

Supplementary Information for

Imaging of Ultrafast Photoexcited Electron Dynamics in Pentacene Nanocrystals on Graphite Substrate

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Table of contents

Supplementary Note S1: Peak assignments of 2P-PES for pentacene deposited on HOPG.	2
Supplementary Fig. S1: $h\nu$ dependence of 2P-PES for pentacene (2 min deposition) on HOPG.	4
Supplementary Fig. S2: UPS spectrum for pentacene (2 min deposition) on HOPG.	4
Supplementary Fig. S3: Wide-view 2P-PEEM for pentacene nanocrystals (28 min deposition) on HOPG.	5
Supplementary Fig. S4: $h\nu$ dependence of 2P-PES for pentacene (28 min deposition) on HOPG.	5
Supplementary Fig. S5: Non-resonant 2P-PEEM of pentacene nanocrystals.	6
Supplementary Fig. S6: 1P-PEEM and 2P-PEEM of pentacene nanocrystals on HOPG.	6
Supplementary Fig. S7: Schematic illustrations of pump-probe optical configuration.	7
Supplementary Fig. S8: Intensities of 2P-PEEM at eight sets of nanocrystal and periphery.	7
Supplementary Fig. S9: Wide-view 2P-PEEM for pentacene nanocrystals after heating (50°C).	8
Supplementary References	8

Separately uploaded supplementally movies

Supplementary Movie S1. Polarization-dependent 2P-PEEM of pentacene nanocrystals on HOPG.

Supplementary Movie S2. Time-resolved 2P-PEEM at $\Delta t = 520\text{--}7800$ fs.

Supplementary Movie S3. Polarization-dependent 2P-PEEM of pentacene nanocrystals after heating (50°C).

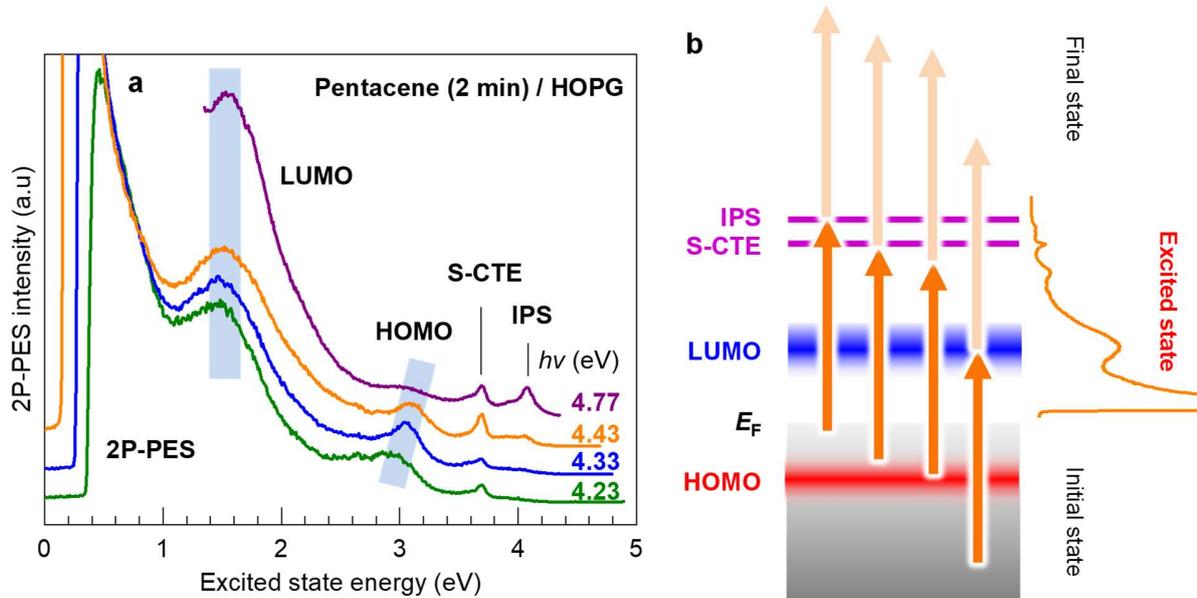
Supplementary Note S1. Peak assignments of 2P-PES for pentacene deposited on HOPG.

From the 2P-PES spectra, both the energies of **HOMO** and **LUMO** can be evaluated to be $E_F - 1.2$ eV and $E_F + 1.5$ eV (E_F : Fermi level), respectively. To assign the 2P-PES peaks to the occupied (e.g., **HOMO**) and unoccupied (e.g., **LUMO**), 2P-PES analyses with various photon energies ($h\nu$) are required. Supplementary Fig. S1a shows the $h\nu$ dependence of 2P-PES spectra for pentacene (2 min) deposited film on HOPG, where the corresponding $h\nu$ s are denoted in the right part of the figure (the blue spectrum ($h\nu = 4.33$ eV) corresponds to the middle one in Fig. 1c in the main text). The horizontal axis represents the excited state energy with respect to E_F . A peak labeled as **LUMO** appears at constant energy regardless of different $h\nu$ s, indicating that the peak can be assigned to an unoccupied state, namely, **LUMO** at $E_F + 1.5$ eV. The value obtained by scanning tunneling spectroscopy corresponds reasonably well to the energy position.¹ On the other hand, another peak labeled as **HOMO** shifts toward higher energy with increasing $h\nu$ s, indicating that the peak is assignable to photoemission from an occupied state through a virtual state. In fact, the HOMO energy estimated by subtracting the $h\nu$ agrees with that evaluated by an ultraviolet photoelectron spectroscopy (UPS, see Supplementary Fig. S2) (*i.e.*, 3.1 eV – $h\nu = -1.2$ eV for $h\nu = 4.33$ eV).

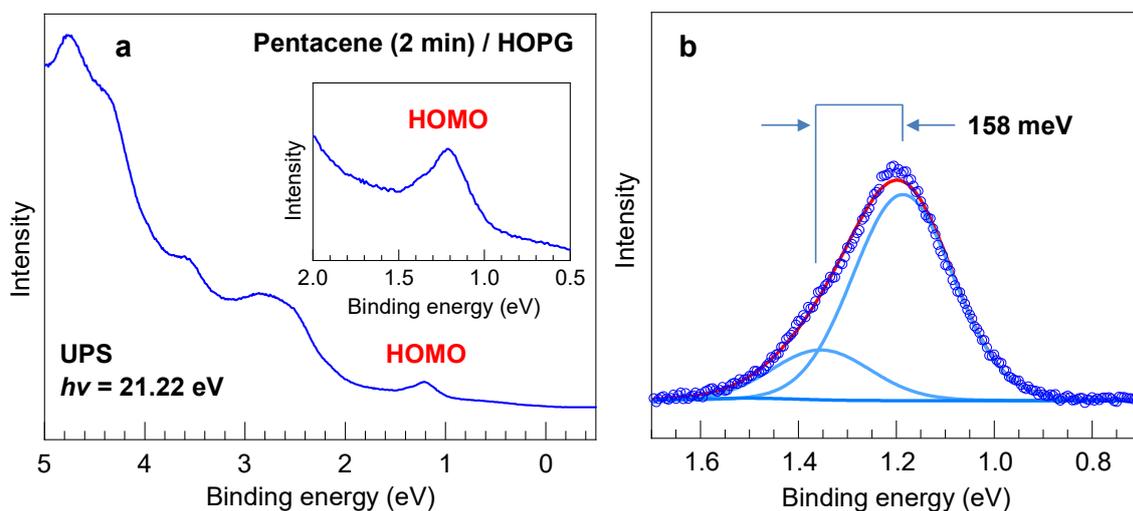
A couple of peaks at the higher binding energy side originate from a surface charge transfer exciton (**S-CTE**) and an image potential state (**IPS**), respectively.²⁻⁷ According to the literature, IPS is a bound state formed by an attractive force with an image charge inside the surface, showing a free electron-like character along with parallel to the surface (see inset in Fig. 1c). The excited electron in **S-CTE** is attracted by both image charge and realistic hole in the molecule, which exhibits a nondispersive character.⁵⁻⁷ Since both quantum states are formed on an atomically flat surface, their presence indicates that the prepared pentacene film (2 min) is sufficiently uniform. Note that the IPS peak is obscured at lower $h\nu$ s because only an electron in the occupied state in the HOPG is energetically accessible to the **IPS**, where the density of states is lower near the E_F . The energy diagram and the excitation scheme are illustrated in Supplementary Fig. S1b.

A series of 2P-PEEM measurements (Supplementary Fig. S3) were performed on thicker pentacene films (28 min deposition). The same $h\nu$ dependent 2P-PES experiment was performed on the pentacene film (28 min) to ensure that the sample remained unchanged throughout the 2P-PEEM measurements. Supplementary Fig. S4 shows typical 2P-PES spectra of the pentacene film (28 min) obtained before and after the current 2P-PEEM measurements. Two broad and $h\nu$ independent peaks are observed, with the peak at lower energy assigned into **LUMO** at $E_F + 1.3$ eV, where it shifts toward lower energy by 0.2 eV from that seen in the thin film (2 min) due to an intermolecular interaction promoted by π -stacked pentacene molecules. For the following reason, another peak at higher energy ($E_F + 2.5$ eV) can be assigned to an excitonic state relevant to the HOMO electron, **HOMO/Ex**. According to differential reflectance spectroscopy, a strong optical absorption occurs at 4.0 eV for thick pentacene film;^{8,9} the excited electron should have $E_F - 1.5 + 4.0$ eV ($= E_F + 2.5$ eV) because the HOMO energy at the multilayered film is $E_F - 1.5$ eV. The result explains the assignment of **HOMO/Ex** in the present 2P-PES. Furthermore, the onset energy of HOMO/Ex shifts toward higher binding energy with increasing $h\nu$ (dotted line in Supplementary Fig. S4a), indicating that the structure of **HOMO/Ex** involves the HOMO-derived component.

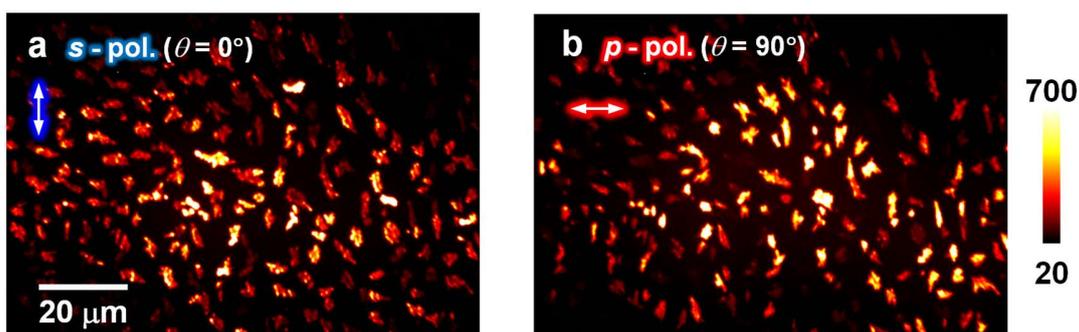
It is crucial to emphasize that the 2P-PES intensities, including the LUMO, are significantly enhanced at higher deposition amounts (28 min). Therefore, the excited electron in the LUMO is supplied through self-dissociation of the hot exciton, where the exciton energy is much larger than the transport gap of pentacene, ranging from 2.2 to 2.8 eV.¹⁰⁻¹² Therefore, we can image the resonantly excited electron in the pentacene nanocrystals using 2P-PEEM.



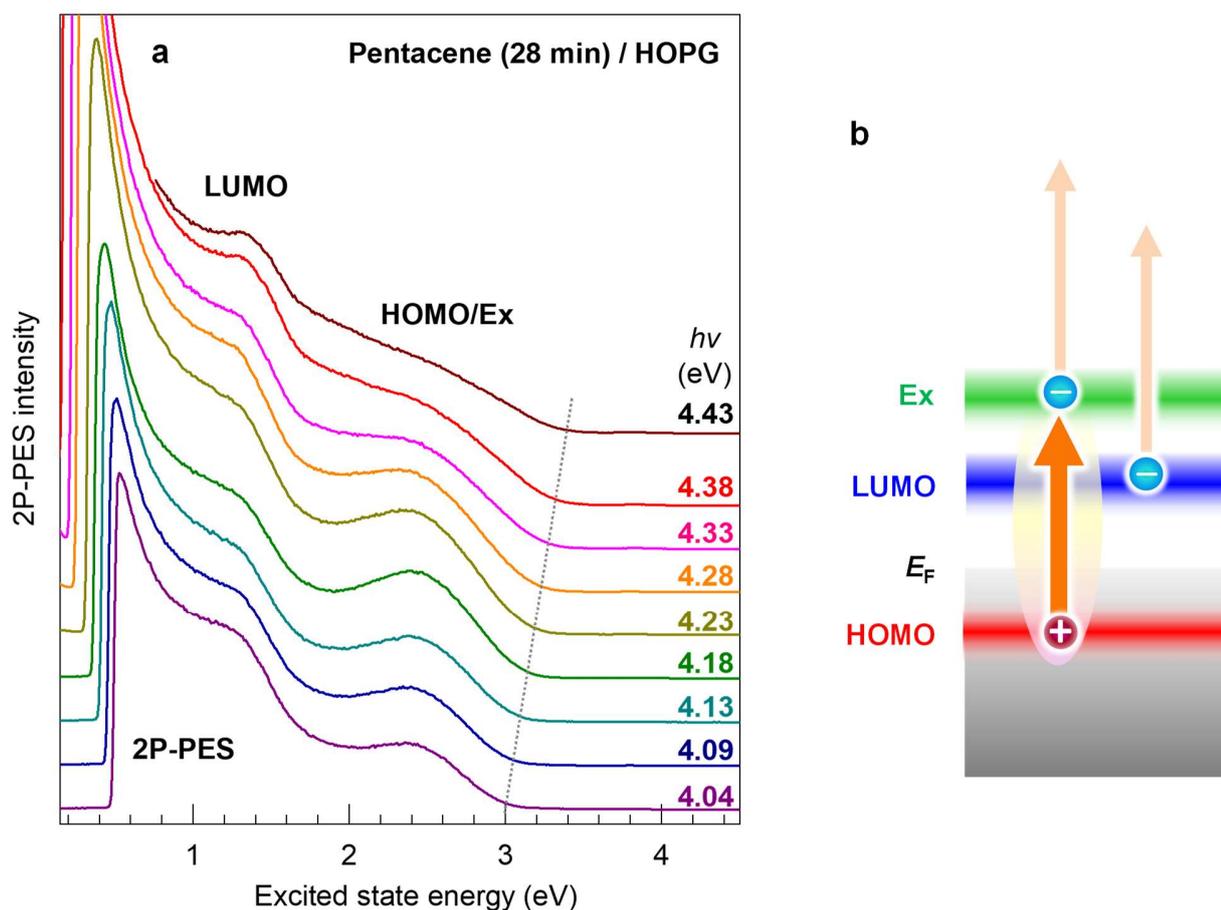
Supplementary Fig. S1. $h\nu$ dependence of 2P-PES for pentacene (2 min. deposition)/HOPG. (a) 2P-PES resolving the spectral features owing to the frontier orbitals (HOMO/LUMO). An image potential state (IPS) and a charge transfer exciton (S-CTE)²⁻⁷ are also resolved at higher energy regions (see Supplementary Note S1 for the assignments). (b) Energy diagram and excitation scheme in the 2P-PES for the pentacene (2 min)/HOPG.



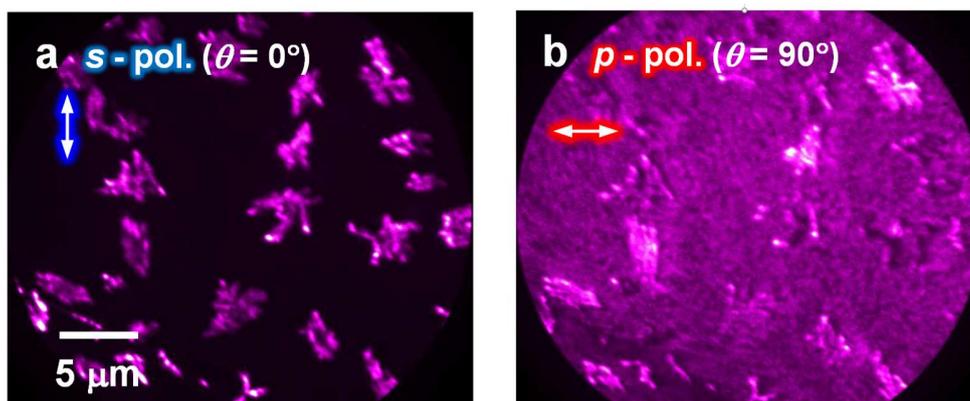
Supplementary Fig. S2. UPS spectra for pentacene (2 min deposition)/HOPG. (a) Raw spectral data showing the HOMO-derived peak at 1.2 eV in binding energy from the Fermi level. A shoulder-like structure appears at the higher binding energy of 1.4 eV, which is attributed to the vibrational satellite. The satellite feature can be observed exclusively for flat-lying pentacene monolayer film.¹³ (b) Peak fitting of the HOMO-derived peak using an energy separation of 158 meV taken from Supplementally ref. 13.



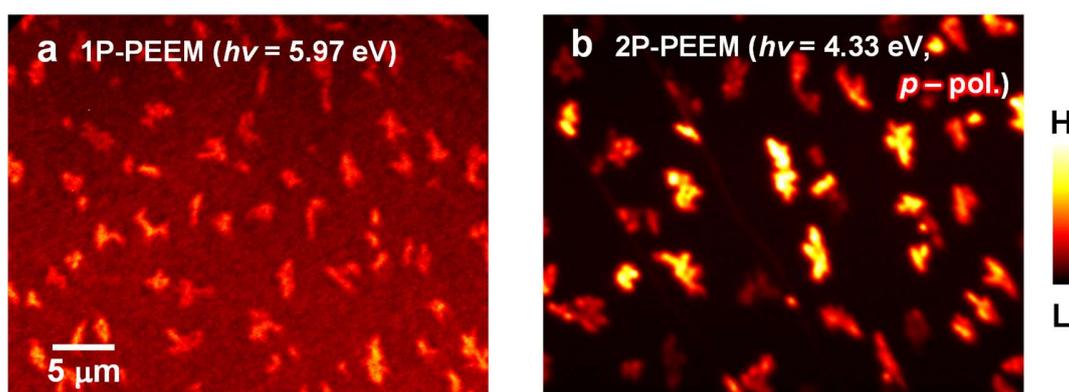
Supplementary Fig. S3. Wide-view 2P-PEEM images for pentacene nanocrystals (28 min deposition) on HOPG. (a, b) 2P-PEEM images with (a) *s*-polarized and (b) *p*-polarized photons. The intensity contrast is shown in the same procedures in both images. Intensities near the center of the images are relatively strong because of the gaussian distribution of the incident excitation laser.



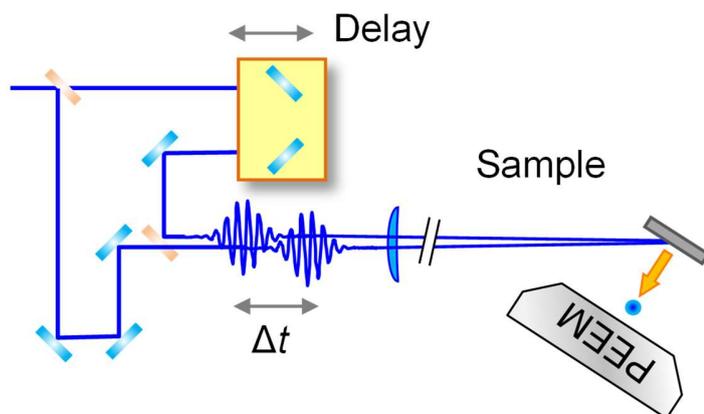
Supplementary Fig. S4. $h\nu$ dependence of 2P-PES spectra for pentacene (28 min deposition)/HOPG. (a) 2P-PES resolving the spectral features owing LUMO and HOMO/Ex. For the peak assignments, see Supplementary Note S1. (b) Energy diagram and excitation scheme in the 2P-PES for the pentacene (28 min)/HOPG.



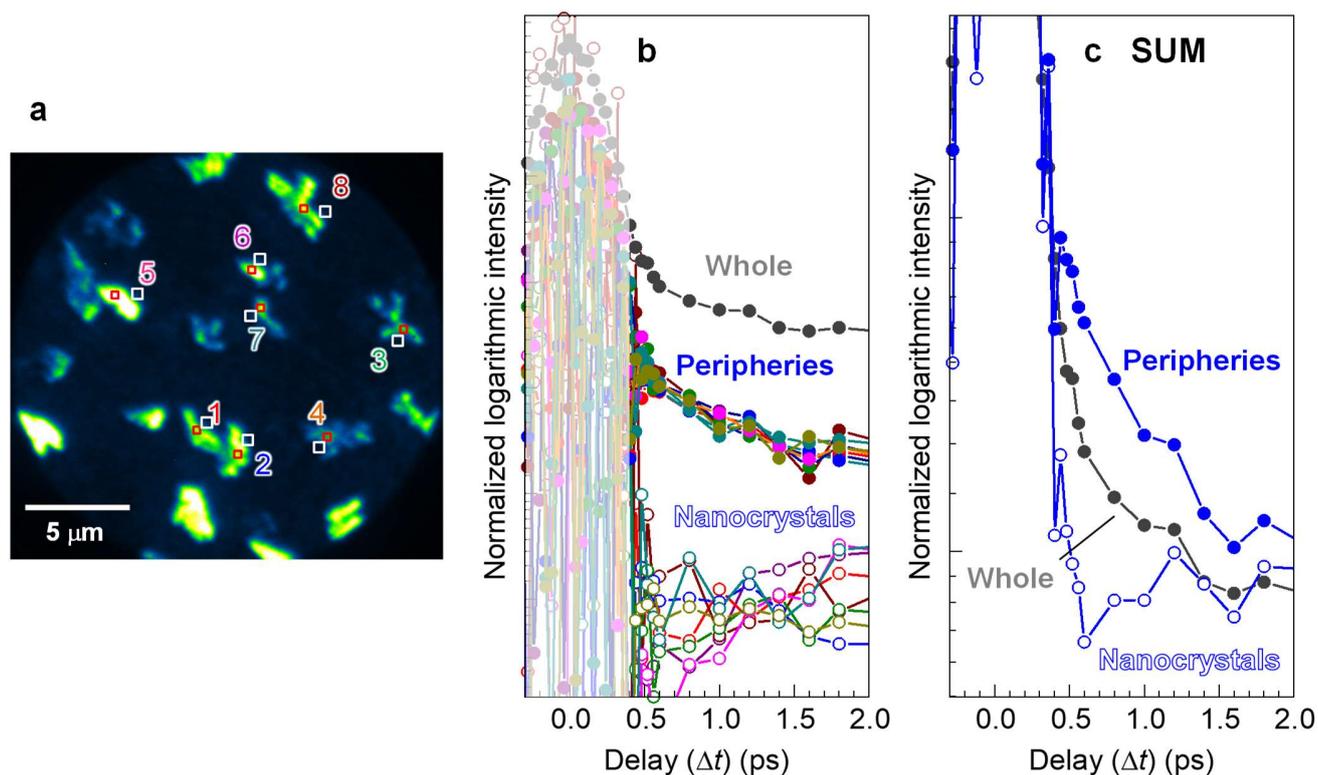
Supplementary Fig. S5. Non-resonant 2P-PEEM images ($h\nu = 3.18$ eV) of pentacene nanocrystals (28 min. deposition) (a, b) 2P-PEEM images with (a) *s*-polarized and (b) *p*-polarized photons. The 2P-PEEM intensities of nanocrystals exhibit fewer intensity variations in both images, while background intensity is enhanced at *p*-polarized photons.



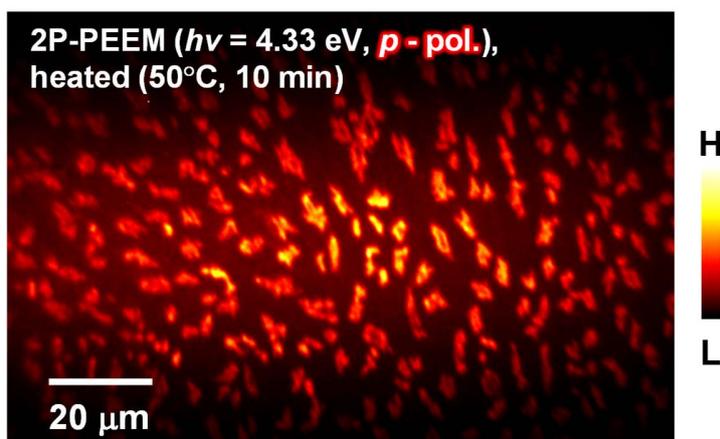
Supplementary Fig. S6. 1P-PEEM and resonant 2P-PEEM of pentacene nanocrystals on HOPG. (a) 1P-PEEM with $h\nu = 5.97$ eV, *p*-polarized photons. (b) Resonant 2P-PEEM with $h\nu = 4.33$ eV, *p*-polarized photons. Intensity variations are more pronounced in (b).



Supplementary Fig. S7. Schematic illustrations of pump-probe optical configuration.



Supplementary Fig. S8. Intensity traces of 2P-PEEM images at eight sets of nanocrystal core and periphery. (a) Area selections from 1 to 8. (b) 2P-PEEM intensities at each area, where they are slightly smeared at $\Delta t < 0.4$ ps because the intensity fluctuates owing to interference between two pulses within their overlapping time. (c) Summated intensities at nanocrystals and peripheries for area datasets numbered one to eight.



Supplementary Fig. S9. A wide-view image of 2P-PEEM for pentacene nanocrystals (28 min deposition) on HOPG taken after heating treatment to 50°C.

Supplementary References

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