0 corresponds to the case of non-solvated [Ir₂(dimen)₄]²⁺ molecules [Fig.S7(a)]. One can see gradual changes in $|\tilde{C}^n_{diff}(q_1, q_2, t)|$ as the number of acetonitrile molecules *k* in the solvation shell increases. At k=20 the difference between the results for non-solvated and solvated molecules is quite pronounced [compare Fig.S7(a) and Fig.S7(d)], and at the same time the agreement with the experimental results becomes poor [compare Fig.S7(d) and Fig.5(c) in the main text]. Therefore, it is tempting to conclude that the effect of the solvation shell is defined by only a few nearest acetonitrile molecules surrounding [Ir₂(dimen)₄]²⁺.

In the previous ultrafast XDS study of [Ir₂(dimen)₄]²⁺ solutions [7] the solvent effects were considered in the form of two contributions to the difference intensity: the "localized" one, due the initial ultrafast desolvation of the Ir atoms followed by slower excited state

coordination, and the "global" one, related to the bulk temperature increase due to energy dissipation from the excited molecules to solvent. Thus, one could assume that the "localized" part will involve only a limited number of solvent molecules, while the "global" heating effect does not lead to a pronounced q-dependent contribution. Results of our simulations (Fig.S7) are, in principle, in agreement with this reasoning, since inclusion of larger numbers of acetonitrile molecules in our attempt to simulate the "local" solvent effect makes the results incompatible with experimental observations. However, one has to recall certain properties of the models of solvated [Ir₂(dimen)₄]²⁺ we employed here. Although in the computations of the correlation maps for undressed molecules (k=0) we excluded all 237 acetonitrile molecules that were originally present in the BOMD simulation box, the effect of solvent on the [lr2(dimen)4]2+ structure is indirectly present in the simulated correlation maps. At the same time, the bulk solvent was not considered in our diffraction simulations, and the solvation shell around each molecule was effectively treated as a part of the host [Ir₂(dimen)₄]²⁺ molecule. Therefore, it is challenging to realistically estimate the effect of solvent using the models applied in the present study. Yet, we would like to highlight the sensitivity of the simulated FCs $|\tilde{C}_{diff}^n(q_1, q_2, t)|$ to the changes in the structure of solvation shell [Fig. S7], giving hope that the correlation analysis can be also applied in the studies of solute-solvent interactions, that are beyond the scope of the present work.



Figure S7. (Log scale, arb. units) The amplitudes of FCs $|\tilde{C}_{diff}^n(q_1, q_2, t)|$ of the orders n=0 and 2 determined at t=2 ps for solvated BOMD structures with different number of acetonitrile molecules k=0,2,10 and 20 in the solvation shell.

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