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Organic Single-Crystalline Whispering-Gallery Mode Microlasers with Efficient Optical Gain Activated via Excited State Intramolecular Proton Transfer Luminogen

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Experimental details

Materials:

Organic compound 1,5-dihydroxyanthraquinone (1,5-DHAQ) was purchased from Shanghai Dibai Biological Technology Inc., and used without further purification. 1-Hydroxy-5-methoxyanthraquinone (HMAQ) was purchased from Atomax Chemicals Co.,Ltd, and used without further purification.

Preparation of 1,5-DHAQ microdisks:

The 1,5-DHAQ microdisks (MDs) were prepared by the facile solution-drying method. with the mixed solvent of dichloromethane (DCM) and acetonitrile. In a typical preparation process, 0.5 mg of 1,5-DHAQ powder was dissolved in 1 mL DCM. Then 1 mL of acetonitrile was added into this 1,5-DHAQ/DCM solution, which means that volume ratio of DCM and acetonitrile was 1:1. After shaking for a while, the well-mixed solution was dropped onto a quartz substrate, which was then covered with a watch glass. The 1,5-DHAQ MDs can be obtained dominantly when the solvents gradually evaporated.

Characterizations:

The steady-state fluorescence spectra of the samples were measured by a HITACHI F-4600 fluorescence spectrophotometer. Meanwhile, the time-resolved femtosecond fluorescence up-conversion measurement were performed using a Pharos femtosecond laser system (Light Conversion; 1030 nm, 250 fs, 200 uJ/pulse and 100 kHz repetition frequency) and a HARPIA-TF upconversion system incorporated with TCSPC module. The fluorescence microscopy images were obtained using a Leica DMRBE fluorescence microscope with a spot-enhanced charge couple device (CCD, Diagnostic Instrument, Inc.). The samples were prepared by placing a drop of dispersion onto a cleaned quartz slide. TEM images were obtained by a transmission electron microscopy (TEM, FEI company, Tecnai G2 F20, United States). One drop of the solution was dropped on a carbon-coated copper grid, and evaporated at room temperature. TEM measurement was performed at an accelerating voltage of 20 kV. Micro-area photoluminescence (μ-PL) spectra were collected on a homemade optical microscopy and the equipment were set up as shown in the Scheme S1. The light was coupled to a grating spectrometer (Princeton Instrument,

ARC-SP-2356) and recorded by a thermal-electrically cooled CCD (Princeton Instruments, PIX-256E). PL microscopy images were taken with an inverted microscope (Olympus, BX43). The single crystal XRD data were collected at 120 K on a Bruker SMART APEX II, Mo *K*α (*λ* = 0.71073 Å). The data were processed with Denzoscalepack. Solution and refinement: Structures were solved by direct methods with SHELXS. Full matrix least-squares refinement on the basis of F^2 with SHELXS-97. Refinement of F^2 was against all reflections. Stacking distances were determined by calculating the best plane through a ring and subsequent determination of the distance of the ring atoms of the neighboring molecule and averaging of these distances.

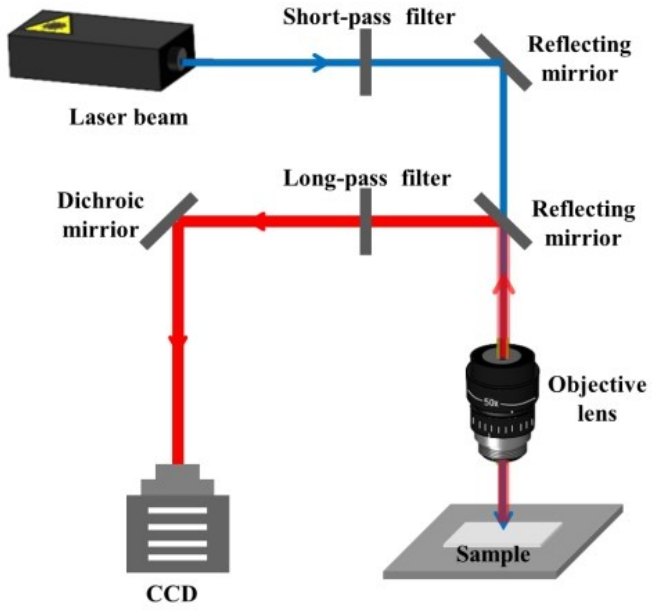

Figure S1. Schematic demonstration of the experimental setup for the optical characterization.

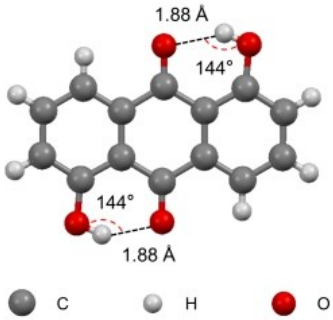

Figure S2. Schematic of the molecular structure of 1,5-DHAQ.

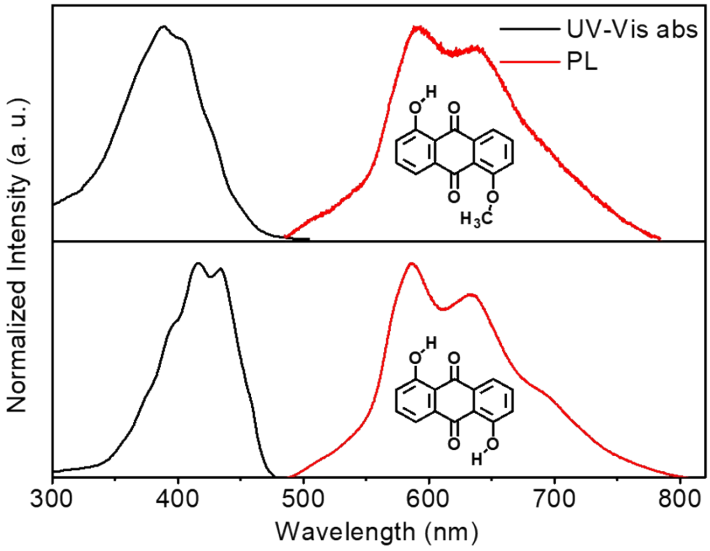

Figure S3. The UV-Vis absorption and PL spectra of HMAQ (top) and 1,5-DHAQ (bottom) doped in polystyrene spheres. The top and bottom insets show the molecular structures of HMAQ and 1,5-DHAQ respectively.

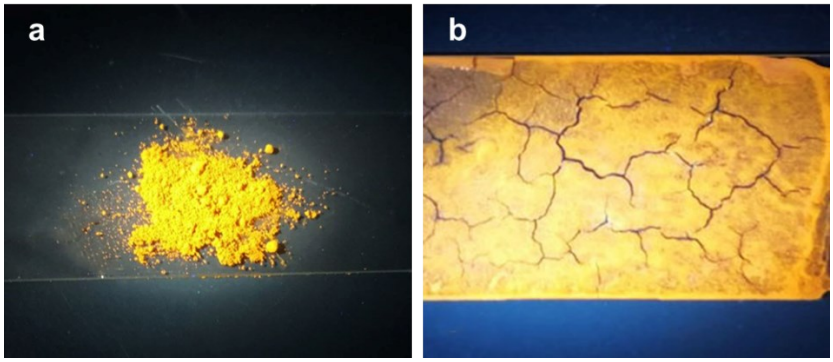

Figure S4. Pictures of 1,5-DHAQ powder (a) and solid state solution (b) under 365 nm UV exposure.

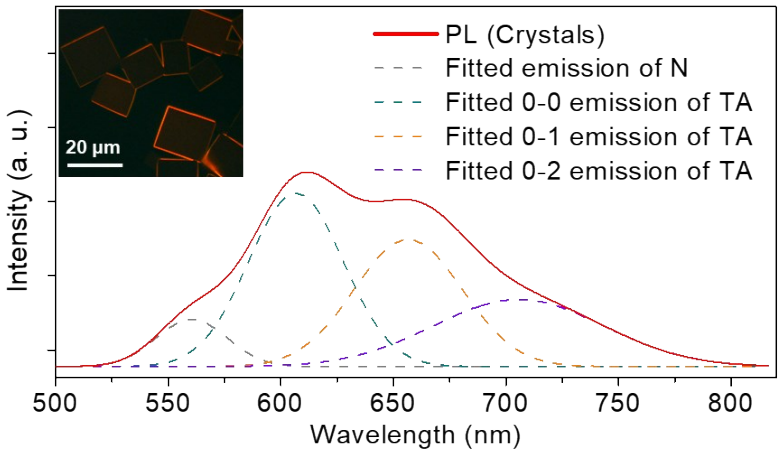

Figure S5. PL spectra of 1,5-DHAQ MDs fitted with lorentzian line shapes displaying the emission bands from the normal form and the vibrational emissions of tautomer A. Inset: The PL image of some MDs of 1,5-DHAQ excited with 375 nm UV beam.

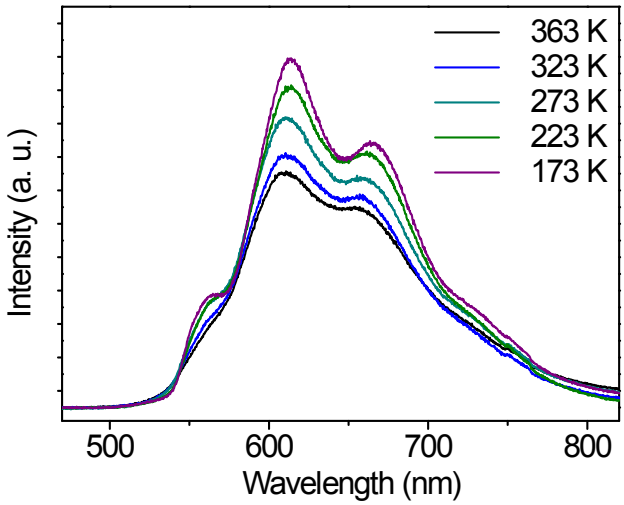

Figure S6. Temperature-dependent PL spectra of 1,5-DHAQ MDs excited with 375 nm UV beam.

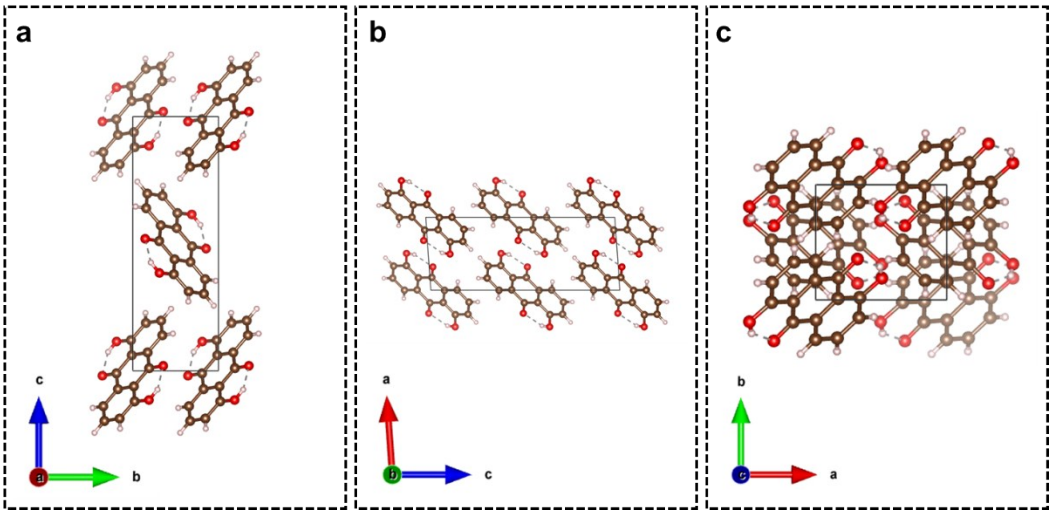

Figure S7. The unit cell structure of 1,5-DHAQ MD from different views along a) *a* axis; b) *b* axis; c) *c* axis.

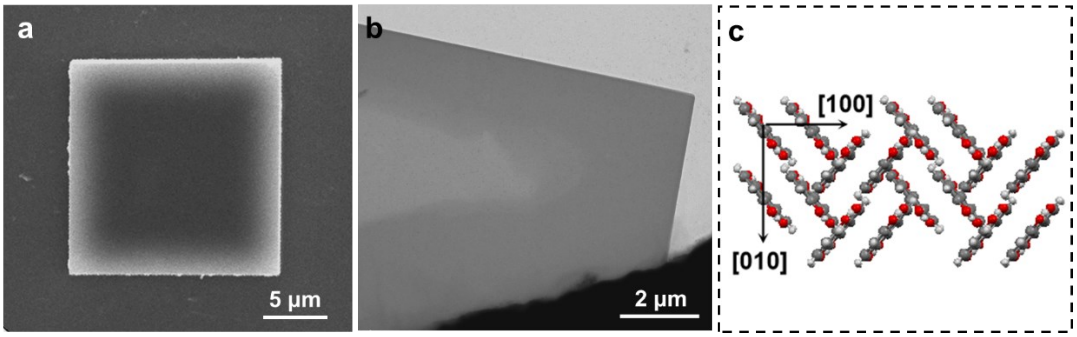

Figure S8. a) SEM image of an individual 1,5-DHAQ MD. b) TEM image of an individual 1,5-DHAQ MD. c) Schematic of the molecular packing in 1,5-DHAQ MDs.

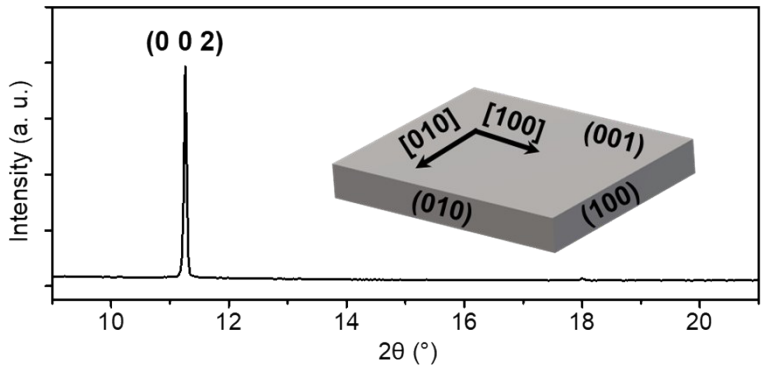

Figure S9. XRD patterns of 1,5-DHAQ MDs. Inset: Schematic of the 1,5-DHAQ crystal morphology with labeled crystal planes.

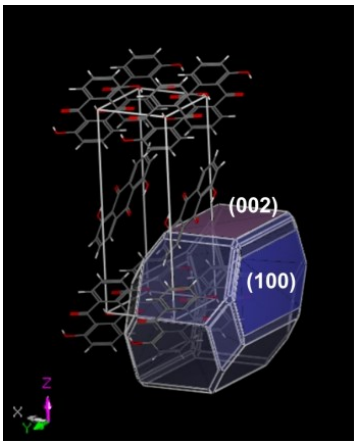

Figure S10. The simulated equilibrium morphology of 1,5-DHAQ crystal by using Material Studio package.

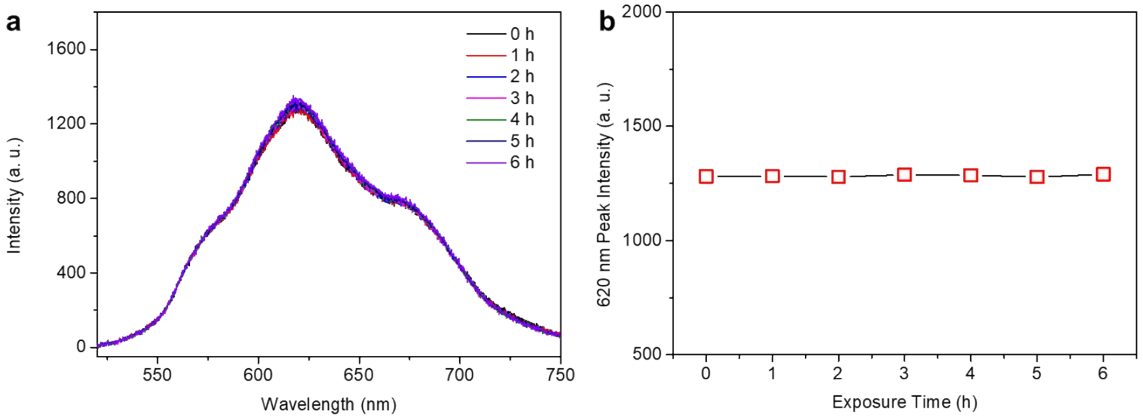

Figure S11. (a) PL spectra of an individual 1,5-DHAQ crystal under 375 nm UV exposure for 6 hours. (b) The 620 nm peak PL intensity change of the 1,5-DHAQ crystal with respect to exposure time.

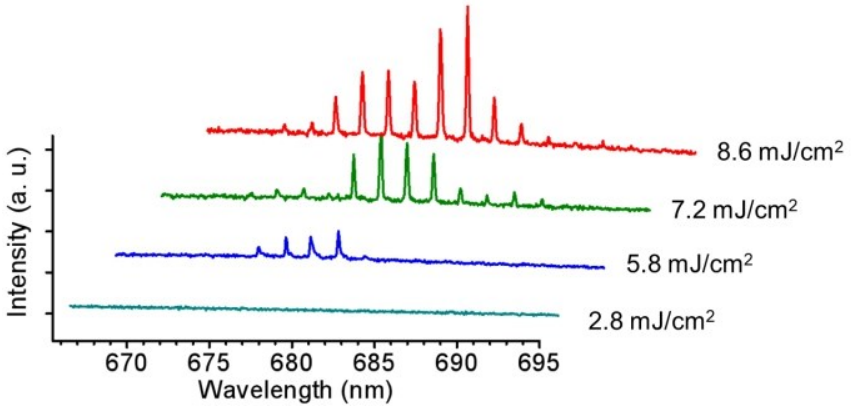

Figure S12. Multiple mode lasing measured from the MDs of 1,5-DHAQ with side length *l* = 16.4 μm

Table S1. The unit cell of the 1,5-DHAQ single crystal (CCDC No. 1965075).

Formula	$C_{14}H_8O_4$
Formula weight	240.0
Crystal system	monoclinic
Space group	*P* $2_1/c$
a (Å)	6.0211
b (Å)	5.2723
c (Å)	15.6347
α (°)	90.000
β (°)	94.048
γ (°)	90.000
V (Å)	495.086
Cell formula units, *Z*	2
R-factor (%)	4.08

Table S2. The simulated parameters of the growth morphology of 1,5-DHAQ single crystals.

hkl	d_{hkl} (Å)	Relative surface area	E_{att} (kJ mol^{-1})	Total facet area (%)

{0 0 2}	7.79784775	31.74504553	-25.39477714	31.22675748
{1 0 0}	6.00607893	82.43082881	-26.39638856	34.45905223
{0 1 1}	4.99461360	99.12399717	-34.06011195	31.88471285
{1 0 -2}	4.92947876	100.43375543	-40.51310733	
{1 0 2}	4.60376350	107.53942148	-33.47947664	2.42947745
{0 1 2}	4.36766418	113.35259398	-39.57575747	
{1 1 0}	3.96225338	124.95063200	-51.84888857	
{1 1 -1}	3.88365974	127.47925858	-53.47258639	
{1 1 1}	3.79827024	130.34513929	-50.25509551	
{0 1 3}	3.70173453	133.74434620	-45.07403014	
{1 1 -2}	3.60076799	137.49457491	-56.99655100	

Table S3. The simulated parameters of the equilibrium morphology of 1,5-DHAQ single crystals.

hkl	d_{hkl} (Å)	Relative surface area	E_{sur} (kJ mol^{-1})	Total facet area (%)
{0 0 2}	7.79784775	31.74504553	0.20067129	15.71804948
{1 0 0}	6.00607893	82.43082881	0.16367914	18.38006913

{0 1 1}	4.99461360	99.12399717	0.17958041	31.24057456
{1 0 -2}	4.92947876	100.43375543	0.24769443	1.04915249
{1 0 2}	4.60376350	107.53942148	0.16412355	13.88432295
{0 1 2}	4.36766418	113.35259398	0.20954184	0.00574329
{1 1 0}	3.96225338	124.95063200	0.22607887	
{1 1 -1}	3.88365974	127.47925858	0.23529001	0.71720738
{1 1 1}	3.79827024	130.34513929	0.20360042	5.37440944
{0 1 3}	3.70173453	133.74434620	0.22209988	2.56309756
{1 1 -2}	3.60076799	137.49457491	0.26027657	