Supporting Information

Two-Dimensional Confinement for Generating Thin Single Crystals for Applications in Time-Resolved Electron Diffraction and Spectroscopy: An Intramolecular Proton Transfer Study

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Table of Contents

Materials and Methods

Materials

1,5-Dihydroxyanthraquinone (1,5-DHAQ, technical grade, > 85%) and chloroform (analytical standard) were purchased from Sigma-Aldrich. V-1 grade 0.26 mm muscovite mica block was purchased from Sungil Industries. Mica is cut and cleaved into proper dimension (edge length 10 to 15 mm and thickness around 0.2 mm) to soak in a 20 ml vial.

Crystallization

Mica sheets were heated at 105 °C for 10 minutes on hot plate and rinsed with acetone to remove surface impurities. Two mica sheets are stacked in a 20 mL vial with diameter of 2 cm and 2 mL of 8.3 mM solution of 1,5-DHAQ in chloroform was added in the vial (Figure S1). The vial is closed with its lid and heated for 10 minutes at 60 °C, which is slightly below the boiling point of chloroform (61.2 °C). Then we set the temperature of the hot plate at 40 °C and left the vial on it for 10 minutes, and then brought the vial to room temperature space. We opened the lid after 10 minutes and covered it with aluminium foil with one pin hole made by 0.8 mm needle. The vial was left in stable place for 5 days for solvent to completely evaporate. The evaporation time is approximately 1-2 days longer in confined area than open area. To prepare samples for Transmission electron microscope (TEM), we put carbon film coated TEM grid on a mica sheet in the batch of crystallization. Crystals having same shape as those on mica sheet grew on the carbon film.

Characterizations

Optical images are taken by Olympus SZX10 with DP27 camera and analyzed by Stream Basic software and ImageJ. Crystal topography was observed with NanoWizard® 4 XP BioScience Atomic force microscope (AFM) in intermittent contact mode [1]. X-ray diffraction (XRD) was measured with 4-Circle Single Crystal Diffractometer SuperNova from Oxford Diffraction. Transmission electron microscopy (TEM) data are taken with CryoTEM JEOL JEM-2100F. We used carbon film coated 200 mesh Copper grid. Crystal structure analysis and powder diffraction pattern simulation was performed with VESTA. TEM images are analyzed with Gatan DigitalMicrograph.

Steady state absorption measurements

Steady state absorption measurements of solution and crystals have been performed on a home-built absorption spectrophotometer. Light sources employed in the set-up are deuterium and halogen lamps, which provide white light in the range of 215 – 2500 nm. The transmitted light is collected by spectrometer (Avantes, AvaSpec-ULS2048-USB2-UA-50). To measure absorption spectra, crystals are placed on a quartz substrate attached on a lens mount and solution sample is contained in a 1 mm quartz cuvette.

Absorption spectrum is plotted as the logarithm of transmitted spectrum through the bare substrate or pure solvent divided by that through a crystal on substrate or solution sample.

Femtosecond Transient absorption measurements

Transient absorption measurements of 1,5-DHAQ in solution and crystalline form have been performed on a home-built transient absorption (TA) set up. The details of the setup have been described previously [2]. Briefly, the TA setup uses Nd based commercial laser, PHAROS by Light conversion. The fundamental beam wavelength is 1030 nm with output power of 1 W at the repetition rate of 1 kHz. The fundamental laser beam is divided to pump and probe beams using a beam splitter: 20% of the beam is guided to focus on a 3 mm YAG crystal to generate a white light as probe beam, and the remaining 80% of fundamental beam is directed to generate 343 nm pump beam using third harmonic generation process. The pump beam is chopped using a Thorlabs chopper operating at 500 Hz, and the pump energy is controlled using set of neutral density filters. The diameters of pump and probe beams at the sample position are 190 μm and 100 μm, respectively. Time delay between pump and probe is controlled by 150 mm linear motorized delay stage from Newport. Probe spectra for each time-delay are detected with the combination of a spectrograph (9055, Sciencetech) and a charge-coupled device linear image sensor (CCD; S11156-2048-02, Hamamatsu Photonics). All the experiments were performed under room temperature. The concentration of the solution sample was 80 μM. Time-resolved absorption spectra were measured with ~200-fs time resolution. Transient absorption data were analyzed with Python GUI coded by Simon Bittmann.

Calculation and data analysis

The vertical excitation energies are calculated with time-dependent density functional theory (TDDFT) using Gaussian 09 package [3]. We adopted coordinates of 8 1,5-DHAQ molecules in a unit cell from CIF file of DHANTQ02 [4] posted at Cambridge Structural Database as crystal model. The geometries of crystal and solution model were optimized at B3LYP/6-31G and B3LYP/6-31G(d) level, respectively. Coulomb coupling between transition dipole moments of two molecules was calculated by Fortran code written by Hong-Guang Duan.

Supporting Figures and Tables

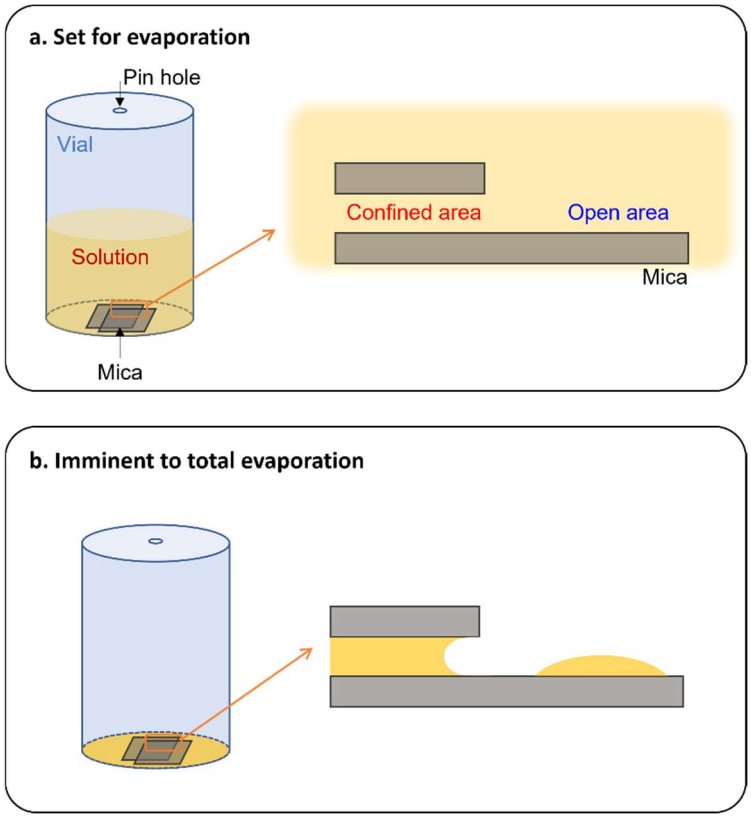

Figure S1. Schematic drawing of crystal growth from solution assisted with spatial confinement.

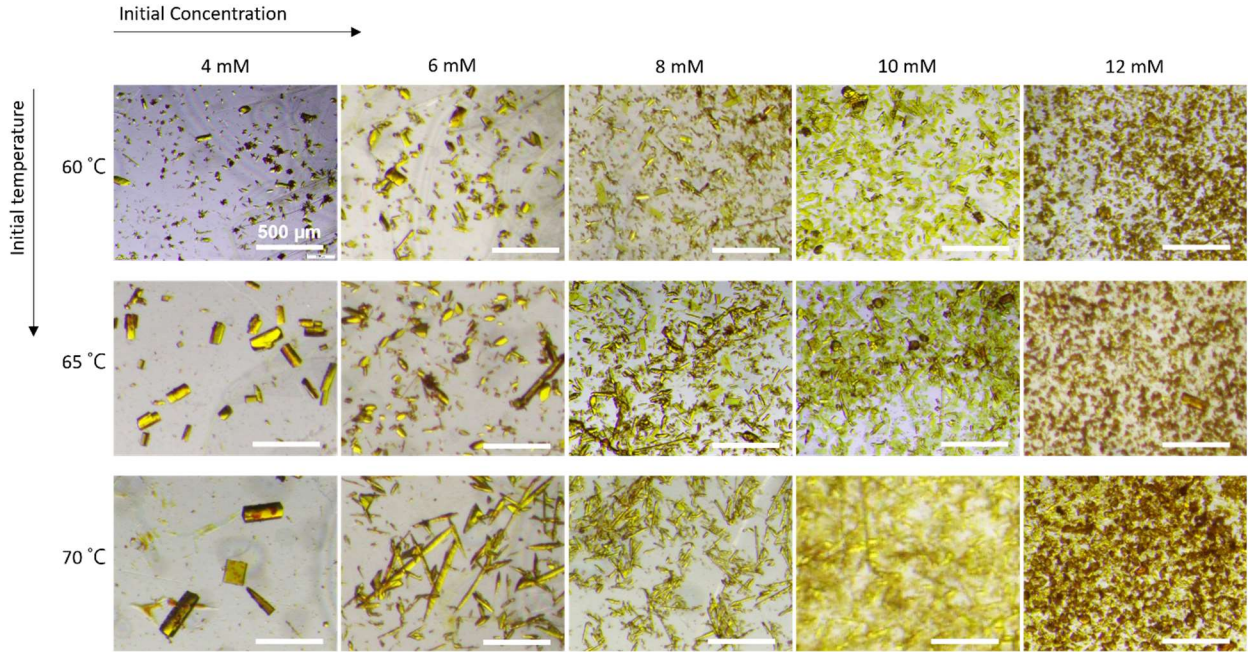

Figure S2. Crystal growth morphology of 1,5-DHAQ in open area by variation of initial concentration and initial temperature. Initial volume is all set to be 2 ml. Initial temperature was maintained for 10 minutes, and then the vials were left under room temperature. The vials were opened for evaporation after 10 minutes. Scale bar is 500 μm for all panels.

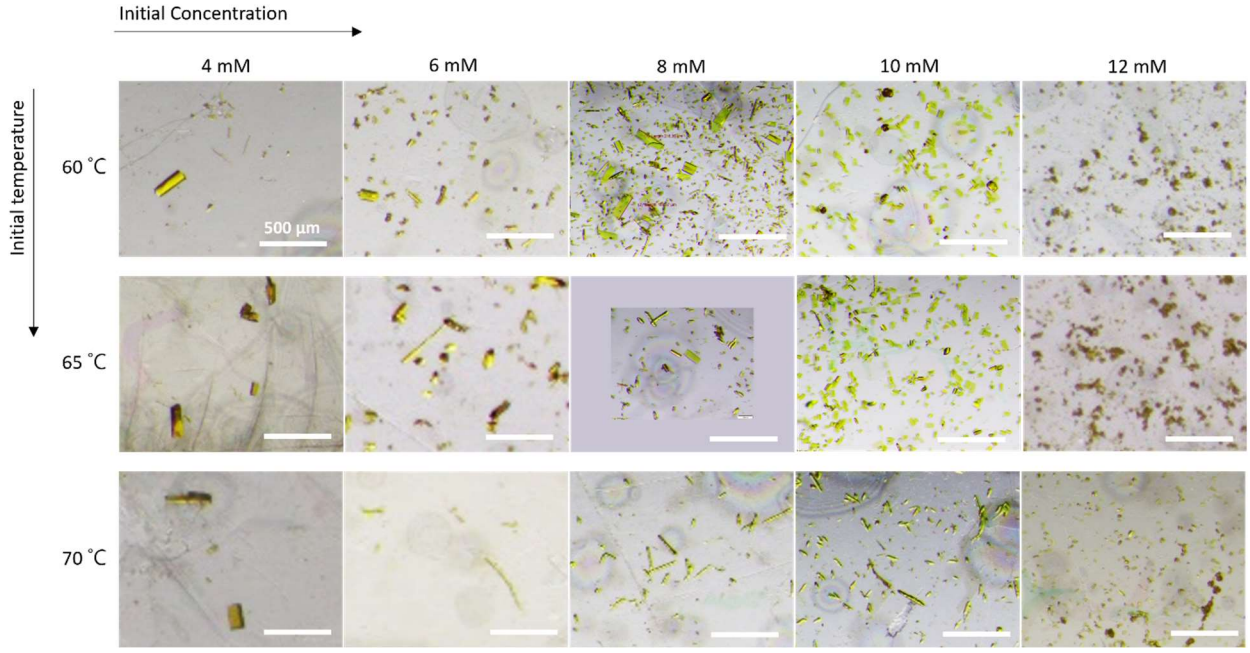

Figure S3. Crystal growth morphology of 1,5-DHAQ in confined area by variation of initial concentration and initial temperature. Scale bar is 500 μm for all panels.

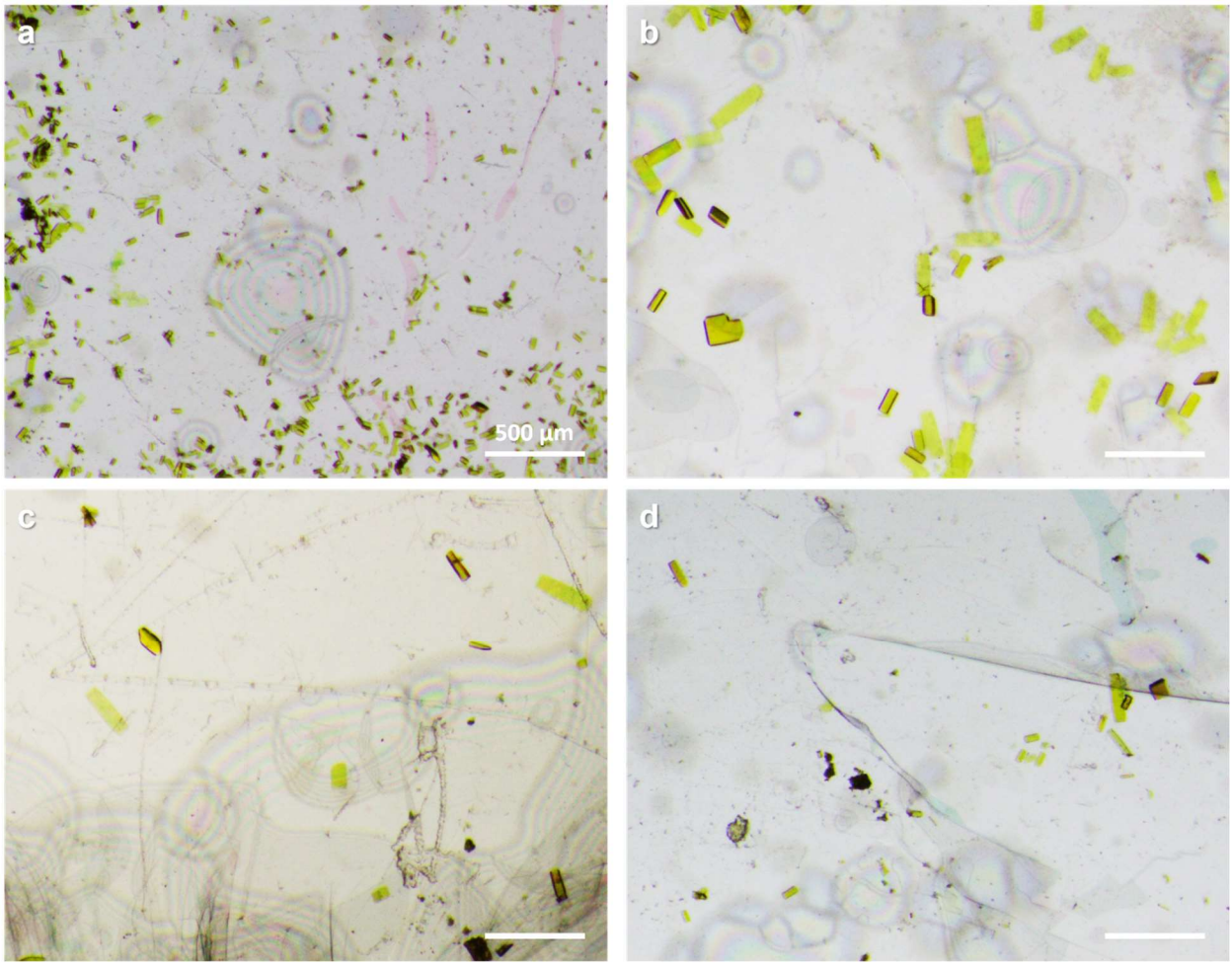

Figure S4. Crystal growth morphology after different temperature treatments. (a) 60 ˚C |10 min – RT | 10 min – Evaporation. (b) 60 ˚C |10 min – 40 ˚C |10 min – RT | 10 min – Evaporation. (c) 60 ˚C |20 min – 40 ˚C |20 min – RT | 10 min – Evaporation. (d) 60 ˚C |10 min – 50 ˚C |10 min – 40 ˚C |10 min – 30 ˚C |10 min – RT | 10 min – Evaporation. Scale bar is 500 µm for all panels.

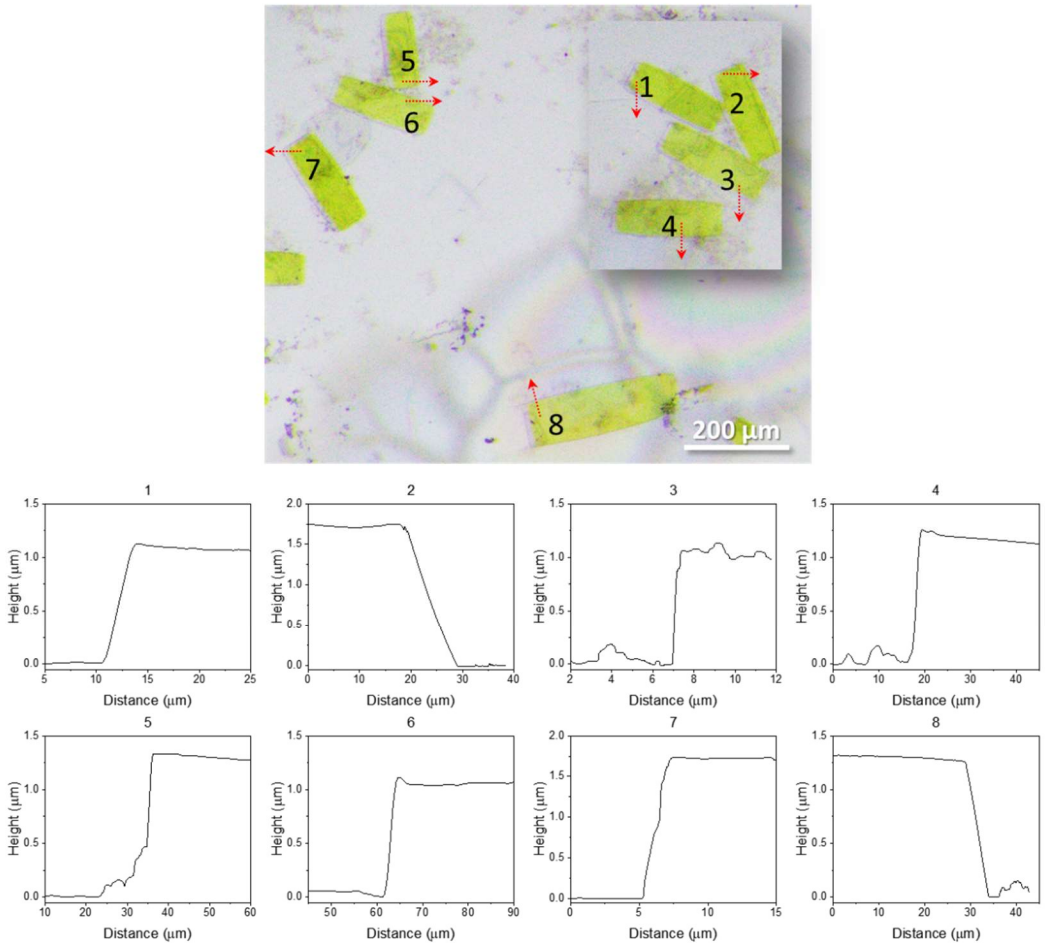

Figure S5. Height profiles at the edges of each crystal by AFM. Red arrows represent tracing direction.

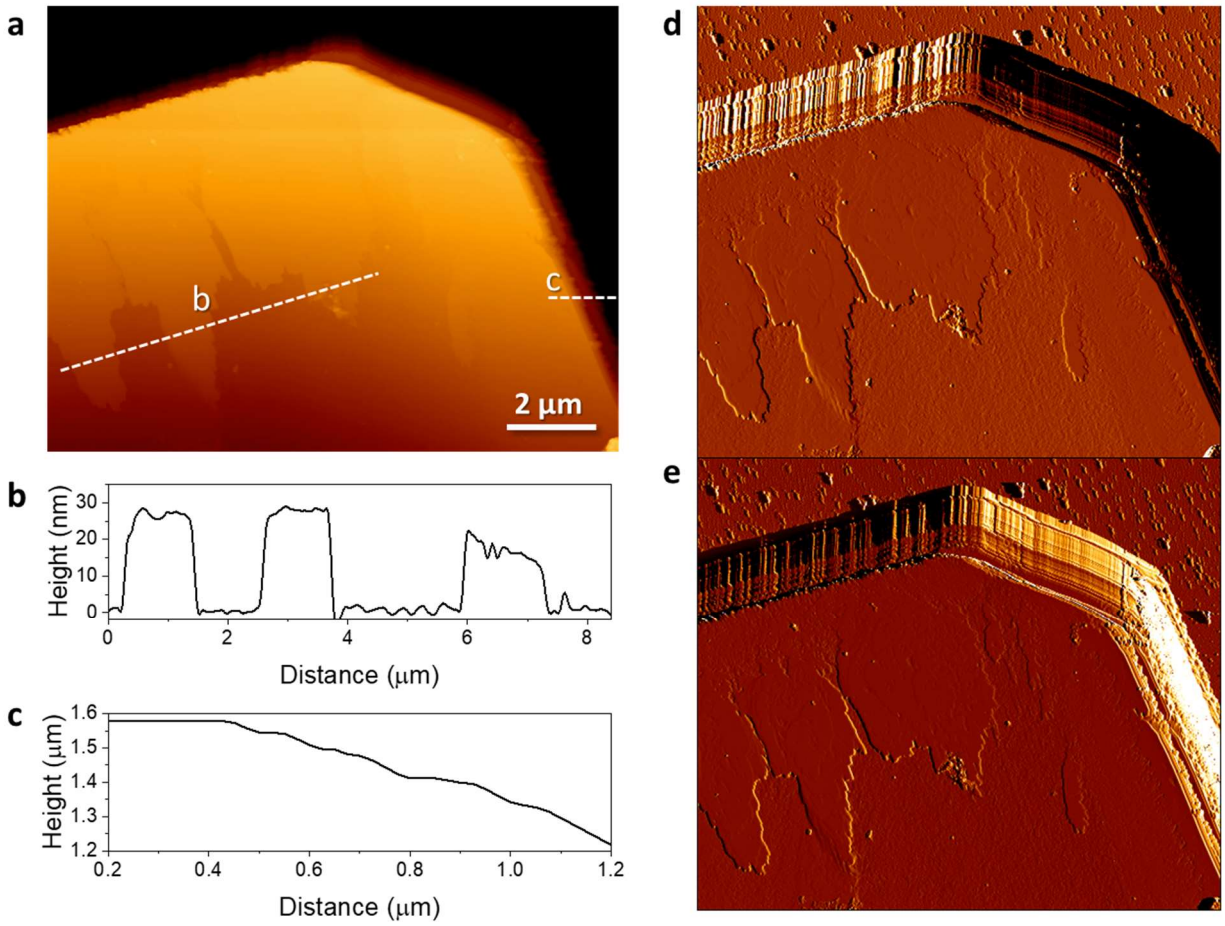

Figure S6. Topography of 1,5-DHAQ thin crystal. (a) AFM height image. (b, c) Height profile. Each profile is traced along the dashed lines in (a) correspondingly. The background of surface is subtracted in profile (b). (d, e) Error signal image of trace and retrace, respectively.

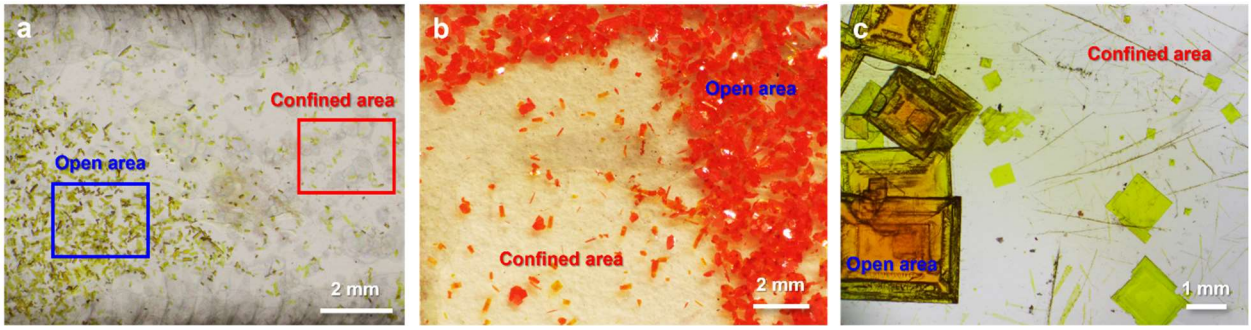

Figure S7. Optical image of crystals using the 2D confinement method. (a) 1,5-DHAQ presented in the main manuscript, (b) 1,4-DHAQ, (c) 1,8-DHAQ.

Table S1. Lattice parameters of 1,5-DHAQ [4].

Crystal system	Monoclinic
Space group (point group)	$P2_1/c$
a (Å)	6.0092(5)
b (Å)	5.3074(2)
c (Å)	15.7538(6)
α (deg)	90
β (deg)	93.672(5)
γ (deg)	90

Table S2. D-spacing of crystal planes shown in Fig. 1e. Calculation with reference data and analysis with selected area electron diffraction (SAED) pattern by TEM.

h	k	l	d (Å), Calculated	d (Å), Analyzed
0	0	2	7.86	7.38
1	1	0	3.97	4.15
1	1	2	3.49	3.62

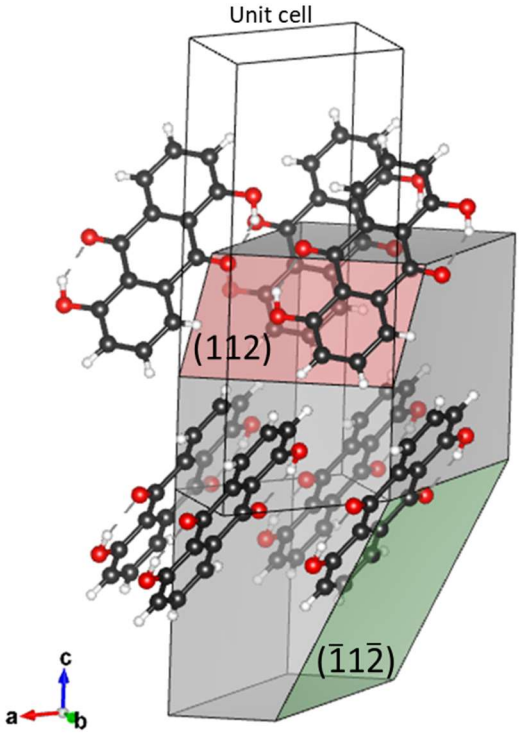

Figure S8. Illustration of crystallographic planes go through molecular planes. Red plane (112) represents the face of upper stacks of molecules in the figure, and green plane $(\bar{1}1\bar{2})$ represents the molecular planes of lower stacks. Grey planes are arbitrary planes.

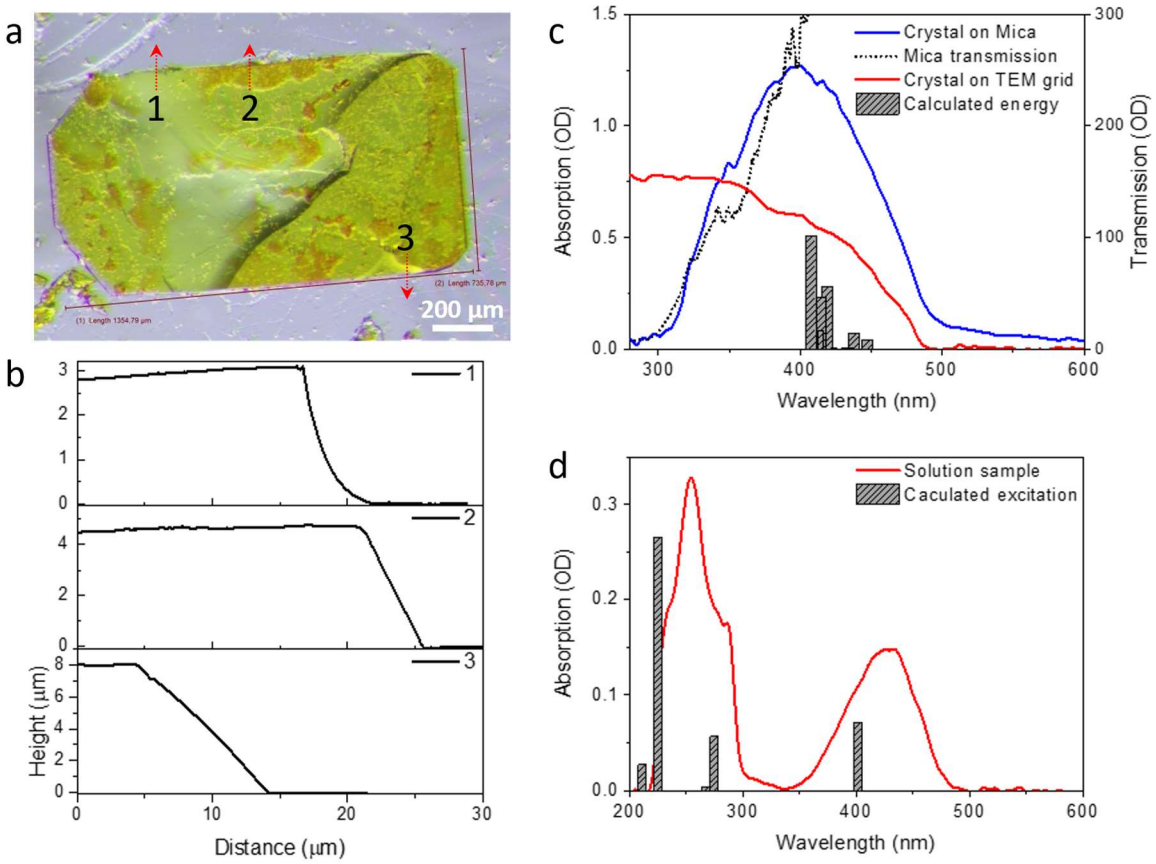

Figure S9. Characterization of TA-measured samples. (a) Optical image of 1,5-DHAQ crystal used for TA measurement. (b) Height profile measured by AFM. Traced line is marked with red arrow in (a) correspondingly. (c) Absorption spectrum 1,5-DHAQ crystal. Spectrum of crystal on mica (blue line) is cut off below 300 nm due to opaqueness of mica in UV region. Dotted line is transmission spectrum measured at mica substrate. Spectrum of crystal on TEM grid (red line) shows continuous absorption below 300 nm. Columns are positioned at the wavelengths of the calculated excitation energies with heights representing relative oscillator strength. (d) Absorption spectra of 1,5-DHAQ solution in acetonitrile. Columns represent the calculated energies with relative oscillator strengths. The values of calculated excitation energies and corresponding oscillator strengths are listed in Table S3.

Table S3. Calculated electronic excited state energies and oscillator strengths of 1,5-DHAQ crystal and solution.

	Excited state*	Excitation energy (nm)	Oscillator strength
Crystal	1	449.01	0.0007
	3	447.30	0.0197
	6	438.10	0.0356
	8	433.02	0.0034
	10	422.25	0.0027
	12	418.76	0.1403
	14	414.48	0.1174
	16	412.20	0.0415
	18	409.11	0.0346
	20	407.40	0.2534
Solution	1	401.00	0.2365
	6	274.59	0.1902
	8	266.85	0.0148
	13	224.78	0.8851
	14	224.64	0.0005
	18	210.92	0.0924
	20	205.32	0.0001

*States with oscillator strength equal to zero are omitted.

Table S4. Transitions contribute to the first excitation.

	Transition	Amplitude
Crystal	HOMO-3 → LUMO	0.13166
	HOMO-1 → LUMO+1	0.31358
	HOMO → LUMO	0.52727
	HOMO → LUMO+2	-0.27189
Solution	HOMO → LUMO	0.70262

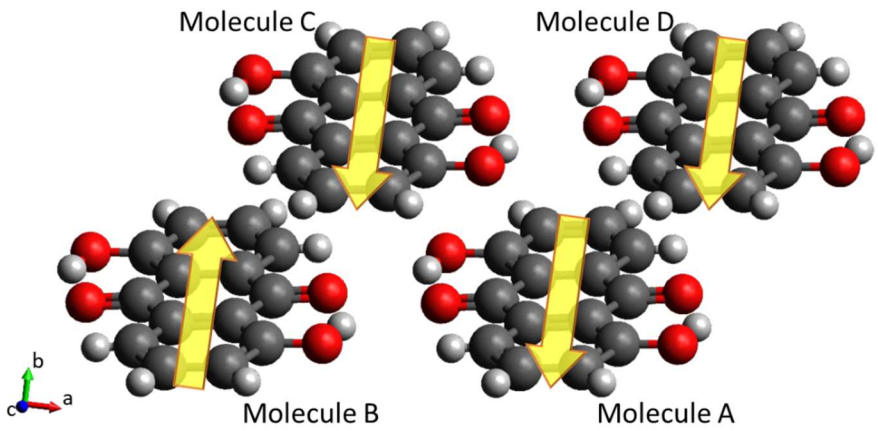

Figure S10. S0 → S1 Transition dipole moments of 1,5-DHAQ molecules. The direction of the dipole moment is depicted with yellow arrows.

Table S5. Calculated intermolecular Coulomb coupling between the transition dipole moments depicted in Fig. S5.

Molecule B ↔ Molecule A	-302.73 cm^{-1}
Molecule C ↔ Molecule A	382.86 cm^{-1}
Molecule D ↔ Molecule A	539.78 cm^{-1}

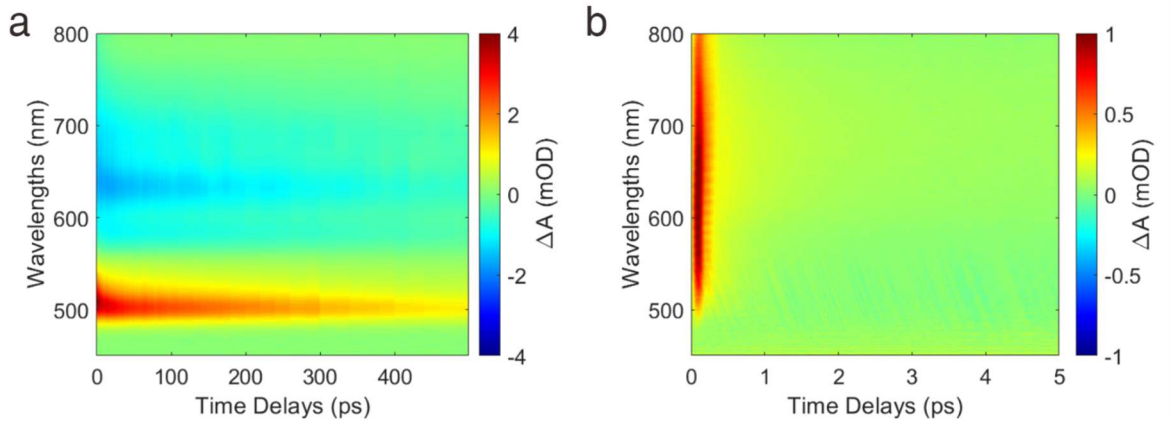

Figure S11. 2-dimensional colour plot of transient absorption spectra of 1,5-DHAQ. (a) Solution and (b) crystal.

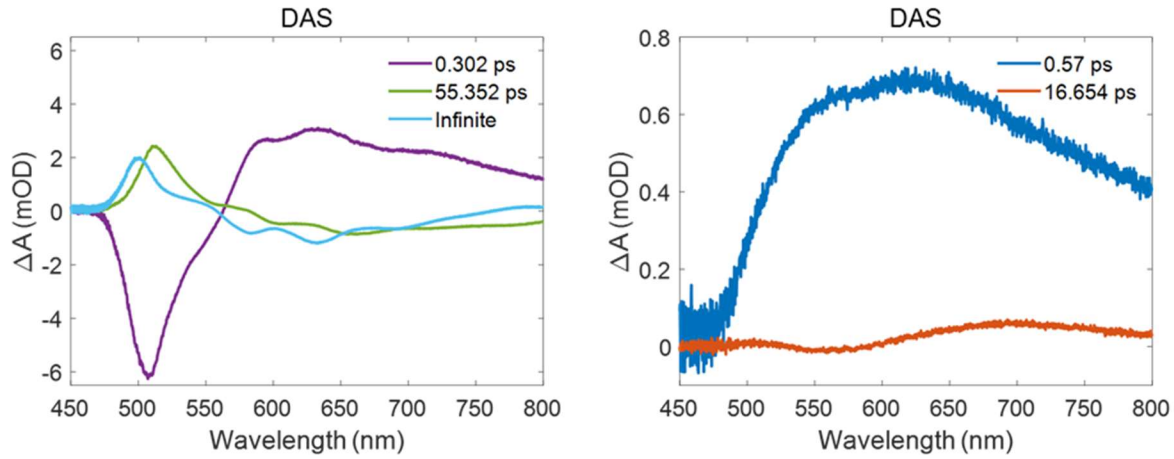

Figure S12. Decay-associated difference spectra of 1,5-DHAQ solution (left) and crystal (right).

Table S6. Specifications of crystal and solution samples measured transient absorption.

	Crystal	Solution
Absorbance at 343 nm	0.84 OD	0.078 OD
Density (crystal)	1.51 $g \cdot cm^{-3}$ [4]	
Thickness (crystal)	3.88 – 8.00 µm	
Concentration (solution)		$7.96 \cdot 10^{-8}$ $mol \cdot cm^{-3}$
Fluence	1.1 $mJ \cdot cm^{-2}$	2.7 $mJ \cdot cm^{-2}$
Cross-section	$2.63 \cdot 10^{-19}$ – $7.02 \cdot 10^{-19}$ cm^2	$1.63 \cdot 10^{-16}$ cm^2
Excitation fraction	0.05 – 0.14 %	7.68 %

Table S7. Time components of the kinetic traces in Fig. 4 given with exponential fit parameters and physical assignments on the components.

	Wavelength	τ_1 (ps) / Assignment	τ_2 (ps) / Assignment	τ_3 (ps) / Assignment
Solution	**500 nm**	0.279 ± 0.014 (rise) Proton transfer	40 ± 11 Non-radiative decay	> 500 S_1 state decay
	630 nm	3.8 ± 1.7 (rise) Vibrational redistribution	250 ± 50 S_1 state decay	
Crystal	**565 nm**	< 0.2	0.56 ± 0.06 Vibrational redistribution	
	670 nm	< 0.2	0.78 ± 0.20 Vibrational redistribution	9 ± 5 S_1 state decay

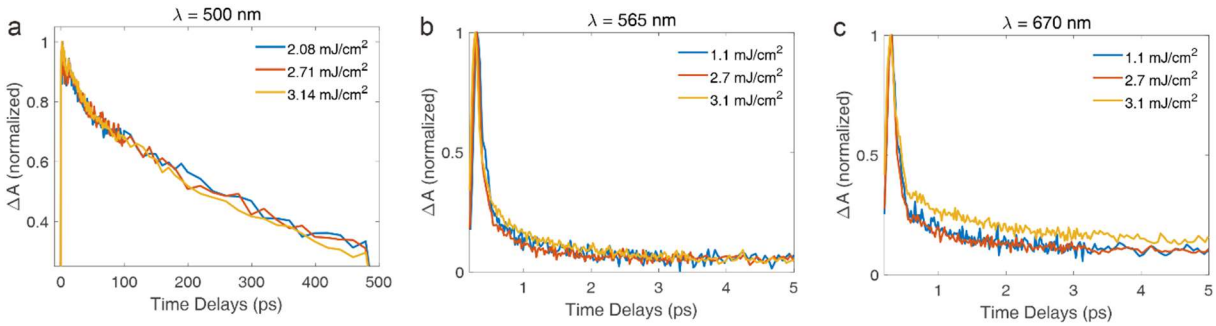

Figure S13. Photon fluence dependence. Normalized kinetic traces of 1,5-DHAQ solution with different photon fluence at 500 nm (a) and crystal at 565 nm (b) and 670 nm (c).

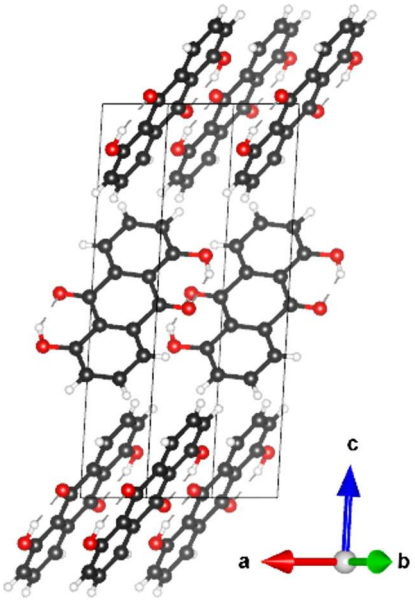

Figure S14. 1,5-DHAQ crystal model containing 8 molecules in a unit cell used for electronic excitation calculation.

Table S8. Coordinates of input files for electronic excitation calculation.

	X	Y	Z
O	2.866014	4.284133	1.812999
O	2.134240	1.023267	13.908460
O	2.638713	1.630433	6.047731
O	2.361542	3.676967	9.673728
O	1.885403	1.879350	0.304053
O	3.114851	3.428050	15.417405
O	3.619324	4.533050	7.556676
O	1.380931	0.774350	8.164782
C	3.866127	5.174715	1.894436
C	1.134127	0.132685	13.827023
C	1.638600	2.521015	5.966294
C	3.361655	2.786385	9.755165
C	3.832780	0.774350	2.947773
C	1.167474	4.533051	12.773685
C	1.671947	3.428050	4.912956
C	3.328308	1.879350	10.808503
C	4.815314	1.712167	3.097127
C	0.184940	3.595233	12.624331
C	0.689413	4.365867	4.763602
C	4.310842	0.941533	10.957856
C	-0.138340	1.792840	2.183711
C	5.138594	3.514560	13.537748
C	5.643067	4.446540	5.677019
C	-0.642812	0.860860	10.044440
C	5.916524	0.907035	1.135089
C	-0.916269	4.400366	14.586369
C	-0.411797	3.560735	6.725640
C	5.412051	1.746665	8.995819
C	4.923783	5.231504	0.966870
C	0.076471	0.075896	14.754589
C	0.580944	2.577804	6.893860

C	4.419310	2.729596	8.827599
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C	4.474023	3.663168	7.703515
C	0.526231	1.644233	8.017944
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H	2.409661	3.359584	4.307680
H	2.590593	1.947816	11.413779
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H	4.307118	0.360903	11.633879
H	3.008102	3.736410	1.069059
H	1.992153	1.570990	14.652399
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H	-1.197610	2.292797	3.773150
H	6.197864	3.014603	11.948309
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C	6.085672	5.383296	14.754589
C	7.681147	3.428050	4.912956

H	6.702337	4.946497	4.087579
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H	7.914389	4.601516	12.168409

C	7.143327	5.440085	13.827023
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H	8.418861	3.359584	4.307680
C	7.647800	2.521015	5.966294
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C	-3.152018	5.174715	17.615894
C	-1.101622	6.214435	16.856548
O	0.876458	7.186751	16.025511
C	6.147540	3.514560	-2.183711
C	7.094617	5.383296	-0.966870
O	7.894604	7.186751	0.304053
H	6.514923	7.732882	2.232447
H	-1.514669	-2.425482	13.489011
O	-2.894349	-1.879350	15.417405
C	-2.094362	-0.075896	16.688328
C	-1.147285	1.792840	17.905169
C	0.138340	-1.792840	-2.183711
C	2.176420	-0.774350	-2.947773
O	3.143186	1.023267	-1.812999
O	1.857069	4.284133	17.534457
C	2.823835	6.081750	18.669232
C	4.861915	7.100240	17.905169
O	-3.143186	-1.023267	1.812999
O	-1.885403	-1.879350	-0.304053
O	8.143440	6.330667	13.908460
O	6.885658	7.186751	16.025511
O	8.647913	1.630433	6.047731
O	-3.647659	3.676967	9.673728
C	6.147540	-1.792840	-2.183711

C	8.185620	-0.774350	-2.947773
O	9.152386	1.023267	-1.812999
O	-4.152131	4.284133	17.534457
C	-3.185365	6.081750	18.669232
C	-1.147285	7.100240	17.905169
H	5.503477	2.881918	-2.232447
C	7.203086	3.595233	-3.097127
C	8.152273	5.440085	-1.894436
C	-3.152018	-0.132685	17.615894
C	-2.202831	1.712167	18.818586
H	-0.503222	2.425482	17.953906
H	-0.505723	-2.425482	-2.232447
C	1.193886	-1.712167	-3.097127
H	2.914134	-0.705884	-3.553050
H	3.001098	1.570990	-1.069059
H	1.999157	3.736410	16.790518
H	2.086121	6.013284	19.274508
C	3.806369	7.019568	18.818586
H	5.505978	7.732882	17.953906
H	-3.001098	-1.570990	1.069059
H	8.001353	6.878391	14.652399
H	8.505825	1.082710	6.791670
H	-3.505571	4.224691	8.929788
H	5.503477	-2.425482	-2.232447
C	7.203086	-1.712167	-3.097127
H	8.923334	-0.705884	-3.553050
H	9.010298	1.570990	-1.069059
H	-4.010043	3.736410	16.790518
H	-3.923080	6.013284	19.274508
C	-2.202831	7.019568	18.818586
H	-0.503222	7.732882	17.953906
H	7.206810	3.014603	-3.773150
C	8.185620	4.533051	-2.947773

O	9.152386	6.330667	-1.812999
O	-4.152131	-1.023267	17.534457
C	-3.185365	0.774350	18.669232
H	-2.206555	2.292797	19.494608
H	1.197610	-2.292797	-3.773150
H	3.802645	7.600197	19.494608
H	7.206810	-2.292797	-3.773150
H	-2.206555	7.600197	19.494608
H	8.923334	4.601516	-3.553050
H	9.010298	6.878391	-1.069059
H	-4.010043	-1.570990	16.790518
H	-3.923080	0.705884	19.274508

Acknowledgement

We thank I. Nevoigt for carrying out the XRD measurements. We thank R. Schubert for carrying out the TEM measurements, and training H. Hwang to operate AFM and analyse the data using their software.

References

1. Han, H., et al., *The XBI BioLab for life science experiments at the European XFEL.* J Appl Crystallogr, 2021. **54**(Pt 1): p. 7-21.
2. Yan, Y., et al., *Fundamental Flaw in the Current Construction of the TiO2 Electron Transport Layer of Perovskite Solar Cells and Its Elimination.* ACS Appl Mater Interfaces, 2021. **13**(33): p. 39371-39378.
3. M. J. Frisch, G.W.T., H. B. Schlegel, G. E. Scuseria, , et al., *Gaussian 09, Revision D.01*. 2013, Gaussian, Inc.: Wallingford CT.
4. Marasinghe, P.A.B. and G.D. Gillispie, *Structure of 1,5-dihydroxyanthraquinone: a redetermination.* Acta Crystallographica Section C Crystal Structure Communications, 1993. **49**(1): p. 113-114.