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Electronic Supplementary Information (ESI)

Active Whispering-Gallery-Mode Optical Microcavity Based on Self-Assembled Organic Microspheres

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Experimental details

1. Materials

The organic compounds of 1-(4-fluoro-2-hydroxyphenyl)ethanone and 4-(dip-tolylamino)benzaldehyde were purchased from Sigma-Aldrich. The solvent of dichloromethane (DCM, analysis grade), ethonal (EtOH, analysis grade), acetonitrile (analysis grade), hexane (analysis grade) and potassium hydroxide (KOH), magnesium sulfate ($MgSO_4$) were purchased from Beijing Chemical Agent Ltd., China. Ultrapure water with a resistance of 18.2 MΩ cm^{-1}, produced by using a Milli-Q apparatus (Millipore), were used in all experiments. Besides, all compunds and solvents were used without further treatment.

2. Synthesis of DTPHP

In a typical preparation process, mixture of 1-(4-fluoro-2-hydroxyphenyl)ethanone (0.92 g, 6 mmol) and KOH (1.01 g, 18 mmol) was dissolved in the EtOH (200 mL) and stirred at room temperature for 1 hour in a 500 mL round-bottomed flask. Then the 4-(dip-tolylamino)benzaldehyde (1.81 g, 6 mmol) in EtOH (30 mL) was then added dropwise into the flask. After being stirred for 48 hours at room temperature, the mixture was then added dropwise into the water and extracted with DCM. The separated organic layer was then dried over $MgSO_4$ and distilled in vacuo at 25 ºC. By further recrystallization from acetonitrile/hexane, the pure (*E*)-3-(4-(dip-tolylamino) phenyl)-1-(4-fluoro-2-hydroxyphenyl)prop-2-en-1-one (DTPHP) powder was obtained (1.92 g, 73 %). 1H NMR (400 MHz, $CDCl_3$) δ 13.47 (*s*, 1H), 7.91 (*t*, *J* = 7.5 Hz, 1H), 7.88 (*d*, *J* = 7.7 Hz, 1H), 7.47 (*d*, *J* = 8.5 Hz, 2H), 7.39 (*d*, *J* = 15.2 Hz, 1H), 7.13 (*d*, *J* = 8.2 Hz, 4H), 7.05 (*d*, *J* = 8.1 Hz, 4H), 6.96 (*d*, *J* = 8.4 Hz, 2H), 6.69 (*d*, *J* = 10.4 Hz, 1H), 6.64 (*t*, *J* = 8.5 Hz, 1H), 2.34 (*s*, 6H).

3. Preparation of the Self-assembled Organic Microspheres

Typically, 5 mL of EtOH, which serves as the poor solvent was added to 1ml DTPHP solution with DCM as the good solvent (5 mg mL^{-1}) and stirred vigorously. After 2 hours' standing, the mixture was dropped onto a glass substrate. When the solvent evaporated, the organic DTPHP microspheres were obtained in a large scale.

4. Structural and Optical Characterizations

The field-emission scanning electron microscopy (FESEM) images of the samples were taken by a FEI Quanta 200F at acceleration voltages of 15 kV. A thin gold layer is coated on the surface of samples with an Edwards Sputter Coater to improve the electrical conductivity. The steady-state fluorescence spectra of the samples were measured on a HITACHI F-4600 fluorescence spectrophotometer. Meanwhile, the time-resolved fluorescence decay of these samples was also measured with a HORIBA JOBTN YVON FLUOROMAX-4 spectrofluorimeter. 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. In addition, Micro-area photoluminescence (μ-PL) spectra were collected by a homemade optical microscopy, and the equipment was set up as shown in the Figure S7. To measure the PL spectra of individual microplate, the plate was excited locally with a 375 nm laser focused down to the diffraction limit. The excitation laser was filtered with a 375 nm notch filter. The light was subsequently 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).

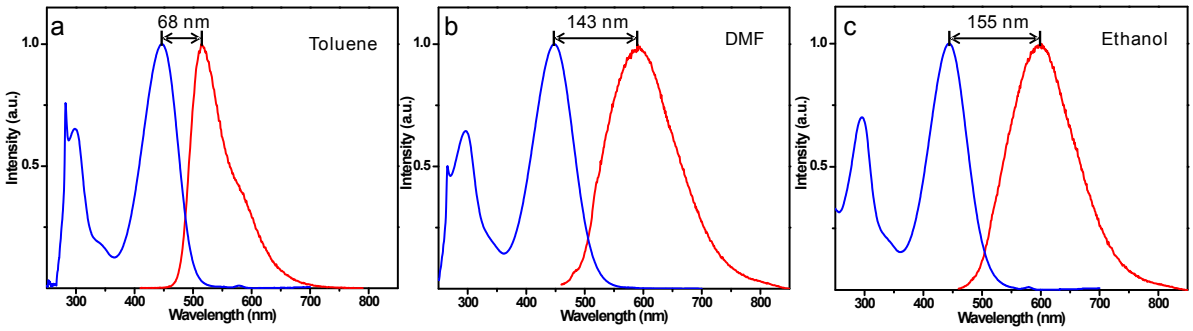

Figure S1. The absorption (blue line) and PL (red line) spectra of DTPHP in (a) Toluene; (b) DMF; (c) Ethanol solution.

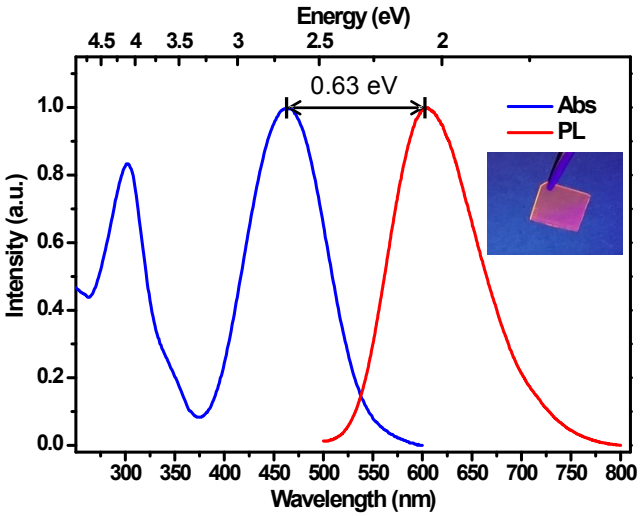

Figure S2. The absorption (blue line) and PL (red line) spectra of the thermal deposited DTPHP film (30 nm). The inset is the photograph of the film and fluorescent microscope image of microspheres.

Table S1. The summary of the parameters of the DTPHP unit cell (CCDC No. 1892054).

Formula	$C_{29}H_{24}FNO_2$
Formula weight	437.5
Crystal system	Monoclinic
Space group	*P* -1
a (Å)	10.300(2)
b (Å)	12.510(3)
c (Å)	19.440(4)
α (o)	96.92(3)
β (o)	101.63(3)
γ (o)	109.63(3)
V (Å)	2262.28
Cell formula units, *Z*	4
R-factor (%)	10.11

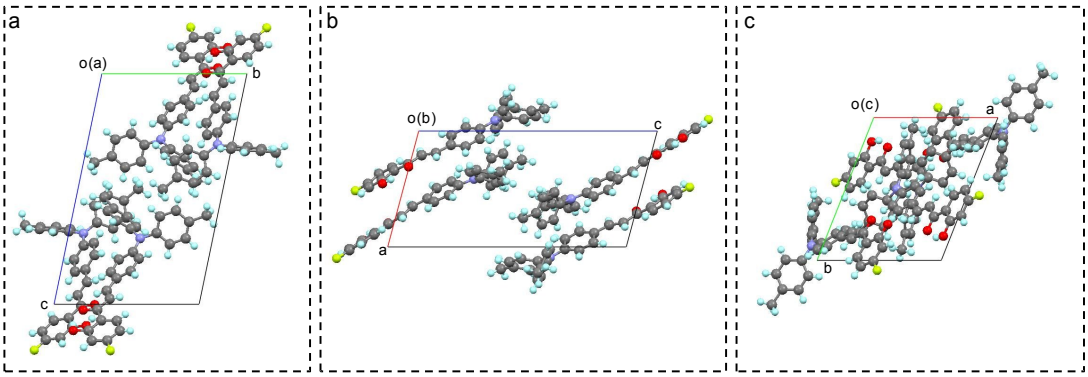

Figure S3. The unit cell structure of DTPHP from different views along (a) a axis; (b) b axis; (c) c axis.

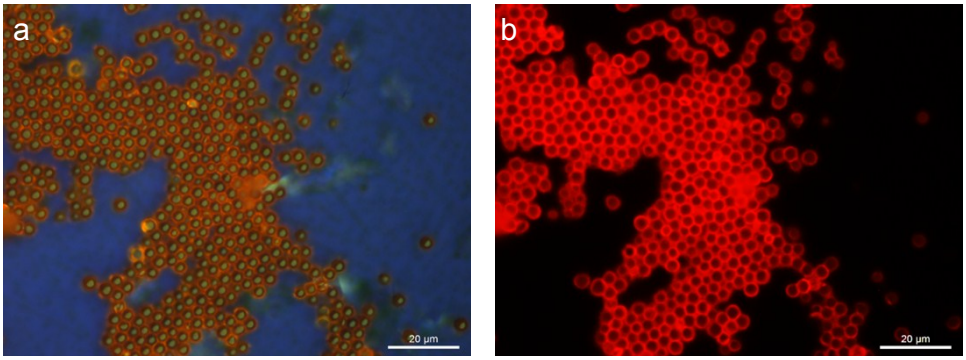

Figure S4. (a) The bright-field and (b) fluorescent microscopy image of densely self-assembled DTPHP microspheres.

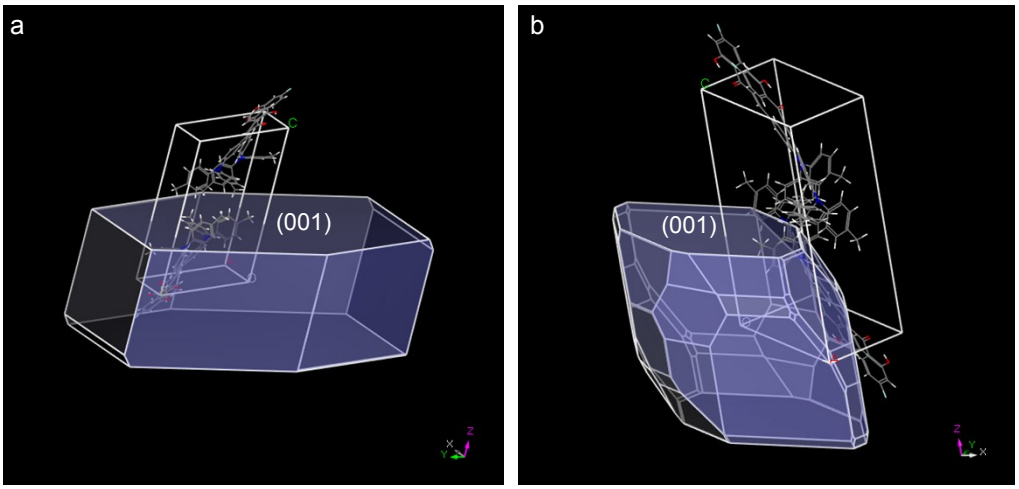

Figure S5. (a) The simulated growth morphology of DTPHP molecules based on the attachment energies utilizing Materials Studio package; (b) The simulated equilibrium morphology of DTPHP based on the surface energies.

Table S2. The simulated parameters of the growth morphology of DTPHP.

hkl	d_{hkl} (Å)	Relative surface area	E_{att} (kJ mol^{-1})	Total facet area (%)
{001}	18.64	121.36	-37.92	54.17
{010}	11.53	196.12	-86.65	17.13
{01-1}	10.85	208.52	-99.28	1.99
{10-1}	9.41	250.51	-128.44	
{100}	9.37	241.42	-101.83	11.42
{1-10}	9.11	248.32	-90.82	15.13
{011}	9.02	250.81	-102.17	
{1-1-1}	8.49	266.34	-118.12	
{101}	7.62	296.96	-97.91	0.17

Table S3. The simulated parameters of the equilibrium morphology of DTPHP.

hkl	d_{hkl} (Å)	Relative surface area	E_{att} (kJ mol^{-1})	Total facet area (%)
{001}	18.64	121.36	15.62	27.67
{01-1}	10.85	208.52	23.90	3.80
{1-10}	9.11	248.32	18.34	14.89
{011}	9.02	250.81	20.46	3.09
{101}	7.62	296.96	16.55	7.44
{1-12}	6.24	362.63	18.37	3.81
{110}	6.23	363.09	18.59	11.99
{1-20}	6.00	376.79	21.18	3.08
{1-21}	5.79	390.45	20.87	3.35

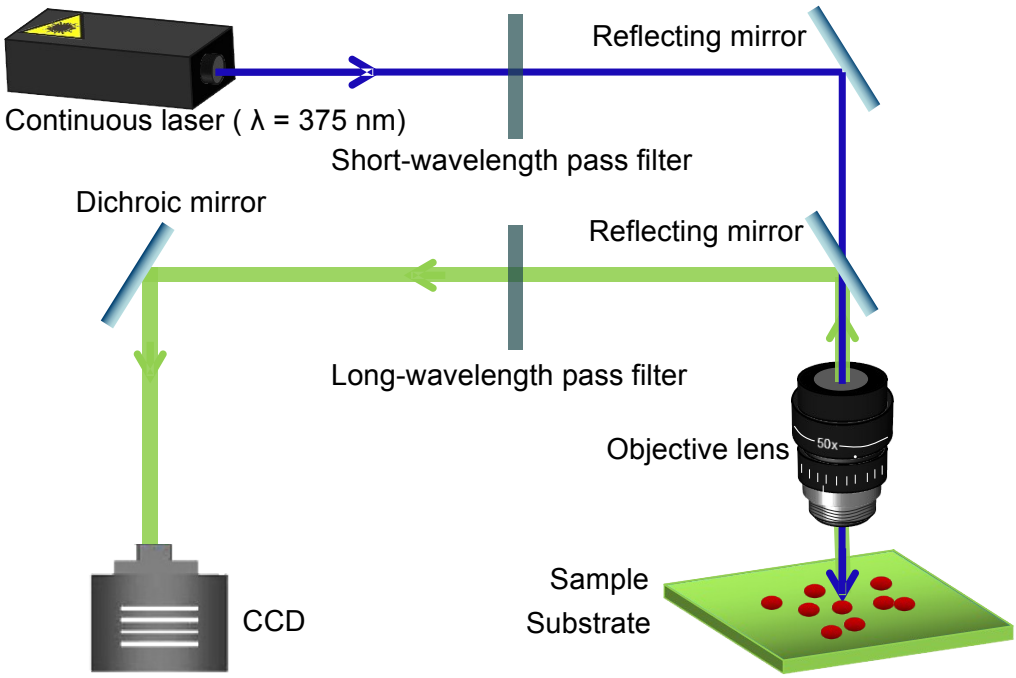

Figure S6. The diagram of the setup of the home-made μ-PL system.

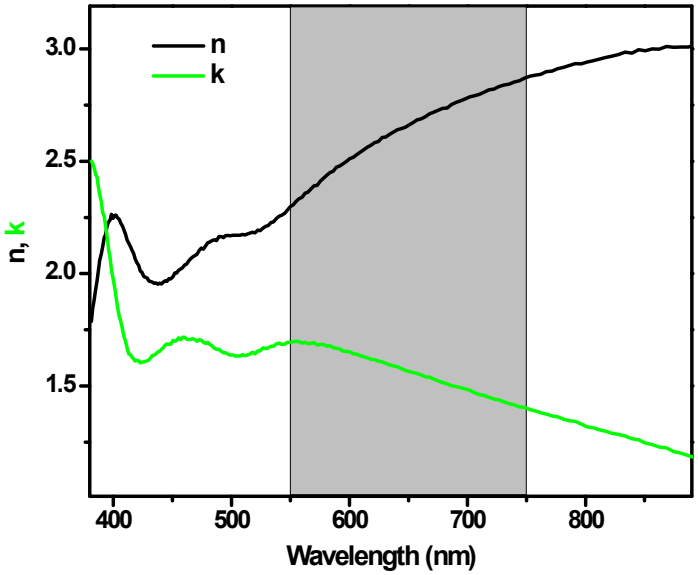

Figure S7. The measured intrinsic refractive index (*n*, black line) and dielectric constant (*k*, green line) of DTPHP film with a 30 nm thickness.

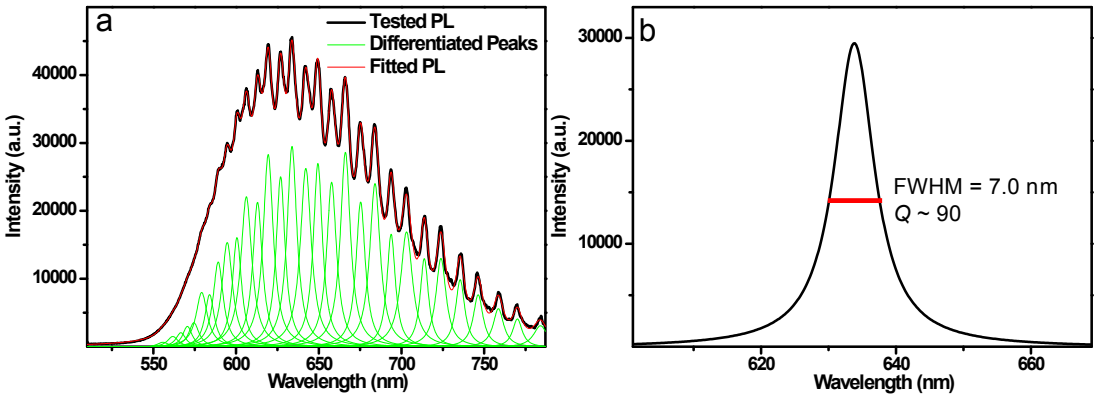

Figure S8. (a) The peak-deafferenting of the resonance peaks appear in the PL of individual DTPHP microsphere with a diameter of 1.7 μm. (b) Individual resonance peak deafferented from the PL spectra with a half width at half height (FWHM) of 7 nm, indicating a quality (*Q*) factor of around 90.