

## SUPPORTING INFORMATION

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### Supporting Information

## Single-photon upconversion in 6-pentaceneone crystal from bulk to ultrathin flake

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## Experimental Procedures

### Materials and Synthesis

Dark-green 6-pentaceneone (P1O) crystal was obtained as a byproduct in the pentacene (98%, Alfa Aesar) purification using the physical vapor transport method. A semi-transparent furnace was used for single crystal growth.<sup>[1]</sup> The scheme of the apparatus is shown in Figure S1. The purified materials were placed into the high temperature zone of the furnace and the single crystals were grown at the low temperature zone. Argon was used as the carrier gas with a flow rate of 40 ml/min. After 8 hours heating at constant temperature 300 °C, the furnace was cooled to room temperature. Then, the single crystals of pentacene and P1O were obtained at the low temperature zone.

### Characterization methods

**Crystal X-ray diffraction (XRD).** A suitable single crystal was selected by hand under an optical microscope and attached to the top of a glass fiber. The single-crystal X-ray diffraction was performed on a SuperNova CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K. The P1O crystal structure was solved and refined by Shelxl and Olex software.<sup>[2]</sup> CCDC 1907538 contains the supplementary crystallographic data for P1O structure. The phase purity of P1O was characterized using a powder X-ray diffractometer (BRUKER D8 Series, Cu K $\alpha$  radiation) between 5° and 65° ( $2\theta$ ) at a scan rate of 5° min<sup>-1</sup>. The Hirshfeld surface was calculated using CrystalExplorer 3.1.<sup>[3]</sup>

**Optical properties measurement.** Photoluminescence measurements were carried out on a triple-grating micro-Raman spectrometer (Horiba-JY T64000). A cryostat (Cryo Industry of America, USA) was used to provide a continuous temperature from 77 K to 300 K by liquid nitrogen flow. The backscattered signal was collected through a 50 $\times$  long focus objective, dispersed with an 1800 g/mm grating, and detected by a liquid nitrogen cooled charge-coupled device. A series of laser source were used to excite the samples: 473, 532, 671 and 785 nm are excitation lines from the solid-state lasers; 693, 700 and 720 nm lines are from a tunable Ti: sapphire laser. The reflectance and transmittance were collected by CRAIC 20 Microspectrophotometer. For photoluminescence lifetime measurement, a Ti: sapphire femtosecond-pulsed laser (800 nm, 80MHz, ~100 fs) was frequency-doubled by a beta barium boron crystal to generate 400 nm pulsed laser for excitation. Signal was collected with a 50 $\times$  long focus objective using a back-scattering mode. The signal was measured with SPAD detectors.

**The atomic force microscopy** was performed using a Cypher S Atomic Force Microscope.

**Table S1. Crystallographic data for 6-pentaceneone.**

Crystal	6-pentaceneone
Empirical formula	C <sub>22</sub> H <sub>14</sub> O
Formula weight	294.33
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub>
<i>a</i> /Å	6.5602(4)
<i>b</i> /Å	14.7939(9)
<i>c</i> /Å	14.8216(9)
$\beta$ /°	91.727(5)
<i>V</i> /Å <sup>3</sup>	1437.80(15)

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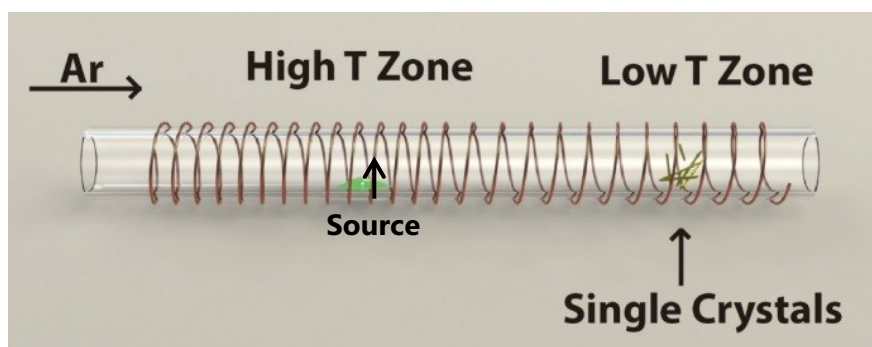
$Z$	4
$T/K$	293(2)
$F(000)$	616.0
$\rho_{\text{calcd}}/\text{g cm}^{-3}$	1.360
$\mu/\text{mm}^{-1}$	0.082
Measured refls.	17319
Independent refls.	5614
No. of parameters	415
$R_{\text{int}}$	0.0373
$R_1 (I > 2\sigma(I))^{\text{a}}$	0.0588
$wR (I > 2\sigma(I))^{\text{b}}$	0.1493
GOF	1.034
CCDC	1907538

[a]  $R_1 = \frac{\sum \|F_o\| - |F_c|}{\sum \|F_o\|}$ , [b]  $wR_2 = \left[ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$ .

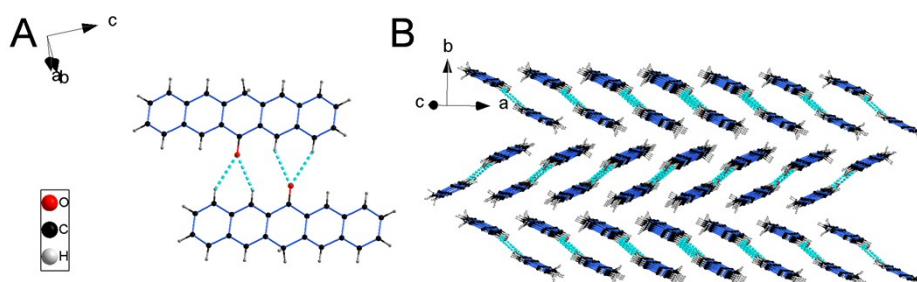
**Table S2 Hydrogen bonds for P10.**

D-H...A	d(D-H) (Å)	d(H...A) (Å)	d(D...A) (Å)	<(DHA) (°)
C(19)-H(19) ..O(2)#1	0.93	2.60	3.399(7)	144
C(21)-H(21) ..O(2)#1	0.93	2.49	3.327(6)	150
C(25)-H(25) ..O(1)#2	0.93	2.49	3.305(6)	147
C(27)-H(27) ..O(1)#2	0.93	2.57	3.368(6)	144

Symmetry transformations used to generate equivalent atoms:: #1 = -1+x, y, z; #2 = 1+x, y, z.

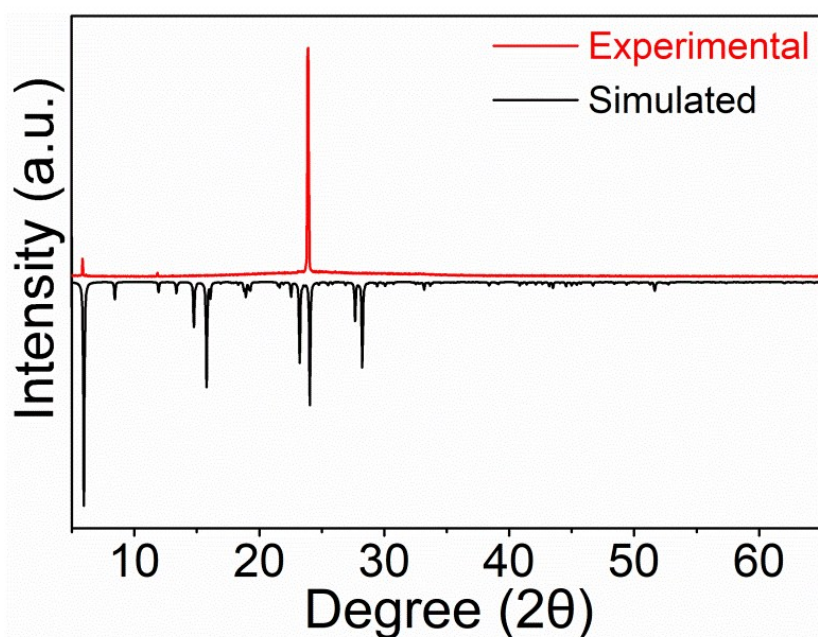


**Figure S1.** Scheme for the single crystals growth of 6-pentaceneone.

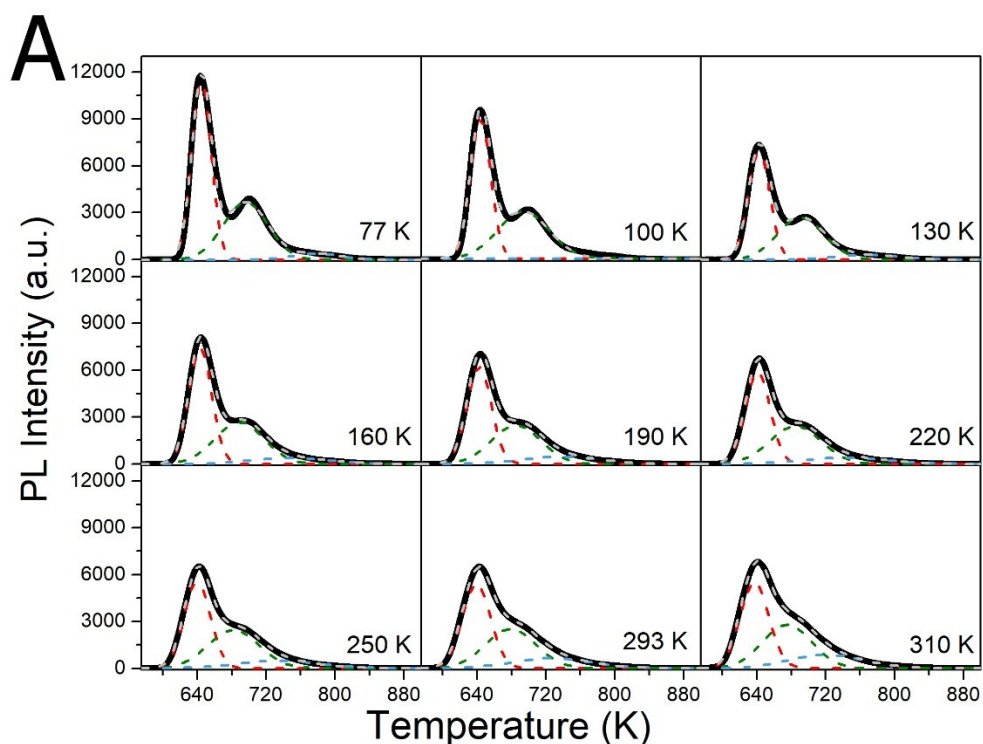


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**Figure S2.** Hydrogen bonds in P1O. The blue dashed lines indicate hydrogen bonding interactions. The red, black, and light grey atoms denote oxygen, carbon, and hydrogen atoms, respectively.

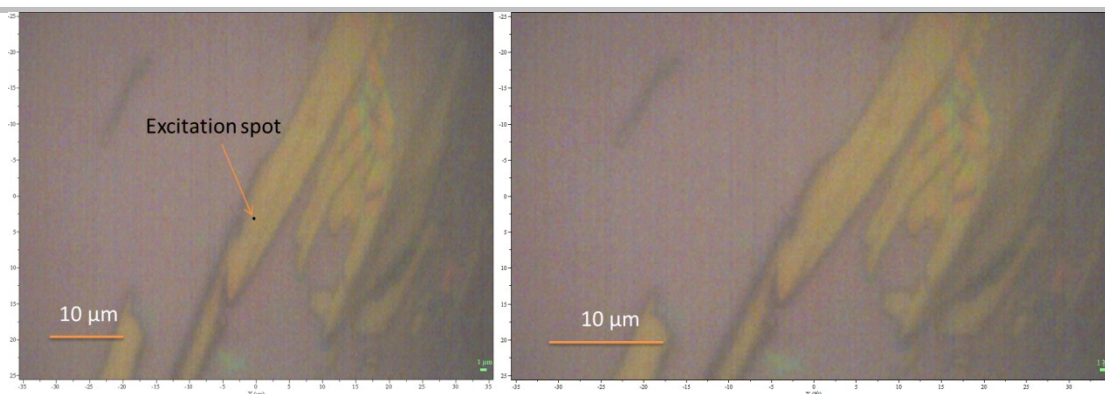


**Figure S3.** The experimental PXRD pattern (red) of P1O compared with the simulated one (black). The black one was simulated from the P1O Cif using the Mercury software. The three peaks in the experimental pattern are (010), (020) and (040).

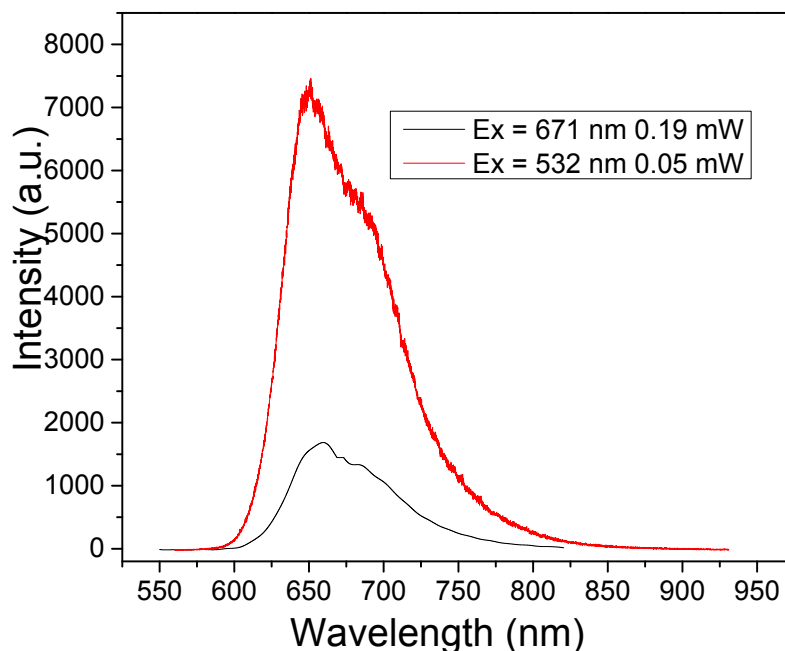


**Figure S4.** The temperature dependent PL spectra of P1O, varying from 77.4K to 310K. The magenta, green and red lines in each graph are the fitting PL curves, corresponding to  $0 \leftarrow 0$ ,  $1 \leftarrow 0$  and  $2 \leftarrow 0$  emission, respectively.

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**Figure S5.** The surface appearance of the samples before (left) and after (right) the excitations of 5.34 mW 671-nm laser, 2.33 mW 693-nm laser and 3.44 mW 700-nm laser.



**Figure S6.** The PL spectra of thin sample (1.2  $\mu\text{m}$ ) with different excitation wavelengths.

### References

- [1] a) P. Hu, K. Du, F. Wei, H. Jiang, C. Kloc, *Cryst. Growth Des.* **2016**, *16*, 3019-3027; b) P. Hu, H. Li, Y. Li, H. Jiang, C. Kloc, *CrystEngComm* **2017**, *19*, 618-624; c) P. Hu, S. Wang, A. Chaturvedi, F. Wei, X. Zhu, X. Zhang, R. Li, Y. Li, H. Jiang, Y. Long, C. Kloc, *Cryst. Growth Des.* **2018**, *18*, 1776-1785.
- [2] a) G. M. Sheldrick, *Acta Crystallogr. C. Struct. Chem.* **2015**, *71*, 3-8; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
- [3] a) Spackman, M. A.; McKinnon, J. J.; Jayatilaka, D, *CrystEngComm.* **2008**, *10*, 377-388; b) Spackman, M. A.; Jayatilaka, D, *CrystEngComm.* **2009**, *11*, 19-32.