Supramolecular Solid-State Microlaser Constructed from Pillar[5]arene-Based Host−Guest Complex Microcrystals

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Supporting Information

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compound **P5**[S1] was synthesized according to previous literature. NMR spectra were recorded with a Bruker Avance DMX 400 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The fluorescence experiments were conducted on an RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). Quantum yield measurements were performed using the absolute method on a FLS920 from Edinburgh Instruments equipped with a $BaSO_4$-coated integrating sphere, a 450W Xe900 Xenon lamp and a R928P PMT detector.

Optical Characterization

The optically pumped lasing measurements were taken on a home-built far-field microfluorescence system (Olympus, IX73 inverted microscope). The crystal was immersed in diethyl ether and then dispersed onto a glass substrate. The excitation light (515 nm) was generated from the second harmonic of the fundamental output that was seeded by a mode-locked Ti:sapphire laser (Light Conversion Pharos, 1030 nm, <300 fs, 1 MHz). The excitation light was filtered with a 515 nm band-pass filter and then diverged with a convex lens (f = 500 mm), and finally focused down to a 140 μm diameter spot through an objective lens (Olympus MplanFLN, 20x, NA = 0.45). The laser beam size was adjusted to cover the whole microcrystal. The emission light was collected by the same objective and focused into a spectrograph (Princeton Instruments, Acton SpectraPro, SP-2300i) with a 600 mm^{-1} grating and detected by a liquid-N_2-cooled CCD (PyLon 100B excelon). The instrument resolution (FWHM) was ~0.1 nm. All measurements were taken at room temperature with pulse picker = 1000. TRPL decay kinetics were collected using a TCSPC module (PicoHarp 300) and a SPAD detector (IDQ, id100) with an instrument response function ~100 ps. The two-photon pumped lasing performance was measured upon excitation at 1030 nm.

*2. NOESY NMR spectrum of a solution of **DASP** and **P5***

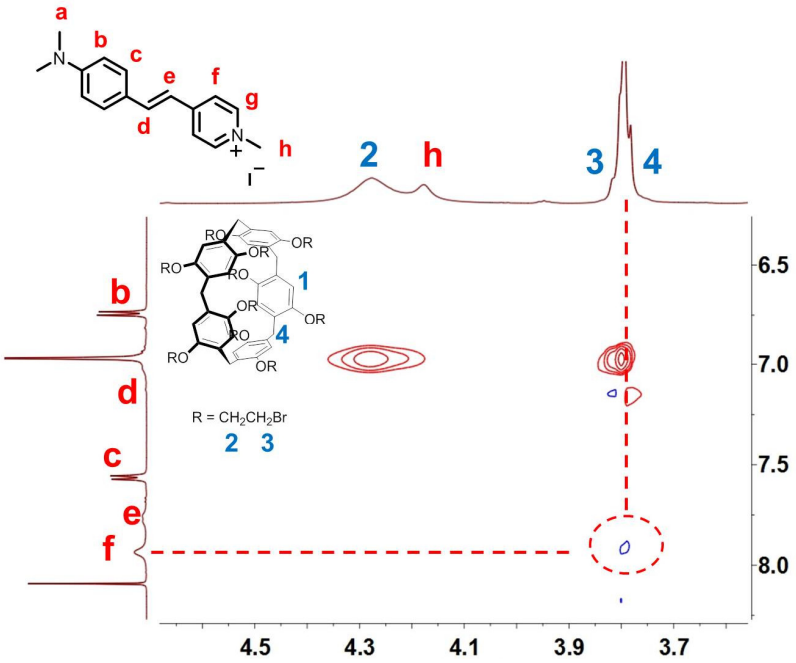

Figure S1. Partial NOESY NMR spectrum (500 MHz, $CDCl_3$:DMSO-d_6 = 1:1, room temperature) of a solution of **DASP** (5.00 mM) and **P5** (5.00 mM).

3. Preparation of **2P5⊃DASP** *microcrystals*

The **2P5⊃DASP** microcrystals were prepared *via* a vapor diffusion method. First, 1.00 mg of **DASP** and 5.00 mg of **P5** were dissolved in 1 mL of chloroform. Subsequently, the mixture was added to a small bottle and the bottle was then placed in a covered beaker containing 2 mL of diethyl ether as the poor solvent. Diethyl ether gradually diffused into the solution of **DASP** and **P5**. After 12 h, a large number of **2P5⊃DASP** microcrystals were obtained. These microcrystals were washed twice with methanol and then kept in diethyl ether for further use.

*4. Optical microscopic images of **2P5⊃DASP** microcrystals obtained at different concentrations*

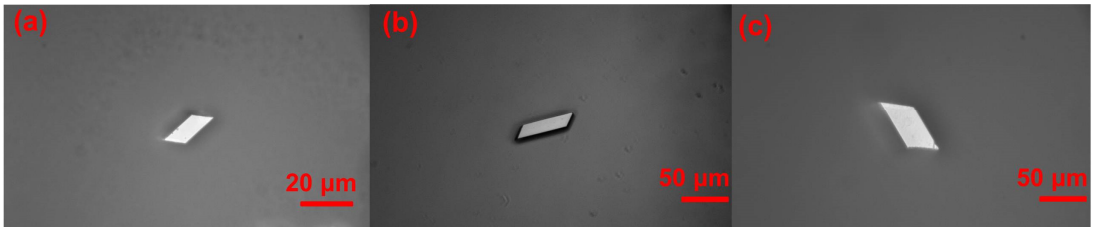

Figure S2. Optical microscopic images of **2P5⊃DASP** microcrystals obtained at different concentrations: (a) 3.00 mM **P5** and 3.00 mM **DASP**, (b) 5.00 mM **P5** and 5.00 mM **DASP**, and (c) 6.00 mM **P5** and 6.00 mM **DASP**.

The size of microcrystals can be efficiently tuned by changing the mixture concentrations of **P5** and **DASP.**

*5. X-ray crystal data of **2P5⊃DASP***

2P5⊃DASP

Crystallographic data: red, $C_{126}H_{139}Br_{20}IN_2O_{20}$, *FW* 3726.28, triclinic, space group P–1, a = 12.3928 (6) Å, b = 15.6251(7) Å, c = 18.2747(9) Å, α = 82.203(4)°, β = 81.506(4)°, γ = 76.519(4)°, V = 3384.5 (3) Å^3, Z = 1, D_c = 1.828 g cm^{-3}, T = 128 K, μ = 6.203 mm^{-1}, 22056 measured reflections, 12814 independent reflections, 876 parameters, 271 restraints, $F(000)$ = 1822.0, R_1 =0.1270, wR_2 = 0.2022 (all data), R_1 = 0.0756, wR_2 = 0.1680 [$I > 2\sigma(I)$], max. residual density 2.291 e•Å^{-3}, and goodness-of-fit (F^2) = 1.034. CCDC 1870965.

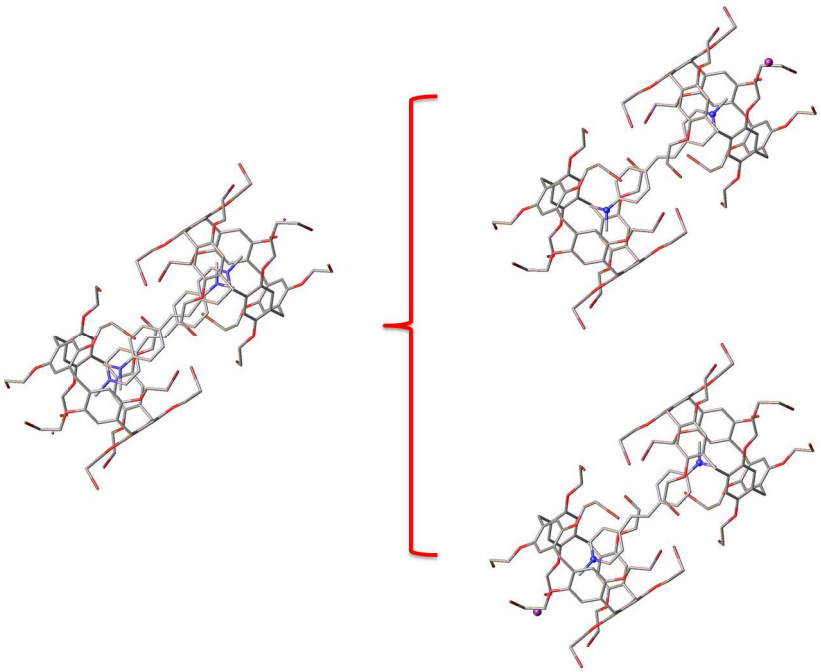

Figure S3. Illustration of the disorder of a guest **DASP** molecule in the void between two host **P5** molecules. The hydrogen atoms are omitted for clarity.

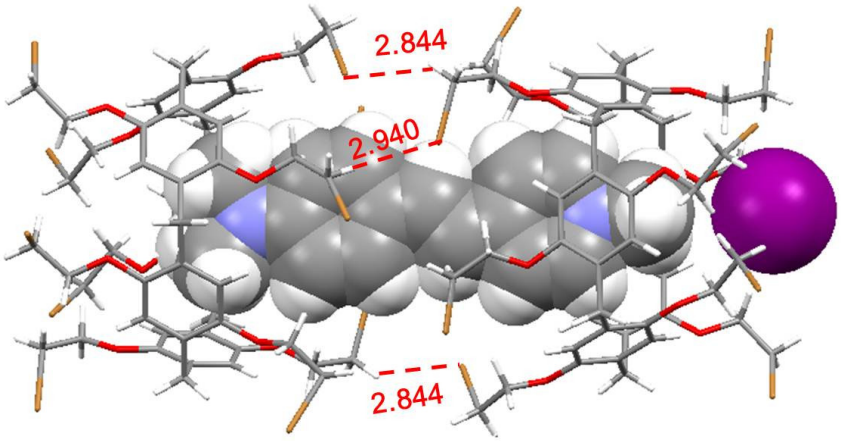

Figure S4. Illustration of the multiple C-H/Br hydrogen bonds in the **2P5⊃DASP** single crystal structure.

In the crystal structure of **2P5⊃DASP**, some H and Br atoms on **P5** were disordered because of the rotation of C-H and C-Br single bonds. The guest molecule **DASP** was disordered because of its reversal in the void made by two centrosymmetric **P5** molecules (Figure S3). The intermolecular distances between the bromine atoms and hydrogen atoms on the **P5** molecules were calculated to be 2.844 Å and 2.940 Å, respectively, which indicates typical C-H/Br hydrogen bonds (Figure S4).[S2]

*6. UV-vis and PL spectra of **DASP** in different solvents*

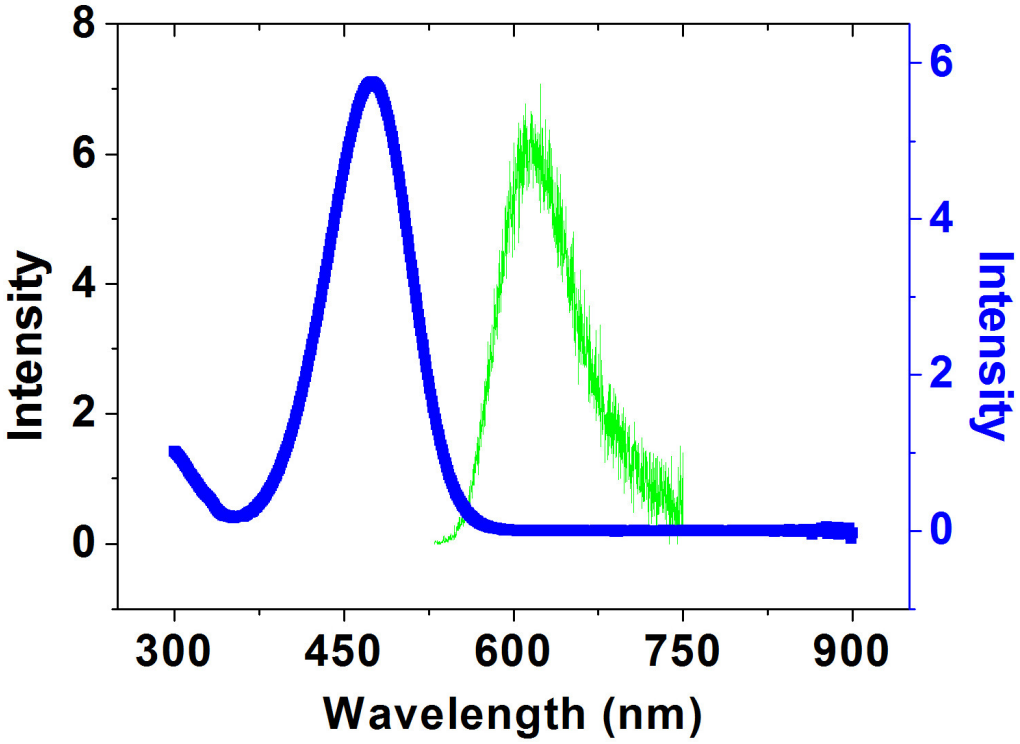

Figure S5. UV-vis (blue) and PL (green) spectra of **DASP** in methanol.

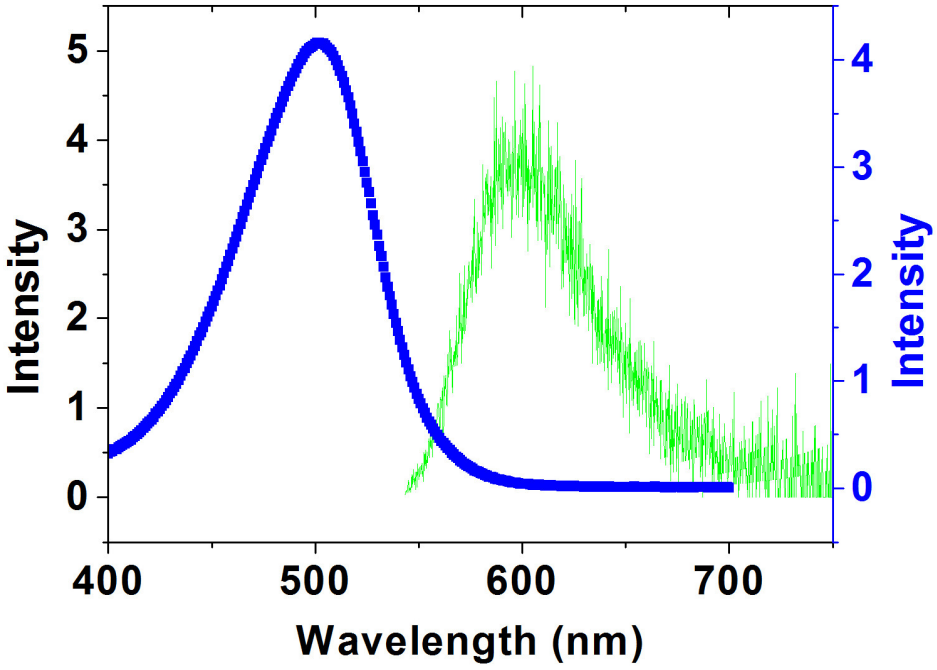

Figure S6. UV-vis (blue) and PL (green) spectra of **DASP** in chloroform.

*7. PL spectra of **DASP** solutions with various **P5** concentrations*

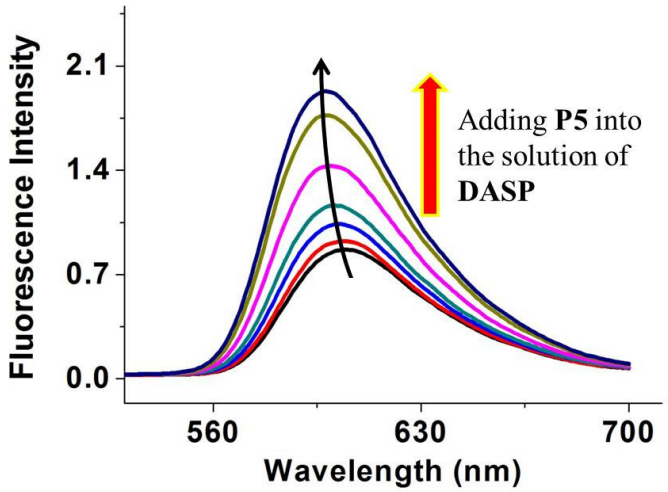

Figure S7. The changes in fluorescence intensity of **DASP** (1.00 mM, λ_{ex} = 500 nm) upon gradual addition of **P5** (0.00, 0.10, 0.30, 0.60, 1.00, 1.50, 2.00 mM) in chloroform.

8. Pump−probe transient absorption spectroscopy

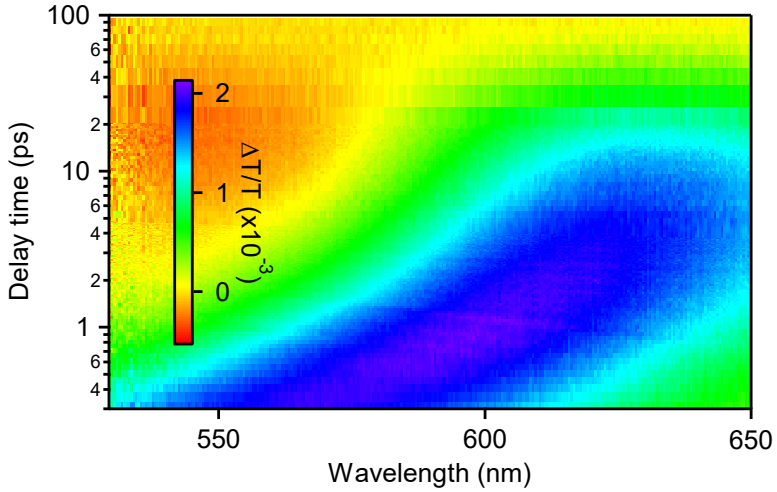

Figure S8. Transient absorption spectroscopy of **DASP** in methanol (λ_{ex} = 370 nm).

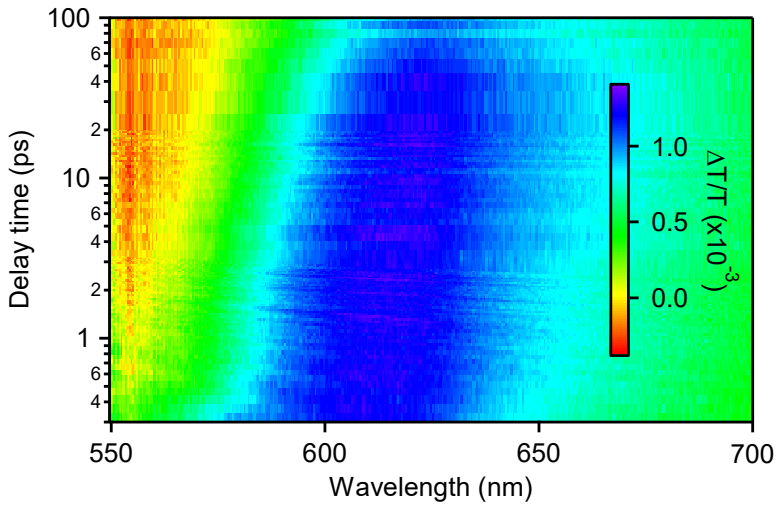

Figure S9. Transient absorption spectroscopy of **2P5⊃DASP** microcrystals (λ_{ex} = 520 nm).

9. Schematic illustration of the experimental setup for the optical measurements

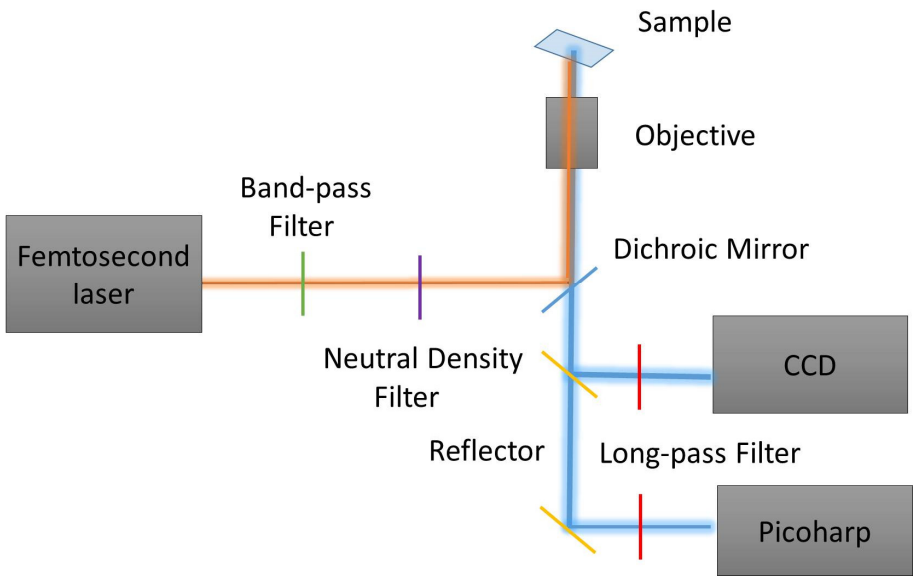

Figure S10. Schematic illustration of the experimental setup for the optical measurements.

*10. Two-photon-pumped lasing of a **2P5⊃DASP** microcrystal*

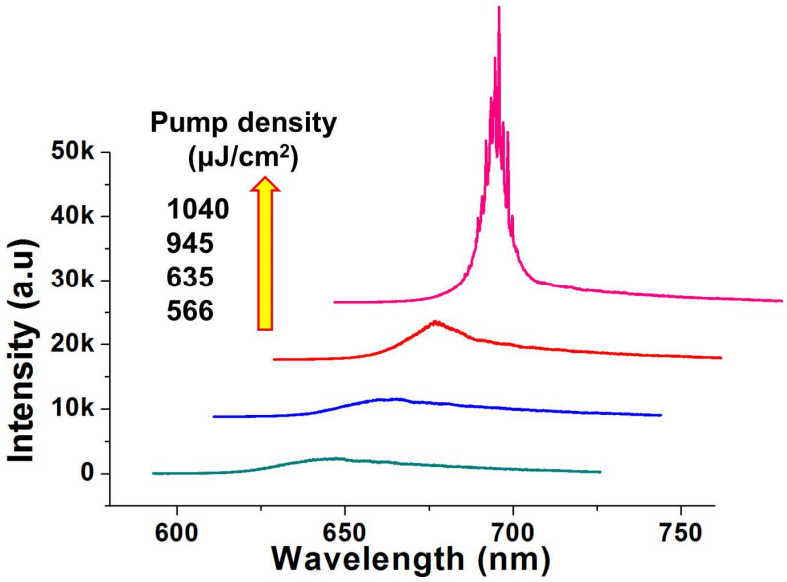

Figure S11. Lasing spectra of a **2P5⊃DASP** microcrystal at different laser energies for excitation at 1030 nm.

11. References

S1. Ma, Y.; Ji, X.; Xiang, F.; Chi, X.; Han, C.; He, J.; Abliz, Z.; Chen, W.; Huang, F. A Cationic Water-Soluble Pillar[5]arene: Synthesis and Host–Guest Complexation with Sodium 1-Octanesulfonate. *Chem. Commun.* **2011**, *47*, 12340–12342.

S2. Arunan, E.; Desiraju, G. R.; Klein, R. A.; Sadlej, J.; Scheiner, S.; Alkorta, I.; Clary, D. C.; Crabtree, R. H.; Dannenberg, J. J.; Hobza, P.; Kjaergaard, H. G.; Legon, A. C.; Mennucci, B.; Nesbitt, D. J. Definition of the Hydrogen Bond. *Pure Appl. Chem.* **2011**, *83*, 1637−1641.